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Multimaterial Nanoscale Printing via Charged Nanoparticle Deposition

By

Daniel Teal

A dissertation submitted in partial satisfaction of the

requirements for degree of

Doctor of Philosophy

in

Engineering — Electrical Engineering and Computer Sciences

in the

Graduate Division

of the

University of California, Berkeley

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Fall 2024

Multimaterial Nanoscale Printing via Charged Nanoparticle Deposition

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Abstract

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Daniel Teal

Doctor of Philosophy in Engineering — Electrical Engineering and Computer Sciences

University of California, Berkeley

Professor Kristofer S.J. Pister, Chair

Microfabrication, the set of manufacturing techniques used to make computer chips, displays, MEMS, and other devices, is famously difficult, slow, and capital equipment heavy. In this dissertation we propose a much simpler path toward rapid prototyping of microfabricated devices by deposition of nanoparticles in vacuum.

We will discuss generation of nanoparticles of standard microfabrication materials such as metals, oxides, and semiconductors, as well as methods to manipulate these as aerosols in low-pressure gas, culminating in a demonstration of multimaterial printing. We will then describe electrical charging of nanoparticles and develop a new method to electrostatically focus and accelerate nanoparticles theoretically capable of printing with sub-1 μm resolution. Finally, we will detail the future work required to 3D print silicon transistors and conclude our new manufacturing process will likely be faster and cheaper than standard microfabrication for making small quantities of simple chips.

Dedicated to a kind and awesome future.

Acknowledgments

With the understanding that the acknowledgments section of a thesis is traditionally freed from the rigid constraints of academic formality:

I need to give huge thanks to **Kris**. You let me pursue this initially-uncertain project despite your wish I spent more time building cooler MEMS robots with traditional microfabrication; I still intend to build plenty of better robots via printing someday. You were simultaneously an excellent advisor, providing proof it's possible to be good at many things, kind to people, and kinda funny sometimes. You set a good example. I also need to give a shoutout to the rest of my thesis committee—**Clark**, **Jeff**, and **Hartmut**—for going along with it and letting me try something a bit unusual. I'm pretty happy with the result.

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To researchers who worked on this and other problems in the past: thanks for your work (and then for publishing it!). Y'all did good, and I hope my work similarly inspires others. Being able to simply look up progress on most problems makes it possible to go so much further. I tried to reference prior work everywhere I could; apologies to anyone I missed.

Thanks to the diffuse group of authors and musicians and artists and engineers whose works of fiction and otherwise have kept me sane these past years then shown me what could be. If anything makes life worth living, it's what we choose to make from it.

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Financially, credit goes to the NSF Graduate Research Fellowship Program (GRFP) (grant DGE 1752814), which gave me the freedom to explore ideas eventually resulting in this dissertation, and to Kris, BSAC, and Berkeley for supporting me the rest of the way.

Minimal thanks to air. Oxygen especially. I love breathing, but I gotta admit this project would have been much easier if everything were in vacuum to begin with.

Finally: thanks to you, reader. I can't resist breaking the fourth wall in order to wish you luck with whatever you're trying to do. I hope you enjoy this show.

List of Symbols

The following are standard symbols used throughout this dissertation and listed here with their SI units for reference. Any symbol with a superscript arrow (\vec{F}) denotes a vector.

Dynamics		Gas Parameters	
t	time (s)	m_g	mass of single gas molecule (kg)
x	position (m)	P	pressure (Pa) (we also use Torr)
r	radial position (m)	T	temperature (K)
v	velocity (m s^{-1})	ℓ	mean free path (m)
a	acceleration (m s^{-1})		
L	distance (m)		
\vec{F}	force (N)		
\vec{E}	electric field (N C^{-1})		
Constants		Ion Traps	
k_B	Boltzmann constant (J K^{-1})	R_T	quadrupole trap radius (m)
e	elementary charge (C)	L_T	quadrupole trap length (m)
ϵ_0	vacuum permittivity (F m^{-1})	ω	trap angular frequency (rad s^{-1})
		f	trap frequency ($2\pi f = \omega$) (Hz)
		V_T	peak-to-peak AC amplitude (V)
		U_T	trap potential energy (J)
		\tilde{U}_T	trap pseudopotential energy (J)
Nanoparticle Parameters		Nanoparticle Beams	
d_p	nanoparticle diameter (m)	r_B	beam minimum radius (m)
m	nanoparticle mass (kg)	d_B	beam minimum diameter (m)
n	number of elementary charges (-)	A_B	beam minimum area (m^2)
q	nanoparticle charge ($q = ne$) (C)	θ	beam half-angle (rad)
β	viscous damping coefficient (kg s^{-1})	Ω	beam solid angle (sr)
D	diffusion coefficient (m^2/s)	v_a	particle axial speed (m s^{-1})
		v_r	particle radial speed (m s^{-1})
		Q	beam volumetric flux (m^3/s)
		N'	beam number flux (particles s^{-1})

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Chapter 1

Introduction

Contemporary life is built on computer chips and displays, LEDs and solar cells, inkjet printers and cell phone RF filters. All these are made with the same set of fabrication tools, which we collectively call microfabrication. Microfabrication is notable for three reasons:

- it lets us build nanometer-scale multimaterial devices;
- it is often the *only* way to build these devices;
- it is very difficult, expensive, and time-consuming.

This last point is unfortunate. As we will show, it means R&D is slow and microfabrication is out of reach of most researchers and engineers. It is a testament to its importance that we've persisted with microfabrication long enough to build computers and the Internet—but how much more could be done if it were easier and accessible? We argue it is worthwhile to investigate new manufacturing methods that achieve similar results with fewer constraints.

In this dissertation, we'll describe our progress developing one such fabrication process¹. It will not replace microfabrication in general but should be capable of creating some of the same devices while being easier, cheaper, and faster in limited circumstances.

What are these nanometer-scale multimaterial devices, and what is the challenge in making them? The prototypical device is a transistor, billions of which are contained in each computer CPU, but other exemplar devices include solar cells and LEDs. All these are nothing more than solid blocks of the right materials put together in the right configurations. Some silicon here, some aluminum there, some oxides between them. This is comparable to games like Minecraft: put particular materials in correct positions, and you have a transistor. The difficulty is that, in reality, this needs extreme precision and control.

For example, a simple MOSFET transistor might consist of at least four different materials: silicon with a small amount of boron, silicon with a small amount of phosphorus, silicon

¹The impatient reader can skip to section 1.3 for details. In short: 3D printing nanoparticles.

dioxide (SiO_2 , i.e., glass), and aluminum, placed together as in figure 1.1 [1][2]. In order for the transistor to work, the thin later of SiO_2 in the center (the “gate oxide”) must be less than 100 nm thick (only several hundred atoms!), while the proportion of boron and phosphorus (“dopants”) in silicon needs to be extremely precise with no contaminants². Increasingly complex improvements (silicon crystal orientation, different gate oxide materials, etc.) raise performance. Other devices, like solar cells and LEDs, or MEMS³ devices like inkjet printer nozzles and cellphone RF filters (which all have air gaps that allow miniature mechanical parts to move), have their own constraints. A solar cell, for example, is just a layer of this phosphorus-doped silicon on boron-doped silicon with metal electrodes on each side.

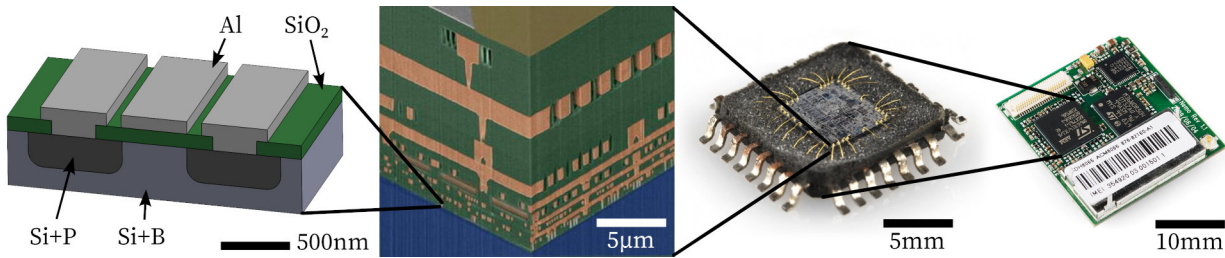


Figure 1.1: From left to right: a minimal transistor, tens of transistors in a cutaway view of a chip that contains millions, the chip in a standard integrated circuit package, and the result mounted to a printed circuit board. Right pictures from [3], [4].

Fortunately some of these constraints can often be relaxed slightly at the cost of reduced performance, but in general interesting devices always have the following requirements:

- **Multimaterial construction:** These devices consist of several different types of material, and each material must be very pure, sometimes to better than one non-silicon atom per billion silicon. Furthermore, the interfaces between two different materials needs to be near atomically perfect. The usual macroscopic approach of making two parts separately then attaching them leaves rough surfaces and dust and grease and is not good enough. Usual materials include metals (as electrical conductors), oxides (like SiO_2 , often electrical insulators), and especially semiconductors (like silicon).
- **High resolution:** At least some parts of the more interesting devices need to be below 1 μm thick (human hair is 80 μm in diameter). Compare this to traditional macroscopic metal machining, where just the roughness of a smooth surface might be around 1 μm !

The combination of these two qualities—multimaterial capability and high resolution—is the main challenge that microfabrication solves and no other manufacturing method has yet reached. Achieving this will be our main challenge in this dissertation.

²Silicon has a density of about 5×10^{22} atoms per cubic centimeter. Common levels of purposely added dopants range anywhere from 1×10^{13} to 1×10^{20} atoms per cubic centimeter, and unwanted impurities must be below that (less than one unwanted atom per billion others). Electrical purity silicon is one of the most precise materials humans have ever produced and is far beyond, e.g., natural gemstones.

³Microelectromechanical systems (MEMS) are tiny gears, vibrating beams, and other mechanical parts made with microfabrication. Moving parts are made by etching away specific materials to leave air gaps and can then be moved around with electrostatics by applying a voltage via an attached electrical circuit.

1.1 Microfabrication is Hard

We now know what microfabrication has to do: it places metals, semiconductors, and oxides together with high resolution. But how does it work, and why is it so slow and difficult?

Microfabrication is a set of different tools combined in what was originally called the planar process, first conceptualized some 65 years ago [5][6]. Starting with a flat substrate—typically a silicon wafer—the substrate is passed through many steps, each performed by a different tool. Some steps deposit a thin layer of a new material across the entire surface, some add a layer of special material onto which a 2D pattern is drawn with light (“photolithography”), and some steps selectively etch some materials but not others. This process makes hundreds of copies in parallel on the same wafer, so a final step cuts this into individual rectangular chips, which are then packaged and attached to PCBs in larger devices [1][7][8].

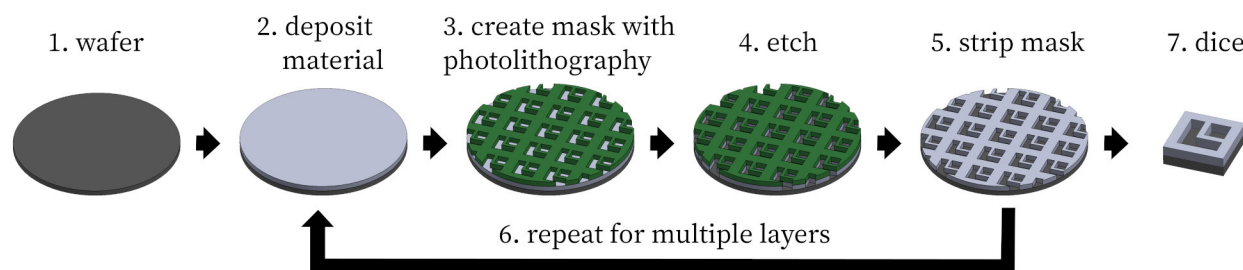


Figure 1.2: The steps of microfabrication. A silicon wafer has material deposited, a mask patterned, the material etched through the mask, and mask removed. These steps are repeated up to tens of times for multiple layers until the wafer is finally diced into complete chips. Each step requires its own precise piece of manufacturing equipment.

This planar microfabrication process can make multimaterial devices by depositing each material in a separate step. These thin-film deposition tools generally work by introducing into a vacuum chamber the wafer and a cloud of atoms, which condense into a solid film on the wafer surface, not unlike the everyday experience of water vapor condensing into fog on a cold mirror except the condensation might be metal. There are many variations⁴, all of which can precisely control film thickness to the nanometer level, sometimes even with atomic precision (via ALD), and all result in pure materials due to the lack of contaminants in a vacuum. Thus our first requirement, multimaterial construction, is achieved.

In order to achieve the second requirement, high resolution, in addition to precisely controlling film thickness we also need to make 2D patterns across the wafer. This is achieved by photolithography, a process in which a layer of light-sensitive polymer photoresist is deposited on the wafer and a pattern of light, made with a patterned mask, is magnified and chemically changes this photoresist in exposed areas. The exposed photoresist can be etched away, and another etching process used to selectively remove material below those areas, after which the photoresist is removed. The resolution of this process is limited mainly by the

⁴Some variations include evaporation and sputtering, which are often described as physical vapor deposition processes, and chemical vapor deposition, in which the vapor reacts on the surface [1].

wavelength of light used and is easily sub-1 μm ; 200 nm resolution is decades old technology while state-of-the-art extreme ultraviolet (EUV) photolithography tools approach 10 nm.

The result is impressively capable. Microfabrication makes not only small multiterminal transistors, but also arrays of many transistors spread across a chip—an integrated circuit (IC)—and easily mass produces them. Early ICs quickly superseded vacuum tubes in size and performance. As microfabrication (and especially photolithography resolution) improved, ICs contained more transistors, quickly increasing from several thousand in the early Intel 4004 microcontroller, to millions in the 1990s, to billions of transistors per chip today (or even trillions in terabyte memories). This rapid increase in capability, known as Moore’s Law [6][9], allowed the rapid adoption of computers in every part of society⁵. Almost as an afterthought, the same microfabrication process is used to build solar cells, LCD displays, hard drives, DVDs, accelerometers, LEDs, microfluidic chips, and more.

That’s how microfabrication works. Why do we emphasize its difficulty?

Briefly: it is too complex. A modern CPU might have 80 layers, each of which needs its own deposition, lithography, and etch steps, not to mention cleaning and metrology steps in between. This means a total of hundreds or thousands of individual steps, each of which is performed in a different piece of machinery. A wafer is moved back and forth between these pieces of equipment⁶ in a process that takes days at minimum, but more often weeks to months, and the warehouse-sized factory (“fab”) holding this equipment must be a cleanroom to minimize dust. Even worse: if a single step messes up, there is often no way to correct it but to start over from the beginning. Thus each tool needs to be precisely built to be as perfect as possible, which is naturally expensive. Simpler devices like MEMS often have fewer layers but the microfabrication process has to be customized to each device, making them almost equally challenging to build.

To convince the reader this is worth improving, we submit the following evidence:

- **2020 chip shortage, due to time constraints:** around 2020–2023, a combination of economic factors resulted in a significant mismatch between which chips were produced by microfabrication fabs and what customers required [11]. This affected many industries in which larger systems (e.g., cars) could not be built without a missing chip. These problems took years to resolve, despite significant financial incentive, because it takes that long for a fab to change the chips it makes or for new fabs to be built.
- **Inaccessibility, due to cost:** the minimum cost to make a single new custom chip, ordered from an existing fab, is typically at least tens of thousands of dollars⁷. Building even a minimal custom fab from used tooling is even more expensive. This limits chip design to large companies. Well-funded startups can only afford one or two tries to make a working chip, and this is even harder for researchers or hobbyists (who are also affected by the multi-month times required to make anything, including MEMS).

⁵As of 2024 we are running out of further iterative improvements to make to microfabrication, slowly leading arguably to the end of Moore’s Law. The effect this will have on the industry is uncertain, although microfabrication and computers are definitely here to stay. We share some thoughts in chapter 7.

⁶Wafers often spend half their time en route between tools as a consequence of queueing theory [10].

⁷For simple chips; recent nodes can cost millions. For details and references, see section 7.2.1.

Thus, unlike fields such as robotics or metalwork, where cheap kits and tools are widely available to teach students, microfabrication has no ecosystem of slowly improving amateur talent. It remains a niche activity despite its massive importance.

- **Supply chain complexity, due to difficulty:** the semiconductor supply chain has become one of the most complex in the world [12], there are many possible points of failure in a fab, and keeping up with the state-of-the-art requires increasingly fragile, precise, and expensive microfabrication tools. The largest challenge in building a new fab is often not the economics, despite its multimillion (or billion) dollar cost, but the technical problem of setting up even a copy of an existing working fab [13].

These problems have inspired worldwide efforts such as the \$52-billion-dollar 2022 US CHIPS Act [14], which tries to address each of these by improving existing microfabrication.

At this point, we believe it makes sense to recognize that since microfabrication is simultaneously important yet difficult, it is worthwhile to spend at least minimal effort investigating alternative fabrication processes not subject to the same time, cost, and difficulty limits⁸. While it is unlikely we will be able to compete with the half-century of intense technological effort that is microfabrication, an alternative can start small and might help in a subset of cases—what if we could iterate minimal designs in days instead of months? What if building a single bad transistor only needed a desktop tool, not a warehouse-sized fab? What if hobbyists could order simple custom chips as easily as PCBs today? Or will there never be another way to make a million-transistor computer? It seems likely alternatives can exist as there’s no law of physics prohibiting construction far faster and with far more precision than microfabrication other than our skill in designing new ways to move atoms around [16][17]. Thus, in the grand academic tradition of asking difficult questions, we’ll follow this thought and see if we get anywhere interesting.

So: in what ways other than the planar microfabrication process can we make high-resolution multimaterial devices, both transistors and beyond?

1.2 Existing Microfabrication Alternatives

The reason we continue to use microfabrication despite its difficulty is we have no alternative simultaneously capable of the multimaterial patterning and high resolution required to make useful devices. But partial alternatives certainly exist. Here we list a number of manufacturing methods⁹ that can get close to microfabrication’s resolution and material capabilities and, despite falling short of this particular goal, often find a niche for themselves.

⁸As the author, I admit a personal motivation: frustration with these limits of microfabrication while teaching Berkeley’s EE143 microfabrication lab course or building MEMS devices [15] even in our excellent research fab. It’s not fun to spend more time waiting for tools to finish than doing more useful research.

⁹The reader may be familiar with a distinction in macroscopic manufacturing tools between subtractive and additive processes: a subtractive process, like woodwork or CNC milling, begins with a block of material and removes mass to carve it to shape, while an additive process like welding or 3D printing adds material. Although this division breaks down for more complex methods, microfabrication is arguably a combination of repeated additive then subtractive cycles. The following processes, excepting FIB milling, are all additive (or “direct write” [18][19]) as this more easily satisfies the requirement to use multiple materials.

1.2.1 Inkjet Printing

Inkjet printing is perhaps the most well-known of all alternative manufacturing methods that pattern multiple materials with high resolution. Small liquid ink droplets are dispensed through a small (microfabricated!) nozzle via mechanical pressure or thermal expansion. Scanning the the dispensing head over a substrate while switching inks allows 2D multimaterial printing. Many nozzles can be operated in parallel for fast printing—at the upper end, 200×10^3 nozzles across 40 printheads, each at 80×10^3 drops per second per nozzle, gives 16 billion drops per second [20][21]. It is possible to layer inks to build 3D structures [22][23]. However, despite these abilities, inkjets still can't compete with microfabrication.

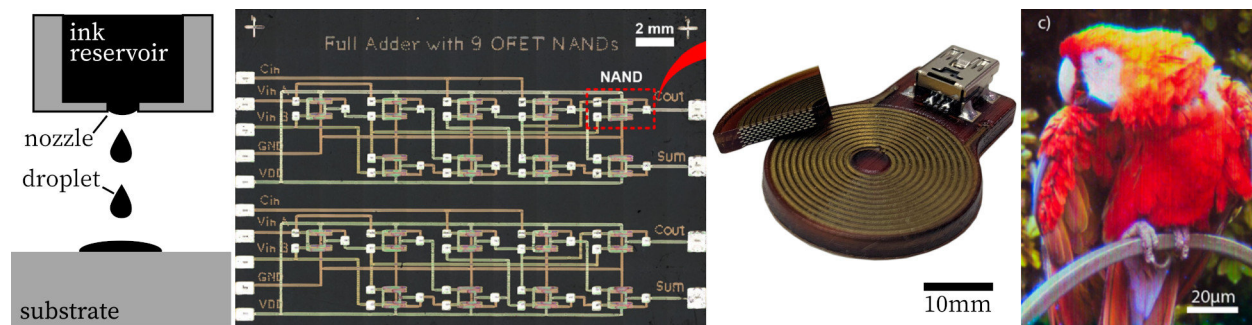


Figure 1.3: Left: the basic inkjet mechanism, in which liquid ink is expelled in droplets from a micron-scale nozzle by piezoelectric mechanical pressure or thermal expansion. Center left: an inkjet-printed full adder circuit [24]. Center right: printed thick insulating and conducting inks makes a 3D coil onto which a connector is soldered [23]. Right: EHD printing achieves 250 nm resolution [25].

A large limitation of inkjets is that they only work with liquid inks within a certain viscosity range. This prohibits the use of standard semiconductor materials—for example, silicon is only a liquid when molten above 1414°C which is infeasible to work with¹⁰. Instead, inks are generally polymer-based in a liquid organic solvent that evaporates after printing. Conductive traces are possible by printing metal nanoparticles in liquid followed by sintering [26][27], but semiconductors are limited to low-performance complex polymers and metal oxides [24][28]. These material difficulties, compounded with reliability and accuracy issues, have limited the largest inkjet printed circuits to about 100 transistors [24][28].

Inkjets also have a low resolution limit: the method cannot print well with resolutions below about $20\ \mu\text{m}$ (in printing industry terms, 1200 dots per inch). It is possible to use the spreading of droplets or chemical forces to achieve smaller features in one dimension [29]. Both resolution and viscosity limits can be improved by changing the deposition process to electrohydrodynamic jet (EHD) printing, where an electric field pulls a liquid into a sharp tip from which a smaller droplet is ejected [30]. This has been shown to reach 250 nm resolution [25][31] and is commercially available at $1\ \mu\text{m}$ [32]. But materials must still start in a liquid phase and the reliability issues of clogged or spreading liquid inks are not improved.

¹⁰Most rocks are silicates, so molten silicon might be considered lava.

1.2.2 Resin 3D Printing and Two-Photon Lithography

Another category in high-resolution manufacturing is 3D printing methods that use liquid polymer resins specially formulated to be light-sensitive to harden to a solid upon exposure to the right wavelength. These can be solidified with a light pattern projected with conventional optics (not unlike photolithography), in which case the process is called stereolithography (SLA), or cured at the small focus of a laser, called two-photon lithography.

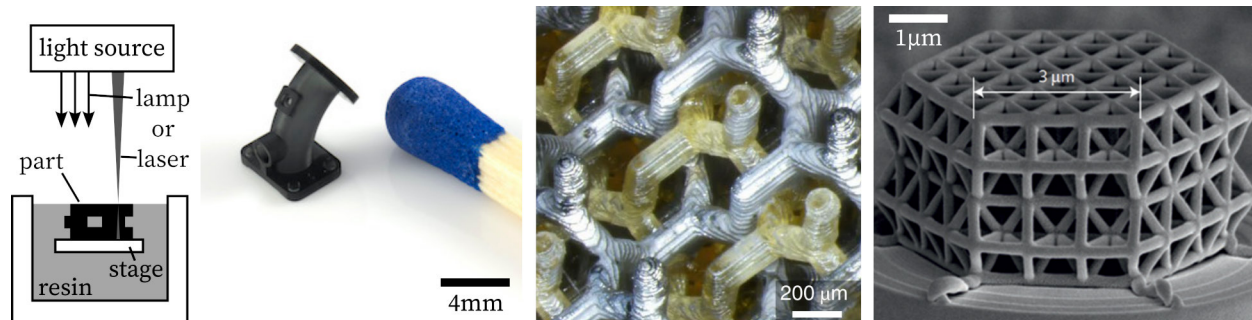


Figure 1.4: From left to right: resin printing techniques use focused light to create one layer of a 3D object at a time, a small tubing adapter made with SLA next to a matchstick [33], a multimaterial lattice printed by switching resin baths during an SLA print [34], and a significantly smaller lattice made with two-photon lithography [35].

These printers are usually only capable of printing a single material at once, and that material must be a light-sensitive polymer resin (a category even more restrictive than inkjet ink). There is some limited multimaterial capability: it is tricky but possible to change materials by moving the part under construction between multiple resin baths during the print. Postprocessing a print with electroless plating can make conductive traces [34], and piezoelectrics can be printed by embedding particles in the resin [36].

But these methods begin to approach interesting resolutions. While SLA 3D printing can only achieve perhaps $10\ \mu\text{m}$ minimum features, two-photon lithography printers, which formulate their resin molecules to require absorption of two photons (not just one) to solidify allowing the intensity of a focal point of a laser to draw below the light diffraction limit, can regularly demonstrate almost $100\ \text{nm}$ resolution [37]. This compares to photolithography (though not precise sub- $100\ \text{nm}$ thin film deposition methods).

The main strength of these resin printing processes is their 3D geometry capabilities, which can build photonic lenses [38] or MEMS actuators [39]. Microfabrication cannot make very complex 3D structures as that would require many photolithography layers which vastly increases fabrication time and cost¹¹. However, the material limitations of resin printing are far too strict for broader applicability in electrical devices.

¹¹Though this has been done in limited circumstances. See [40], which “3D prints” complex sub-millimeter metal mechanisms by microfabricating tens of layers of electroplated metal.

1.2.3 Aerosol Deposition and Cold Spray

Both inkjet and resin printing were limited primarily by their materials. There exists a different category of fabrication methods capable of printing more interesting metals and ceramics: small particles of material, either solids or liquid ink and from the nanometer to micrometer scale, are shot onto a surface in an air jet. This is vaguely similar to the sputtering or evaporation thin-film deposition methods of microfabrication, but faster, less controllable, and with some ability to draw patterns instead of uniformly coating a surface. Many varieties exist: cold spray [41], aerosol deposition [42], cluster beam deposition [43].

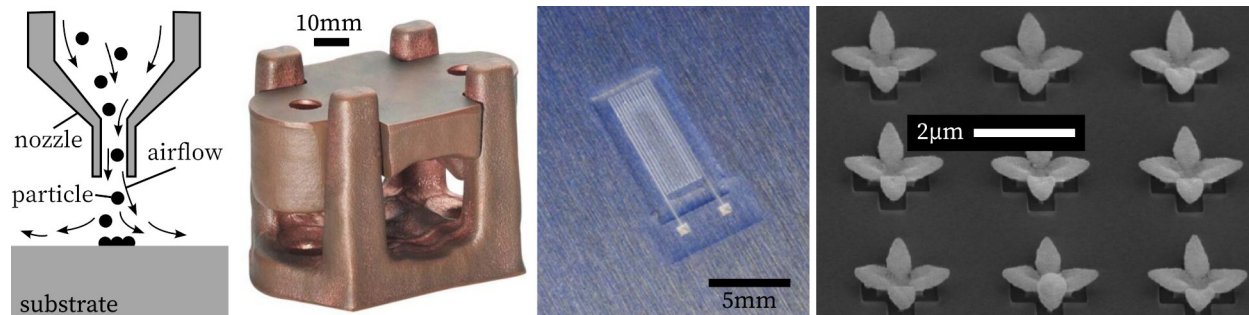


Figure 1.5: Left to right: a diagram of cold spray and aerosol deposition, which differ merely in scale, a copper cable clamp printed by cold spray [44], a silver and polymer strain gauge aerosol jet printed on aluminum [45], and 3 nm copper nanoparticles deposited into 3D shapes by an electric field formed by crosses in a microfabricated mask [46].

Material capabilities are very good and comparable with microfabrication [47]—cluster beam deposition has even been used as a microfabrication thin-film deposition tool [48][43]. It is possible to use liquid inks [49] or solid metals and ceramics which deform then form covalent bonds to the substrate (for details, see chapter 3) [50][51]. Multimaterial structures are easily made via serial deposition. Cold spray methods are used industrially [41] to produce hard ceramic coatings reaching over 90% of bulk properties and to 3D print large metal items [52][42][44]. Transparent ceramics and piezoelectrics are possible [42], and mixing particles gives material gradients [53]. Transistors have been aerosol jet printed with semiconducting inks [54][55][56][57], and depositing pure and doped silicon works [58][47][59].

The main limit of these methods is resolution [60], which requires extremely precise airflow. An aerodynamic lens is a particular fluid dynamic structure that focuses a given particle diameter [61]; sufficiently good control allows resolution down to $\approx 10 \mu\text{m}$ [62] but is ultimately limited by Brownian motion (section 4.2.1). Some promising experiments¹² use electric fields from charged masks to direct charged nanoparticles during deposition with sub-micron results [63][69][68], but this has not been explored fully or developed into a general printing method. As we will see shortly, the method proposed in this dissertation is essentially aerosol deposition with a better electrostatic focusing method bolted on top.

¹²These papers [46][63][64][65][66][67][68] were among the strongest a priori evidence that this dissertation's proposal could eventually work. [64] demonstrates minimum feature sizes as low as 35 nm!

1.2.4 Other Methods

Besides inkjet, resin printing, and aerosol deposition, there are many less common fabrication techniques still worth mentioning [70]. Some scale to higher resolutions than microfabrication with impressive capabilities, but all currently have some material or practicality limit that has prevented their use for semiconductor device manufacturing.

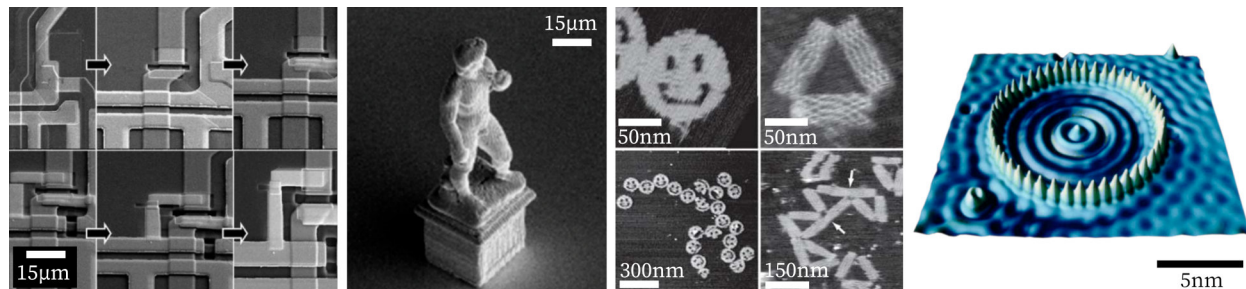


Figure 1.6: Left to right: circuit traces from tungsten and SiO_2 made with FIB [71], a statue electrochemically printed in copper [72], geometrical patterns made from assembled DNA molecules [73], and 48 iron atoms arranged on a copper surface via STM [74].

Focused beam tools: some methods electromagnetically focus a beam of electrons or atoms in vacuum, then use the narrow beam to interact with the surface of a material [75][76]. This includes scanning electron microscopes (SEMs), but the beam can locally initiate a chemical reaction with a surrounding gas to deposit material [77] as in focused electron (or ion) beam induced deposition (FEBID and FIBID)—or cure photoresist, in electron beam lithography. A focused ion beam (FIB) tool etches away material. These methods can reach sub-10 nm resolution but are very slow with limited material choices (e.g., no doped semiconductors). Combination “multibeam” FIB, FIBID, and SEM tools are used commercially to investigate, debug, and rewire small parts of microfabricated integrated circuits¹³ [71][78][79]. Extensions of these methods have managed to deposit single atoms with sub-100 nm resolution [80]. All these are similar to what we propose; see section 6.5.4 for a detailed comparison.

Spatial atomic layer deposition (ALD): standard ALD, which creates films of atomically precise thickness by repeatedly layering certain gas precursor molecules, is common in microfabrication. By focusing these gases through a small nozzle scanned over a substrate it is possible to draw 2D patterns [81][82][83][84] (for CVD: [85][86]). However, the chemistry limits materials to what chemical precursors are available, and the nozzle resolution is a large $100\ \mu\text{m}$ giving its atomically thin prints somewhat unwieldy large width-to-height ratios, making any devices simultaneously wider and slower to make than is practical¹⁴.

Electrochemical printing: it is possible to deposit pure metals electrochemically [87] on a substrate submerged in a liquid bath through a small (microfabricated) nozzle with near $1\ \mu\text{m}$ resolution [72][88]. Parallelism to print large objects is possible [89]. This method is restricted to metals capable of electrochemical deposition, i.e., no insulators or semiconductors.

¹³A FIB tool was likely used to make the chip cross-section in figure 1.1.

¹⁴It is possible that spatial ALD/CVD makes a good companion method to this dissertation’s nanoparticle printing process, which should be generally more capable but worse at controlling film thickness.

Laser direct write: like focused beam tools, a laser can induce local material deposition [90]. Laser chemical vapor deposition (LCVD) directs a gas-to-solid reaction that can print metal [91] but is very slow. In laser induced forward transfer (LIFT), a thin film of material is suspended over a substrate where it (or a donor layer) is selectively hit by a focused laser to expand and fly off onto said substrate [92]. This can work with a broad range of materials including solid metals, but minimum resolution is typically limited to 1 to 20 μm .

DNA nanotechnology: in a dramatically different approach, it is possible to generate DNA strands that fold in liquid solution into nanoscale structures with near 1 nm resolution and atomic precision [93][94][73]. This makes millions of copies of the same structure, randomly arranged. Significant research is in progress, but there is not yet a reliable way to make electrical devices from these or connect them to even microfabricated circuitry.

Scanning probe lithography: in atomic force microscopy (AFM) and scanning tunneling microscopy (STM), a near atomically sharp tip is dragged over a surface with subatomic resolution to image it. This can instead be used for fabrication by selectively heating a substrate, transferring ink (“dip-pen lithography”), or even electrostatically pushing individual atoms [95][96][74]. These methods reach the highest resolution of anything discussed (comparable to or exceeding focused beam methods) and have been used to build parts of transistors [97], but are impractically slow and generally only capable of moving a single type of material at a time. Best used in combination with other methods.

1.3 Our Proposal: Nanoparticle Printing

We are now well-positioned to design a new fabrication method that avoids the limitations of existing methods to achieve the multimaterial high-resolution capabilities that semiconductor devices require.

In order to print standard materials—metals, semiconductors, and oxides—we’ll use vacuum deposition similar to aerosol deposition or focused beam tools (or the physical and chemical vapor deposition processes used in microfabrication itself). Methods that operate with or in a liquid, like inkjet printing, two-photon lithography, and electrochemical printing, are too strongly restricted by chemical compatibility and material properties of their liquids. The ability to control the pressure, temperature, and composition of the environment around any part under construction is much more likely to provide in high-quality results than remaining in standard atmosphere or liquid.

To reach sufficiently high resolution, we’ll ignore the small nozzle approaches of inkjet and electrochemical printing (which are limited to about 1 μm and can be unreliable due to clogged nozzles), focused light methods like photolithography and two-photon lithography (which are mostly diffraction-limited and constrain material properties), and gas jet focusing of aerosol deposition (which is limited to 10 μm by Brownian motion and inability to more precisely control fluid flow). We’ll instead use the electrostatic focusing found in EHD printing and focused beam tools. This has no fundamental resolution limit as the electromagnetic field scales well below atomic level; the final theoretical resolution (which will be sub-1 μm) will come from other implementation details (chapter 6).

Specifically, we'll try to make the following idea work: begin with nanoparticles (clumps of atoms, as individual atoms would be too slow) of standard microfabrication materials, focus these electrostatically in vacuum, and impact them onto a substrate, where they should meld with the surface as in aerosol deposition methods. Switching between types of particles would allow multimaterial prints. If successful, nothing should prevent manipulation and printing of pure (and doped) semiconductor nanoparticles at very high resolutions.

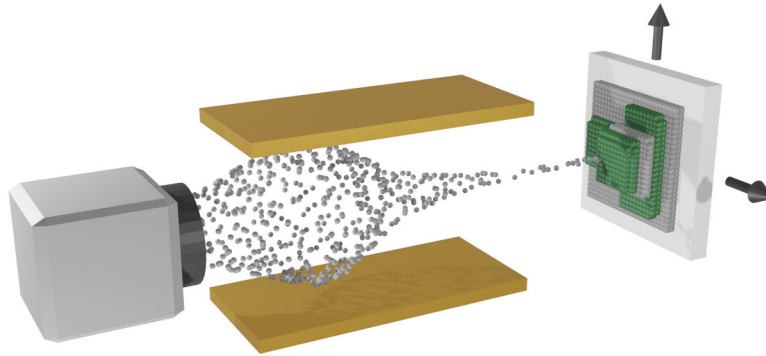


Figure 1.7: A cartoon of the basic idea: nanoparticles are generated (left), focused and accelerated in vacuum via electric fields between electrodes (gold, center), and finally shot onto a substrate, which is moved by a motorized XY stage in two dimensions to draw a pattern. Switching between types of nanoparticles would allow depositing different materials.

As we saw in the prior art, this idea is fundamentally similar to gas jet processes like cold spray, aerosol deposition, and cluster deposition, but we add electric fields to focus particles beyond the limits of fluid dynamics. It has been recognized that focusing resolution is the main limit to using aerosol deposition for nanoscale manufacturing [60], and several groups have previously proposed using electric fields for this [98][99][100][64][63], but none have figured out an ideal general solution. As we will see, this thesis develops a more capable electrostatic focusing mechanism that should achieve higher resolution. Our method is also similar to focused ion beam tools (see section 6.5.4) but uses nanoparticles instead of single atoms and at lower impact velocities.

In the rest of this dissertation, we'll discuss our progress engineering each part of this system. In chapter 2 we will see how to create nanoparticles in inert gas, and chapter 3 will theorize what needs to be done to print them. Some minimal low-resolution but multimaterial deposition is surprisingly straightforward with aerosols in chapter 4. To achieve higher resolution we describe the process of electrically charging nanoparticles in chapter 5 as a prerequisite for chapter 6, where we find electrostatic focusing mechanisms are common across particle accelerators and mass spectrometry then design our own with techniques theoretically capable of printing with sub-1 μm resolution. Finally, in chapter 7, we will summarize our results: although we didn't manage to demonstrate a complete system or print a transistor, we came close, showed partial success, and have a short roadmap toward a full demonstration with no major roadblocks. We'll show this printing process has the potential to be easier, cheaper, and faster than microfabrication for some limited applications, achieving our original goal.

Chapter 2

Nanoparticle Generation

The first step in printing nanoparticles is to, well, somehow obtain nanoparticles. We'll discuss what this means then detail our construction of two custom nanoparticle sources.

What is a nanoparticle? For our purposes, a nanoparticle is just a clump of atoms. Assume it is roughly spherical and we can define its size by its diameter, which we'll typically want to be between 5 nm and 50 nm or so (in the nanometer range, thus “nanoparticle”). We'll use nanoparticles of all the same type of atom: all silicon or all aluminum, perhaps, though sometimes we might use slightly doped silicon¹ or an oxide like SiO₂.

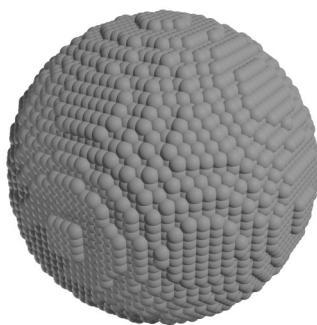


Figure 2.1: A cartoon representation of a simple example nanoparticle. Each gray sphere is an individual atom. This is about 42 atoms wide, or perhaps 10 nm in diameter, with about 40000 atoms in total. Note many inorganic nanoparticles are small enough that their crystal structure becomes monocrystalline or amorphous, not polycrystalline [101].

Nanoparticles are common [102]. Any aerosol, like smoke or fog, is simply small solid or liquid nano (or micro) particles moving around in a gas. Many more complex biological molecular structures, like viruses or organelles, could arguably be considered nanoparticles. For our purposes, however, we'll stick to spherical nanoparticles of a single solid material.

¹This is important—it is why printing semiconductor devices with reliable doping should be possible.

Why do we want nanoparticles in particular? The trouble comes from our desire to place small bits of matter serially. We could try printing single atoms one at a time, but that would be slow²: even at a ridiculously fast 1 million atoms per second, even a tiny 100x100x1 μ m chip would take multiple years to print, not to mention this is overkill as we probably couldn't place those atoms with atomic resolution anyway. We could speed this up at the cost of spatial resolution by printing a cloud of several atoms hitting the same area at once³—but at this point we might as well use nanoparticles, which we'll see squish together on impact to give a similar result (see chapter 3) and print faster than atoms when charged (see section 6.5.3). On the other hand, if we printed even larger clumps of atoms (say, 10 μ m diameter), we couldn't get the sub-1 μ m resolution we need for semiconductor devices.

For reference, here are the approximate number of atoms in and total masses of nanoparticles of some particular diameters and materials, assuming the same densities as in bulk:

	Au (gold)	SiO ₂ (glass)	Si (silicon)	Cu (copper)
atoms, 1 nm	31	42	26	44
atoms, 10 nm	30900	41700	26200	44500
atoms, 100 nm	30900000	41700000	26200000	44500000
mass, 1 nm	1.01×10^{-23} kg	1.39×10^{-24} kg	1.22×10^{-24} kg	4.69×10^{-24} kg
mass, 10 nm	1.01×10^{-20} kg	1.39×10^{-21} kg	1.22×10^{-21} kg	4.69×10^{-21} kg
mass, 100 nm	1.01×10^{-17} kg	1.39×10^{-18} kg	1.22×10^{-18} kg	4.69×10^{-18} kg

Table 2.1: Some example nanoparticle properties calculated with densities from [103].

2.1 Nanoparticle Generation Methods

Because nanoparticles are so prevalent, significant study has gone toward simple reliable ways of making them. Breaking down larger material by physical grinding or aerosolizing a liquid tends to make larger particles, but nanoparticles are small enough they can be grown from individual atoms sticking to each other under the right conditions.

The most common particle generation methods include:

- **Mechanical milling:** Large chunks of material are ground down into powder via mechanical action [104][105]. Resulting particles are larger than at least 100 nm as smaller particles melt together (elaborated on below). Can be used to alloy materials together (frequently used in metallurgy).
- **Atomization:** Also referred to as nebulization or aerosolization. Gas is blown through a liquid, making small droplets carried as an aerosol in the gas [106]. Used for aerosol deposition, paint guns, and air fresheners. It is also possible to atomize molten (liquid) metal, which is a common way to mass-produce metal powder in industry [107], or even

²This has kind of been done, excruciatingly slowly: see [80] or [74], and section 6.5.4.

³Microfabrication thin-film deposition processes like evaporation, sputtering, and CVD arguably deposit clouds of single atoms over an entire wafer (without patterning), in minutes to hours.

blow air through a metal powder instead of a liquid. All these result in fairly large particle sizes in the micrometer range.

- **Electrospray:** A high voltage can be used to draw a liquid out from a narrow nozzle (a “Taylor cone”) and break it into droplets [108][109]. This can make liquid nanoparticles, but the liquid can also evaporate to leave molecular ions or nanoparticles that were already in the liquid solution [110][111][30][112]. Commonly used in mass spectrometry to remove molecules from a liquid solution. Slow compared to other methods⁴.
- **Liquid nucleation:** One of most reliable ways of making particles truly in the nanometer size range. Atoms or molecules are dispersed in a liquid solution carefully engineered so these atoms nucleate and stick together to grow nanoparticles [113]. Commonly used in biomedical applications or research. Pre-grown nanoparticles in liquid are commercially available in many different materials [114].
- **Vapor nucleation:** Also called gas phase nucleation, vapor synthesis, or aerosol synthesis. Similar to liquid nucleation but in a gas. Commonly occurs in the atmosphere (for example, cloud formation) [115][116], and making metal particles is possible. Can even happen in microfabrication processes like CVD [117] or PVD [118].

Note several more methods exist to generate individual atoms as ions for focused ion beam sources (see chapter 5 and section 6.5.4), but these are generally too small and the production rate and efficiency too low for what we want.

Of all these methods, which do we choose? Vapor nucleation is the most promising.

Recall our materials need both very high material purity and dimensions below 100 nm. The need for high purity to sometimes better than one part per billion (see chapter 1) by itself rules out mechanical milling—which might contaminate particles with atoms worn off the milling apparatus by mechanical contact—or atomization, liquid synthesis, and electrospray methods, in which case the particle might be somewhat contaminated by the surrounding liquid. Vapor nucleation is a promising option because no atoms are involved save the material we want and a background gas, which can be chosen to be an inert noble gas (He, Ar, etc.) that should not react with the nanoparticles.

The nanoparticle size also matters significantly. Sufficiently small nanoparticles (below our approximate threshold of 1 μm or so, not entirely coincidentally) react very easily with their surroundings. Because of their size and geometry, a large fraction of their atoms are near their surface with freedom to move. The resulting surface energies are much higher than in bulk [119]. This also decreases the melting point of nanoparticles—in fact, nanoparticles often melt into to each other slightly at room temperature. The result is that nanoparticles packed together as a powder, like an everyday bag of flour⁵, will tend to agglomerate until

⁴We briefly tried electrospray, without much success. Dr. Williams of [111] informed us producing up to 10k 100 nm particles per second is typical for use in charge detection mass spectrometry. That is a mass rate of $1 \times 10^{-3} \text{ mg h}^{-1}$, 3 orders of magnitude slower than our spark ablation and laser ablation sources.

⁵The reader may be familiar with dust explosions from clouds of flour or metal. These are a result of particle surface reactivity: an exothermic reaction with a surrounding gas, multiplied by the large surface area of a collection of particles, is a significant amount of energy. Dust explosions are often from more easily manufactured microparticles; nanoparticles, due to higher surface energies, would be worse.

their clumps reach at least micron size scales⁶ [120]. In order to store nanoparticles, we'll need to either keep them in a liquid (which has contamination concerns, as noted previously) or levitate them in a gas. This last option best fits vapor nucleation.

2.1.1 Vapor Nucleation

This is how vapor nucleation creates nanoparticles [121][122][123][124]:

The material we want to make nanoparticles of is first vaporized into a cloud of its constituent atoms. This is easy enough to do by any of several methods: add enough energy and any solid or liquid will evaporate, sublime, or otherwise break up into a gas or plasma.

As this cloud of atoms cools down, it loses thermodynamic stability (is supersaturated), at which point multiple effects occur at different rates: atoms condense and form clusters (another name for very small nanoparticles with mere tens of atoms), these clusters collide and coagulate into larger clusters (which coalesce into uniform crystalline structures), and some atoms evaporate off existing clusters to make them shrink again. These processes happen simultaneously at different rates. According to classical nucleation theory, which compares the growth of cluster surface area (increasing instability due to evaporation) vs. volume (increasing stability from bulk energy), clusters become stable and continue to grow above a critical diameter; below this they dissipate [43][125][126][127]. The result is a distribution of particle sizes (often lognormal [128][102]) around some nonzero mean value. Particles are mostly rather chunky polyhedra but are close enough to spherical for our purposes.

This can work in vacuum [47][43] but also in gas⁷ (preferably an inert gas that does not react). This gas can modify the process by, e.g., adjusting the cooling rate or atom collision frequency. It is also possible this gas reacts with the nanoparticles to add an oxide layer or other coating, possibly making multimaterial nanoparticles [60][128], and trace contamination levels can be maintained below the limits required in microfabrication [129]. As we will see in chapter 4, using a gas medium also lets us conveniently move nanoparticles.

Many options exist to implement vapor nucleation [130][101]. The atom vapor can be generated by directly heating a solid [131], magnetron sputtering [132], electrical joule heating, or a laser, and the resulting cloud moved through assorted pressure differentials and geometries. Accurate quantitative analysis of nucleation is possible but somewhat involved [125], so for purposes of this work we'll start with trial and error based on existing literature results.

In order to develop our proposed nanoparticle printer, we began by building a spark ablation nanoparticle generator but eventually switched to laser ablation to improve consistency, material capability, and system compatibility.

⁶Selective laser sintering (SLS) 3D printing, which melts together layers of metal or plastic powder with a laser, is limited in resolution by its particle diameter, which cannot be below 1 μm for this reason [120]. If we successfully print nanoparticles, we will have turned this previously undesired effect to our advantage.

⁷This nucleation process also works in liquid—that's what aforementioned liquid nucleation is—and is closely related to how crystals grow in general.

2.2 Spark Ablation

As the first step in developing a nanoparticle printer, we built a spark ablation nanoparticle generator as a source with which to test nanoparticle manipulation and printing.

Spark ablation begins with repeated electrical spark discharges between two electrodes of the desired material. The large current of each spark through a small area on the surface of the electrodes results in localized joule heating, vaporizing that part of the electrodes, from which vapor nucleation proceeds. A background gas at significant pressure is required for the initial spark and can also carry the nanoparticles away to a point of use.

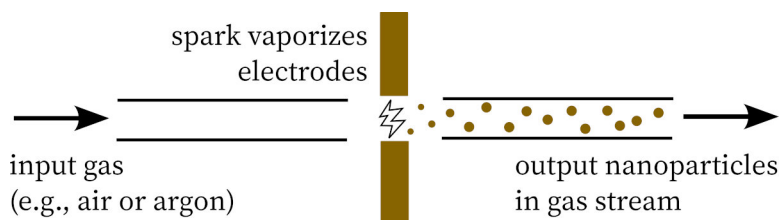


Figure 2.2: A minimal cartoon illustrating spark ablation nanoparticle generation. A spark locally heats and vaporizes two electrodes, the vapor from which condenses into nanoparticles which are pushed along in a gas flow.

This method was first introduced in 1988 [133] and has since seen wide use [134][128][68] with little change to its fundamental principles⁸. Its advantage is simplicity⁹: the only equipment required for a minimal system is several electrodes and tubing assembled with merely millimeter precision in atmosphere and a small high-voltage circuit. Metal nanoparticles are easy, and spark ablation has also been shown to make doped silicon nanoparticles [58]. Although the electrodes must be conductive so creating insulating nanoparticles directly is not possible, metal nanoparticles can be oxidized if the surrounding gas contains oxygen [128], giving us all the basic materials semiconductor devices need.

We constructed the system shown in figure 2.3. The spark discharge apparatus itself is held in an airtight KF-25 6-way cross vacuum fitting to allow control of pressure and gas movement. Two metal electrodes of the material we want to create nanoparticles out of and about 1 mm in diameter are held in miniature brass drill chucks, which are connected to custom vacuum feedthroughs built of stainless steel KF-25 fittings, copper wire, SLA 3D printed parts from Formlabs Durable resin [135], and Loctite Hysol 1C epoxy¹⁰. The electrodes are connected to external spark circuitry by alligator clips¹¹ on the feedthroughs. The electrodes can be

⁸Spark ablation generators are commercially available from [51] (a company founded by Dr. Schmidt-Ott of [133] and [128]). These off-the-shelf generators are well-engineered with optimized electrode geometry and improved circuitry but cost (quoted) \$80k each. We chose to build our own for better system integration, to more easily handle multiple materials in the future, and to avoid dwarfing the rest of the nanoparticle printer cost as tabulated in section 7.2.1.

⁹Contrast this with cluster beam synthesis methods, which more conventionally heat metals to increase their vapor pressure and need a high vacuum [43], or laser ablation which needs a sufficiently capable laser.

¹⁰Which is compatible with high vacuum systems and cheaper than competing Torr Seal brand epoxy.

¹¹Carefully monitored. Please do not use alligator clips for high voltages on a production system.

removed and replaced by unfastening the KF-25 clamps holding them to the 6-way cross and are adjusted until the gap between the electrodes is 1 mm to 2 mm¹². We were thus able to change the electrode material to anything in a thin cylindrical form factor including off-the-shelf copper, steel, and gold wire¹³, or even pieces of a shattered p-type silicon wafer fit into the chuck¹⁴.

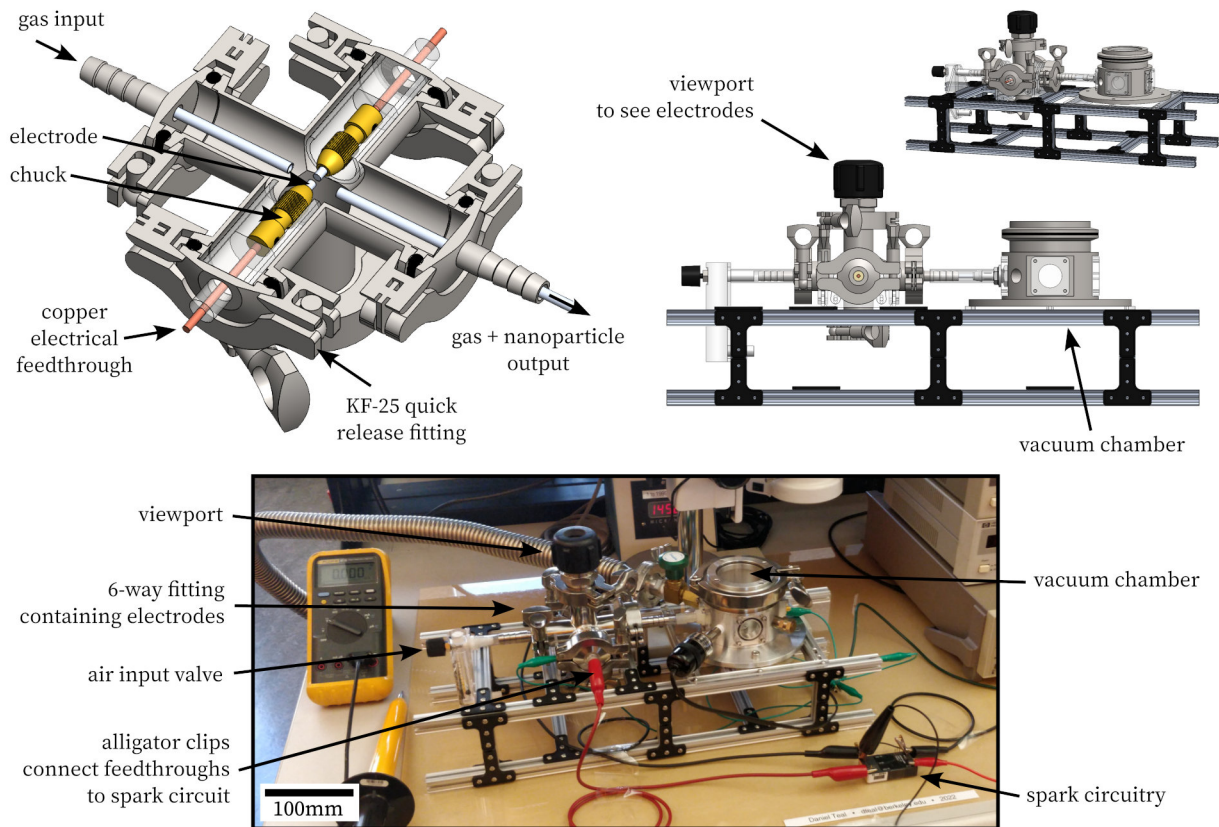


Figure 2.3: Spark ablation nanoparticle generation system. Top right: a CAD model cross-section showing the spark electrodes and tubing. Top left: CAD model of entire spark ablation test setup including input gas flowmeter/valve, generator, and secondary vacuum chamber. Bottom: physical implementation of the above system also including a small high-voltage spark circuit and a high voltage multimeter.

¹²While this worked, we recommend future engineers build a system to more easily finely adjust the distance between these electrodes, which is an important quantity in spark behavior.

¹³A 55 mm long 0.38 mm diameter 24K (0.9995 purity) gold wire was purchased from an eBay vendor for \$29, equal to the raw material cost plus a significant markup. This demonstrates the extreme material efficiency possible in nanoparticle printing (elaborated on in section 7.2.3). A minimal microfabrication gold evaporation or sputtering target needs to be significantly larger and thus often costs \$10k or more.

¹⁴Cylindrical silicon rods are available but much less common than flat wafers, especially in electrical semiconducting grades. This is another point in favor of laser ablation, which can use flat material targets.

Perpendicular to the electrodes are two aluminum tubes of 4 mm inner diameter, each about 1 cm from the electrode centerpoint. One tube about 150 mm long connects to a vacuum chamber continually pumped to a steady-state pressure of about 1 Torr (below 1% of atmospheric pressure, 760 Torr), while the other is about 100 mm long and connected to a needle valve (and rotameter for flow measurement) to atmosphere. Air is continually pulled at about 1 L min^{-1} through the needle valve, past the spark discharge electrodes—where it hopefully picks up nucleated nanoparticles from spark-generated vapor—and into the vacuum chamber. Note replacing air with argon would reduce oxidation, but in both cases our small nanoparticles should primarily follow the airflow rather than gravity (see chapter 4). We estimate the pressure of the air around the spark electrodes to be between 0.5 and 1 atmospheres. An ideal setup might increase this pressure up to several atmospheres of pressure, which results in higher breakdown voltage¹⁵ and spark energy and thus more material vaporized and a higher nanoparticle generation rate [136].

The next step is to create sparks between the electrodes. A spark can be created by applying a high voltage that exceeds the breakdown voltage of the surrounding gas at its pressure and distance, which is given by Paschen’s law as in figure 2.4. The resulting electron avalanche makes a conductive plasma pathway that short-circuits the electrodes, causing a large current and significant heat. The longer this current can be sustained, the larger the spark¹⁶. Repeat this process to continually generate nanoparticles.

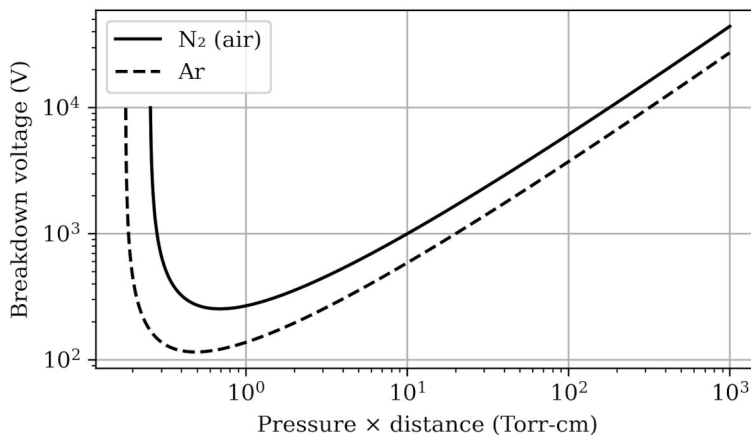


Figure 2.4: A graph of Paschen’s law, which gives the voltage required to cause gas breakdown via electron avalanche (Townsend discharge) between two electrodes at a given pressure and distance (which are not independent). Curve data (from [137]) is approximate; these curves can vary significantly [138]. At high pressures, the lower gas mean free path requires a larger voltage to accelerate electrons to avalanche energies. At low pressures, there are too few stray electrons and gas atoms to produce an avalanche. Our spark discharge setup is slightly to the right of center. Note also there is never breakdown below a minimum of a couple hundred volts even if electrodes are very close together. This will be important in chapter 6.

¹⁵The dependency of spark behavior on pressure means the pressure cannot be varied solely to optimize nanoparticle nucleation. This is another downside of spark ablation that laser ablation does not share.

¹⁶This is a miniature lightning bolt.

We created these sparks with the circuit of figure 2.5. An XP Power FS20-12 2kV DC 5mA power supply was connected in parallel with a 47nF high voltage capacitor and the spark electrodes. The power supply slowly charged the capacitor until it exceeded the gas breakdown voltage, typically around 1.5 kV, at which point the full charge of the capacitor, around 50 mJ, was discharged in a spark. Increasing spark energy should increase vaporized material and, somewhat, particle size [136][134]. This process repeated at about 10 Hz to 20 Hz, with random fluctuations [136], rate limited by the power supply current. Nanoparticle production rate is proportional to frequency; the literature exceeds 150 Hz [136].

Safety note: high voltage is dangerous. The low kilovolt level and 50 mJ spark energy used here is enough to potentially cause electrical injuries. As safety measures, high voltage wires were placed safe distances apart to avoid breakdown in air between wires, the vacuum chamber was connected to earth ground, a bleeder resistor discharged the capacitor, and the system was completely disconnected when not in use.

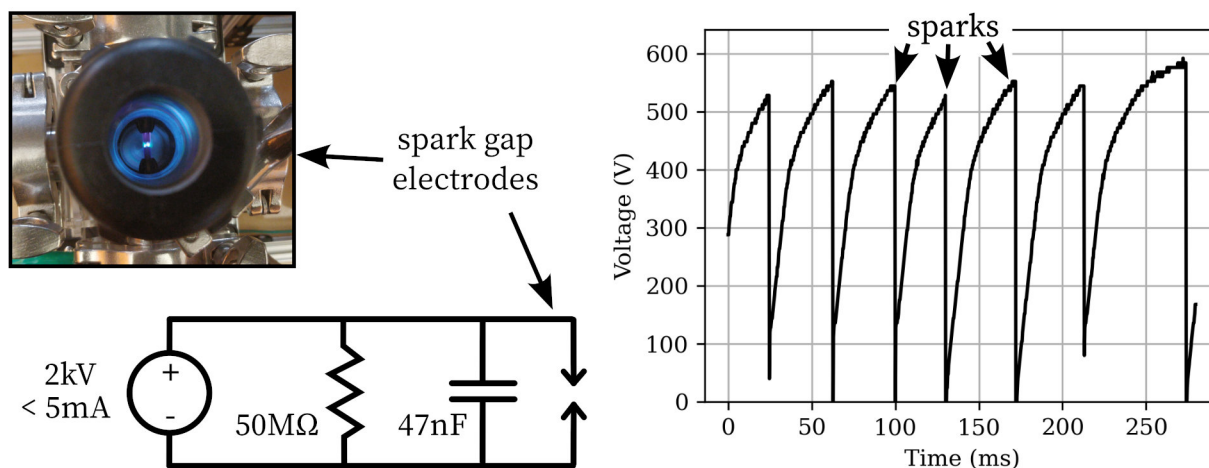


Figure 2.5: Top left: picture of a spark between electrodes seen through viewport. Bottom left: spark circuit diagram. Right: measured voltage across electrodes vs. time (albeit at a lower pressure and voltage than typical), showing multiple sparks with variable timing.

At this point we almost have all the hardware required to implement spark ablation except that we are missing a way to detect and measure the resulting nanoparticles to know whether it worked. This is nontrivial as each sub-100 nm particle is too small to be visible in the 1 μm diffraction-limited resolution of an optical microscope and even a cloud of nanoparticles in gas is still too diffuse to be seen. Instead, the standard tool for nanoparticle and aerosol detection and measurement is a differential mobility analyzer (DMA) from aerosol science [102]. A DMA takes as input a stream of nanoparticles in gas (precisely like we hope to make), electrically charges these nanoparticles (typically via radiation-based diffusion charging; see chapter 5), then detects an electric current from particles hitting a conductive plate (a

Faraday cup). Carefully deflecting particles with an electric field allows only a subset of particles with a particular air drag mobility coefficient to be detected, and scanning over these subsets produces a histogram of nanoparticle diameters. But although DMAs are widely used in the literature [136], we were not able to access one. This does not matter too much yet—this project’s focus is on nanoparticle deposition and manipulation; the particles themselves can be characterized further in future work.

Instead, we chose to directly deposit nanoparticles on a surface where a sufficiently large deposit built up over time should be visible and perhaps measurable via optical or electron microscope. This is also a common practice in aerosol science, where it is called impaction [102] (and is also the principle behind aerosol deposition): nanoparticles are either caught in a gas-permeable filter or shot out of a nozzle where their inertia suffices to make them impact a surface (for more details, see chapter 4). We implemented these methods by adding a filter¹⁷ or a 0.21 mm ID nozzle 1–3 mm from a substrate, respectively, to the setup vacuum chamber as shown in figure 2.6. After initial filter paper tests, we continued only with nozzle-based impaction to allow the use of many kinds of substrates.

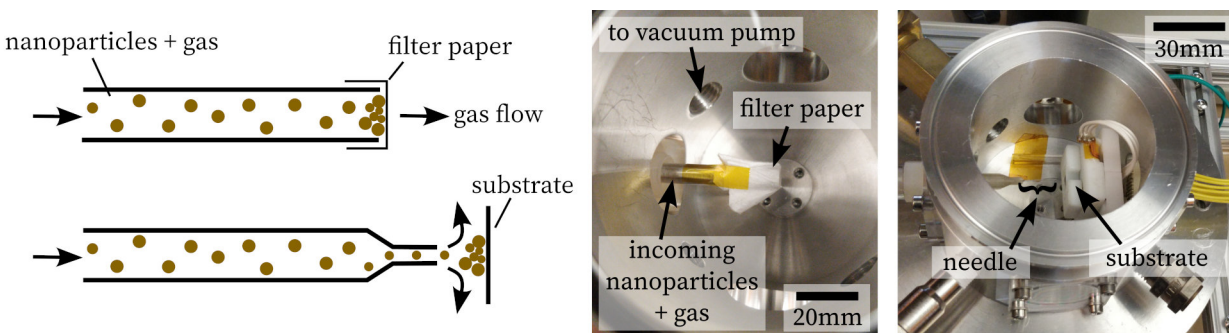


Figure 2.6: Left top and bottom: cartoons illustrating aerosol collection via filter or impaction, respectively. Center: nanoparticles moving through metal tubing from spark ablation generator into secondary vacuum chamber are captured by a filter attached to the open tube end. Right: the filter is replaced by a dispensing needle placed several millimeters from a substrate (that could be any flat surface but here is actually a custom XY stage).

We are finally ready to test nanoparticle generation. As pictured in figure 2.7, we began with copper electrodes and observed reliable deposits on filter paper, steel, and silicon after a deposition time of tens of seconds. Gold deposits well on steel but not glass, in which case it adheres to itself but flakes off the substrate. This is frequently seen in standard microfabrication due to gold’s inability to oxidize; an adhesion layer of chromium or titanium is placed between SiO_2 and gold. All these are excellent signs: we successfully transferred material from electrodes to substrate and can conclude nanoparticle (or microparticle) generation is at least minimally functional.

¹⁷As filter paper we used Filtrete Ultra Allergen vacuum bags, which claim to trap 99% of airborne particles 1 μm or larger. For a more repeatable result, [58] chose Millipore Durapore 0.45 μm PVDF filters.

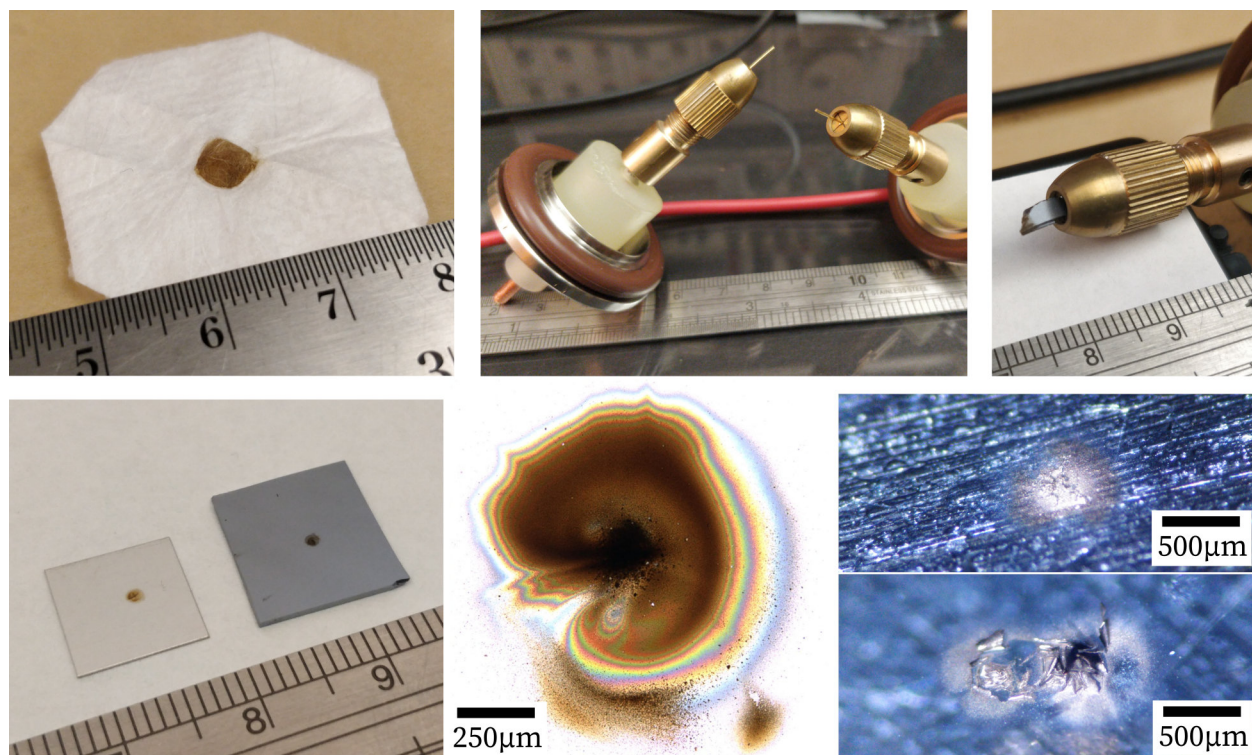


Figure 2.7: Spark ablation results. Clockwise from top left: copper deposited on filter paper. Gold wire electrodes mounted to chucks and feedthroughs. A silicon wafer shard as electrode. Gold deposited on steel (above) and glass (below); note the gold adheres to itself but not to the glass. A micrograph of a very large copper deposit on silicon demonstrating variation in particle diameter and airflow. Finally, copper on steel (left) and silicon (right).

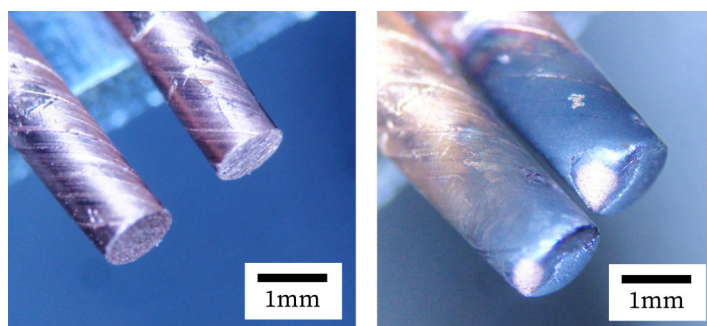


Figure 2.8: 1.3 mm diameter copper electrodes before (left) and after (right) being used as spark discharge electrodes. SEM EDS analysis suggests the black film may be carbon.

Now that we have a working spark ablation nanoparticle generator, we can perform at least some minimal characterization as previously noted before continuing to study nanoparticle movement in later chapters.

Rate measurement: we approximated the production rate by measuring copper electrodes (figure 2.8) before and after generating nanoparticles for 1 hour (spark rate 1 Hz to 5 Hz). We found a total mass loss of 0.6 mg, i.e., nanoparticles are made at 0.6 mg h^{-1} (if 10 nm, 3.5×10^{10} particles/s). The literature, using a better spark power supply capable of 100 Hz operation, reports anywhere from 1 to 30 mg h^{-1} [136]. This is a good sign we have successfully replicated the prior art. These are also convenient numbers for microfabrication: at only 0.6 mg h^{-1} a reasonably sized $10 \times 10 \times 0.01 \text{ mm}$ chip¹⁸ could be printed in 15 hours.

Nanoparticle size: as stated earlier, the nanoparticle size distribution can be approximated by analysis of deposits. We impacted copper nanoparticles on a clean silicon wafer for 2 min to create the large deposit pictured in the bottom center of figure 2.7. Based on that image as well as the SEM¹⁹ results shown in figure 2.9, it appears the majority of particles fell below $\approx 100 \text{ nm}$ and formed a thick solid (and cracked) film; a minority of particles were $1 \mu\text{m}$ to $10 \mu\text{m}$ in diameter. This is excellent: we are generating sub-micron particles and future work should be able to characterize and control this further.

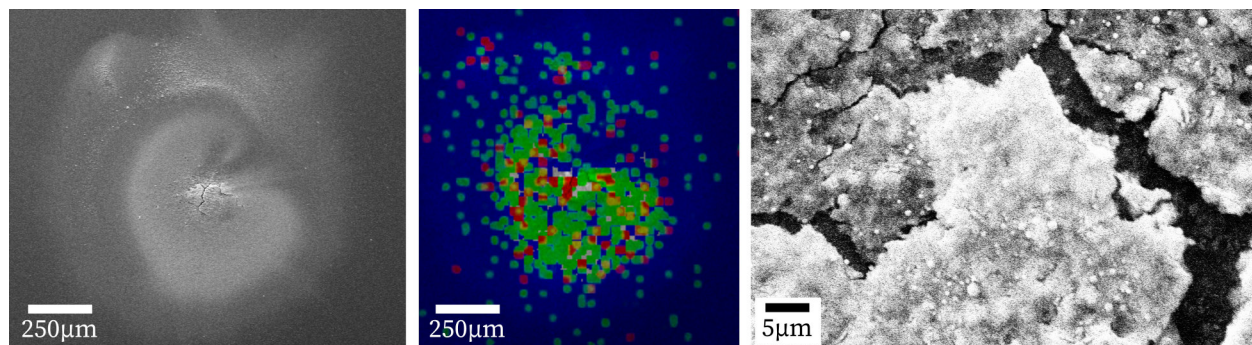


Figure 2.9: Left: SEM image of copper deposit on silicon. Observe the thick cracked film in the center and some larger particles near the top. Center: energy dispersive x-ray spectroscopy (EDS) image showing elemental composition. Blue is Si, green is O, red is Cu: apparently the copper is heavily oxidized (as expected due to our use of air; see section 4.3.3). Right: close-up SEM image of deposit center showing a cracked film presumably formed of agglomerated sub-100 nm particles plus several larger particles.

Although our spark ablation nanoparticle generation appears to be a success, the method has several problems. First, it cannot create insulating nanoparticles without inconvenient gas-phase oxidation reactions [128]. Second is its inconsistent generation rate: nanoparticles are generated in groups at each spark instead of in a continuous stream. Finally, the sparks creates very significant²⁰ electromagnetic interference (EMI). These limitations all have workarounds (conductive particles can be oxidized, particles can be buffered into a steady stream, and EMI can be shielded), but were enough to prompt us to experiment with a second vaporization method: laser ablation.

¹⁸This is typical. Chips made with the SkyWater SKY130 130 nm microfabrication process are $12 \mu\text{m}$ of transistors and wiring atop a silicon substrate [139], and most chips are several millimeters on a side.

¹⁹After testing the sample to ensure no particles would be released into the SEM chamber as required by its maintainers. We chose to minimize SEM usage for the rest of this dissertation over these concerns.

²⁰We observed 9 V oscillations on a nearby 12 V DC lab power supply due to spark-generated EMI.

2.3 Laser Ablation

We implemented a laser ablation nanoparticle generator after finding the previously mentioned limits of spark ablation. This laser-based process is very similar. Instead of vaporizing electrodes with joule heating from a spark, material targets are instead vaporized by a laser; the rest of the apparatus can remain identical. Compared to spark ablation, EMI should be insignificant, the generation rate more constant, and material capabilities broader.

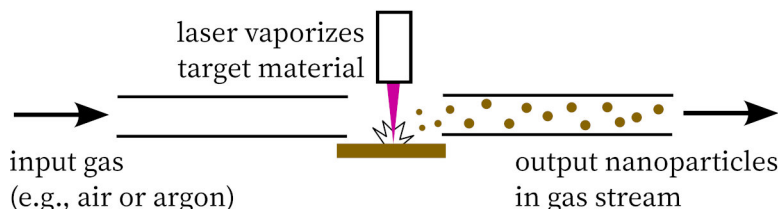


Figure 2.10: A simple cartoon illustrating laser ablation nanoparticle generation. A laser of the correct wavelength and intensity heats and vaporizes material, which condenses into nanoparticles which are pushed along in a gas flow.

This method is widely used with a variety of conducting, semiconducting, and (unlike spark ablation) insulating oxide materials [140] and has existed since at least 1981 [141][142]. The fundamental laser vaporization process is the same as used in laser cutting and machining [91] since 1962 [143]: a laser is absorbed in a material, generally via exciting electrons, and the energy is quickly coupled to the surrounding nuclei as heat²¹. If the incoming laser power is sufficiently larger than the rate at which heat is conducted and spread throughout the material, part of the material will become hot enough that it vaporizes. The material target can be a flat surface or a microparticle aerosol [147][148][149].

For our purposes, we need only that the laser (a) is of the correct wavelength to be quickly absorbed and (b) has peak intensity sufficient to heat material to vaporization. Metal machining most commonly uses 1064 nm wavelength lasers [150], and higher intensities can be achieved by pulsing the laser (in nanoseconds or shorter) instead of a lower constant average power (“continuous wave”). The laser ablation source of [142] used a 1064 nm Nd:YAG pulsed laser (5 ns and 10–30 mJ per pulse) to evaporate metals within a helium carrier gas at 1 to 2 atmospheres of pressure. Adjusting gas flow controlled nucleation conditions.

Historically, these lasers have been rather expensive (above \$10k), but diode-pumped solid state (DPSS) lasers have recently become significantly cheaper and accessible. We acquired an xTool 1064 nm DPSS laser module designed for metal etching [151] with 2 W average optical power, 15 kW peak power, 20 kHz pulse rate, 7 ns pulse width, and 100 μ J per shot for less than \$400 new. Its stock lenses produce a 30 μ m diameter spot size with 20 mm throw and perhaps 1 mm depth of field. It is controlled by a standard 3.3 V PWM signal and 24 V power supply, making it easy to integrate into our own custom systems.

²¹There are minor variations to this basic physical process, e.g., a sufficiently intense and fast (femtosecond) laser can completely strip electrons via thermionic emission before they transfer heat elsewhere, and the remaining positively-charged nuclei undergo Coulomb explosion [144][145][146].

Safety note: high-intensity lasers are very dangerous as they can easily blind you. Above around 500 mW optical power (a class 4 laser), even scattered light can cause eye damage. The 1064 nm 2 W pulsed laser used in this work is easily in this category. To ensure safety, we built a full enclosure around the laser, added safety interlocks to only turn on the laser with the enclosure closed and software in the correct state, and ran it only when wearing high-quality laser safety glasses (ThorLabs LG10) rated to bring the worst-case intensity below maximum permissible exposure limits.

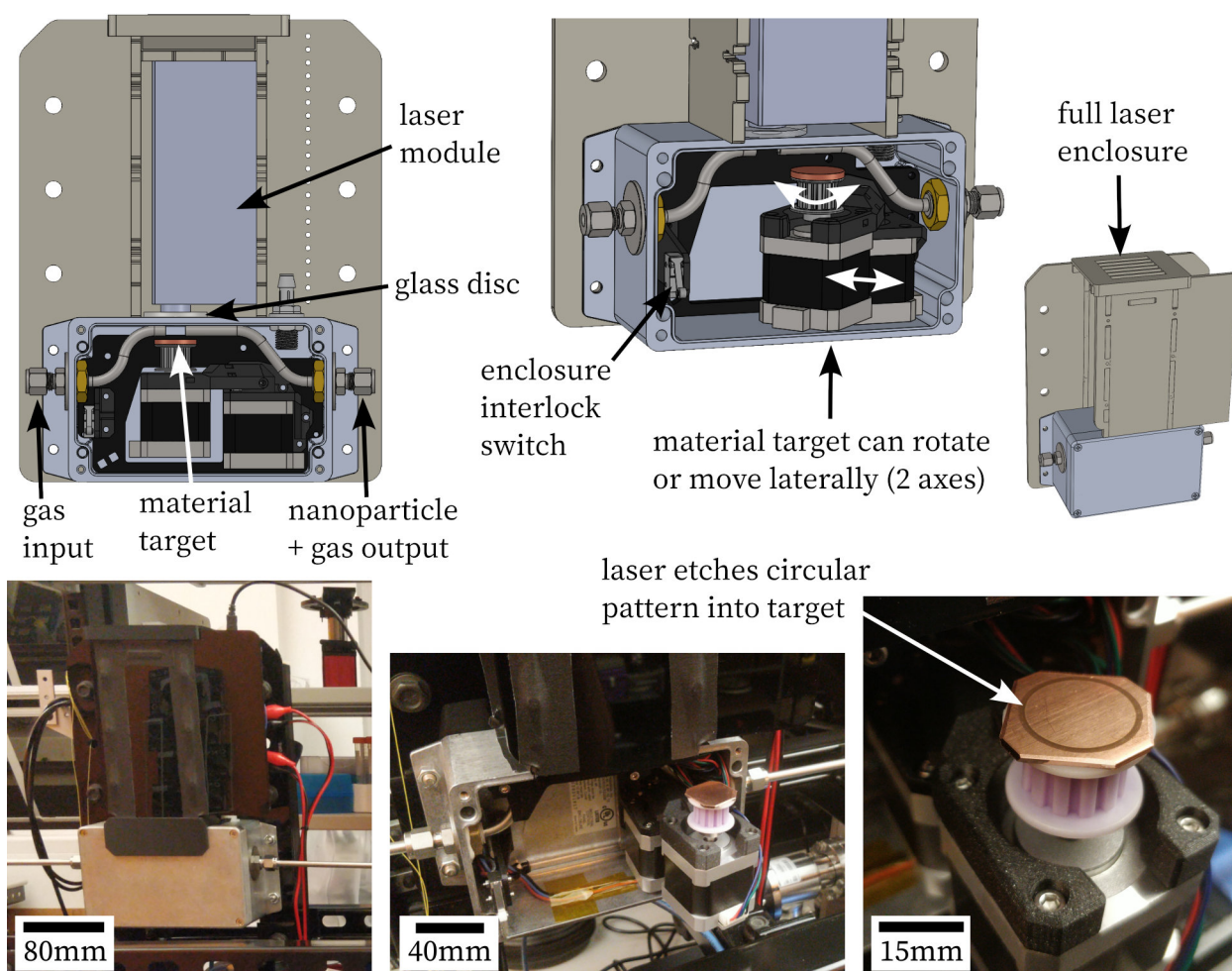


Figure 2.11: Top: CAD models of laser ablation nanoparticle generator, some with cover removed to show interior workings. Bottom left: assembled laser generator. Bottom center: material targets can easily be moved out of generator to be changed out with different materials. Bottom right: rotation causes the laser to etch a characteristic circular trace.

Similar to our spark ablation nanoparticle generator, we designed an airtight chamber with 4 mm ID gas tubing input and output. A 1064 nm-transparent borosilicate glass disc allows

the laser to enter the chamber and hit a material target in a 10 mm wide space between the tubing. All material targets are flat discs 10 mm to 25 mm in diameter which are easy to acquire. Because the laser is focused on a sub-1 mm² spot much smaller than the targets, it is typical to use some system to scan the laser across the target surface [142][140]. We built a motorized rotary two-axis scanning mechanism. The result is the system shown in figure 2.11. This was attached to a nanoparticle impaction setup similar to the spark ablation generator but with a larger vacuum chamber described in section 4.3.

As an initial experiment, we scanned the laser across a copper target at 0.3 mm s⁻¹ at 50% of its maximum power for a total time of 15 s, impacting the result onto glass. The result is shown in figure 2.12: this created a large 700 μm deposit implying copper nanoparticles were successfully generated, transported, and impacted. This speed is comparable to (if not faster than) our spark ablation nanoparticle generator results.

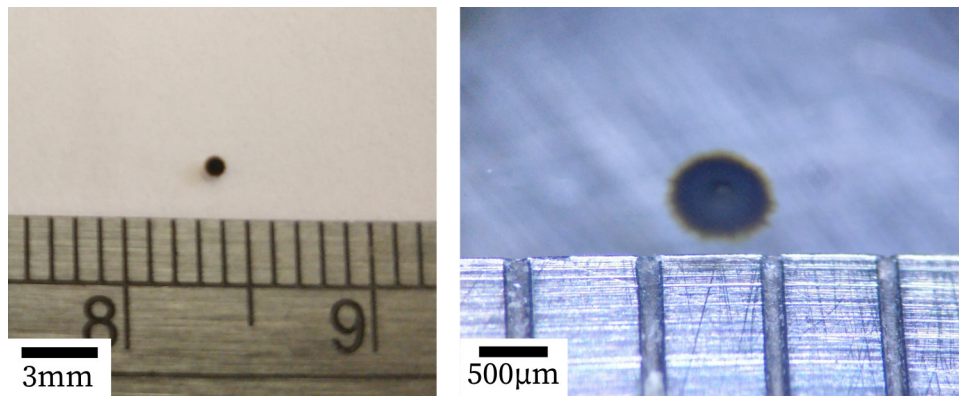


Figure 2.12: Left: copper deposited on a glass slide. Right: a close-up view showing the deposit may have 100 μm tall topography at its center.

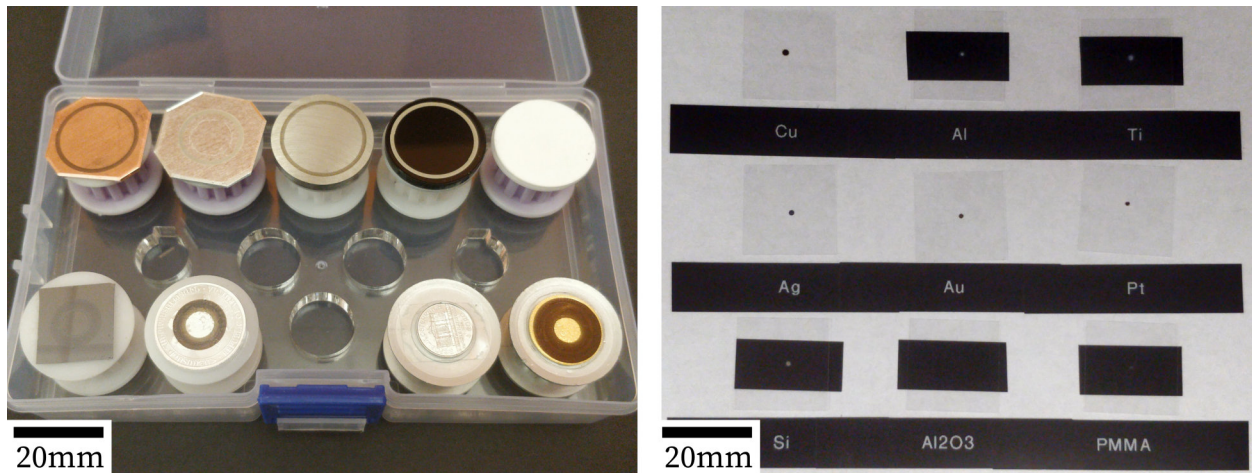


Figure 2.13: Left: material targets. Clockwise from top left: copper, aluminum, titanium, black acrylic (PMMA), alumina, gold, silver, platinum, silicon. Right: materials impacted onto glass slides. All materials work save for alumina. The PMMA deposit is barely visible.

Given our initial success with copper, we next tested a wide range of materials. Our generator was constructed to allow quick and easy material changes by swapping out the material target to any flat disc of diameter below 25 mm, letting us try the following: copper (101 alloy, 99.99% Cu, McMaster-Carr), aluminum (1100 alloy, > 99% Al, McMaster-Carr), titanium (99.995% Ti sputter target, ACI Alloys Inc), black acrylic (PMMA), alumina (96% Al₂O₃, remainder SiO₂), gold (2024 Armenia 1 gram gold 100 Dram Noah’s Ark BU coin)²², platinum (2024 Austria 1/25 oz platinum Philharmonic BU coin), silver (2024 Armenia 1/4 oz silver 100 Drams Noah’s Ark coin), and silicon (boron p-doped wafer).

Each material was etched with the laser moving at 10 mm s⁻¹ over the surface and at 50% maximum power. Gas flow rate was set to approximately 0.5 L min⁻¹. Deposition was continued for 1 min for each sample onto a glass slide. The results are shown in figure 2.13: copper, silver, gold, and platinum produced dark deposits. Titanium, aluminum, and silicon produced white deposits. Alumina produced no visible deposit, and PMMA resulted in a very faint deposit with uncertain molecular structure. These are excellent initial results; it appears laser ablation nanoparticle generation works, and future characterization and improvement efforts can likely make a reliable convenient nanoparticle source.

We did attempt to quantify the nanoparticle production rate by measuring the mass change of both the material target and substrate during the material experiments of figure 2.13 but found no measurable difference above 0.1 mg over our 1 min deposition time²³. This implies the generation rate is below 6 mg h⁻¹, but the similarity of deposits to our spark ablation results suggests the generation rate is at least 0.6 mg h⁻¹. This rate, between 0.6 mg h⁻¹ to 6 mg h⁻¹, is again reasonable for printing chips in hours.

2.4 Metrics and Improvements

We are now able to generate nanoparticles via either spark ablation or laser ablation and are ready to proceed with considering their deposition in chapter 3. However, we have only achieved the bare minimum. Although we can generate particles, we only have rough proxy measurements of their diameters and other properties. While this is fine for the moment—we thought it more important to confirm we can print nanoparticles before spending time refining the nanoparticle sources themselves—this characterization and refinement is an ideal target for future work.

An advanced nanoparticle printer might add the following:

Nanoparticle characterization: we would like to know the precise distribution of nanoparticle diameters as well as their shape, optionally using this to optimize the ablation and vapor nucleation processes—are the particles crystalline? Are they actually spherical or instead multiple smaller particles necking together? Are they oxidized? As mentioned earlier when

²²Gold, silver, and platinum are most readily available in a flat cylindrical form factor as minted coins. We chose the cheapest coins commercially available of sufficiently large diameter. Costs were < \$100 on average per metal, making this as affordable as spark ablation wire and again significantly cheaper than microfabrication material sources which typically have to be much larger.

²³Longer deposition times were not attempted for fear of overheating the laser module.

we approximated particle sizes from SEM images, precise size distributions can be better measured via a differential mobility analyzer (DMA), a cascade impactor (which uses a combination of aerodynamic lenses and inertia to similarly select particles of a certain diameter [102]), or charge detection mass spectrometry [111]. Size as well as particle geometry can be determined to some extent by inspection of particles with a scanning or tunneling electron microscope (TEM) [149] or atomic force microscope (AFM) after deposition.

Nanoparticle size control: to make a very precise and repeatable manufacturing method, it would be preferable to control (and not just measure) the distribution of nanoparticle sizes—perhaps we want nanoparticles of exactly 5 ± 0.5 nm. However, all discussed nanoparticle generation methods result in a wide distribution of particle diameters (say, a lognormal distribution [128][102] from 5 nm to 30 nm) and more precise control is notoriously difficult and may not be possible without using a process other than vapor nucleation. But there is an alternative: it is relatively straightforward²⁴ to sort particles by diameter in the same DMA or cascade impactor tools used for characterization, a similar but less precise virtual impactor [102], a time-of-flight filter based on mobility in gas [152], or a quadrupole mass filter as used in mass spectrometry and discussed in section 6.3.2 [132][153]. We can simply select the subset of nanoparticles of the correct diameter to print and recycle the rest.

Deposition efficiency: ideally 100% of the material vaporized from target electrodes is transformed into nanoparticles and deposited onto the substrate. That this is theoretically possible is a strong benefit of nanoparticle printing that is not possible in microfabrication, where a significant fraction of material (easily far above a majority, depending on how one calculates) goes to waste (see section 7.2.3). This efficiency can be quantified by measuring the mass of a target material and deposition substrate before and after moving material from the former to latter. One spark ablation paper in the literature [136] found a 22–38% efficiency, i.e., at least 62% of vaporized material was lost by deposition onto tubing sidewalls before being deposited as desired on the substrate, but noted this is mainly due to diffusion and can be reduced by increasing gas flow to minimize transfer time.

All these results and possibilities make us confident that precise reliable multimaterial nanoparticle sources are feasible and practical. With that determined, we are ready to consider what happens to nanoparticles after they are made: how we will deposit them and how this can be achieved by manipulating them with a combination of gas drag and electrostatic forces.

²⁴The company [51] that sells a spark ablation generator also sells an aerosol-based particle size selector with claimed 0.1 nm diameter resolution for 1 nm to 10 nm particles.

Chapter 3

Deposition Theory

Now that we have nanoparticles, we can get to the fun part: printing.

More specifically, we need to consider what physical processes need to happen to attach these nanoparticles to the substrate or part under construction. Understanding this is a prerequisite for designing any printing mechanism. We'll review the physics and literature of similar nanoparticle deposition processes to find out what is possible and in what conditions (e.g., nanoparticle impact speeds). We'll then briefly discuss systems to move nanoparticles around and conclude we should focus on the gas/aerosol and electrostatic systems we later pursue in chapters 4, 5, and 6.

3.1 Deposition Review

When proposing our nanoparticle printing process in section 1.3, we wanted nanoparticles to hit the surface of a part under construction, then stick. What does that mean? How does that work? Most macroscopic things don't spontaneously stick together.

Roughly speaking, the materials we're interested in (metals, semiconductors, and oxides) consist of individual atoms bonded equally to all their neighbors; they are near-infinite 3D grids of atoms. Now suppose you were to take two pieces of the same metal with atomically flat surfaces and push these flat pieces together with no air or grease or other contaminants¹ in between. The atoms would line up, the electrons forming bonds would spread across the now-nonexistent gap, and the pieces would meld together into one as if they were never two separate parts [154]. In Feynman's words [155], "there is no way for the atoms to "know" that they are in different pieces". This process is often called cold welding².

In our case, we want to cold weld nanoparticles to larger surfaces, which turns out to be particularly effective due to high nanoparticle surface reactivity (as in chapter 2).

¹Another common contaminant is an oxide layer from the surface reacting with atmospheric oxygen.

²Why don't we see this more often on the macroscale? It's extraordinarily difficult to make metal surfaces flat and clean enough, especially at large sizes. But galling on tight screw threads is in part cold welding, and spacecraft can experience cold welding between their metal parts in vacuum.

We'll begin by considering what happens when a nanoparticle hits a flat surface at some velocity. Sometimes the nanoparticle will deform and cold weld to the surface. This interaction has been widely studied in several research areas that approach the same problems from separate directions³. These methods mainly differ in particle size and impact velocity (or, equivalently, the kinetic energy per atom of the moving particle before impact).

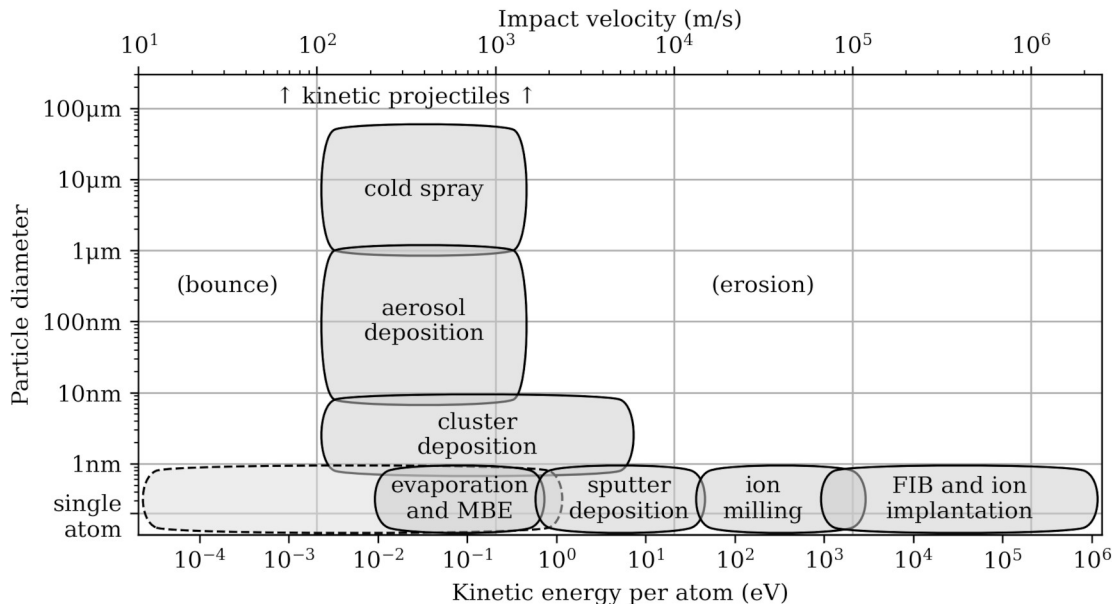


Figure 3.1: Assorted effects when nanoparticles hit surfaces, graphed by approximate particle sizes and impact velocities. Kinetic energy is computed as $KE = \frac{1}{2}mv^2$ assuming particles consist of 40 amu atoms. Thermal energy $k_B T$ at 25 °C is 26 meV. Single atomic bonds are 1 eV to 10 eV [103]. Inspired by similar graphs in [42] and [158]. See also figure 3.2.

Single atoms: suppose a single atom hits a surface [156]. This is a common part of many microfabrication thin-film physical vapor deposition (PVD) tools (which have many atoms impacting in parallel). If the atom was moving slowly, with some probability (the sticking coefficient) it will form temporary bonds then move around on the surface with thermal energy as an adatom. Eventually it may form a stronger bond. Many atoms make a thin film. This describes evaporation and molecular beam epitaxy (MBE) [118] but applies to any low-speed collision [159]. The structure zone model [160][161] notes a transition from porosity to small then large grains with substrate temperature, and film stress varies significantly [162]. If the incoming atom velocity and thus kinetic energy were greater than $k_B T$ thermal energy or the ≈ 1 eV of chemical bonds, the extra energy is enough to modify film properties slightly [163]. This is also the regime sputter deposition tools typically operate in [164]. At even higher velocities, the incoming atom has enough kinetic energy to collide with many atoms in the substrate, sometimes making some fly off the surface (“sputter”) so material is removed instead of added. This applies to ion milling, FIB, and ion implantation [75][1].

³For a broad overview, we can recommend the combination of [118], [156], [43], [42], and [157].

Clusters (1–10nm): the next smallest⁴ particles, clusters⁵, are clumps of several to several thousand atoms, that is, small nanoparticles with diameters up to tens of nanometers. These have a variety of behaviors similar to single atoms [43]. At low impact velocities, below about 0.1 eV per atom, these clusters merely bond as-is to the surface. Depositing multiple clusters can stack them without deformation, making a porous film. However, increasing the impact velocity and energy to 1 eV is enough to allow the clusters to deform and make solid films, which are good enough to form metallic ohmic contacts and PN junctions [171][172][47]. Varying process conditions can produce amorphous, nanocrystalline, and polycrystalline films [47] and, especially with a heated substrate, these clusters move around the surface similar to single adatoms (but surprisingly far: up to microns [171]) and form epitaxial films [173][174]. Higher velocities (10 eV per atom) begin to cause sputtering and erosion effects, and even faster speeds with small clusters still gives ion implantation⁶.

Industrially, clusters in the erosion regime can be used to smooth microfabricated surfaces⁷ in gas cluster ion beam (GCIB) processing [176][48][177]. Cluster deposition [125] is less common. It (specifically ionized cluster beam deposition, ICBD, from 1975 [178][47]) has been used commercially for DRAM contact hole filling [179] but, in general, the complexity of cluster sources [43] means it has no significant benefit over evaporation and sputtering for standard microfabrication (for our printing process, however, using larger particles than atoms is worthwhile to allow higher print speed in chapter 6).

Larger particles act progressively more macroscopically. Specifically:

Low-speed bounce (large particles below 100m/s): when a particle hits a surface at low speeds, it can bounce⁸. Below $\approx 100 \text{ m s}^{-1}$, there is not enough kinetic or thermal energy available to reform bonds or bond the particle to the surface except for Van der Waals forces, so the particle elastically compresses slightly then rebounds, its inertia overcoming any minor surface attraction (unless it is so slow, perhaps below 5 m s^{-1} [157], that surface attraction dominates [102]) [157][158][181][182][183]. Single atoms can somewhat bounce: they adsorb then desorb from a surface (with sticking coefficient probability) [184].

Aerosol Deposition, Cold Spray (10nm–100 μm): when particles larger than clusters hit a surface at intermediate velocities, typically 100 m s^{-1} to 1000 m s^{-1} , they can undergo plastic deformation to conform to the surface while cold welding [42][185][41][52]. This works at room temperature (though more heat helps) with only a partial temperature increase (not necessarily to melting) at the collision point as kinetic energy is converted to heat [186]. There is both a material-dependent [187] minimum critical velocity (which can be predicted with solid mechanics as the onset of shear instability) and maximum velocity (notably a bit below the 1 eV per atom milestone) above which a particle fragments, does not fully adhere, and leaves an impact crater (hydrodynamic penetration) [186][188].

⁴Deposition of organic molecules exists as soft landing in mass spectrometry [165][166][167][168][169].

⁵Clusters were widely studied in the 1960s through 1990s for their interesting physics [170][43]. This research also led to vapor nucleation nanoparticle generation methods [142] and the C_{60} buckyball molecule.

⁶Molecular ion implantation used for shallow MOSFET doping is arguably a form of cluster deposition.

⁷EUV photolithography mirrors are smoothed with single argon atoms (ion beam figuring, IBF) [175].

⁸This is relevant for sub-1 μm tin droplets in EUV light sources [180].

Impacting these large particles over wide areas can produce thick solid films that exceed 95% of bulk density, are gas-tight, and have high optical transparency [185][42]. This is used in the semiconductor industry to apply nanocrystalline yttria coatings to semiconductor equipment plasma chambers [189] and to manufacture some sputtering targets. To clarify nomenclature: aerosol deposition and cold spray are so called because the main method to accelerate 10 nm–100 μm particles to impact speeds is as an aerosol in an air jet (see sections 3.3, 4.2.1). Cold spray is feasible at atmospheric pressures; the smaller particles of aerosol deposition have higher air drag and require partial vacuum for deposition (see section 4.2.1). Thermal spray methods are cold spray at high temperatures. Other names exist⁹.

High-speed erosion (above 1000m/s): sufficiently fast particles have enough kinetic energy to vaporize a good bit of both themselves and the surface they impact. This is the hypervelocity regime [197]. Hypervelocity acceleration of micrometer-scale particles is useful for studying in-space micrometeoroid or cosmic dust impacts [198][199][157]. Particles above 1 mm and from low speeds to hypervelocity are common as kinetic projectiles.

3.2 Deposition Parameters

Given the above deposition regimes, what parameters should our proposed nanoparticle printer use? The literature suggests four properties are most important to control deposition: impact velocity, particle size, temperature, and material.

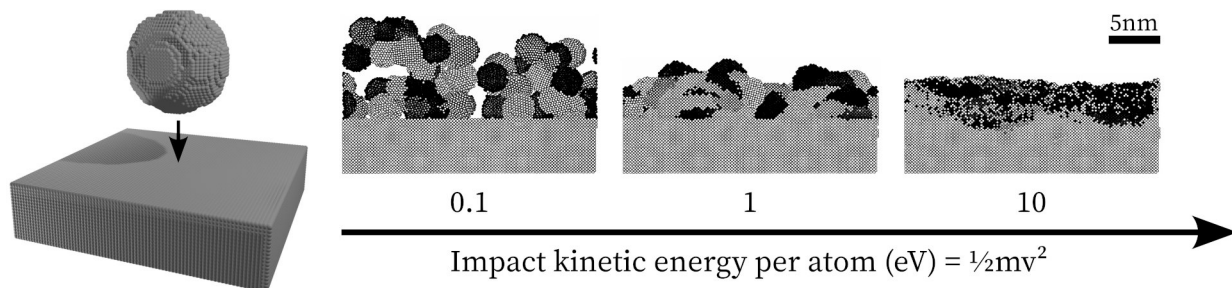


Figure 3.2: Left: what happens when a nanoparticle hits a surface? Right: depending on their initial velocity, particles can cohere, deform, and meld together (molecular dynamics simulations from [200]). This can be explained by noting that when a particle is at a given velocity, all its atoms have that same velocity, and the kinetic energy of each atom ($\frac{1}{2}mv^2$) turns into heat on impact and is available to reform the 1 eV to 10 eV chemical bonds between atoms. The total kinetic energy of the pre-impact particle is this multiplied by the (large) number of atoms. 1 eV per atom is equivalent to about 2000 m s^{-1} . See also figure 3.1.

Velocity: the most important parameter in any of these physical deposition processes is the speed at which nanoparticles impact a surface (for us, the substrate and part under construction). This is because deforming then bonding the particle to the surface requires

⁹Other names for air jet deposition include micro cold spray [190], hypersonic plasma particle deposition (HPPD) [191][59][192][193][194][60], vacuum kinetic spray [195], and nano-particle deposition system [196].

reforming chemical bonds, which needs energy, and the most convenient source is the kinetic energy of impact as in figure 3.2. According to figure 3.1, we probably want to choose impact velocities between 100 m s^{-1} and perhaps 3000 m s^{-1} . Because the ideal velocity varies with material and particle size [188], we would ideally be able to precisely control the velocity within that window to fine-tune deposition conditions experimentally.

Particle size: as mentioned in chapter 2 (and later chapter 6), printing larger nanoparticles is faster than printing single atoms, and we’ll also see in chapter 4 that larger particles are easier to focus to high resolutions. But there is a tradeoff: larger particles have more mass and are harder to accelerate to the required impact velocities, and, of course, we can’t reach sub-100 nm printing resolution if the particles are larger than 100 nm in diameter. The best size range for our purposes—achieving high-quality materials with high resolution—is probably 1 nm to at most 50 nm, mostly within the cluster deposition regime that is known to be able to deposit films with high-quality electrical properties. This is also (not coincidentally) the size range the nanoparticle generators we built in chapter 2 are optimized for.

Temperature: kinetic energy is not the only source of energy for deforming and bonding particles; thermal energy can also help. At an absolute temperature T , atoms vibrate with energy on the order of $k_B T$ (where k_B is the Boltzmann constant). At room temperature $T = 298 \text{ K} \approx 25^\circ\text{C}$, $k_B T \approx 0.026 \text{ eV}$, and at silicon’s melting point of $T = 1687 \text{ K}$ we have $k_B T = 0.15 \text{ eV}$, sufficient to cause by itself the initial conglomeration in figure 3.2—which is why silicon becomes liquid there (but note this is still less than the kinetic energy velocity can deliver locally to the particle). Furthermore: both the substrate and particle can be heated. Heating the particle doesn’t mean anything for a single atom but can provide significant energy with larger particles as in cold spray (giving thermal spray methods) [186][188][192]. This is why single atom methods like evaporation purely heat the substrate as described in the structure zone model [161]. What should we use? We’ll ignore particle temperature, start with the substrate at room temperature¹⁰, and can eventually add capability to heat up to the 500°C used by Takagi for cluster epitaxy [47] (being aware that this might cause adatom movement of up to microns [171], potentially reducing print resolution).

Material: although velocities and other parameters vary with material [188], our material choices will mainly be determined by the requirements to build useful semiconductor devices as described in chapter 1: metals, semiconductors, and oxides. Fortunately, these all appear feasible with minimal variation. It might eventually be useful to also deposit polymers¹¹ as sacrificial release materials for MEMS devices, but we leave this for future work.

In conclusion: we suspect we need to move particles of 1 nm to 50 nm at velocities of 100 m s^{-1} to 3000 m s^{-1} and can eventually add temperature control. Varying parameters might allow printing assorted materials with a variety of crystal structures: amorphous, nanocrystalline, polycrystalline, and monocrystalline (epitaxial). This is exactly what we need to print our desired multimaterial nanoscale devices—if we can achieve these high nanoparticle velocities while simultaneously aiming the particles with high printing resolution.

¹⁰This will allow us to print on low-temperature substrates, like plastics.

¹¹See PVD evaporation/MBE of organics [118] or mass spectrometry soft landing [165][166][167][168][169].

3.3 Manipulation Methods

According to section 3.2, we might be able to achieve the high-resolution multimaterial printing we want if we can shoot nanoparticles of 1 nm to 50 nm diameter at a substrate at well-controlled velocities somewhere between 100 m s^{-1} and 3000 m s^{-1} , and with positioning accuracy below our final desired printing resolution, e.g., $1 \mu\text{m}$.

But how can we do that? These are tiny particles (only tens of atoms wide), high speeds (supersonic), and high resolutions (accuracy within ten thousand atoms)!

Of the four fundamental forces—weak and strong, gravity, and electromagnetism—the weak and strong forces are irrelevant at these scales and gravity is far too small to be useful¹². We need to use electromagnetism somehow. This includes long-range electrostatic and magnetic forces, photons, and matter interactions (since all matter is simply atomic nuclei and electrons held together by electromagnetism).

- **Matter interactions:** also called touching stuff. We could put some nanoparticles on the end of a robot arm then move it extremely fast. But as noted in chapter 2, we want to avoid having the nanoparticles contact anything else made of atoms before deposition to minimize the chance those atoms rub off and contaminate the particles, compromising the sub-part-per-billion atomic purity we require. It is difficult to have good enough control of chemistry to reliably do better. But there is a notable exception: many gases, especially the noble (inert) gases (helium, argon, etc.), are single atoms or molecules that can impact nanoparticles without reacting.
- **Photons (light):** it is possible to move nanoparticles with photon momentum (optical tweezers [201][202][203]), but simultaneously achieving velocity and resolution is tricky. We will use photons instead for electrical charging in chapter 5.
- **Electrostatics and magnetics:** an electrically charged nanoparticle will experience a force directly from electric or magnetic fields. This is promising. The nanoparticle can alternatively have a nonzero magnetic moment, but this is harder to control.

That leaves us two options: moving our nanoparticles (otherwise isolated in vacuum) either with gas atoms collisions somehow or with electrostatic forces. This conclusion is well-supported by the prior art¹³ in section 3.1: aerosol deposition, cold spray, and some cluster methods [125] use gas to accelerate particles, while other cluster methods [47] and nanoparticle hypervelocity tests [198] use electrostatic acceleration. We also used gas already in our nanoparticle generators in chapter 2.

In chapter 4, we will discuss gas-based manipulation of nanoparticles and be able to demonstrate some minimal multimaterial printing. But it will prove insufficient to reach the full velocity and resolution we want, so we will turn to electrostatics in chapters 5 and 6.

¹²Any size particle falling a long 100 m distance in Earth-standard 9.8 m/s^2 gravity in vacuum gains a total kinetic energy of only about 0.0004 eV per atom compared to the 1 eV we need.

¹³Evaporation and MBE instead use thermal energy to release atoms from a solid of the same material, but this neither scales up well to larger particles or allows efficient velocity control—the velocity distribution is Maxwell-Boltzmann [118] instead of the single value we want. Sputtering uses gas impacts.

Chapter 4

Aerosols and Printing

As proposed in chapter 3, we will try moving 1 nm to 50 nm diameter nanoparticles by having gas molecules collide with them, ideally accelerating the nanoparticles to precise high-speed velocities (up to 3000 m s^{-1}) with high spatial resolution ($< 1 \mu\text{m}$). If we succeed, we can print them. How can we go about doing this? First consider how gas collisions work.

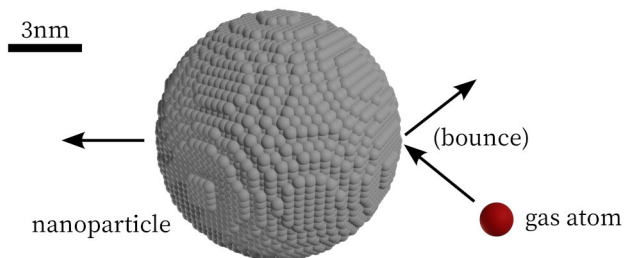


Figure 4.1: Cartoon of a single gas atom (or molecule) bouncing off the right side of a nanoparticle. This causes the nanoparticle to move slightly to the left.

By a gas, we mean a collection of individual atoms¹ moving around in what is otherwise a vacuum. When a single gas atom hits a nanoparticle, it acts like a nanoparticle hitting a large surface as in chapter 3. If the atom is unreactive and moving slower than perhaps $10 \times 10^4 \text{ m s}^{-1} \approx 10 \text{ eV}$ (often the case; larger velocities risk deforming or breaking the nanoparticle [204], so we'll avoid that), it will bounce off the nanoparticle and head in a different direction. Conservation of momentum dictates this acts like macroscopic collisions (just like billiard balls) and is at least partially elastic², so the nanoparticle will be pushed slightly away from the collision point. Repeat this many times (a nanoparticle is significantly heavier than a gas atom, so it takes a while), and the nanoparticle can be pushed in whatever direction we like. (The other relevant interaction is electrons can move between atom and nanoparticle, which is usually negligible but will matter in chapter 5.)

¹A gas can be molecules like N_2 , not just atoms, with little difference. We use “atom” for convenience.

²Although most collisions are specular (and elastic on average), the atom can temporarily adsorb (stick) to the nanoparticle giving a diffuse reflection [184][205], and some energy can also be lost or gained from vibrations (phonons) in the particle to bring it to mean gas temperature [206].

Unfortunately, we don't have a way to precisely shoot gas atoms at a nanoparticle to make it go exactly where we want³. Instead we'll allow millions of gas atoms to randomly hit each nanoparticle, and their average behavior will determine what happens. We will control the overall gas behavior—fluid dynamics⁴—to indirectly control the nanoparticles.

An aerosol is exactly this: a collection of nanoparticles in a gas. Aerosols are very common; examples include smoke, fog, steam, and clouds. Aerosol science [102], the study of aerosols, has produced useful results and tools like the differential mobility analyzer (DMA) mentioned in chapter 2. We'll quickly discuss gases in general then focus on aerosol-specific results.

4.1 Gas Physics

We will briefly review some basic gas behavior. Consider a large number of gas atoms inside an airtight chamber. The atoms move around, bouncing off the walls and each other just like they bounce off nanoparticles. This is the kinetic theory of gases, and statistical mechanics can be used to derive some useful average properties [102].

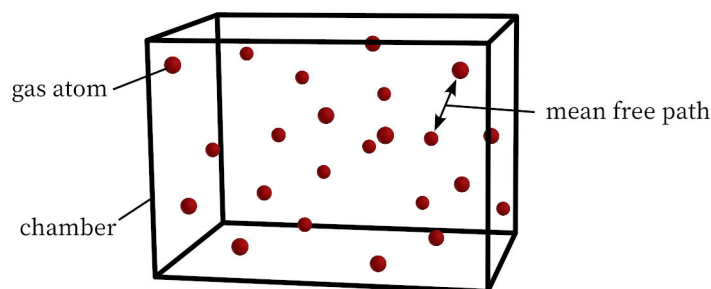


Figure 4.2: A 3D rectangular chamber holding gas atoms bouncing off the chamber walls and each other. The mean free path is related to the average distance between gas atoms.

As with nanoparticles, each collision between gas atoms and the surface is elastic on average⁵, so at nonzero temperatures the gas atoms never stop moving even if their velocity might change on each bounce. The atoms' range of velocities is given by the Maxwell-Boltzmann distribution and is fairly broad (some atoms move slowly; other quickly). The average velocity increases with temperature and with smaller gas atoms. Standard air is just the particular gas consisting of about 78% N₂, 21% O₂, and some Ar, CO₂, and other trace elements, each part of which acts independently according to this same distribution.

³Atomic billiards! But collisions are only somewhat elastic on average; single shots might be unpredictable.

⁴In continuum mechanics, "fluid" refers to both gases and liquids since both continuously deform under applied shear stress and otherwise act similarly.

⁵Collisions equilibrate the temperature of the gas and chamber until this is the case; the atoms of the chamber surface vibrate according to their temperature and transfer energy to or from colliding gas atoms.

From the Maxwell-Boltzmann distribution we can derive that the average kinetic energy of the gas atoms (each moving in a random direction) at absolute temperature T is $\frac{1}{2}k_B T$ in each of the x, y, and z directions for a total of (again, in a random direction)

$$\frac{3}{2}k_B T \quad (4.1)$$

where $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} = 8.617 \times 10^{-5} \text{ eV K}^{-1}$ is the Boltzmann constant. At 25 °C, any gas atom has about 0.039 eV of kinetic energy. An argon gas atom, for example, would move on average (root mean square velocity⁶) at 431 m s^{-1} . Nanoparticles will also randomly bounce around and eventually gain the same $\frac{3}{2}k_B T$ kinetic energy, but this applies to the entire particle (not its individual atoms), so a 10 nm nanoparticle would only move at 2 m s^{-1} . This doesn't help us achieve the high velocities (up to 3000 m s^{-1}) we want to accelerate nanoparticles to, and it might make positioning nanoparticles with sub-1 μm resolution difficult. We'll address this shortly as Brownian motion.

Also relevant is that gas atoms hitting a surface, whether it be part of the chamber sidewall or the side of a nanoparticle, apply a force. The average force (over time) per area is the pressure, which is often the best way to measure the number of gas atoms in the chamber. These are related by the ideal gas law

$$PV = Nk_B T \quad (4.2)$$

where P is the absolute pressure, V is the total volume of gas, and N is the total number of gas atoms. Normal Earth atmosphere is air at a pressure of about 101 325 Pa or 760 Torr⁷. Removing gas molecules from the chamber reduces the pressure; if below atmospheric we call it a vacuum. Pressure is always positive (achieving perfectly zero pressure is near-impossible), and for some applications (including ours; see sections 4.2.1 and 4.3.3) the difference in otherwise small pressures (say, 1 Torr and 1×10^{-7} Torr) can be significant.

The rate at which atoms hit a surface (creating a pressure) is the impingement rate

$$J = \frac{P}{\sqrt{2\pi m_g k_B T}} \quad (4.3)$$

where J (gas atom impacts per unit area per unit time) is the impingement rate and m_g is the mass of a gas atom. In standard 760 Torr atmosphere, the surface of a 10 nm diameter particle is hit by about 9×10^{11} gas atoms per second. This is an extremely large number.

A final important parameter is the distance between gas atoms⁸. It is often more convenient to use the average distance a gas atom travels before a collision with another gas atom. We call this the mean free path ℓ , calculated by

$$\ell = \frac{k_B T}{\sqrt{2\pi} d_g^2 P} \quad (4.4)$$

where d_g is the kinetic diameter of the gas atom, about 0.36 nm for Ar, N₂, and O₂ [103]. The mean free path of 760 Torr air is about 70 nm—larger than a 10 nm nanoparticle!

⁶Computed from $\frac{3}{2}k_B T = \text{KE} = \frac{1}{2}mv^2$. The true (non-RMS) mean velocity is $\sqrt{\frac{8}{3\pi}} \approx 0.92$ of this value.

⁷Or 1.01 bar, 14.7 psi, or 1 atmosphere. Of all these units, torr are common in vacuum engineering.

⁸The mean spacing between gas atoms, about 3 nm in atmosphere, is smaller than the mean free path.

4.1.1 Nanoparticle Air Drag and Brownian Motion

Given how gases behave, we can now consider how they make nanoparticles move.

We'll consider the simple case where a nanoparticle with initial velocity v suddenly appears in the center of a chamber with gas otherwise in equilibrium at some pressure and temperature. This will take us surprisingly far. Note this is equivalent to the case where the nanoparticle has no initial velocity but the gas is moving with velocity $-v$ on average. It is only the relative velocity that is important.

If there are no gas atoms (zero pressure), the nanoparticle will of course move forever at velocity v . But in a gas, the nanoparticle collides with the gas atoms, transferring its kinetic energy to the gas until the gas temperature is raised and the system is at equilibrium. The nanoparticle is slowed down until it has the same relative velocity as the surrounding gas (plus its randomly-directed thermal motion from section 4.1). This is air drag⁹!

Air drag is the main interaction between a nanoparticle and a gas. As suggested in the introduction to this chapter, if we make gas atoms move somewhere on average, air drag will drag nanoparticles along (and if we move nanoparticles without moving the surrounding gas, those nanoparticles will quickly slow down). If we want to precisely move nanoparticles, we should quantitatively understand the effects of air drag as well as its interaction with the previously mentioned thermal (Brownian) motion.

Other nanoparticle-gas interactions besides drag include chemical reactions (unlikely with noble gases, common with oxygen) or exchanging electrons (important in chapter 5), and air drag itself has many subtle effects (e.g., thermophoresis). We will ignore these for now.

There are two ways to analyze drag: bottom-up statistical mechanics calculations accounting for how nanoparticles are randomly bumped around, or a top-down approximation¹⁰ that treats the gas as a continuous viscous fluid. We'll start with the latter.

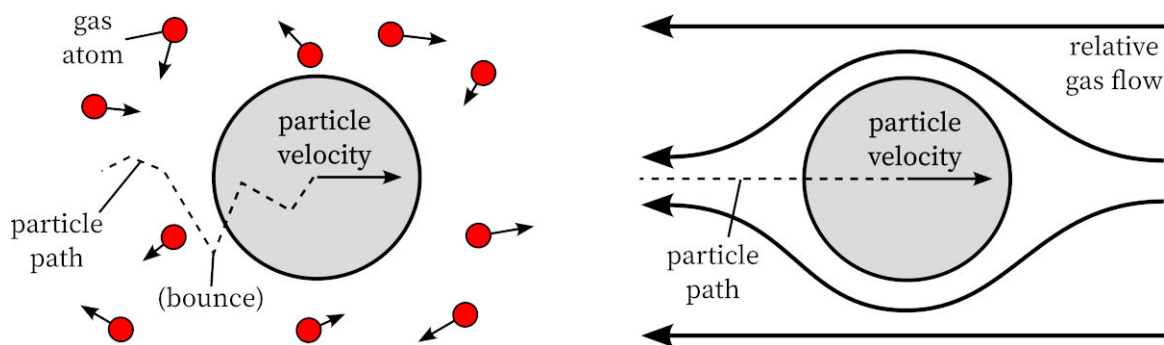


Figure 4.3: Two ways to analyze gas-particle drag. Left: a particle moving to the right experiences many collisions with gas atoms, each of which slightly redirects the particle course and, on average, slows it down. Right: as the number of gas atoms approaches infinity (a continuum), collisions are averaged out so a particle moving to the right (shown with gas streamlines moving to the left) has a straighter path but is still slowed down.

⁹Drag exists in all gases, not just air, but the term “air drag” is more common than “gas drag”.

¹⁰Navier-Stokes can be derived from the kinetic theory of gases with Chapman-Enskog theory.

The reader may be familiar with Stokes’ law, which says the force \vec{F} due to drag on a sphere of diameter d_p moving at velocity \vec{v} through a fluid of dynamic viscosity μ is

$$\vec{F} = -3\pi\mu d_p\vec{v}. \quad (4.5)$$

In other words, a particle moving relative to a gas experiences a force in the direction opposite its motion, proportional to its current (relative) velocity, vaguely similar to friction.

This equation is derived by assuming the surrounding gas is a continuum, then simplifying the incompressible Navier-Stokes equations at low speeds around a sphere with a no-slip boundary layer. The result is accurate¹¹ for large everyday objects.

However, this equation is often incorrect for nanoparticles since they are much smaller than the mean free path ℓ between air molecules (compare $\ell = 70$ nm in atmosphere to a 10 nm particle) so the no-slip boundary condition does not hold. In other words, the nanoparticle is so small the approximation that the gas is a smooth continuum breaks down. This is quantified by the Knudsen number $\text{Kn} = \frac{\ell}{d_p}$, the ratio of mean free path ℓ to particle diameter d_p . Kn can be thought of as the degree of non-continuous fluid behavior and in our case is much greater than 1, a region referred to as free molecular flow¹² [207].

It is sometimes possible to add a term to Stokes’ law to compensate for small nanoparticle diameters. Specifically, the Stokes drag force is multiplied by $1/C$ defined by

$$C = 1 + \frac{2\ell}{d_p} \cdot (c_1 + c_2 e^{-c_3 \frac{d_p}{2\ell}}) \quad (4.6)$$

where c_1 , c_2 , and c_3 are empirical constants, approximately $c_1 = 1.17$, $c_2 = 0.52$, $c_3 = 0.78$ for air [102][205]. This is called the Cunningham-Millikan-Davies slip correction factor and has the distinction of being used in the Millikan oil drop experiment that demonstrated the existence of charge quantization [208]. The downside of this method is limited applicability due to the empirical fit (which assumes standard pressure and temperature air).

An alternate and more general method to compute the drag comes from a first principles analysis of hard sphere collisions. There are many minor variations to this method; see [205] for an excellent discussion. We will use the form (referred to as “Epstein’s Law”):

$$\vec{F} = -\frac{8 + \pi\varphi}{12} \sqrt{\frac{2\pi m_g}{k_B T}} P d_p^2 \vec{v} = -\beta\vec{v}, \quad (4.7)$$

where \vec{F} is the drag force, $\varphi \approx 0.9$ is a constant indicating the fraction of diffuse vs. specular collisions, m_g is the mass of each gas molecule, k_B and T are the Boltzmann constant and temperature, P is the gas pressure, d_p the particle diameter, and \vec{v} the particle velocity. For convenience, we will sometimes abbreviate this as the viscous damping coefficient β .

¹¹Stokes’ law applies at low Reynolds numbers. Assuming continuum flow, a 10 nm particle at 3000 m s⁻¹ in 25 °C 760 Torr air has Reynolds number $\text{Re} = 2$, well below the $\text{Re} \approx 2000$ onset of turbulence.

¹²“Free molecular flow” also refers to the point at which the mean free path is larger than the vacuum chamber holding the gas, which is not quite the case for most of our systems.

Advantages of Epstein’s law include a clear relation to temperature, pressure, and gas molecular mass. The major downside is this only applies to the free molecular flow $\text{Kn} \gg 1$ regime, but this is satisfied for our nanoparticles in almost all cases¹³. Importantly, note the drag is directly proportional to velocity as in Stokes’ law, just with a modified magnitude.

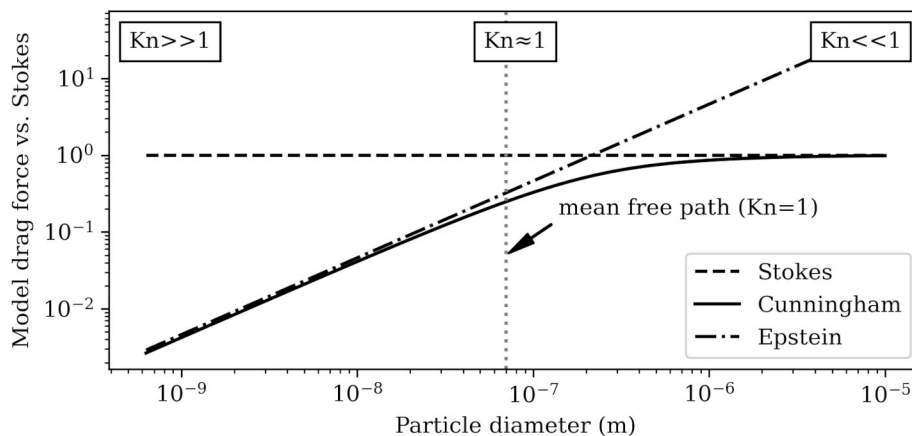


Figure 4.4: A comparison of Stokes, Cunningham, and Epstein drag models in 25 °C 760 Torr air, where the mean free path is about 70 nm. Air drag of nanoparticles larger than the mean free path (low Knudsen number) is modelled by Stokes drag, while Epstein drag is accurate for smaller particles. Cunningham drag interpolates between the two.

Minor model refinements exist for additional accuracy¹⁴. Small nanoparticles might require a lower Epstein φ parameter [184][205][213], and gas-particle temperature differentials might require additional corrections [206]. If particles were larger we might want to add secondary fluid continuum forces including the Basset force, gravity buoyancy, Magnus or Saffman lift due to particle rotation or shear flow; Saffman forces help model aerosol deposition [50]. For our smaller particles in large Knudsen numbers (and compared to the larger electrostatic forces in chapter 6), we will ignore these (unless particles are nonspherical [102]) [214].

One additional effect we cannot ignore is diffusion due to Brownian motion.

Earlier, we noted there were two ways of calculating drag. The first is the simple velocity-dependent force we just discussed, which we will refer to as viscous drag. The other method accounts for each individual collision of a gas atom with a nanoparticle.

Gas atoms hitting a nanoparticle cause it to have jagged motion: short straight-line movements changing directions upon each collision as shown in figure 4.3. With sufficiently many gas atoms, the force on the particle almost averages out to viscous drag—but not quite¹⁵.

¹³A 10 nm diameter particle in 760 Torr atmosphere has $\text{Kn} \approx 7 \gg 1$, and Kn increases at lower pressures.

¹⁴See ion mobility spectrometry [209][210][211][212], which makes very precise nanoscale drag calculations.

¹⁵That gas collisions cause both drag and Brownian motion is the fluctuation-dissipation theorem.

The remaining motion is slow, random, and omnidirectional (though for a particle moving quickly, it is more noticeable perpendicular to the particle’s primary direction of motion). This is called Brownian motion or diffusion¹⁶ and is not accounted for in viscous drag. Given time, a particle will move arbitrarily far from the path we would otherwise predict.

Brownian diffusion is very significant for small particles [102] but can be tricky to analyze because of its large number of collisions and discrete nature. It does not have a single simple analytical formula like viscous drag. There are several ways of dealing with this:

- Computer simulation of random gas collisions is accurate and also replicates viscous drag but does not simplify analysis and is computationally expensive¹⁷ [215][216][217].
- Average Brownian motion (ignoring motion with viscous drag) can be probabilistically but analytically approximated with Fick’s laws of diffusion.
- Brownian motion gives particles $\frac{3}{2}k_B T$ mean kinetic energy. If a particle is trapped in a potential energy field, this can give us a probability distribution for its position.

We’ll approximate particle motion as viscous drag plus independent Brownian movement (this is the Langevin equation [217]) given by one of the latter two approaches.

Using diffusion, a statistical mechanics analysis [102] can find that Brownian motion makes particles move an average (randomly oriented) distance¹⁸ (beyond viscous drag) of

$$x_{\text{diffusion}} = \sqrt{4Dt} \tag{4.8}$$

where t is time and D is a diffusion coefficient computed by equating (the Stokes-Einstein-Sutherland relation) diffusion force from osmotic pressure to (Epstein) drag [102][205] as

$$D = \frac{12}{8 + \pi\varphi} \cdot \frac{k_B T}{Pd_p^2} \cdot \sqrt{\frac{k_B T}{2\pi m_g}} \tag{4.9}$$

	D (760 Torr)	D (1 Torr)	RMS Velocity
(single atom)	$4.0 \times 10^{-5} \text{ m}^2/\text{s}$	$3.1 \times 10^{-2} \text{ m}^2/\text{s}$	431 m s^{-1}
1 nm	$5.2 \times 10^{-6} \text{ m}^2/\text{s}$	$4.0 \times 10^{-3} \text{ m}^2/\text{s}$	69 m s^{-1}
10 nm	$5.2 \times 10^{-8} \text{ m}^2/\text{s}$	$4.0 \times 10^{-5} \text{ m}^2/\text{s}$	2.2 m s^{-1}
100 nm	$5.2 \times 10^{-10} \text{ m}^2/\text{s}$	$4.0 \times 10^{-7} \text{ m}^2/\text{s}$	0.07 m s^{-1}

Table 4.1: Some diffusion coefficients at 25 °C in air. Particles are of 5 g/cm³ density or argon. Velocities due to thermal motion (in between Brownian collisions) shown for comparison.

In a 2D plane, a 10 nm nanoparticle diffuses 460 μm on average each second in atmosphere. It is clear this will be important when we attempt to achieve sub-1 μm resolution.

¹⁶“Brownian motion” generally refers to the random movement of a single particle and “diffusion” to the average behavior of a group. In this dissertation we will use both terms interchangeably.

¹⁷Recall we calculated a 10 nm particle has 9×10^{11} collisions per second in atmosphere.

¹⁸Specifically, the mean squared displacement is $2nDt$ where n is the dimension (1D, 2D, or 3D). Here we are mainly concerned about 2D particle motion perpendicular to the main direction of travel.

4.2 Aerosol Transport

We've established that nanoparticles are moved with a gas flow according to a viscous drag force (given by Epstein's law) with simultaneous diffusion (Brownian motion). These laws are enough to analyze particle motion in gas flow in tubing like we used in chapter 2.

First we'll establish how long a nanoparticle takes to react to a gas flow [102]. As suggested earlier, suppose a nanoparticle of mass m starts with velocity \vec{v}_0 relative to the surrounding gas (for example, it is moving 10 m s^{-1} while the gas is still, or the particle is still while the gas moves 10 m s^{-1} in the other direction). The particle follows Newton's second law while drag applies a force proportional to velocity by¹⁹ viscous damping coefficient β giving

$$\vec{F} = m\vec{a} = -\beta\vec{v} \quad (4.10)$$

where, for Epstein drag (though our results apply to any velocity-proportional drag law),

$$\beta = \frac{8 + \pi\varphi}{12} \sqrt{\frac{2\pi m_g}{k_B T}} P d_p^2. \quad (4.11)$$

Solving for how the velocity evolves over time, we see this particle slows exponentially with a time constant (the relaxation time) $\tau = \frac{m}{\beta}$ until it reaches the gas velocity:

$$\vec{v}(t) = \vec{v}_0 e^{-\frac{\beta}{m}t} \quad (4.12)$$

In the time it takes to equilibrate velocity, the particle will travel a finite maximum distance \vec{x}_{max} , which is called [102] the stopping distance S :

$$\vec{x}(t) = \int_0^t \vec{v}_0 e^{-\frac{\beta}{m}t} dt = \vec{x}_{max} - \frac{m}{\beta} \vec{v}_0 e^{-\frac{\beta}{m}t} = \vec{x}_{max} \left[1 - e^{-\frac{\beta}{m}t} \right] \quad (4.13)$$

$$S = |\vec{x}_{max}| = \left| \frac{m}{\beta} \vec{v}_0 \right| = |\tau \vec{v}_0| \quad (4.14)$$

That is, the gas will push the particle until the particle is moving at the same relative speed as the gas, and in this time (about 3τ) the particle will move a distance $S = |\tau \vec{v}_0|$.

	τ (760 Torr)	S (760 Torr)	τ (1 Torr)	S (1 Torr)
(single atom)	$6.5 \times 10^{-10} \text{ s}$	$6.5 \times 10^{-7} \text{ m}$	$5 \times 10^{-7} \text{ s}$	0.0005 m
1 nm	$3.3 \times 10^{-9} \text{ s}$	$3.3 \times 10^{-6} \text{ m}$	$2.5 \times 10^{-6} \text{ s}$	0.0025 m
10 nm	$3.3 \times 10^{-8} \text{ s}$	$3.3 \times 10^{-5} \text{ m}$	$2.5 \times 10^{-5} \text{ s}$	0.025 m
100 nm	$3.3 \times 10^{-7} \text{ s}$	$3.3 \times 10^{-4} \text{ m}$	$2.5 \times 10^{-4} \text{ s}$	0.25 m

Table 4.2: Example relaxation times and stopping distances in 25°C air. Particles start at $|\vec{v}_0| = 1000 \text{ m s}^{-1}$ and are of 5 g/cm^3 density or argon.

We can see that even at high 1000 m s^{-1} initial velocities a particle will stop and match the gas flow movement within nanoseconds and micrometers in atmospheric pressure and can take microseconds and move millimeters in 1 Torr vacuum. Incidentally, this is one place where the precise vacuum pressure matters: if we want particles to travel multiple meters against the gas flow without an additional force²⁰, this would require a significantly lower

¹⁹Sometimes mechanical mobility $B = 1/\beta$ is used instead of β [102]. See electrical mobility in chapter 6.

²⁰In chapter 6 we'll consider adding an additional electrostatic force.

vacuum below 1×10^{-3} Torr (in the high vacuum regime), even though both it and 1 Torr are close to zero compared to 760 Torr atmospheric pressure.

Let's consider particle motion through a series of chambers and pressure gradients, which illustrates a number of important and useful effects.

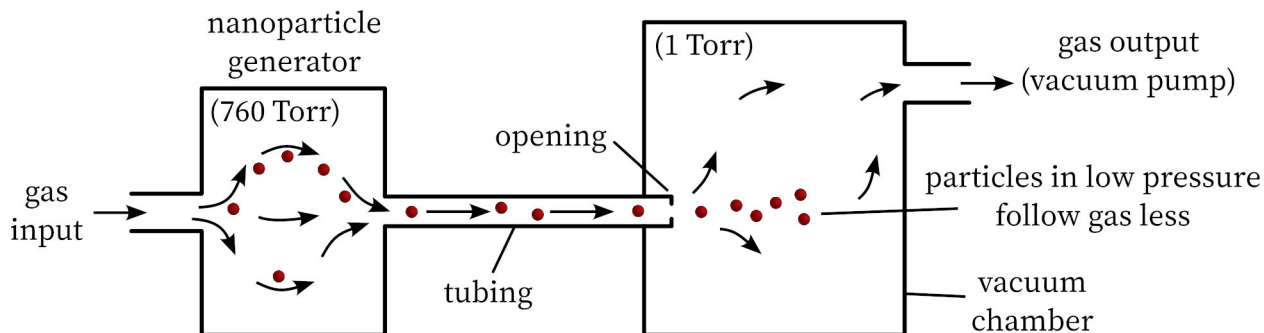


Figure 4.5: Gas (black arrows) flows into a left chamber (perhaps a nanoparticle generator), through tubing and a narrow opening into a right (vacuum) chamber at significantly lower pressure, and out into a pump. Nanoparticles (red circles) follow the gas as soon as they are created but start to deviate from gas streamlines in the low-pressure vacuum chamber.

Gas flow and pressure gradient: Before considering nanoparticle motion, note how the gas moves through this system. Gas is continually added on the left, removed from the right, and flows as one might intuitively expect²¹. The two chambers are each mostly at constant pressure, but the pressure can drop through the thin tube connecting them (in vacuum engineering, this is quantified as the conductance²² [207]), and especially across the small opening into the right vacuum chamber. This leaves the chambers at different pressures (gas flow is driven by pressure gradients). We will assume gas flow is independent of particles (which are sufficiently small and sparse).

Flow into vacuum chamber: It is worth elaborating on how the right vacuum chamber is at low pressure at steady state even though gas is flowing into it. This is a differentially pumped vacuum system²³. Similar setups are common in semiconductor process equipment to keep process gas at a specific pressure or in scanning electron microscope electron guns. In mass spectrometers these move analytes from high pressure to vacuum, and the opening is referred to as a skimmer²⁴ [219][220][221]. The small opening can be engineered (e.g., as an orifice plate or de Laval nozzle) to create a large pressure differential and often operates in the choked flow regime [207].

Particle motion: Due to short relaxation times and stopping distances as in table 4.2, particles almost exactly follow gas streamlines to move from the left chamber (where they

²¹A full treatment of fluid dynamics is out of scope of this dissertation.

²²Conductance allows simple analysis of vacuum systems in free molecular flow. It acts similar to networks of electrical or thermal conductivities.

²³A larger differentially pumped system might have separate vacuum pumps for each chamber.

²⁴Skimmers have variations from simple to complex. For example, an ion funnel [218] uses ponderomotive force to guide charged particles toward an orifice, similar to the quadrupole we will investigate in chapter 6.

were perhaps created by vapor nucleation), through the tubing, and into the right. Once in the right chamber, however, their stopping distance is long enough that they start to break away from streamlines due to inertia; the lower the pressure the larger this effect. If they hit a chamber wall or surface, assume they stop moving. We will want to deposit particles on surfaces, but if any make it to the vacuum pump they can be caught by a filter.

Particles in tubing: Besides air drag, particles in flow through a narrow tube experience three major effects: Brownian diffusion (as previously discussed), thermophoresis, and electrostatic forces. Diffusion causes nanoparticles to move throughout the tube and possibly stick to the tube sidewall [102]. Thermophoresis, the effect that gas atoms near a hot surface have higher kinetic energy, can cause nanoparticles to move away from the tube wall if the tube is warmer than the gas flow or toward it if cooler [222][102][126][223]. Finally, charged particles will be attracted to electrically conductive tubing walls via image charge or possibly to charge built up on electrically insulating tubing [224][225]. We typically want particles to move through tubes like this without being lost by sticking to their walls, so we might choose to use large tube diameters, maximize gas speed to minimize residence time, or heat the tubes to induce thermophoretic force [126].

Gravity: So far we have ignored the effect of gravity on particle motion, and we can justify continuing to do so. Equating the force from $g = 9.8 \text{ m/s}^2$ Earth gravity to air drag in atmosphere gives a 10 nm particle a terminal velocity $v = \tau \cdot g$ of only $3 \times 10^{-7} \text{ m s}^{-1}$ compared to the much larger²⁵ $4.6 \times 10^{-4} \text{ m}$ diffusion in 1 s we computed in section 4.1.1.

All that suffices to understand basic particle motion in a gas. In order to achieve our goal of printing particles on a surface at 100 m s^{-1} to 3000 m s^{-1} with sub-1 μm resolution, we'll need to carefully consider the motion of gas and nanoparticles through velocity-increasing nozzles and around surfaces.

4.2.1 Nozzles and Why We Want Vacuum

Consider what is required to print particles onto a surface via aerosol manipulation. When a gas flow is aimed at the surface, it breaks and turns to either side. If particles follow the gas streamlines exactly, as happens at high pressures (due to low stopping distances), they will be blown off to the side and will not reach the surface²⁶. In order to print particles, we need their stopping distance to be long enough that they can diverge from the gas streamlines and instead travel straight onto the surface via inertia. This is done by making the gas pressure above the substrate be low: a partial vacuum²⁷.

We then need to design the gas flow to focus particles to a narrow area (our sub-1 μm resolution) and high speed (we want 100 m s^{-1} to 3000 m s^{-1}). This is the job of a nozzle.

²⁵This is subtly misleading because diffusion increases with square root of time, but the conclusion holds.

²⁶Except maybe through Brownian diffusion, which is very imprecise.

²⁷This won't be high vacuum because we're continually adding gas into the area.

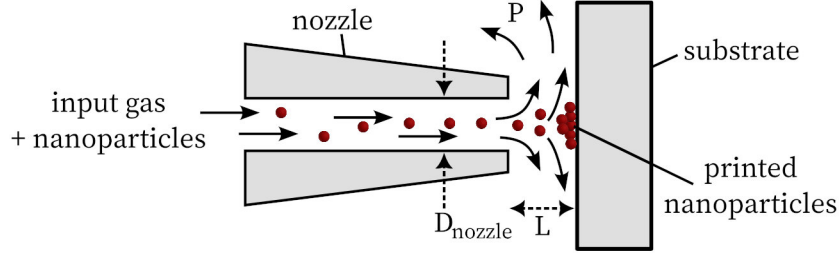


Figure 4.6: In order for nanoparticles (red circles) to be printed onto a surface, they can be accelerated and focused within a nozzle, but once exiting the nozzle they must continue to travel straight to reach the surface despite gas streamlines (black arrows) turning to the side, which can be achieved by making pressure P low. The distance L between nozzle and substrate is often comparable to nozzle diameter D_{nozzle} . Also, Brownian diffusion causes particles to spread out from the centerline anyway, decreasing resolution.

We can approximate what the pressure P above the surface must be even before knowing more specifics of the gas airflow. Particles travel a distance L between nozzle and substrate, and L must be nonzero and often greater than nozzle diameter D_{nozzle} so the gas has somewhere to go. D_{nozzle} is limited by manufacturing and flow rate concerns to be larger than 0.1 mm to 1 mm, so assume $L \geq 1$ mm. We know the particle stopping distance S has to be significantly larger than this, i.e., $S > L$ (preferably $S \gg L$ because we want particles to have nonzero velocity upon impact). This dimensionless quantity S/L is called the Stokes number [102]. According to table 4.2, particles above 1 μm diameter might have $S > L$ in 760 Torr atmosphere, but below 100 nm a lower pressure closer to 1 Torr is required. This explains the divide between cold spray and aerosol deposition we saw in chapter 3: cold spray uses large particles so it works at atmospheric pressures, but aerosol deposition needs vacuum; its literature reports pressures of 0.1 Torr to 10 Torr²⁸ [185]. Even lower pressures are counterproductive as they require bringing the gas closer to the free molecular flow regime even upstream of the nozzle, limiting focusing drag force and increasing diffusion.

How much particle focusing and acceleration is possible? We want high resolution ($< 1 \mu\text{m}$) and high speeds (100 m s^{-1} to 3000 m s^{-1}). The literature has several nozzle geometries:

Aerosol impactors: at its most basic, a nozzle can be just a narrow cylinder through which particles travel as in figure 4.6. Printing resolution is larger than the nozzle diameter D_{nozzle} (generally $> 100 \mu\text{m}$) due to gas drag and Brownian diffusion. Velocities are limited by choked flow to about sound speed ($< 400 \text{ m s}^{-1}$). This simple mechanism finds use in the aerosol (cascade) impactors (as mentioned and used in chapter 2) that aim to efficiently collect nanoparticles on a substrate for later analysis with no need for high resolution or velocity [102][226][227][228]. Mass spectrometer interfaces are similar sans substrate [219]. These were briefly applied as “gas deposition”, a precursor to aerosol deposition [229][230].

Converging-diverging (de Laval) nozzles: Initial work in the 1980s [231][232][233] found that in a converging-diverging nozzle²⁹, nanoparticles are given inertia to move toward the

²⁸This pressure range is why we used 760 Torr and 1 Torr as example pressures throughout this chapter.

²⁹These de Laval nozzles are also found on rocket engines.

nozzle center as the gas flow through the nozzle converges, and as the flow diverges (often at lower pressure) the drag force pulls particles away from the center. Proper nozzle design balancing these forces with particle inertia can result in focusing particles in the gas flow into a beam significantly more narrow (100x in theory) than the mechanical diameter of the nozzle, so a 100 μm nozzle, about the smallest feasible to build, can print with down to 1 μm theoretical resolution (ignoring Brownian motion). These nozzles are now ubiquitous in cold spray and aerosol deposition [234]. The gas velocity through these nozzles can be somewhat supersonic (in practice, below about 1000 m s^{-1} [59]); particle impact speed is somewhat lower than this (often $< 700 \text{ m s}^{-1}$) [235] after particles slow down as they cross gas streamlines (bow shock, in supersonic nozzle flow [236][237]) between the nozzle and substrate [238]. Also, focusing depends strongly on particle diameter [236][237][239].

Sheath gas and collimation: Modifications can be made to converging-diverging nozzles, e.g., gas relief channels can reduce pressure for higher impact speeds [235], a stream of gas with particles can be surrounded by a sheath gas stream and the result compacted in a nozzle [240][239], or a collimating section can be added [241]. These latter methods can provide additional focusing and also help increase pressure upstream of a nozzle to maintain choked flow for high speeds. Some setups achieve experimental 10 μm to 20 μm printing resolution (the best demonstrated with aerosols to our knowledge) and 2 μm theoretically (neglecting Brownian motion), but with only 100 m s^{-1} velocity [239][241][242][240].

Aerodynamic lenses: Serially stacking converging-diverging nozzles (which can be as simple as a single orifice each) can better focus nanoparticles: this is called an aerodynamic lens [214][243][244][245][246][247]. A calculator exists for easy design [61][248]. Though smaller particles are harder to focus due to their lower inertia and higher diffusion, aerodynamic lenses provide a design framework that has been used to focus particles as small as 1 nm to 10 nm [244][125], though focusing resolutions are generally $> 100 \mu\text{m}$, velocities are usually $< 100 \text{ m s}^{-1}$, and many particles are lost by adhesion to the lens sides. Deposition works [249], but the end of such a lens often opens into high vacuum to create particle beams for mass spectrometry or spectroscopy. [214] gives an expression for particle beam broadening due to the initial angular spread from Brownian motion when entering high vacuum.

We can see these aerosol nozzle particle focusing methods can approach the printing velocities and resolutions we want but cannot quite reach them. They are somewhat further suboptimal for deposition as discussed in chapter 3 for the following reasons:

- Velocity limits: gas flows are generally limited to slightly-supersonic $< 1000 \text{ m s}^{-1}$, and particle speeds are somewhat slower than this. Though aerosol deposition and cold spray reach the 100 m s^{-1} to 500 m s^{-1} minimum speeds required for deposition, the higher velocities (3000 m s^{-1}) we hypothesized may be useful do not seem feasible.
- Resolution limits: the highest printing resolution experimentally demonstrated to date is only 10 μm [241] (for $> 500 \text{ nm}$ particles; smaller is harder) and it is not clear whether better is possible. Below we give another argument that sub-1 μm resolutions are unlikely due to Brownian diffusion.
- There is significant gas flow around the part under construction, which may damage fragile printed objects or be affected by substrates heated for epitaxy.

As a final argument that further development of aerosol-based focusing is unlikely to lead to our desired printing resolution, consider limits due to Brownian diffusion. In the setup of figure 4.6, suppose particles are perfectly focused into a tight beam (< 10 nm diameter) within a nozzle then leave at a maximum 1000 m s^{-1} and travel a minimum 1 mm distance to the substrate (again, the surrounding gas pressure must be sufficiently low for the particle to make it to the substrate). In the $1 \mu\text{s}$ of travel time, we can approximate how far particles can diffuse perpendicular to their direction of travel using equation 4.8; twice this is the minimum particle placement resolution. The printing resolution is limited both by diffusion/placement and by particle size ($1 \mu\text{m}$ particles cannot print a line $< 1 \mu\text{m}$ wide).

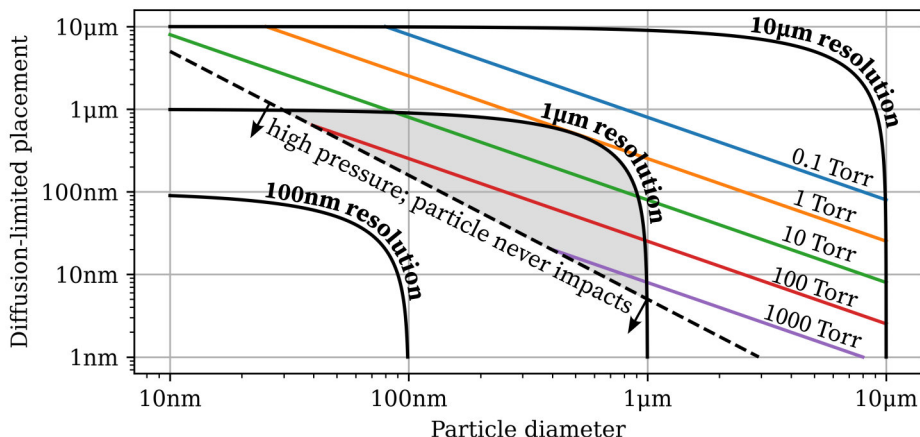


Figure 4.7: A rough model of aerosol printing resolution limits as described above. Achieving a given resolution (100 nm , $1 \mu\text{m}$, 10 nm) requires both a small particle size and low Brownian diffusion, but increasing the pressure to minimize diffusion eventually means the particle stopping distance is too short and it never hits the substrate. There is only a small region (shaded light gray) where $1 \mu\text{m}$ printing may be possible; 100 nm never is, and unfortunately this requires large ($> 100 \text{ nm}$) particles less likely to make high-quality electronic thin films. It makes sense that the literature’s best printing resolutions are just under $10 \mu\text{m}$.

We can conclude that aerosol nanoparticle manipulation is close but insufficient; it can neither focus nor accelerate particles as much as we would like to make interesting devices.

In order to achieve higher velocities and resolutions, we will have to consider methods not limited by Brownian diffusion, i.e., electrostatic forces in vacuum (as a limit, recall single-atom focused beam methods can achieve sub- 10 nm resolution and $> 1 \times 10^4 \text{ m s}^{-1}$). It is worth dedicating our effort (chapters 5, 6) to investigating these instead of pure aerosols.

However, aerosol manipulation is still useful. It is convenient for moving nanoparticles around before printing (we used it already in chapter 2) and might be used for bringing nanoparticles into vacuum in a controlled way before further electrostatic manipulation. Furthermore, aerosol focusing will let us test multimaterial deposition albeit with low impact speeds and bad resolution. We’ll try that now.

4.3 Experimental Implementation

Although aerosol deposition cannot by itself reach the full range of deposition velocities and high resolutions we want, it can print nanoparticles with the minimum 100 m s^{-1} to 500 m s^{-1} velocity required for minimal particle-substrate adhesion and with sub-1 mm (not sub-1 μm) resolution. We constructed such a system to demonstrate multimaterial printing with the nanoparticle sources we built in chapter 2. Because the system includes moving nanoparticles into a vacuum chamber, it is also an excellent starting point to build a future electrostatic focusing and acceleration apparatus as described in chapters 5 and 6.

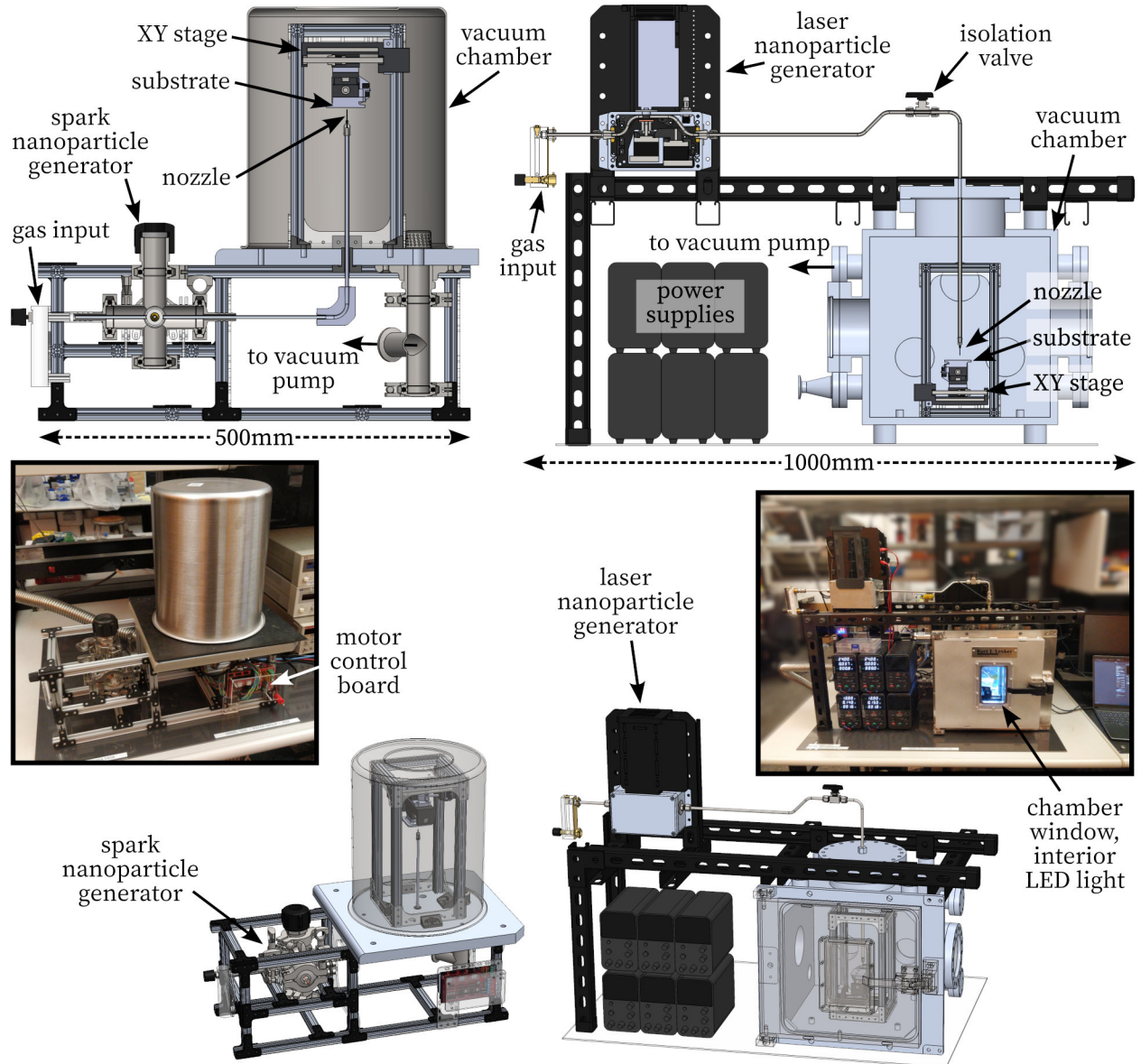


Figure 4.8: Two versions of the same system. Left: first version with spark ablation nanoparticle generator. Right: second version with larger chamber and laser nanoparticle generator.

Safety note: vacuum chambers are generally safe except for minor implosion concerns. Placed in standard atmosphere, a 300 mm cube vacuum chamber has a pressure differential of one atmosphere (101 kPa or 760 Torr) giving a potential energy of 2.7 kJ that can be suddenly released. This risk is easily minimized by sufficiently robust construction. This is also significantly safer than pressure vessels (like gas cylinders or common workshop air compressors): even the best vacuum chamber has a pressure differential of at most one atmosphere, but pressure vessels can be pressurized to potentially tens or hundreds of times atmospheric pressure with proportional stored energy.

We actually made two iterations of the same system. The first was built around the spark ablation nanoparticle generator from chapter 2. This system was replaced with the second which instead used the the laser ablation nanoparticle generator and also added a larger, higher-quality vacuum chamber. The systems otherwise worked similarly.

Both systems were constructed with a vacuum chamber as required for printing nanoparticles (see section 4.2.1). The first system used a custom³⁰ cylindrical chamber (220 mm diameter by 270 mm tall); the second had a commercially-built³¹ high-vacuum-capable chamber with a 300 mm cubical interior. Both were pumped with an 160 L min⁻¹ Edwards RV8 rotary vane vacuum pump and monitored by an Edwards APG-M-NW16 Pirani vacuum gauge. The chambers could both reach a base pressure of under 5×10^{-2} Torr within a couple minutes as expected. Progressively lower vacuum levels need progressively better hardware (see [207]). In our case, we needed only 1 Torr pressure, well within the low vacuum range that only requires a single pumping stage, and only used air (any semiconductor process gas, for example, would need much more attention paid to safe usage, venting, and exhaust). This meant we were able to take shortcuts for the first chamber: wire feedthroughs were custom made with laser-cut acrylic³² bolted with o-rings to the aluminum baseplate, for example. The second chamber was made with significantly more care including CF flanges and commercial electrical feedthroughs and should be capable of reaching high vacuum ($< 1 \times 10^{-5}$ Torr) if a second pumping stage (e.g., turbopump) were later added.

After leaving the nanoparticle generators, aerosols were moved through standard 1/4 inch (4.6 mm ID) stainless steel instrumentation tubing connected with compression and VCR face seal fittings, eventually reaching the nozzle, a 20 mm long 0.21 mm ID (27 gauge) steel dispensing needle inside the vacuum chamber positioned 1 mm to 3 mm from the substrate. Total flow distance from the nanoparticle generator to nozzle was 380 mm or 800 mm for the two system versions, respectively. During operation, an input gas valve was adjusted to allow about 0.5 standard liter per minute gas flow (air) through the nanoparticle generators to each chamber. When entering the vacuum chamber through the nozzle and with our vacuum pump, this gas flow resulted in steady state chamber pressures of 0.5 Torr to 1 Torr. Based on the choked flow assumption and similarity to mass spectrometer inlet capillaries [219][220], we estimate nozzle gas (and particle) exit velocities were 100 m s⁻¹ to 350 m s⁻¹.

³⁰An epoxy degassing pot on top of a custom aluminum faceplate with a neoprene rubber gasket.

³¹From the Kurt J. Lesker Company. This chamber was bought cheap at auction; new it is worth >\$10k.

³²With wires through holes sealed with (sometimes) hot glue. Don't do that on better vacuum systems.

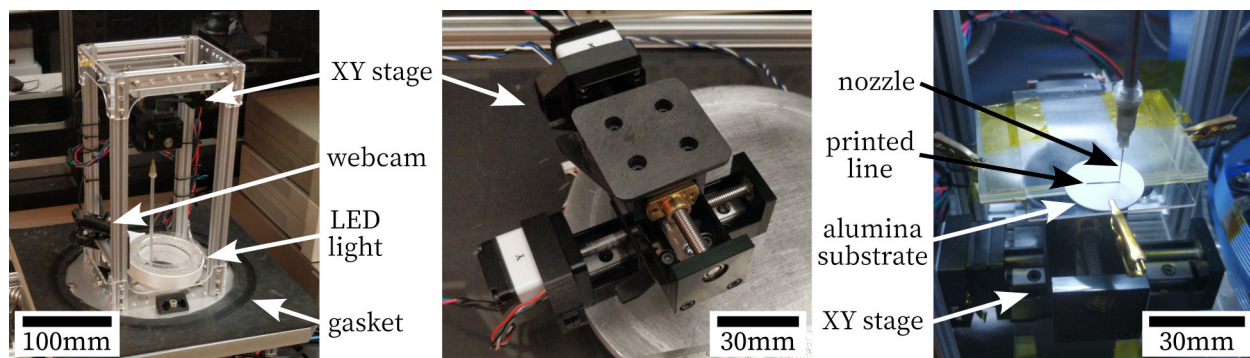


Figure 4.9: Left: first version with vacuum chamber cover removed to show XY stage, nozzle, webcam, and light. Center: custom XY stage. Right: inside of second version while printing the gold line from section 4.3.3 on an alumina substrate clamped to the XY stage.

Besides the large vacuum chambers, the largest addition to these systems beyond the basic impaction setup we used in chapter 2 was a motorized XY stage able to move the substrate (clamped on top of the stage) with respect to the nozzle in order to print 2D patterns. It is preferable to move the small and light substrate while keeping the nozzle, which is connected to rigid tubing, fixed in place³³. Small vacuum-compatible XY stages with nanometer precision are commercially available³⁴. We built our own stage from stepper motor linear slide modules, open loop stepper motor drivers, and open source 3D printer control software. This XY stage could move about 40 by 40 mm with estimated 10 μm repeatability. Besides the stage, we also added a USB webcam camera and LED light inside the vacuum chambers to observe the printing process. None of the XY stage, webcam, or light needed special care to survive the vacuum³⁵.

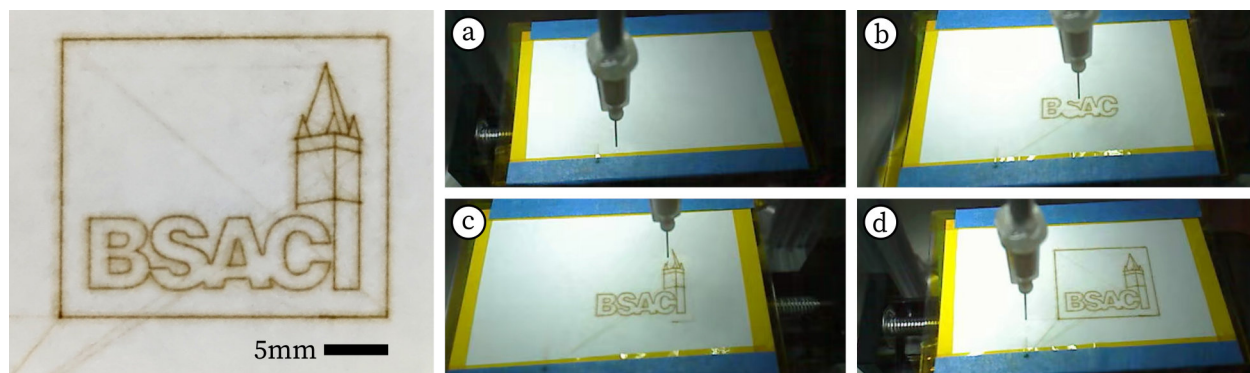


Figure 4.10: Left: BSAC logo in copper on paper, printed in 45 min. Right: the printing process at (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min.

³³The electrostatic focusing system of chapter 6 replaces the nozzle and is larger and heavier. But then, given charged particles, we might additionally deflect particles electrostatically in XY (like scanning electron microscopy) for fast small motion. A mechanical XY stage is still necessary for long-distance movement.

³⁴Piezo motor or voice coil stages with optical feedback are >\$5k from [250][251][252].

³⁵This worked because (a) we used no harmful process gases and (b) we did not need high vacuum which offgassing or virtual leaks from these parts might prohibit. We also found no heat dissipation problems.

As an initial test, we printed the logo of the Berkeley Sensor and Actuator Center (BSAC) with copper nanoparticles on paper. Using the deposition conditions outlined above with the spark ablation nanoparticle generator and moving the XY stage created the successful result shown in figure 4.10. The stage was moved at 0.1 mm s^{-1} below the nozzle; at this speed, the total print took 45 min to complete. This could be sped up significantly by increasing the nanoparticle flow rate or printing thinner lines. The printed lines had a dense inner portion about $160 \text{ }\mu\text{m}$ wide and a fainter $400 \text{ }\mu\text{m}$ outer portion, respectively thinner and thicker than the 0.21 mm nozzle. Nanoparticles were continually generated, so in order to print disconnected patterns (the “B” and rectangular border, for example), the stage was moved at a faster 1 mm s^{-1} between these thereby creating only faint (diagonal) lines³⁶.

It is interesting to note standard microfabrication cannot replicate this. Specifically, microfabrication cannot deposit a metal shape on paper substrates³⁷ because the paper would not survive the wet chemical photoresist developing and removal steps required to pattern the metal, not to mention whatever process is used for etching.

4.3.1 Multimaterial Printing

As emphasized in chapter 1, semiconductor devices are made of multiple electronics-grade materials, and one of the most interesting possibilities of a nanoparticle printer is the ability to pattern multiple such materials in a single tool.

We already demonstrated generation of nanoparticles from 8 different materials and printing on glass, steel, and silicon in chapter 2. We have also printed copper on paper. What remains to be shown is that multiple materials can be added to the same part³⁸.

To prove this is possible, we printed lines of copper, silver, gold, and silicon (in that order) on an alumina substrate. Specifically, we began with a 25 mm diameter alumina disk (96% Al_2O_3 , remainder SiO_2) then deposited one material at a time, moving the substrate at 0.1 mm s^{-1} for 2.5 min each with the same parameters used previously, to create 15 mm long lines. After each line, the laser nanoparticle generator was stopped, opened, and had its material target changed out, all while the substrate remained at vacuum.

The successful result is shown in figure 4.11. All lines were about $500 \text{ }\mu\text{m}$ wide; more detailed geometry measurements are shown in section 4.3.2. This is significantly wider than the 0.21 mm nozzle. Interestingly, each material demonstrated subtly different behavior despite being deposited in the exact same conditions (including laser nanoparticle parameters, gas flow rate, and print speeds). Copper and silver stuck to the substrate and printed well-defined clean lines. The gold adhered to both itself and copper and silver lines beneath but not to the substrate, resulting in a film that flaked off (especially when blown away by gas escaping the nozzle). As briefly noted in chapter 2, the poor adhesion of gold to alumina is due to its inability to oxidize. This is a known effect in microfabrication solved by depositing gold films instead on an intermediate Cr or Ti film as an adhesion layer. The printed silicon, finally, produced a thin yet tall ridge (see section 4.3.2).

³⁶In future work this could be replaced with a proper beam blanking mechanism.

³⁷Except maybe with a shadow mask, which has other drawbacks. See elaboration on this in section 4.3.1.

³⁸Given a functional printer this might seem trivial. It somewhat is—that’s why printers are interesting.

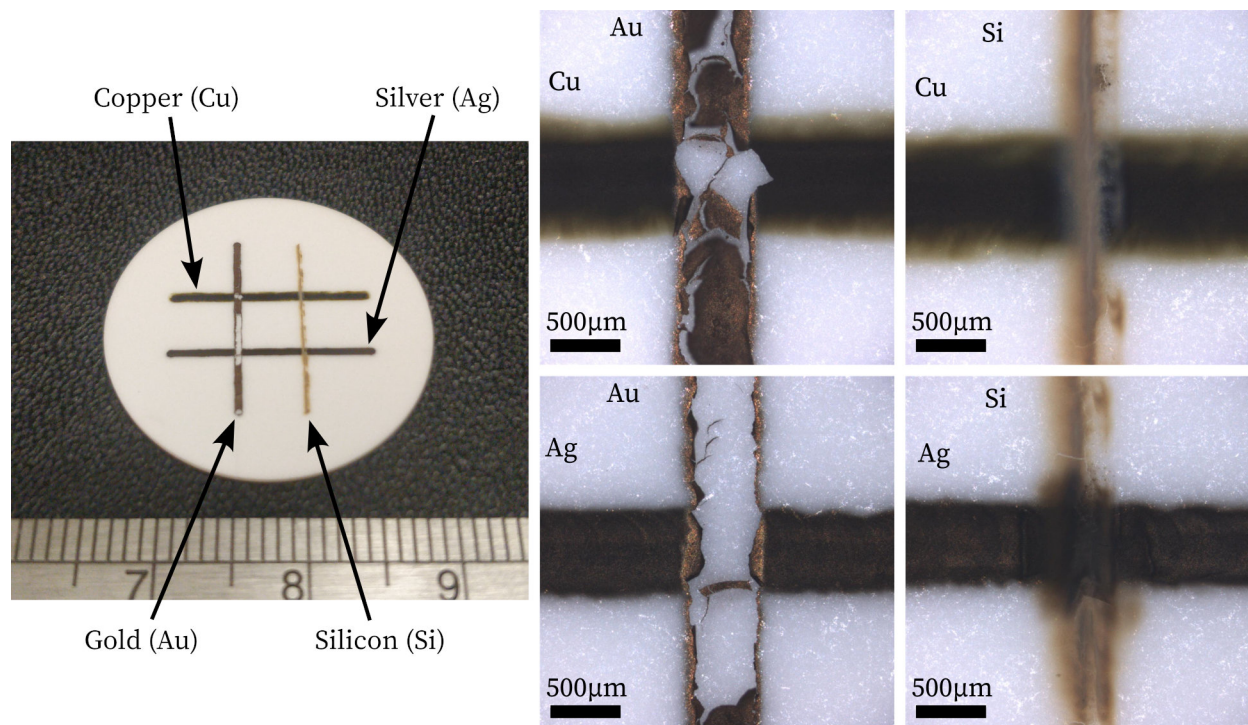


Figure 4.11: Left: copper, silver, gold, and silicon lines printed (in that order) on an alumina disk. Right: clockwise from top left, the intersection of Cu/Au, Cu/Si, Ag/Si, and Ag/Au.

Despite this result, more work remains to produce a working multimaterial semiconductor device (for example, a diode); we have yet to reliably print even simple conductors besides gold. We believe this is solvable: we discuss the major roadblock, oxidation, in section 4.3.3. The other problem is low film quality: as hypothesized in section 4.3.2, these lines are porous with sub-bulk qualities. The way to fix that (see chapter 3) is to print with higher particle impact velocities using something better than aerosol deposition.

But we have still shown another feat microfabrication cannot replicate: this simple pattern was printed in 10 min, but it would have taken microfabrication many hours to make this because each different material requires its own deposition, lithography, and etch steps.

For completeness, there is one microfabrication technique that can achieve similar results: stencil lithography [253][254], where a thin membrane with holes (a shadow mask) is placed in between an evaporator material source and a substrate in high vacuum³⁹. The mask can be moved to change where material is deposited [255]; switching materials allows multimaterial deposition. Sub-100 nm patterning has been achieved. However, deposition rates are slow (1 nm s^{-1}), so patterning large arbitrary custom structures takes unreasonably long, and the stencil can become clogged over time. As a result, this is used only for occasional nanoscale research tasks. Nanoparticle printing, though it has yet to achieve the same printing resolutions, has neither of these limits and should be better suited to general applications.

³⁹This can be modeled as apertures subject to the emittance theorem (see chapter 6).

4.3.2 3D Printing

Up until now, we have only discussed printing in 2D⁴⁰. Theoretically a nanoparticle printer can easily extend this to 3D: simply print multiple 2D patterns on top of one another⁴¹. Doing this requires each layer to be thick but might allow printing MEMS.

We can get some preliminary evidence that printing thick layers is possible. We used a 3D laser confocal microscope to measure the cross-section of the Cu, Ag, Au, and Si lines we printed in section 4.3.1 with results shown in figure 4.12. These lines were about 500 μm wide and 10 μm tall with the exception of silicon that formed a 50 μm high peak.

We can also use these cross-sections to estimate the volume of the printed lines and, from there, the rate at which material was deposited. The volumes of these 15 mm long lines are, for Cu, Ag, Au, and Si, 0.033 mm^3 , 0.039 mm^3 , 0.053 mm^3 , and 0.095 mm^3 . Since each was printed in 150 s, this gives possibly unrealistically high mass deposition rates of 7.1 mg h^{-1} , 9.9 mg h^{-1} , 25 mg h^{-1} , and 5.3 mg h^{-1} . In chapter 2, we estimated the laser ablation nanoparticle generation rate at only 0.6 mg h^{-1} to 6 mg h^{-1} . We can conclude that a large fraction of material was successfully transferred as nanoparticles from material target to substrate (i.e., high efficiency) and these lines are probably porous with lower density than bulk, as expected from low particle impact velocities (see chapter 3).

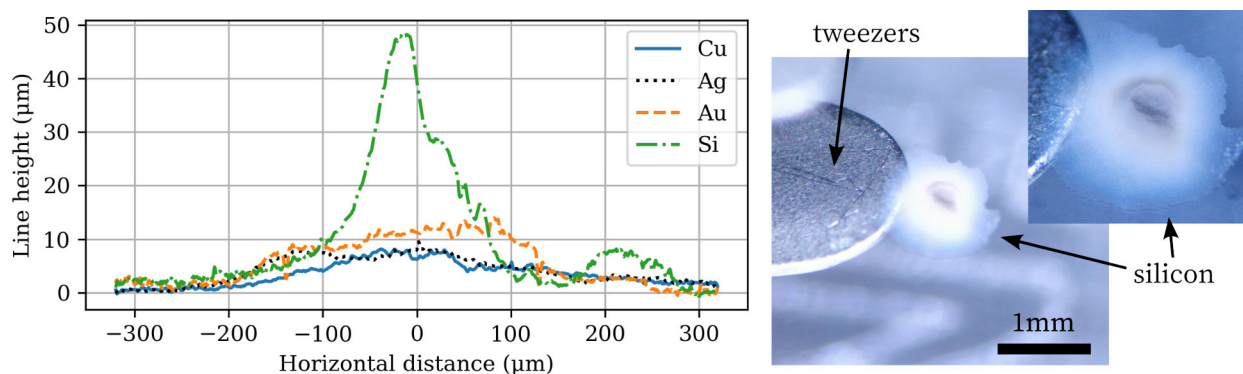


Figure 4.12: Left: height profiles of the lines printed in figure 4.11 showing 3D geometry. Right: a 3D conical silicon deposit in midair stuck to tweezers.

These deposits may be thick enough for 3D printing, but we can do better: focusing the same nanoparticles to a smaller area (and with higher impact velocities) as we eventually hope to do should produce thinner yet taller lines. It might also improve the rough surface (which is likely due in part to forces from impacting gas).

Also, in a separate experiment while printing silicon on glass, we noticed a large silicon deposit detached from its glass substrate (see figure 4.12). It stuck to a pair of tweezers used to pick it up, technically becoming a freestanding structure. This supports the hypothesis that nanoparticle-printed structures are sufficiently solid to form 3D shapes.

⁴⁰Aside from mentions of aerosol 3D printing in chapter 1, which remain promising.

⁴¹Overhanging geometry can be made by printing then later etching away a sacrificial support material.

4.3.3 Conductors and Oxidation Problems

We can print multiple materials, but we should also show they still exhibit the electrical behavior necessary to make semiconductor devices. A good first step is confirming expected conductors (and semiconductors) are electrically conductive and insulators are not.

We confirmed printed gold is conductive. We deposited another 15 mm gold line on alumina (an insulator) with the same parameters as in section 4.3.1. As previously noted, the gold formed a solid film that flaked off due to poor adhesion to the alumina substrate, but it was still sufficiently solid to confirm conductivity. On a probe station, we positioned two micromanipulator probes about 100 μm apart atop one gold flake and measured a resistance of about 4 Ω fluctuating slightly with time (and removing the probes left visible scratches). This is conductive; we attribute the somewhat high⁴² resistance and fluctuations to the hypothesized porous structure and resulting minor local joule heating. This should be fixed by creating a more solid film by increasing particle impact velocity as in chapter 3.

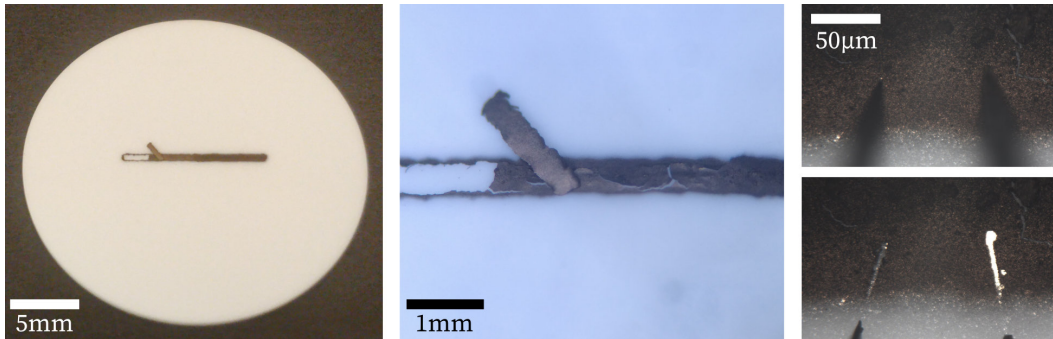


Figure 4.13: Left: gold line printed on alumina. Center: gold flakes off substrate. Right top: two probe tips on edge of gold line. Right bottom: visible scratches with probes removed.

However, repeating this with copper gave no measurable conductivity. It seems metals (and Si) other than gold are not conductive when they should be. This is problematic.

The problem is almost certainly oxidation: oxygen molecules that hit a surface will often react with the exposed atoms⁴³ to form an oxide that happens to be an electrical insulator. Copper becomes⁴⁴ CuO or Cu_2O , aluminum becomes Al_2O_3 , silicon becomes⁴⁵ SiO_2 . The gas flowing through our system was air, which contains much more than enough oxygen to oxidize the surface of nanoparticles nearly as soon as they are created, so the final printed material might be mostly insulating oxides with, at best, small isolated pockets of conductive metal that were incompletely oxidized. Gold is the exception as it is the only metal without a thermodynamically stable oxide. Oxidation is why welding needs inert gas, soldering needs flux, and why iron rusts⁴⁶. The oxidation hypothesis is further supported by our EDS image of printed copper in chapter 2 which found significant oxygen.

⁴²A solid 100 by 100 by 5 μm gold film should have 0.0049 Ω resistance.

⁴³Sometimes oxygen can also diffuse through a material to oxidize more atoms underneath.

⁴⁴Copper oxides are P-type semiconductors, but it is hard for us to take advantage of that right now.

⁴⁵This is useful in microfabrication to purposely grow thin films of SiO_2 on silicon [1].

⁴⁶Rust is just iron's oxide, but it happens to expand and become mechanically unstable when grown.

In other words: if our experiments were repeated but all oxygen were magically removed from the surrounding air, everything would still work and our printed copper, silver, and other metals would be conductive, and the silicon would likely be properly semiconducting. If not for oxygen, we might have printed diodes and transistors by now.

The best solution⁴⁷ to the oxidation problem is exactly this: to remove oxygen (and water vapor, which contains oxygen and can act similarly) from the chamber. Perfect removal is near-impossible, so we should ask exactly how much oxygen our process can tolerate.

We would like nanoparticles to remain (at least mostly) oxide free from their creation until they are printed⁴⁸ and covered with another layer of particles. Suppose this takes several seconds. Using equation 4.3 we can calculate it takes about 1 s for oxygen at a partial pressure of 1×10^{-6} Torr to completely cover a surface; this is a good minimum pressure target to aim for though lower is of course preferable.

Reaching oxygen pressures below 1×10^{-6} Torr is well within vacuum technology capabilities and is commonly used in microfabrication evaporation for this same reason [118]. This falls within the high vacuum regime (8×10^{-5} Torr to 8×10^{-9} Torr [207]); the typical approach is to bring a sufficiently good vacuum chamber down to a full vacuum (no gases including oxygen) then optionally backfill it with some other non-oxygen gas if desired (as used in sputtering [118]). What makes things a little more difficult is we need near-atmospheric pressure for the nanoparticle generators; those sections of our system need gas with part-per-billion oxygen levels. Argon is sold with part-per-million oxygen impurities but can be further filtered before flowing into a gas chamber to reach these low levels [58]. All this does require significant attention paid to chamber materials, cleanliness, and vacuum pump stages, but it may be worthwhile: another benefit of high vacuum is a large gas mean free path with negligible Brownian motion, and we may be able to take advantage of this to achieve high precision as discussed in chapter 6.

It is also useful to monitor oxygen and water vapor levels to confirm the desired low oxygen pressures are reached. Monitoring methods include [257] electrochemical sensors, optical sensing (spectrometry) [149], and residual gas analyzers [207].

Unfortunately we were unable to obtain a sufficiently good vacuum system within the time and budget constraints for this dissertation⁴⁹, so we will have to postpone printing non-gold conductors and semiconductors to future work.

However: we can still conclude multimaterial nanoparticle printing, the first half of what we need to create a better device fabrication technology, seems feasible. Since we were not able to reach the second half—high particle resolutions and impact velocities—with aerosols, as proposed in 3 we will now consider electrostatic manipulation of nanoparticles to further refine their movement.

⁴⁷An alternative solution is to make the gas actively reducing (often “forming gas”, a 5% H / 95% N₂ mixture) to counteract oxide growth, but this might create other problems.

⁴⁸Interestingly, the impact and deformation of the larger particles of cold spray can break through their surface oxide coating, allowing printing metals in atmosphere. This doesn’t work on our smaller scales [256].

⁴⁹We did briefly try using 1ppm nitrogen gas flow instead of air, but we saw no benefit as expected as the resulting 1×10^{-3} Torr oxygen partial pressure in the nanoparticle generator remained too high.

Chapter 5

Nanoparticle Charging

So far we have created nanoparticles, moved them in a low-pressure gas, and achieved some limited multimaterial printing success, but also found we need additional control over nanoparticle motion if we want to print truly small or high-quality structures. That control will come from electrostatic manipulation in chapter 6, but in order to move nanoparticles with electric fields, we must first electrically charge the nanoparticles.

That is, we must somehow add or remove electrons from each nanoparticle without affecting the positively-charged atomic nuclei thus leaving the particle with a negative or positive charge, respectively—and we need to do this while the particles remain suspended in midair to avoid compromising their material purity. This is nontrivial.

5.1 Charging Methods

Fortunately for us, plenty of nanoparticle charging prior art exists in the academic literature. Aerosol studies often charge nano- to micron-scale particles as the first step in measuring, collecting, or otherwise manipulating them. Charging (albeit for single atoms and molecules) is also fundamental to mass spectrometry, focused ion beam tools, and trapped-ion quantum computing. Charging methods include (but are not limited to) [102][76]:

- **Diffusion charging:** Suppose particles are in a gas and some gas molecules are ionized (unipolar, i.e., either positive or negative, not both). When an ionized molecule collides with a particle via Brownian motion, an electric charge is sometimes transferred. Repeated collisions can build up a large charge. If the gas has both positive and negative ions (a bipolar distribution), this can instead discharge.
- **Field charging:** This is diffusion charging in the presence of a uniform electric field, which more efficiently charges larger particles due to electric field distortions around the particles. Diffusion and field charging are often combined.
- **Corona, flame, radioactive, and photoelectric charging:** These are all methods to charge the gases that then charge particles via diffusion and field charging. Corona

charging uses high voltage breakdown of the gas, flame charging uses thermionic emission via the high temperature of a flame, radioactive charging uses an α or β source, and photoelectric charging uses the photoelectric effect.

- **Photoelectric charging:** Photoelectric charging can directly charge nanoparticles without diffusion or field charging as an intermediary [258]. Photons of sufficient energy (often UV or x-ray) hit a surface, are absorbed by electrons, and give them sufficient kinetic energy to leave the particle. This is the dominant mechanism for charging dust around a star or in the interstellar medium [259].
- **Electron impact ionization:** Bombarding nanoparticles with electrons can give them a negative charge or, via secondary electron emission, a positive charge [260][261]. Used in mass spectrometry for charging molecules; has been used for cluster beam deposition [178][47]. Requires high vacuum for the electron mean free path to be sufficiently long. Important in lunar dust behavior along with photoelectric charging [262].
- **Electrospray ionization:** A way to simultaneously generate and charge nanoparticles using a liquid medium (see also its description in chapter 2). Used as a mass spectrometry ion source or a liquid metal ion source (LMIS) for focused ion beam tools [76][108][109]. It is possible to charge nanoparticles [112], but we will ignore this as the process is messy, material-dependent, and might compromise material purity.
- **Field and thermionic emission:** More a fundamental physical effect than a charging method. Electrons are pulled from a material surface with a sufficiently strong electric field (field emission) or break away with sufficiently high kinetic energy from high temperature (thermionic emission). Commonly used for, e.g., electron microscopes. Is used for electron impact ionization. Sometimes flame charging makes nanoparticles emit electrons via thermionic emission in addition to field and diffusion charging. Field emission is also responsible for charging limits as described later.
- **Spark ablation:** The same spark ablation process used to generate nanoparticles can also allow some to end up with a charge due to the large ion concentration in the spark arc, not dissimilar from corona charging. The resulting nanoparticles have a distribution of positive, negative, and neutral charges [128].

All these methods have different capabilities. They result in different charge distributions (some percentage of nanoparticles are positively charged, neutral, and negative) and have different efficacies on nanoparticles of different diameters (e.g., field charging is more effective for larger particles). Many nanoparticle charging applications, such as mass spectrometry or the differential mobility analyzer (DMA) previously mentioned as a way to sort nanoparticle diameters, prefer methods that more reliably give a single electrical charge to all sizes of nanoparticles. This makes it easy to sort nanoparticles based on mass-to-charge ratio.

What qualities do we want from a charging method? As we will see later, we prefer nanoparticles to have as high a charge as possible, and we would also like to ensure all nanoparticles (instead of only a small fraction) are charged. To choose a method, we should first discuss maximum charge limits.

5.1.1 Charging Limits

There is a limit to how much charge can be put on a nanoparticle. If the negative charge is increased by adding electrons, the nanoparticle can have such a negative charge that any additional added electrons are spontaneously repelled. Likewise, if electrons are removed to leave a positive charge, there is a point at which repulsion between the positively charged nuclei is sufficient to break up the nanoparticle. This limit can be approximated [102] by comparing the surface electric field strength E_s needed to remove an electron (i.e., field emission) or nucleus to the field present on the surface of a charged particle of diameter d_p from Gauss's law $E_s = (ne)/(\pi\epsilon_0 d_p^2)$, where n is the number of elementary charges on the particle, $e \approx 1.60 \times 10^{-19}$ C is the elementary charge, and $\epsilon_0 \approx 8.85 \times 10^{-12}$ F m⁻¹ is the permittivity of vacuum. This maximum number of charges n is

$$n \leq \frac{\pi\epsilon_0 E_s d_p^2}{e}. \quad (5.1)$$

The precise value of E_s , often modeled with Fowler-Nordheim theory, is heavily dependent on the surface. For a rough estimate, Hinds [102] suggests $E_s \approx 9.0 \times 10^8$ V m⁻¹ and $E_s \approx 2.1 \times 10^{10}$ V m⁻¹ for electron and nucleus emission, respectively.

There are limits for the diffusion and field charging methods mentioned above: a charged nanoparticle will electrostatically repel similarly charged gas molecules, reducing the likelihood of further charging[102]. All these charge limits can be quantitatively graphed:

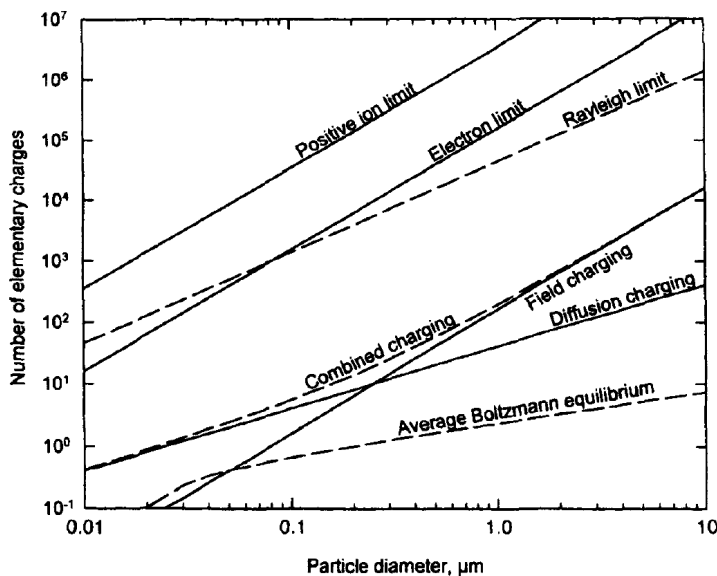


Figure 5.1: The limits to nanoparticle charging, from [102]. Above the positive ion limit, removing additional electrons will cause a nanoparticle to break apart via repulsion between positive nuclei; above the electron limit, adding more electrons is impossible as any new electrons are spontaneously repelled due to excess negative charge. The Rayleigh limit is the point at which liquid droplets break up overcoming surface tension. Contrast these with the much lower maximum charging limits achieved by field and diffusion charging or the average charge achieved in standard atmosphere due to background radiation.

For our desired nanoparticle diameters of approximately 5 to 50 nm, we see that positive charge is limited to hundreds of unit charges and negative charge sometimes to the low tens: if we positively charge nanoparticles, we can fit a higher net charge. But also note that field and diffusion charging may struggle to add even a single charge to a sufficiently small nanoparticle, far from the theoretical maximum.

The best nanoparticle charging method for us is likely photoelectric charging. It is theoretically able to charge particles to their maximum limits, unlike diffusion and field charging, and is much more capable at charging sub-100 nm diameter nanoparticles. It also results in a positive charge which has a higher maximum charge limit than negative charging, giving an advantage over electron impact ionization. Finally, it may be the simplest to implement in whatever printing system we build because it depends little on the nanoparticle material, gas, or ambient electric field: arbitrarily high photon densities have negligible effect on electrostatic nanoparticle movement, unlike the high densities of gas ions or electron densities needed for other charging methods.

5.2 Photoelectric Charging

How does photoelectric charging work, in detail, and how do we implement it? The fundamental idea is the photoelectric effect: when a photon arrives at the surface of a material, it can be absorbed by an electron which converts that photon into energy (kinetic and potential). If this step change in energy is sufficiently high, the electron might escape the surface of the material. Famously¹, this requires each individual photon to have sufficient energy². Increasing the number of photons (the intensity) will not affect the photoelectric effect; it will merely be able to move more electrons at the same time.

Simply put: if we shine light of sufficiently high energy (low wavelength) photons at nanoparticles, electrons should jump off, leaving the nanoparticle positively charged.

How much energy does it take to remove an electron from a nanoparticle? First consider some edge cases. The energy required to remove an electron from a (neutral) atom is customarily termed the ionization energy, while the energy to remove an electron from an infinitely large surface of some material is called the work function Φ . The ionization energy is typically higher than the work function. The energy required to remove an electron from a (neutral) nanoparticle of intermediate diameter is somewhere between these. Furthermore, as soon as one electron is removed from a nanoparticle, the particle will have a positive charge, making it more difficult to remove the next electron, and so on.

This energy can be approximated in the same way as we previously computed the maximum charge limit in equation 5.1, but more care is required to match empirical data [264][265]. Specifically, the energy is well-modeled by the bulk work function, plus the energy required to move an electron from a spherical particle with a given charge, plus a correction to the original work function due to image forces on a sphere instead of a plane. This energy to remove the n^{th} electron from an initially neutral nanoparticle of diameter d_p is:

¹This won Einstein the 1921 Nobel Prize in Physics.

²Usually. Sometimes lower-energy photons can combine to ionize material (multiphoton ionization) [263].

$$E(n) \approx \Phi + n \frac{e^2}{\pi \epsilon_0 d_p} - \frac{5}{8} \frac{e^2}{\pi \epsilon_0 d_p}. \quad (5.2)$$

To more easily visualize the implications of equation 5.2, we can generate a table of the excess energy beyond the work function required to charge a nanoparticle a given amount.

n	1 nm	2 nm	5 nm	10 nm	20 nm	50 nm	100 nm	∞
1	1.08	0.54	0.22	0.11	0.05	0.02	0.01	0
2	3.96	1.98	0.79	0.40	0.20	0.08	0.04	0
3	6.84	3.42	1.37	0.68	0.34	0.14	0.07	0
4	-	4.86	1.94	0.97	0.49	0.19	0.10	0
5	-	6.30	2.52	1.26	0.63	0.25	0.13	0
7	-	9.18	3.67	1.84	0.92	0.37	0.18	0
10	-	13.50	5.40	2.70	1.35	0.54	0.27	0
30	-	-	16.92	8.46	4.23	1.69	0.85	0
100	-	-	-	28.62	14.31	5.72	2.86	0

Table 5.1: The additional energy (measured in eV) beyond the work function Φ required to remove the n^{th} electron from a spherical particle of the given diameter according to equation 5.2. Sufficiently small particles have a maximum charge as previously noted with equation 5.1. The rightmost column labelled “ ∞ ” shows the limit as the particle diameter approaches infinity, i.e., it becomes the infinite surface used to define the work function, and is zero by definition. As an example of using this table, a 10 nm diameter nanoparticle of work function 5 eV would require photons of at least $5 + 0.40 = 5.4$ eV to reach a charge of +2.

Material	Work Function	Ionization Energy
Al	4.3 eV	6.0 eV
Si	4.7 eV	8.2 eV
Ti	4.3 eV	6.8 eV
Cr	4.5 eV	6.8 eV
Fe	4.8 eV	7.9 eV
Ni	5.1 eV	7.6 eV
Cu	4.7 eV	7.7 eV
Ge	5.0 eV	7.9 eV
Ag	4.3 eV	7.6 eV
Pt	5.6 eV	9.0 eV
Au	5.3 eV	9.2 eV

Table 5.2: The approximate work functions and first ionization energies of some assorted materials [103]. Work functions vary with crystal orientation; average values are used here. Note that ionization energy is not defined for compound materials such as SiO_2 .

Work functions themselves are material-dependent and typically determined empirically. Some are listed in table 5.2 for reference along with ionization energies.

For any given material, we can condense the information from equations 5.1 and 5.2 and table 5.2 into a single graph as shown in the figure below for copper. This sort of plot makes it clear that charging will be most reliable with photon energies significantly higher than the work function, perhaps around 10 eV.

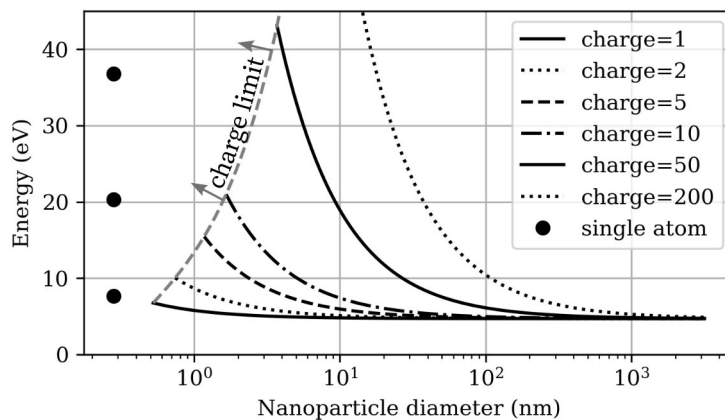


Figure 5.2: A graph of the energy required to positively charge a copper nanoparticle vs. its diameter, created from equations 5.1 and 5.2 and table 5.2. We see that smaller particles require more energy to reach a given charge and also have a lower maximum charge limit (above which a particle will break apart). The first three ionization energies of a single copper atom are shown on the left for comparison. The regime between the single atom and our models is not entirely empty but is complex due to quantum effects; atomic cluster studies report that energies fluctuate with single digit numbers of atoms [142][266][170].

5.2.1 Photoelectric Quantum Yield

There is another relevant factor we have not yet considered: how many photons are required to charge a nanoparticle? We can assume each photon results in at most one emitted electron (so a +10 charge requires at least ten photons), but not all photons impacting a surface succeed. The fraction of photons that successfully remove an electron is called the photoelectric quantum yield, and this also varies with nanoparticle diameter—fortunately in our favor, in that smaller nanoparticles are easier to charge [259][267][265]. The photoelectric quantum yield is another complex material-dependent property, but approximate typical values might be [259] on the order of 0.5 for 1 nm diameter nanoparticles (i.e., 50% of photons result in an emitted electron), 0.1 for 10 nm, and 0.01 in diameters above 100 nm, though efficiencies can easily be lower, e.g., 0.001 is not uncommon. Higher energy photons tend to give higher yields, which suggests it may be more efficient to choose photons with energies above the minimums previously calculated.

5.3 Photoelectric Engineering Considerations

We now know the minimum photon energy required to charge our nanoparticles. From figure 5.2, we want 5 eV to 20 eV, where the higher end of the range is preferable to reach higher charge and increase quantum yield. How can we build a charging system out of this?

5.3.1 Light Sources

The first step in nanoparticle photoelectric charging is to generate the light used to do so. Light is more commonly classified by wavelength than energy per photon, so recall that a photon of a particular wavelength has a fixed energy given by the relation

$$E = \frac{hc}{\lambda} \quad (5.3)$$

where E is the photon energy, $h = 4.14 \times 10^{-15}$ eV s is Planck's constant, $c = 3.0 \times 10^8$ m s⁻¹ is the speed of light, and λ is the photon wavelength. Our desired 5 eV to 20 eV light sources have wavelengths 248 nm to 62 nm (with lower wavelengths preferred). Visible light is 400 nm to 700 nm; we are well past this into ultraviolet (UV) light. UV is often divided into the approximate categories [268] UVA (400 nm to 315 nm), UVB (315 nm to 280 nm), UVC (280 nm to 200 nm), and vacuum UV (VUV) (200 nm to 10 nm)³ [269].

Photon energy	Wavelength	Notes and availability
1.8 eV	700 nm	(end of infrared light regime)
3.1 eV to 1.8 eV	400 nm to 700 nm	(visible light)
3.40 eV	365 nm	mercury arc lamp (i-line)
4.03 eV	308 nm	XeCl excimer lamp
4.88 eV	254 nm	mercury arc lamp
5.00 eV	248 nm	KrF excimer laser
5.28 eV	235 nm	lowest wavelength available UV LEDs
5.58 eV	222 nm	KrCl excimer lamp
6.42 eV	193 nm	ArF excimer laser
6.70 eV	185 nm	mercury arc lamp
7.21 eV	172 nm	Xe ₂ excimer lamp
7.75 eV to 3.10 eV	160 nm to 400 nm	deuterium arc lamp
9.84 eV	126 nm	Ar ₂ excimer lamp
10.2 eV	122 nm	H spectrum peak (Lyman-alpha)
21.2 eV	58 nm	He gas discharge lamp (He I peak)
40.8 eV	30 nm	He gas discharge lamp (He II peak)
124 eV	10 nm	(end of UV and start of x-ray regime)

Table 5.3: Some notable UV light sources sorted by wavelength.

³This includes the extreme ultraviolet (EUV) range in 13.5 nm EUV lithography. Other common photolithography wavelengths are 365 nm (mercury lamps), 248 nm, and 193 nm (KrF and ArF excimer lasers).

There are limited known good ways to generate UV light in the range we want, and many are fixed to certain UV wavelengths; some are shown in table 5.3. An additional difficulty (and the reason the vacuum UV range is so-called) is that below 100 nm wavelengths (above 10 eV) there is no solid material transparent to these wavelengths that can be used as a window, so lower wavelengths must both be generated and used within vacuum chambers⁴ [270]. Specifically, the best SiO₂ glass (crystalline quartz) is transparent down to at most 142 nm; materials such as LiF and MgF₂ reach 100 nm to 110 nm [271].

Gas-based lamps are the most common of UV light sources [269]. In gas discharge lamps (also called arc lamps), a low-pressure gas is electrically ionized into a plasma that emits a gas-dependent spectrum of light. This includes mercury arc lamps, the most historically prevalent UV source, which has a spectrum including peaks at (among others) 365 nm, 254 nm, and 185 nm. Also notable are H and He lamps. He gas discharge lamps are used for UV photoelectron spectroscopy [272]; broad-spectrum deuterium arc lamps for UV-vis spectroscopy. The 13.5 nm source for EUV lithography is made with a tin plasma gas [273]. An improvement over gas discharge lamps are excimer lamps [274][275], which drive particular gases in particular excitation states to produce mostly monochromatic light [276]. Excimer lamps are mechanically simple and robust [277]. Particularly common are Xe₂ excimer lamps at 172 nm that balance low wavelength with the ability to use cheap glass windows.

Excimer lasers output in the UV range [273]. These use similar principles to gas lamps with high power focused output at the cost of complexity and efficiency. They are available in (mostly) fixed wavelengths, the most common of which are the 248 nm KrF and 193 nm ArF lasers used for photolithography, pulsed laser deposition [146], and medical purposes. It is also possible to use nonlinear optics to convert frequencies of other lasers to UV, e.g., to generate 118 nm from tripling the 355 nm third harmonic of an Nd:YAG laser [278].

LEDs are solid state and can be made to emit UV light [279][280][268]. These are currently popular for UV curing, sterilization, gas analysis, and more in the UVA–UVC range. However, current UV LEDs are limited (and an active research area): efficiency drops with lower wavelength, and the current lowest wavelength research LEDs are about 230 nm. 235 nm is commercially available [281]. These are not suitable for our wavelength requirements.

Synchrotron light sources achieve high energies (e.g., 5 eV to 30 eV or 40 nm to 250 nm) within a tunable precise wavelength band (millielectronvolts) [270][282][283]. Photon intensities are much higher than what can be achieved by filtering a broad-spectrum gas UV lamp to that wavelength band but total power is somewhat low in absolute terms. These are useful for photoionization and photodissociation chemical studies but are large and expensive. We do not need their wavelength resolution or tunability.

Of all these methods, gas-based excimer lamps may be our best option: they combine high energy (low wavelength), high output, high efficiency (both in light generation and in that their spectrum is narrow), simplicity, and relatively low cost. The 172 nm wavelength seems particularly promising except for its somewhat low 7.21 eV energy, which would limit us to single-digit charges for particles below 10 nm according to figure 5.2.

⁴Fortunately, we happen to be moving nanoparticles specifically within a vacuum chamber.

5.3.2 Light Intensity

We now know what wavelengths of light will work, but how much of it do we need? To reach a charge of n , each nanoparticle will need to be hit by at least n photons but needs more if the photoelectric quantum yield ϕ , the fraction of photons that result in an emitted electron, is low. With $\phi = 0.1$, a nanoparticle charge of $+10$ would require 100 photons. Also note that, as will be discussed later with ion optics, we want nanoparticle charge to be as high as possible and some variation in the number of charges per particle is acceptable.

Suppose nanoparticles of diameter d_p move at velocity v across an distance of length L over which UV light of sufficiently low wavelength shines at some irradiance (photons per area) J_e , some fraction of which ϕ are absorbed and result in an electron emission.

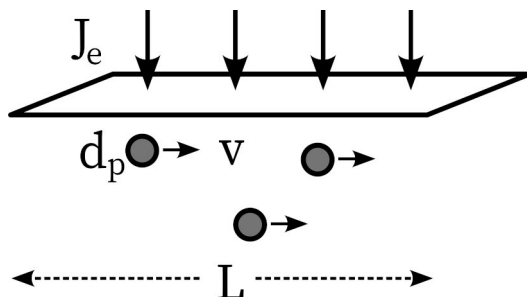


Figure 5.3: Nanoparticles of diameter d_p moving at velocity v through a region of length L into which UV light shines at intensity J_e .

Then the resulting positive charge n of each particle is approximately

$$n = \frac{\pi d_p^2 L \phi J_e}{4v}. \quad (5.4)$$

If we want a charge $n \geq 10$ with $d_p = 10$ nm, $L = 100$ mm, $\phi = 0.1$, and $v = 100$ m s⁻¹, we find $J_e = 1.27 \times 10^{21}$ photons/m²s. At a wavelength of 172 nm, $J_e = 1470$ W/m² = 147 mW/cm². This is somewhat high but feasible to achieve, especially over a small area. 172 nm Xe₂ excimer lamps are commercially available with irradiance above 100 mW/cm² (before focusing) [277][284]. Recent promising work in microfabricated flat microcavity plasma lamps can achieve higher intensities in smaller form factors with over 20% efficiency [285].

5.3.3 Charge Loss Mechanisms

Once nanoparticles are charged, there are several ways they might become discharged or lost that we should be aware of. First, as discussed in 4, charged particles moving in gas through narrow tubing have a greater attraction to its sidewalls (where they can stick and thus be lost) via image charges or adsorbed charges. Second, field and diffusion charging mechanisms can also discharge particles by transferring their charge to gas (in our case, by electrons moving from gas atoms to nanoparticles when they collide) [286][287]. Finally, a related effect is that sufficiently high-energy UV light [288] or electrons [289] can be absorbed by and ionize gas atoms instead of nanoparticles (the first ionization energies of Ar and N₂ are 15.8 eV and 15.6 eV [103]; interestingly, Ar⁻ is unstable—its electron affinity is negative).

5.4 Experimental Tests

We now know roughly how to charge nanoparticles in theory: shine a sufficiently strong UV lamp at them. Furthermore, the literature confirms this works experimentally: many groups have successfully built similar nanoparticle photoelectric chargers for studying common aerosols [286][258][290], fundamental nanoparticle photoemission tests [291][267], and mass spectrometry ion sources [292][293].

We attempted to build our own photoelectric nanoparticle charger. Unfortunately we were unsuccessful, but we ran several partial experiments with useful lessons that can be applied in future work. Building a charger continues to seem feasible.

Safety note: UV light is invisible and harmful to humans, capable of causing eye damage and long-term skin cancer (though diffuse UV lamps are less dangerous than a laser, which concentrates power). There is some evidence the human maximum permissible exposure limit to 200 nm to 222 nm light might be larger than at longer UV wavelengths [294], but for safety we considered the worst-case UV scenario. The UV lamp was operated away from skin, usually in a closed container, and while also wearing UV-blocking safety glasses (ThorLabs LG10, which also block 1064 nm laser light in chapter 2).

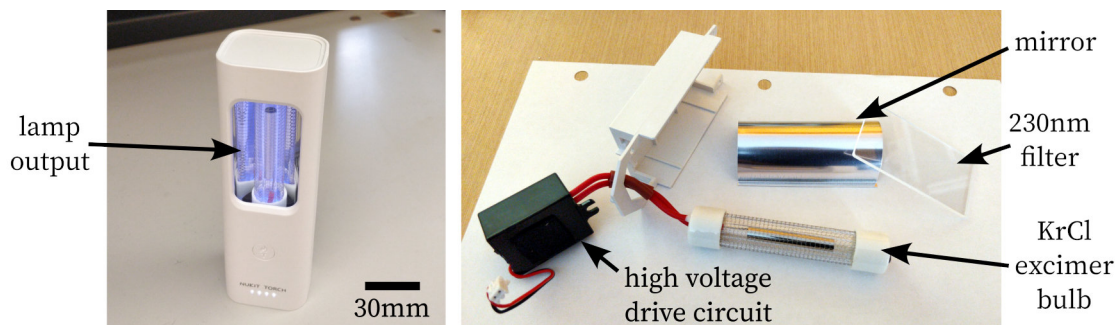


Figure 5.4: Left: UV lamp, operating (imaged safely with a camera). Although its 222 nm light is invisible, its output spectrum also contains some visible violet light. Right: the important optical components inside the lamp (its original control board excluded). The drive circuit converts low voltage DC to high voltage to drive the lamp bulb, whose output is partially reflected out of the lamp with a mirror then filtered to block UV above 230 nm.

The most important part of a photoelectric nanoparticle charger is its UV lamp. Although we predicted good results with a 172 nm lamp with over 100 mW/cm^2 power and noted in section 5.3.2 that these capabilities are commercially available, the best UV source we were able to obtain⁵ was a \$100 222 nm KrCl excimer lamp [295] meant for disinfection purposes with a reported UV optical power output of 0.12 mW/cm^2 (with 90% of this between 214 nm to 226 nm) at a 5 cm distance from the lamp (or 0.0107 mW/cm^2 at 20 cm). We confirmed

⁵This lamp was affordable compared to other sub-230 nm lamps, well-constructed, and easy to work with.

these specifications by measuring current generated in a UV photodiode (SD008-2171-112, Advanced Photonix) sensitive to 220 nm to 280 nm with a 0.019 A W^{-1} response at 222 nm and a 0.076 mm^2 active area. Placing the diode 5 cm from the lamp generated 15 nA from which we calculated an intensity of 1.04 mW/cm^2 , about 10x higher than specified (this error is likely due to our poor-quality uncalibrated measurement setup, but, if correct, the higher intensity would be helpful for our purposes). We will conclude the lamp outputs about 1×10^{18} photons/ m^2s to 1×10^{19} photons/ m^2s at 5 cm.

To demonstrate nanoparticle charging, we chose to take our existing aerosol deposition setup from chapter 4 and, between generating nanoparticles and impacting them, charge the nanoparticles by flowing them through a 7 mm ID UV-transparent glass tube (quartz; we measured over 50% transmittance at 222 nm via photodiode) while irradiating them with our UV lamp. This general strategy appears to work in the photoelectric nanoparticle charger literature [258]. To detect nanoparticle charge, we deposited the nanoparticles onto an electrically isolated but conductive steel substrate attached to a Keithley 487 picoammeter (i.e., we built a Faraday cup).

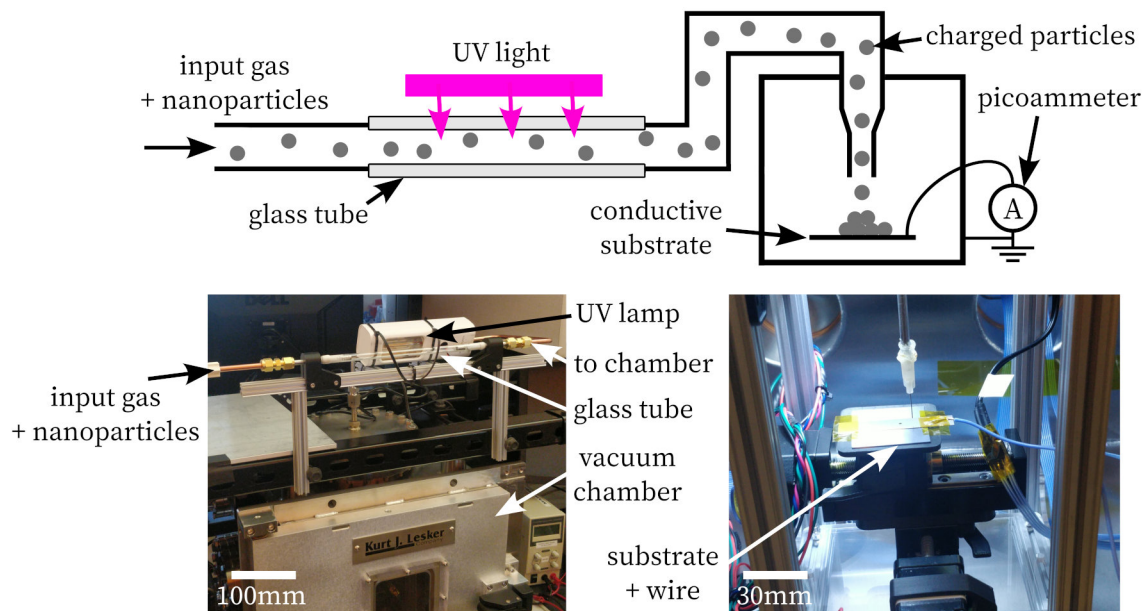


Figure 5.5: Top: cartoon of charging experimental setup built into chapter 4 apparatus. Nanoparticles are charged by UV light then deposited onto a conductive substrate where their charge creates a current detected by a picoammeter. Bottom: pictures of implementation. The UV lamp was covered for safety (not shown) while in operation.

Although this setup was crude, we calculated it might work. According to tables 5.1 and 5.2, 222 nm light (5.58 eV) should charge 10 nm copper particles up to +3. The nanoparticles travel 80 mm through UV light of our calculated lamp intensity (1×10^{18} photons/ m^2s to 1×10^{19} photons/ m^2s). Nanoparticle velocity was determined by gas flow speed, which, assuming the flow conditions as chapter 4, is likely about 1 m s^{-1} through the 7 mm diameter

glass tube. Assuming 10 nm diameter particles with a photoelectric quantum yield of $\phi = 0.1$, equation 5.4 suggests each particle (depending on lamp intensity) obtains a charge of 0.6 to 6, i.e., at least one charge per particle on average.

To compute the rate at which nanoparticles deposit charge, assume from chapter 2 we produce particles at 0.6 mg h^{-1} . Assuming 10 nm diameter copper particles, this is 3.5×10^{10} particles/s. Assume 90% are lost in the system for assorted reasons, so a net total of 3.5×10^9 particles/s are generated, sent through tubing, and deposited. At one charge per particle, the charge deposition rate should be 3.5×10^9 charges/s or 0.6 nA.

We ran the experiment with copper nanoparticles and observed particles depositing on the substrate, but we measured an average charge deposition of $(0.00 \pm 0.01) \text{ nA}$ (controlling for presence of UV light and signal noise). Noise limits only let us measure down to 0.01 nA, less than two orders of magnitude below our expected 0.6 nA signal. That is: we are confident particles moved through the UV charger and deposited on the substrate with whatever electric charge they possessed, but we observed no current meaning we remain unsure whether they were charged or not.

We hypothesize that particles were successfully charged when hit with a photon but a range of factors lowered the resulting signal below the range we were able to detect:

- Perhaps charging was successful but the increased charge increased particle loss sticking to tubing walls between charging and deposition. A more careful reading of the existing literature [258] reveals charged particles are often collected quickly after charging.
- From chapter 2, the particles have a range of diameters; they are not uniformly 10 nm. If the average particle size is larger but charge per particle is constant, the deposited current decreases. Smaller particles might not be charged with our 222 nm light.
- Diffusion (dis)charging—gas atom collisions—may have reduced charge per particle.
- The photoelectric quantum yield might have been less than the assumed 0.1.
- Because particles were insulators, their charge might not have transferred to the substrate (Faraday cup). Solving the oxidation problem as outlined in chapter 4 would fix this. We used copper nanoparticles due to their low work function; gold nanoparticles do not oxidize but have a higher work function (see table 5.2).

Any of these could easily have decreased the signal by an order of magnitude; all together, we are not surprised our signal was not above the 0.01 nA we could measure.

This suggests useful steps to build and successfully demonstrate a working nanoparticle generator in future work. Increasing UV lamp energy and intensity can increase charge per particle, using non-oxidizing conditions might deposit charge reliably, collecting particles quickly minimizes losses, and increasing measurement resolution is also helpful.

Finally, as a separate test, we tried operating the UV lamp inside the vacuum chamber. This might be useful in the future for charging nanoparticles in vacuum to minimize gas interactions. Unfortunately, as shown in figure 5.6, at pressures below 10 Torr the lamp stopped working; its light output changed. Further experimentation suggested an amusing

reason: the lamp construction consisted of a low-pressure KrCl gas in a sealed glass tube with metal electrodes on each side (i.e., both outside the tube and touching atmosphere). In standard operation, a high voltage AC potential between these electrodes capacitively couples to the gas inside to drive a plasma: this is a dielectric barrier discharge lamp [277]. However, when the surrounding atmosphere reached sufficiently low pressures, the lamp drive electrodes instead coupled to this atmosphere to make a gas discharge plasma from this surrounding gas (in our case, air) instead of the desired KrCl. Fixing this problem is straightforward but requires a different lamp geometry⁶.

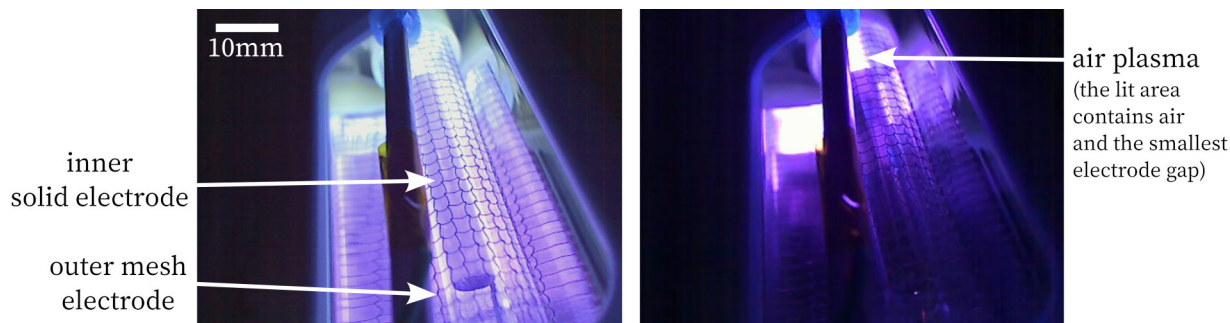


Figure 5.6: Left: close-up picture of the UV lamp bulb in normal operation. The lamp tube is a double-walled hollow cylinder; low-pressure Kr and Cl gas is contained between the walls. There is a mesh electrode around the outside cylinder and a solid electrode in the center area (also at atmospheric pressure). Right: at low exterior pressures, the indicated small cylindrical area (the closest distance between outer and inner electrodes at exterior pressures) becomes an excited air (nitrogen and oxygen) plasma. The color has changed due to different plasma composition.

In conclusion, we understood the theory behind charging nanoparticles but were not able to convincingly demonstrate this in experiment. However, we believe we understand our failure and can modify our apparatus to work in the future; problems included inability to obtain a sufficiently bright UV lamp, insufficient measurement resolution, and poor setup. The literature [258] still provides a convincing existence proof that a charger is possible.

We are now ready to continue our journey to figure out how to manipulate and focus nanoparticles with electric fields in chapter 6, though our current lack of charged particles to experiment with means we will have to continue in theory only.

⁶We were not able to fit the construction of a custom deep-UV lamp within our project's scope.

Chapter 6

Electrostatic Manipulation

We are finally ready to discuss the final step required for nanoparticle printing: using electric fields to move the particles. The approaches of previous chapters were not sufficiently precise or fast to build a good nanoparticle printer, but electrostatics can do better. Furthermore, contemplating this will let us write down quantitative theoretical limits on how good and fast nanoparticle printing can ever possibly be¹. We will have some success.

Recall that chapter 3 concluded printing semiconductor devices requires shooting particles of 1 nm to 50 nm diameter at a substrate at well-controlled velocities somewhere between 100 ms^{-1} and 3000 ms^{-1} and with positioning accuracy below our final desired printing resolution, perhaps $1 \mu\text{m}$. (Afterward, all we have to do is move the substrate back and forth on an XY stage while switching materials to have a multimaterial nanoscale printer, and these last parts are—relatively—easy, as demonstrated in chapter 4.) Furthermore, we argued the two feasible methods to do this are manipulating the nanoparticles with gas molecules or with electric fields.

We considered the first nanoparticle manipulation approach, colliding nanoparticles with gas atoms, in chapter 4. Although we found these aerosol methods were capable of conveniently transporting particles in several ways (and we were able to successfully print some basic multimaterial structures with them), theoretical limits from Brownian motion meant this would never be able to focus nanoparticles to achieve printing resolutions below $1 \mu\text{m}$ (in practice, $10 \mu\text{m}$, and only for larger particles). These methods also had poor control over nanoparticle impact velocity. Achieving convenient semiconductor device manufacturing as contemplated in chapter 1 requires something better, and the only remaining possibility is electrostatic manipulation.

Thus, in this chapter, we investigate moving nanoparticles with electric fields. We will assume nanoparticles have a fixed electric charge (perhaps $1e$ to $100e$) according to our methods in chapter 5, then design electric fields to move them to our desired positions and velocities. Since we were unable to implement nanoparticle charging in chapter 5, we will run computer simulations instead of physical experiments, which we leave to future work.

¹The superlative language in this chapter introduction may not be perfectly justified, but we think our arguments (see, for example, section 6.5.3) are sufficiently solid to excuse our use of the literary device.

6.1 The Focusing Problem

The one problem we haven't solved yet is how to deliver nanoparticles to a very small area. We have solutions for everything else (nanoparticle generation, large-scale manipulation, and charging), so let's simplify this last problem as far as possible.

Suppose we take our printer from chapter 4, add a photoelectric charger from chapter 5, and deliver charged nanoparticles into a vacuum chamber. The chamber would be at our choice of gas pressure, possibly down to high vacuum if desired².

We now have what appears to be a simple physics problem: charged particles start with random position, speed, and direction in a circular area 100 μm to 1000 μm wide (depending on aerosol nozzle qualities). We want to move as many particles as possible into a much smaller area, printing them onto a substrate within 1 μm or better. How can we do this?

The answer—the rest of this chapter—turns out to be surprisingly complex and nuanced.

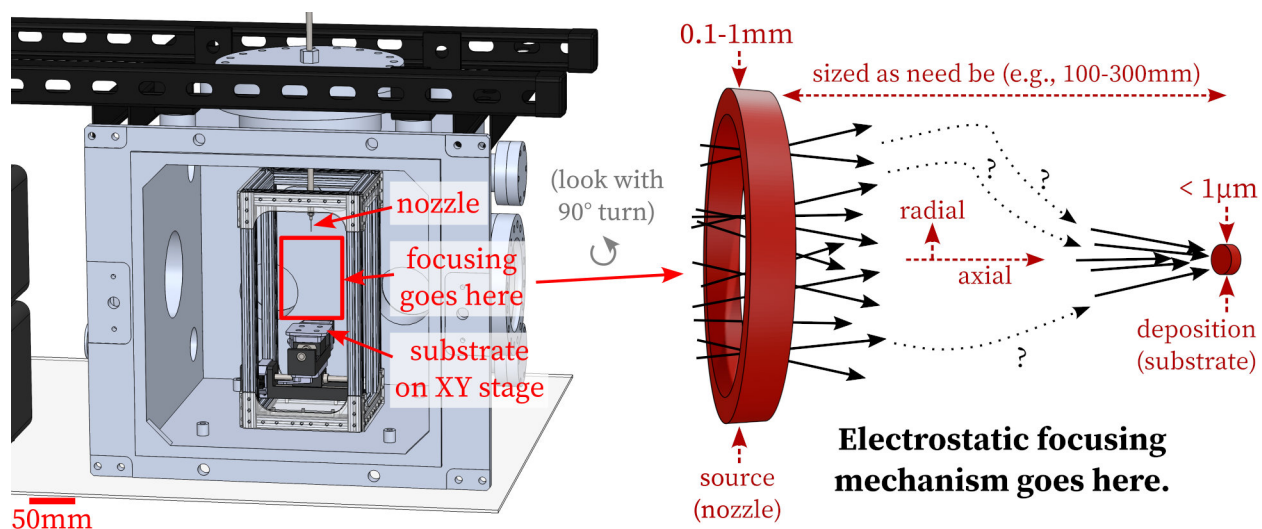


Figure 6.1: Left: starting with an aerosol printer as built in chapter 4, move the nozzle away from the substrate and there is room to add an electrostatic mechanism to focus particles. Right: an annotated cartoon of how this mechanism has to work (drawn turned 90 degrees). A wide beam of particles needs to be focused to a smaller area. Call the direction of movement from source to substrate “axial” and the perpendicular direction(s) “radial”.

To analyze this problem, we will assume³ particles mostly travel forward in a single direction (they won't stop or travel sideways very much, for example), which forms a nanoparticle beam (that particles travel close to the average beam position is called the paraxial approximation). Name the direction from nanoparticle source to substrate the axial direction, and movement perpendicular to that the radial⁴ direction (a cylindrical coordinate system). A particle with

²Nanoparticles can be moved to high vacuum with a skimmer as briefly mentioned in chapter 4.

³We will justify this assumption in many cases in section 6.3.1, but we will also actually find reasonable circumstances where particles travel backward for a short while in section 6.4.2.

⁴Sometimes “transverse” is used instead of radial and “longitudinal” instead of axial [296].

a radial position of zero is centered on the beam axis; our particles start with random radial positions in 0 μm to 500 μm and need to end with positions less than 0.5 μm —100x to 1000x smaller! We also want particles to end up with a high and well-controlled axial velocity.

For later reference, record the starting and ending conditions we want:

	Start (exit nozzle)	End (deposit)
Beam diameter	0.1 mm to 1 mm	< 0.001 mm (< 1/100th input)
Axial velocity	$\pm 50\%$ in 100 m s^{-1} to 300 m s^{-1}	$\pm 10\%$ in 100 m s^{-1} to 3000 m s^{-1}
Particle diameter	$\pm 50\%$ in 1 nm to 50 nm	(no change)
Particle charge	± 2 in 1 e to 100 e	(no change)

Table 6.1: Particle input and desired output conditions. We will add additional constraints (emittance) later in table 6.3. The beam diameter is double the maximum radial position of any particle. We can choose mean values for speed, diameter, and charge inside the given range, at which point the tolerance represents variance around that mean. Particle charges are integer multiples of the elementary charge e . Tolerances are approximate.

All these parameters vary, and the combined wide parameter range is the primary reason focusing is so difficult: the same mechanism that focuses a +3 charge 20 nm particle moving at 300 m s^{-1} is unlikely to also focus a +1 5 nm particle at 100 m s^{-1} by the same amount. Initial particle speed is determined by aerosol nozzle (chapter 4) and is dependent on particle size. As in chapter 2, particle generation results in a broad size distribution (perhaps a 500% spread in diameters, almost an order of magnitude—e.g., 5 nm to 25 nm), though we can select a narrow slice of this via filtration (at the expense of lower throughput). We assume a 50% variation is a good compromise between consistency and nanoparticle generation rate, but note particle mass scales with the cube of the diameter, so 50% diameter variance is a 350% mass variance! Finally, particle charge is somewhat controllable as discussed in chapter 5 but may vary (different diameters give different photoionization thresholds, etc).

6.2 Electrostatic Nanoparticle Movement

To analyze particle movement, we will begin by reviewing basic electrostatic forces. The fundamental law governing charged particle movement is the Lorentz force, which states a particle with charge q and velocity vector \vec{v} in an electric field \vec{E} and magnetic field \vec{B} experiences the force $\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$. We also have Newton’s second law, of course, with $\vec{F} = m\vec{a}$ for particle mass m and acceleration \vec{a} . Together, these laws completely determine how a particle moves inside a given time-varying electromagnetic field⁵. Assume for now the particles and fields are inside a perfect vacuum. Applying a voltage across two conductive electrodes makes an electric field \vec{E} in the empty space between them.

To simplify calculations we make several assumptions. First, assume each particle is merely

⁵To a good first approximation. This ignores relativistic effects and emitted radiation (cyclotron or bremsstrahlung/braking), for example, but the effect on our particular calculations will be negligible.

a point mass and charge⁶. Second, ignore magnetic fields—since particles are relatively slow, the force from electric fields will be much greater⁷. Finally, assume electrode electric fields are quasielectrostatic, i.e., depend only on electrode voltages at that instant⁸, and are unaffected by the particles (image charge effects). Thus the force on each particle is merely

$$\vec{F} \approx q \cdot \vec{E} \quad (6.1)$$

(that is, a particle in an electric field experiences a force in the direction of the field, scaling with charge and field strength), and now we can proceed with straightforward calculations.

A basic demonstration of electrostatic movement is as follows. In a perfect vacuum, add two conductive pieces of metal (“electrodes”) and apply a constant voltage between them. This creates an electric field in the space in between and around the electrodes. The strength of the field is approximately the voltage divided by distance (measured in volts per meter). Now put a particle of nonzero charge q in midair between these electrodes (if the particle has no charge, nothing happens). The particle will be pushed with force $\vec{F} = q \cdot \vec{E}$, and its trajectory can be determined by $\vec{F} = m\vec{a}$ (we use vector notation \vec{v} for any 3D vector).

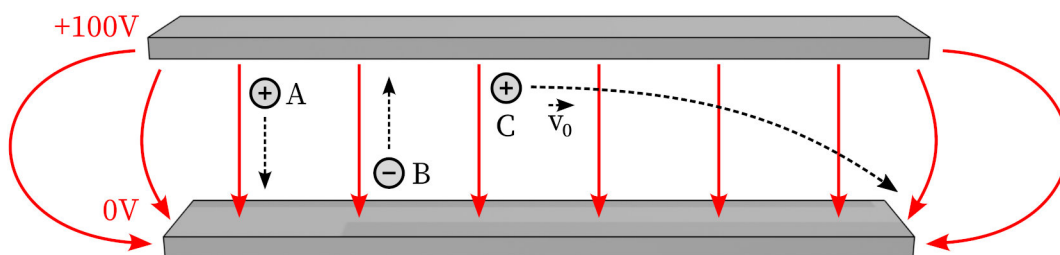


Figure 6.2: An electric field (red arrows, conventionally drawn from high to low potential, which we call the direction of the field) is created between electrodes, in this case by applying a 100 V potential difference. Note the field curves at electrode edges. Positively charged particle A is pushed in the field direction (from chapter 5, our particles will generally have a positive charge). Particle B has a negative charge, so it is pushed in the opposite direction. Positively charged particle C has initial velocity \vec{v}_0 and continues in that direction but is also pushed down like particle A, resulting in a parabolic trajectory.

These basic ideas are enough to start considering what it takes to achieve particle movement to solve our focusing problem of section 6.1: how can we focus a beam of particles?

⁶This is valid as the nanoparticle diameter is much smaller than any other system dimension. We assume also negligible effects from magnetic moments, which is reasonable given we use no magnetic fields.

⁷A 1000m/s particle in a reasonably large 100 mT field experiences a force equivalent to a single charge in a 100 V m^{-1} electric field, but most fields in this work are orders of magnitude greater, perhaps $100 \text{ V cm}^{-1} = 10 \text{ kV m}^{-1}$ or more. SEMs and particle accelerators have much higher particle velocities resulting in larger magnetic Lorentz forces and therefore make more use of magnetic fields instead of electric fields.

⁸This is valid because we use no magnetic fields and also because the frequencies at which electric fields change will be below 1 MHz with wavelengths (300 m) far greater than the size of the system or nanoparticle travel path. This will simplify electric field calculations.

6.3 Radial Focusing

Now that we have a way to create electric fields and analyze their effects on particle motion, it is time to turn to solving the particle movement challenge presented in section 6.1 and table 6.1. We can divide this problem into two parts:

- We need to focus particles in the radial direction, from a broad beam over $100\ \mu\text{m}$ wide to a much more narrow beam less than $1\ \mu\text{m}$ wide. This gives high printing resolution.
- Simultaneously, we want to adjust particle velocities in the axial direction so the impact velocity is well-controlled and within the $100\ \text{m s}^{-1}$ to $3000\ \text{m s}^{-1}$ range.

It will turn out the final solutions for these two subproblems are somewhat independent, so we will address them one at a time. Radial focusing is more difficult; we will start there.

As an illustrative partial solution, consider a broad beam of positively-charged nanoparticles we would like to print on a substrate as in figure 6.3. If the substrate is at a known voltage and a ring-shaped high voltage electrode is set just above, an electric field will be formed that pushes particles inward radially (in addition to some axial acceleration) to move through the hole in the high-voltage electrode before impacting the substrate. The final printed deposit is smaller than the original beam diameter; the particles are focused. This setup also has some significant drawbacks, but we can use it to introduce some important ideas.

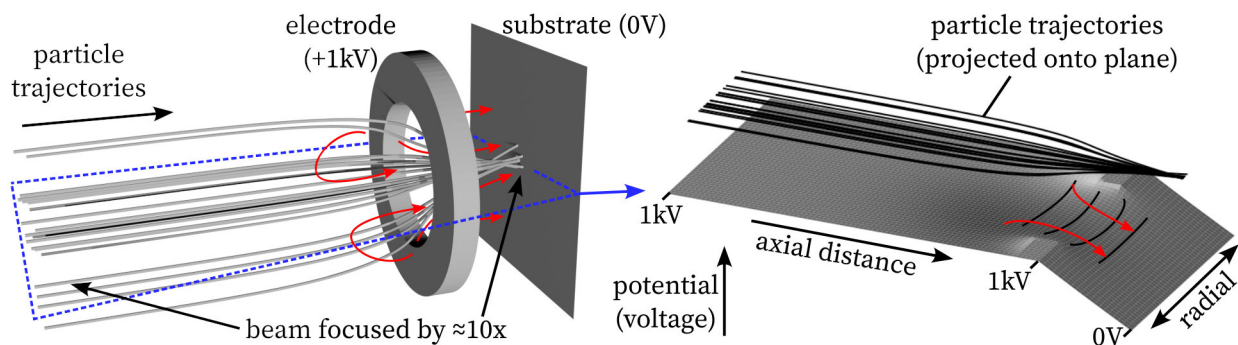


Figure 6.3: Left: 3D computer simulation of a beam of nanoparticles deflected inward by an electric field (red arrows) to impact a smaller area on the substrate. Right: the electric field in a 2D plane (blue) can also be visualized as a potential energy surface (height measured in volts) that particles travel through, with 2D projections of particle paths above.

The first idea is we can use computer simulation to calculate the exact shape of the electric field and resulting particle motion. Although we also use hand calculations and intuition to make some approximate broad statements and check the simulation (e.g., comparing the magnitudes of particle kinetic energy and electric potential can suggest how much focusing happens), the full field shape is complex. The specific software we use is SIMION 8.2⁹ [297].

⁹SIMION [297] is industry-standard software for simulating particles in electric fields to design ion optics. Fields are computed by solving the Laplace equation via a finite difference method, then particle trajectories are found by integrating $\vec{F} = m\vec{a}$ over time. (We also use Python [298] and Blender [299] to display results.)

Second, instead of visualizing the electric field as arrows, we can draw an electric potential surface as shown in the right of figure 6.3. We take a 2D cross-section of the 3D geometry and graph the potential at each point on it. Higher potential is higher voltage; electric field lines point downhill. Particles move in this potential like how large objects would fall down a slope due to gravity. These plots are more exact and easier to draw than arrows.

Now: this radial focusing method partially works; what are the downsides?

One primary drawback is the need for substrate charge. The method has actually already been used to good effect in the literature to print structures from nanoparticle aerosols [46][63][300][69][68] (also cited in chapter 1) or electrohydrodynamic jets [30][301][302][303]. But the substrate must be at a known voltage or charge¹⁰, which conflicts with our desire to print arbitrary geometry with both conductors and insulators (for transistors, for example), which change the field shape (section 6.5.2). We'd like to focus particles without relying on the substrate's electrical properties, so we need a different method.

Other important flaws are that focusing requires very low particle axial velocities or very high voltages, and there is a fundamental minimum to how much focusing is possible—we would never be able to fit the entire 0.1 mm incoming beam of table 6.1 into a sub-1 μm spot. These limits are the same as for Einzel lenses, which we will discuss in the next section.

6.3.1 Ion Optics, Einzel Lenses, and Emittance Limits

We still need to figure out how to focus particles radially, but we now have the additional constraint that the focusing mechanism shouldn't include the substrate as an electrode. This makes things harder. Fortunately, significant prior art exists, and there is a beautifully simple expression (emittance) that tells us what we need to do.

Ion optics (or charged particle optics, or electron optics) is the study of moving electrically charged particles (electrons or atomic ions) with electric and magnetic fields in vacuum [296][304][305]. The name comes from certain behavior analogous to light ray optics. Ion optics sees use in scanning electron microscopes, particle accelerators¹¹, mass spectrometers, trapped ion quantum computing, cathode ray tube displays, and focused ion beam tools (see section 6.5.4), among others (see appendix A). The field is mature, and the focusing problem as laid out in section 6.1 is very familiar—it is almost identical to concerns in SEMs and FIBs except that the use of large nanoparticles is uncommon. Ion optics has a simple (partial) solution to the focusing problem: the Einzel lens [305][306].

An Einzel lens focuses a beam of charged particles. The beam travels through the lens and is made to converge, just like a converging optical lens does for light [306]. The Einzel lens itself consists of three ring electrodes with the center ring at a different voltage from the other two; the particle beam travels through the holes in the rings. Particles are slowed down by the first pair, slightly change direction depending on their distance from the beam axis, then are sped up to their original velocity (and energy) by the second pair. To a first-order approximation, the direction change is proportional to radial position.

¹⁰Attracting particles to a charged pattern is xerography; this is how paper laser printers work.

¹¹SEMs and particle accelerators can use magnetic instead of electric fields due to higher particle velocities.

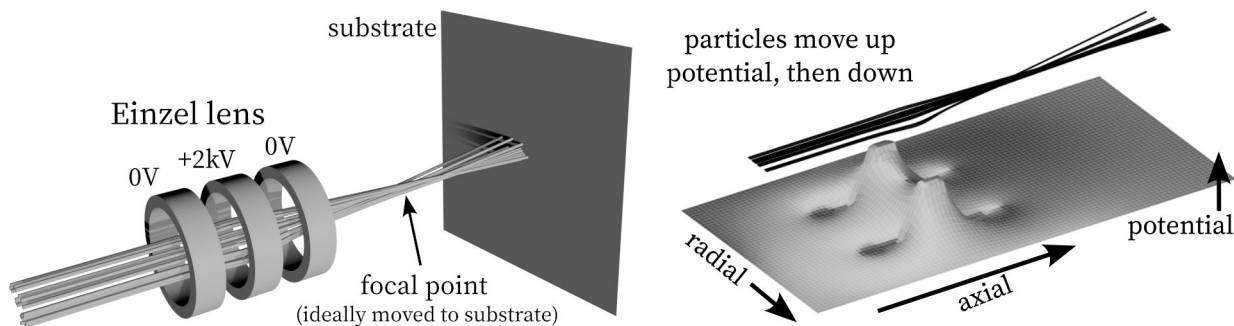


Figure 6.4: Einzel lens simulation in the same style as figure 6.3. Left: 3D render of lens and particle trajectories. Right: the potential energy field of the lens. The particles don't meet exactly at the focal point (the beam diameter is nonzero) due to some variation in incoming particle mass, velocity, and nonzero incoming angle.

In order to focus a beam, the height of the Einzel lens potential surface (its voltage times particle charge) must be close to the incoming kinetic energy of the particles. If the lens energy is low, particles are focused more gradually (the focal point is further away); if too high, the particles are reflected backward.

This is the first indication an Einzel lens is not the right tool for us. Our nanoparticles have a wide range of masses and thus kinetic energies (possibly 350% variation; see table 6.1). Thus different particles will be focused significantly differently or not at all (more correctly, particles with a different mass-to-charge ratio will be focused differently; with the laws $\vec{F} = q\vec{E} = m\vec{a}$, we have $\vec{a} = (q/m)\vec{E}$ so the ratio is the only determinant of particle trajectory). This is an extreme case of chromatic aberration¹². A second related problem is large fast particles need unrealistically high voltages to focus.

Diameter	100 m s ⁻¹	300 m s ⁻¹	1000 m s ⁻¹	3000 m s ⁻¹
1 nm	0.146 eV	1.32 eV	14.6 eV	1.32×10^2 eV
10 nm	1.46×10^2 eV	1.32×10^3 eV	1.46×10^4 eV	1.32×10^5 eV
100 nm	1.46×10^5 eV	1.32×10^6 eV	1.46×10^7 eV	1.32×10^8 eV

Table 6.2: The kinetic energies (total, not per atom as in chapter 3) of assorted copper nanoparticles at different velocities, in electronvolts. A 1000 m s⁻¹ 10 nm particle with a single charge needs an Einzel lens voltage of up to 14 600 V to be focused. Note this requires high vacuum; it would cause Paschen breakdown (see figure 2.4) at higher pressures.

If we were to filter particles even more to reduce variation in diameter and thus energy, and only use smaller particles at low speeds, this might start to work; there already exist several papers studying Einzel lenses to focus nanoparticles for deposition [308][309][99][100]. But there is another reason Einzel lenses are insufficient for what we want to do.

¹²In ion optics, chromatic aberration primarily refers to focusing imperfections due to a spread in particle kinetic energies. Reducing chromatic aberration is possible in only limited cases [307]. Spherical aberration is imperfect focusing due to lens shape, separate from the more fundamental emittance limits we will discuss soon. Astigmatism is deformation of the beam radial symmetry; we neglect it here. See [305] for more.

Einzel lenses have a second fundamental limit: emittance. Perfect focusing is impossible.

The emittance limit actually applies to virtually all ion optics, including our first radial focusing method in section 6.3, and even if all particles were the same diameter with the same charge and velocity (so there is no chromatic aberration).

The limit goes like this. Any beam of nanoparticles spreads out at some nonzero angle and at its narrowest point has some nonzero diameter—a beam is never perfectly collimated or focused. We can define a quantity called the beam “emittance” equal to the beam diameter times the spread angle at some point. It turns out this is a conserved quantity: no matter how we bend and focus the beam, the emittance will never decrease (but it can increase). If we want to focus the beam by decreasing its diameter, the beam angle must increase to compensate—and basic geometry limits the half-angle to 90° .

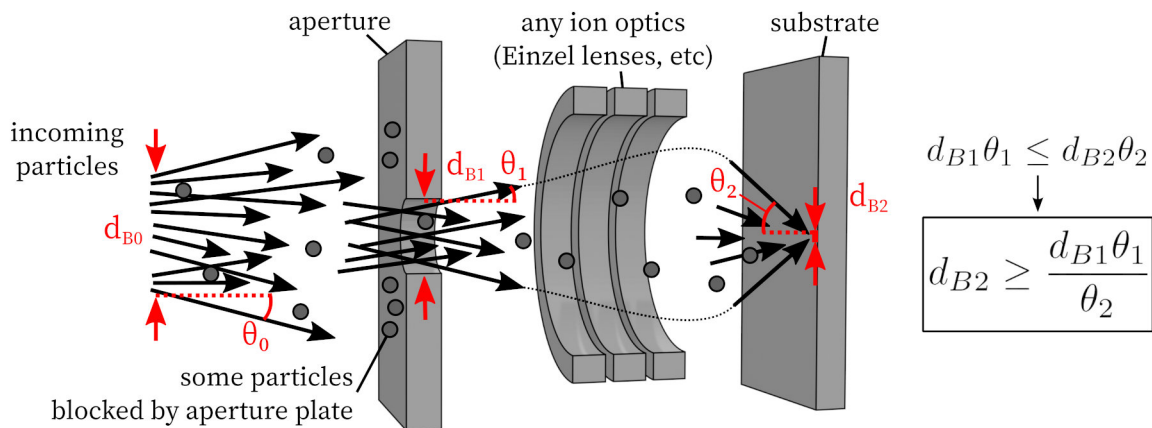


Figure 6.5: Cross-section cartoon of theoretical focusing limits due to emittance. Any beam of particles has nonzero half-angle θ_0 and at its narrowest some nonzero diameter d_{B0} . The diameter-angle product $d_{B0}\theta_0$ is the emittance. In an energy-conserving system (like particles moving in electrostatic fields in vacuum), the only way to reduce emittance is by removing some of the beam, e.g., with an aperture, giving a beam with a different diameter d_{B1} and angle θ_1 (though brightness will decrease). Focusing the beam while keeping all particles will at best preserve emittance giving $d_{B1}\theta_1 = d_{B2}\theta_2$, and $\theta_2 < 90^\circ$ limits how small d_{B2} can be. (Also, the diameters and angles can be replaced with areas A_B and solid angles Ω .)

This theorem is well-known in ion optics (with minor variations; for a better discussion see [296]). Stated with a bit more precision: consider the movement of ions in a perfect vacuum through a non-time-varying electric field (potential). It can be shown the Lorentz force in this case is conservative, i.e., particle energy is shifted between kinetic and potential but always remains constant. Now consider a group of particles, each with their own initial positions and velocities. According to Liouville’s theorem from Hamiltonian mechanics, the density of this group in phase space is constant, so if particles start and end at the same potential they end with an equally large group of positions and velocities. Alternatively: the system is time-reversible (could be run backward), so there is no case where two particles with different initial conditions end up in the same final position.

There are several mostly-equivalent ways to define emittance¹³. In figure 6.5 we define the minimum diameter¹⁴ d_B of a beam and the half-angle θ it spreads out at; $d_B\theta$ is constant. Note θ is approximately the ratio of radial to axial velocity (when θ is small, i.e., the paraxial approximation). Instead of $d_B\theta$, we can also use the minimum beam area $A_B = \pi d_B^2/4$ and the solid angle $\Omega \approx \pi\theta^2$ and conserve $A_B\Omega$, but the 2D version remains simplest to use.

$$d_{B1}\theta_1 \leq d_{B2}\theta_2 \quad \text{or} \quad A_{B1}\Omega_1 \leq A_{B2}\Omega_2 \quad (6.2)$$

Again, emittance cannot decrease, given the theorem’s assumptions, though it can increase via nonlinearity or focusing imperfection¹⁵. This is unfortunate as we want both small diameter and small angle (for more reliable impact and larger depth of field), i.e., we want small emittance. But there are minor loopholes.

One main way to decrease emittance in a vacuum is physically removing some of the beam, maybe by blocking it with an aperture (a hole in a flat plate). The remaining beam can have lower emittance but contains fewer particles (in our case, this would make printing slower). To account for this, define the volumetric flux Q (the total volume of nanoparticles moving in the beam per second) (units m^3/s), and define the volumetric brightness $Q/(A_B \cdot \Omega)$. This volumetric brightness¹⁶ is conserved even through an aperture.

The other way to decrease emittance is accelerating particles to a higher axial velocity, which stretches out the beam to give a smaller solid angle while keeping area constant. Particles must start and end at different potentials. This is called an “immersion lens” for analogies to light optics; a basic Einzel lens is not one as its start and end potentials are identical. Increasing axial velocity v_a while preserving radial velocity v_r reduces angle θ approximately linearly (and Ω scales with $1/v_a^2$), so $v_a\theta$ or $v_a^2\Omega$ is conserved¹⁷.

These quantities are the main figures of merit for a particle beam: the minimum beam area A_B (or diameter d_B), solid angle Ω (or half-angle θ), axial velocity v_a (note radial velocity v_r satisfies $\theta \approx v_r/v_a$ and $\Omega \approx \pi(v_r/v_a)^2$), and volumetric flux Q . We can write these together as the “reduced volumetric brightness”, which is conserved similar to emittance:

$$\frac{Q_1}{v_{a1}^2 A_{B1} \Omega_1} \geq \frac{Q_2}{v_{a2}^2 A_{B2} \Omega_2}. \quad (6.3)$$

This is enough to understand how much focusing is theoretically possible¹⁸.

(Incidentally, the same theorems can apply near-identically in light optics [314][315], specifically linear optical systems. For a given beam of light, define the “étendue” $G = n^2 A \Omega$ (units m^2sr) for area A , solid angle Ω , and index of refraction n , then also define the “radiance” $L = \Phi/(A\Omega)$ (units $\text{W}/\text{m}^2\text{sr}$) using radiant power Φ (units W). Combine these together as “basic radiance” $L/n^2 = \Phi/G = \Phi/(n^2 A \Omega)$ (units $\text{W}/\text{m}^2\text{sr}$). Basic radiance is conserved

¹³Accelerator physics in particular uses more complex but precise definitions [296][310].

¹⁴Sometimes the minimum diameter is called the size of a virtual source.

¹⁵Aberrations preserve emittance but can deform it so much it acts increased for practical purposes [296].

¹⁶Ion and electron beam systems measure flux as a current and call the result “brightness” [311][304][296].

¹⁷Ion beam systems define “reduced brightness” with voltage V instead of squared axial velocity v_a^2 [312].

¹⁸It is possible to refine this limit slightly with spherical and chromatic aberration calculations [313].

analogous to equation 6.3. In 2D cross-section using the half-angle $\theta \approx \sqrt{\Omega/\pi}$, one can also define the numerical aperture $\text{NA} \propto n\theta$ and lens f-number $N \propto 1/\theta$. Immersion microscopy is moving light into a medium of higher refractive index n . Synchrotron brilliance is radiance per wavelength. All this describes focusing limits to light¹⁹.)

To apply emittance limits to our focusing problem, first rewrite table 6.1 to list all conditions including relevant parameters we did not previously consider:

	Start (exit nozzle)	End (deposit)
Beam minimum diameter d_B	0.1 mm to 1 mm	< 0.001 mm
Beam half-angle θ	$\approx 5^\circ$ (90 mrad)	< 30° (520 mrad)
Axial velocity v_a	$\pm 50\%$ in 100–300 m s^{-1}	$\pm 10\%$ in 100–3000 m s^{-1}
Particle diameter d_p	$\pm 50\%$ in 1–50 nm	(no change)
Particle charge q	± 2 in 1 e to 100 e	(no change)
Volumetric flux Q	1×10^4 to $1 \times 10^6 \mu\text{m}^3/\text{s}$	(no change)

Table 6.3: Approximate particle input and desired output conditions. This is the same as table 6.1 but we also specify the beam half-angle and clarify the diameter is the minimum anywhere along the beam at that angle. The 5° initial half-angle is based on our results from chapter 4. Volumetric flux is the range chapter 2 indicated is feasible.

We can now use equation 6.3 (which includes equation 6.2) to easily calculate whether ion optics can achieve the focusing we want. For example: unrealistically assuming no chromatic aberration for the moment, we can focus the beam to a minimum diameter of

$$d_{B2} = \frac{d_{B1}\theta_1}{\theta_2} = \frac{0.1 \text{ mm} \cdot 5^\circ}{30^\circ} = 16 \mu\text{m}. \quad (6.4)$$

That’s not great; we want resolution over an order of magnitude better. This doesn’t improve much on aerosol focusing (though it should handle small particles better), and chromatic aberration from the spread of particle sizes and charges would significantly reduce the benefit as previously noted. We would get some additional improvement from increasing particle velocity, but our only way to do that is electrostatic acceleration, suffering from the same chromatic aberration flaws as lenses (see section 6.4.1).

We could also use an aperture to reduce the diameter by another 10x at the cost of reduced volumetric flux. Since beam area scales with diameter squared, that would leave approximately $1/10^2 = 1/100$ of the original flux, reducing print speed by orders of magnitude (see section 6.5.3). This might also run into clogging issues—such a small aperture is microscale, making this essentially stencil lithography as briefly mentioned in chapter 4.

¹⁹The reader may know that a magnifying glass on Earth can focus sunlight to start a fire [314]. Radiance and étendue calculations show this can also work with starlight (albeit with a 10 km wide lens), but not moonlight. When a sunbeam bounces off the moon, it reflects in a diffuse (Lambertian) way, spreading over an entire hemisphere and only partially reaching Earth. The resulting étendue of moonlight is about 1×10^5 times larger and even an infinitely large lens would fail to achieve sufficient intensity. A solution is to make the moon surface a mirror (avoiding étendue change).

At this point we see ion optics may be close to achieving our 1 μm resolution—and we can maybe get there if we’re willing to accept impractical particle filtering and slow print speed constraints—but we’re uncertain how feasible the result will be. Can we do even better?

There is one final loophole [316] in the emittance theorem: breaking the premise that particle motion is conservative. We can add a force other than time-invariant electrostatic fields.

6.3.2 Damping and Quadrupole Ion Traps

We just deduced time-invariant electrostatic fields by themselves are not quite good enough. If we want to focus particles radially with sub-1 μm resolution, we need to actively add or remove energy from each nanoparticle to get around the emittance theorem.

One (impractical) approach is to change the electric fields with feedback. For example, if we were able to somehow track the position of a nanoparticle, we could adjust the electric fields around it in real time (by changing electrode voltages) to direct its motion. Unfortunately, tracking each individual particle is infeasible²⁰: we might have over 1×10^{10} particles per second, each moving at 1000 m s^{-1} over tens of millimeters, where each particle is less than 100 nm wide and has charge $q < 100e$ (not very far from single atoms), and tracking needs sub-1 μm precision with microsecond time resolution. These tracking system specifications are somewhat ridiculous to meet. We must make do without closed-loop control²¹.

Instead, our solution is to add a damping force. In addition to time-invariant electric fields, add a force that slows down (dampens) particle motion in all directions²². Over time, each particle will lose both kinetic and potential energy until it has moved to the local minimum²³ of the the electrostatic potential energy field. This is like marbles rolling around in a round bowl (a potential energy field, albeit due to gravity). Without damping, like our previous ion optics, the marbles move forever, never stopping. With damping (air drag and friction) they slow down until they rest at the center of the bowl (the potential local minimum). Setting the shape of the electric potential lets us direct where the particles end up.

This damping approach is widely used in particle accelerators, mass spectrometers, and other trapped ion applications. It is simple, works well, and moves all particles to known positions without needing to track them individually. It is sometimes called “cooling” because slower organized movement generally means lower temperature²⁴. Commensurate with its importance, many ways to create the damping force have been developed [316][318][319][320]:

- **Buffer gas cooling:** This is just air drag as discussed in chapter 4. Impacts from (ideally inert) gas atoms, here called buffer gas, slow down particles. This is fairly universal and common in mass spectrometry [321][322][323], particle accelerators [324], and elsewhere [325], but cools to a nonzero limit. Also called “collisional cooling” [326] or “collisional focusing” [327][328].

²⁰Tracking and controlling only one particle (not many) is sometimes possible; see feedback cooling.

²¹Without per-particle closed-loop control. Control of total beam behavior (e.g., current) is possible.

²²Damping a beam only in the radial direction would be preferable but we have no way to do so.

²³Electric potentials have no local minima; we will address and fix this with ion traps and in appendix A.

²⁴This is tricky as it requires a new definition of temperature for the (usually isolated) particles, e.g., [317].

- **Laser cooling:** A class of techniques that exploit the quantum behavior of particles to absorb and re-emit photons in specific ways, using photon momentum to slow down the particle [329] (Doppler cooling, for example, uses the fact that a particle traveling in one direction will see incoming photons blueshifted and, if those photons' frequencies were carefully chosen, will only absorb photons and their momentum from that direction). Usually only works for single atoms with certain quantum energy levels.
- **Cavity cooling:** Although standard laser cooling doesn't work on nanoparticles which have much messier band structures than single atoms, similar results can be achieved by clever arrangement of nanoparticles scattering a laser in an optical cavity. This might be able to cool nanoparticles to near their ground state but methods are still in development; it is not obvious how we would implement it²⁵ [332][333][330][334][335][336].
- **Sympathetic cooling:** Buffer gas cooling but improved by using laser cooling on the buffer gas (not nanoparticles) to reach lower temperatures [323][337].
- **Feedback cooling:** In well-controlled circumstances, it actually is sometimes possible to sense individual particles (either via their electric image charge when resonating [111][338][321] or optically via scattered light) and sometimes apply electrical or optical feedback to control their position [339][340][341][342][343]. This remains infeasible for our large number of particles. Currently investigated mainly for quantum experiments.
- **Stochastic cooling:** This is the one known way to make feedback cooling practical, used in particle accelerators: sensing average particle beam asymmetries and applying a correcting electrical pulse, many times over as the beam circulates [344][345]. Won the 1984 Physics Nobel [346]. Is not easily applied to our nanoparticles.
- **Radiation damping:** When sufficiently fast (near lightspeed) particles accelerate, they emit light with significant momentum, slowing the particle; this can be used to cool a particle accelerator beam [347][319][318]. Related to synchrotrons.
- **Electron cooling:** Like gas cooling, except the gas is replaced with a beam of electrons [348][349]. Used in particle accelerators.
- **Ionization cooling:** Like gas cooling, except the gas is solid matter (in which nuclei are ionized as the beam passes through). Shown for muon particle accelerators [350].
- **Evaporative cooling:** When multiple particles in a beam interact, they share energy (again like gas cooling) with some distribution; if the fastest are removed (evaporated) from the beam or trap, the remainder are slower on average [351][352][353].

Of all these methods, buffer gas cooling seems the only feasible option for our nanoparticle printer. Other methods don't work on nanoparticles (laser cooling), require much higher speeds and longer times (stochastic cooling), or lose nanoparticles (evaporative cooling). Fortunately, buffer gas cooling is also simple to implement: all we have to do is let some small amount of gas float near the nanoparticles (instead of using high vacuum), and the particles will be slowed as discussed in section 4.1.1. Ideally the gas should be inert (e.g., argon, not oxygen; see section 4.3.3) to avoid chemical reactions with the particles.

²⁵There is some evidence cavity cooling might eventually work for particle beams [330][331].

How can we use this buffer gas cooling method to focus particles?

We must create an electric potential field such that an incoming beam of particles, when slowed by the buffer gas, falls into our desired beam shape. This potential must be lower at the center of the beam and higher elsewhere. As discussed in appendix A, this cannot be done with static electric fields due to Earnshaw’s theorem. However, an oscillating field of the correct shape, generally formed by four parallel rods—a quadrupole—creates an average potential that pushes particles toward the center, focusing the beam like we want!

Specifically, as detailed in appendices A and B, the oscillating field causes particles to vibrate back and forth (micromotion), but asymmetry causes particles to feel a time-averaged force (the ponderomotive force) toward regions of lower electric field magnitude, which acts like the conservative force of a potential field (the pseudopotential).

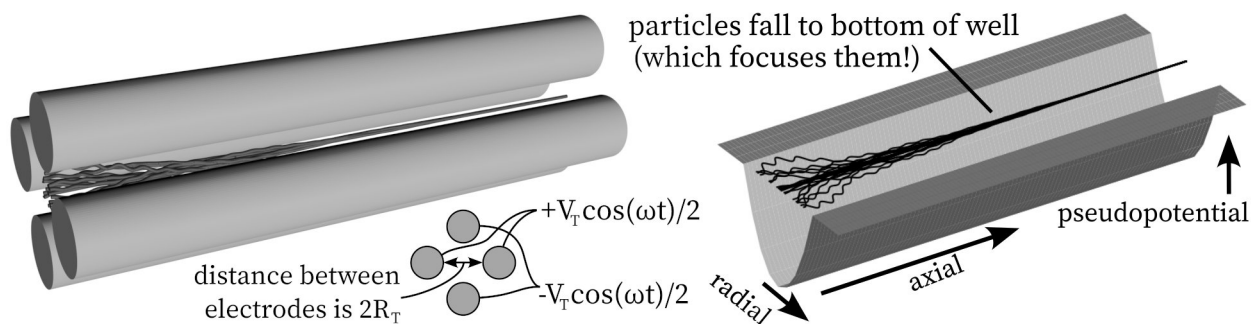


Figure 6.6: Particles moving left to right through a quadrupole ion trap with buffer gas, in the style of figures 6.3 and 6.4. Left: the trap consists of four electrode rods with oscillating voltages. Right: although the fields oscillate, particles experience an average force over time which forces them toward the center like a quadratic potential well (the pseudopotential); see appendix A. When air drag is applied, particles fall down the potential into the center of the well, focusing the particle beam in a completely different way from an Einzel lens.

This quadrupole setup is relatively easy to design and build reliably. This same configuration is common for focusing beams of heavy atoms or molecules, either in particle accelerators, where it is called a radio frequency quadrupole (RFQ) beam cooler [317][354][355][324][356][357], or in mass spectrometers, called a linear quadrupole ion trap [358][321][359][328].

There is one major problem with quadrupole focusing: because buffer gas is omnidirectional, it also slows down particles in the axial direction. Particles will slow down and eventually stop over time due to air drag (according to the stopping distance in chapter 4) [328], as shown in figure 6.7. This is unavoidable since particle motion is exponentially damped with the same time constant in all directions, so by the time a particle loses 95% of its radial velocity, for example, it has also lost 95% of its axial velocity. Particles cannot be fully focused without becoming stuck. A straightforward solution to this axial slowing problem is superimposing an additional axial electric field to keep particles moving. There are multiple ways to do this, so we address it in depth in section 6.4. For the remainder of this section, we assume this is a solvable problem and only consider particle radial motion.

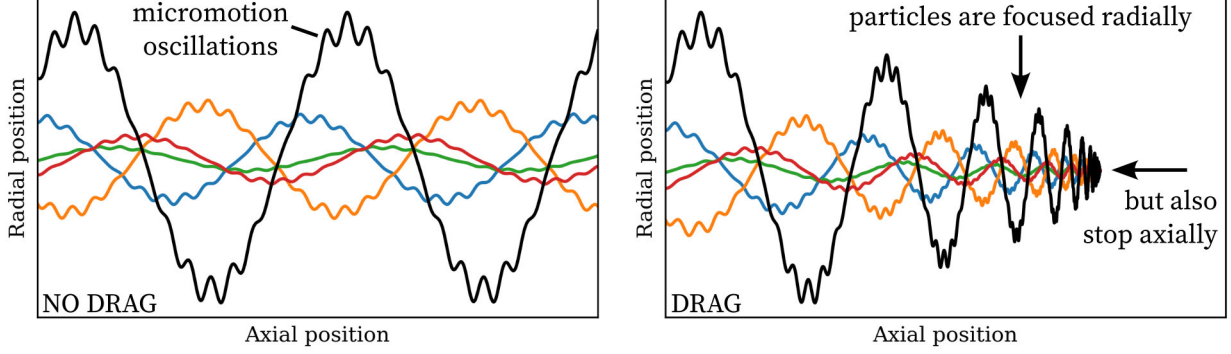


Figure 6.7: Trajectories of particles (different colors) moving left to right in a quadrupole trap. Left: with no air drag, particles move in simple harmonic motion plus an additional micromotion oscillation. The beam diameter stays the same size it was initially. Right: when air drag is added, particles move toward the center, falling down the potential shown in figure 6.6. The beam is focused! However, the particles slow down and eventually stop in the axial direction; they'd never make it to a substrate. We will fix this in section 6.4.

Assuming axial motion works, we are ready to consider how much we can focus particles.

Consider a single particle in a quadrupole trap. The pseudopotential is formed by electric fields with nearly infinite resolution, so if a particle were perfectly damped the particle could be centered nearly exactly. However, the buffer gas molecules continue to hit the nanoparticle and shift it off center. We've brought back Brownian motion! Brownian motion is our main limit to focusing; for several other considerations see section 6.3.3.

We can approximate the smallest beam diameter we can focus particles to by comparing the quadrupole pseudopotential, which narrows the beam, to Brownian motion, which expands it. In appendix A we found the quadrupole pseudopotential (equation A.9) has height

$$\tilde{U}_T(r) \approx \frac{qV_T r^2}{8R_T^2} \cdot \frac{q}{q_0} \cdot \frac{m_0}{m} \quad (6.5)$$

where r is the distance of a particle from the trap center, R_T is the distance from trap center to closest quadrupole electrode, V_T is the peak-to-peak voltage amplitude between quadrupole electrodes, and the particle has mass/charge ratio m/q while the oscillation frequency is optimized²⁶ (equation A.6) for particles with slightly smaller ratio m_0/q_0 .

Brownian motion is random, not a force in a single direction, but we can conveniently analyze it (as noted in chapter 4) by noting it gives particles some amount of kinetic energy. Particles can move in the 2D radial plane perpendicular to the beam and Brownian motion gives $\frac{1}{2}k_B T$ per dimension of movement, so on average particles have a total of $1k_B T$ of radial energy (in a random direction) when cooled to the temperature of the gas. Since this is only an average effect, some particles will have more kinetic energy and make the beam slightly wider, but here we use only $1k_B T$ in our calculations for simplicity.

²⁶Increasing frequency by $\omega = s \cdot \omega_{min}$ gives $\tilde{U}_T = \tilde{U}_{Tmin}/s^2$ and (equation 6.6) $d_{Bquad} = s \cdot d_{Bquad,min}$.

If we set Brownian energy $1k_B T$ equal to $\tilde{U}_T(r)$, we can find an expression for the average radius of displacement r , and the resulting particle beam diameter d_{Bquad} is twice that:

$$d_{Bquad} \approx 2R_T \sqrt{\frac{8k_B T}{qV_T} \cdot \frac{q_0}{q} \cdot \frac{m}{m_0}} \quad (6.6)$$

This equation gives the best resolution²⁷ (minimum beam diameter d_{Bquad}) a quadrupole particle focusing system can achieve. Let's compute some example beam diameters:

n	$R_T = 0.5 \mu\text{m}$	$R_T = 5 \mu\text{m}$	$R_T = 50 \mu\text{m}$	$R_T = 500 \mu\text{m}$	$R_T = 5 \text{mm}$
1	45.3 nm	453 nm	4.53 μm	45.3 μm	453 μm
2	32.0 nm	320 nm	3.2 μm	32.0 μm	320 μm
5	20.3 nm	203 nm	2.03 μm	20.3 μm	203 μm
10	14.3 nm	143 nm	1.43 μm	14.3 μm	143 μm
20	10.1 nm	101 nm	1.01 μm	10.1 μm	101 μm
1	26.3 MHz	2.63 MHz	263 kHz	26.3 kHz	2.63 kHz

Table 6.4: The beam diameter d_{Bquad} nanoparticles of charge $q = n \cdot e$ can be focused to with a quadrupole built with electrodes of size R_T , calculated with equation 6.6 using $V_T = 100 \text{ V}$ and $T = 298 \text{ K}$. We can beat $1 \mu\text{m}$ resolution, perhaps even 100 nm ! Eventually resolution is limited instead by the diameter of the nanoparticles themselves. These resolutions require the trap to have particular frequencies as described in appendices A and B; the last row computes these with equation A.6 for 10 nm Cu particles with $q = 1e$.

This is excellent: quadrupole ion traps with buffer gas theoretically allow us to focus particles to sub- $1 \mu\text{m}$ resolutions, finally achieving our original goal from chapter 1! This entire idea of nanoparticle printing might yet work! However, it requires significant detail.

First, note that with $V_T = 100 \text{ V}$, $T = 298 \text{ K}$, and $q = 1e$, the beam diameter d_B is focused to $\approx 5\%$ of the space between the electrodes ($2R_T$). A beam starting at $d_B = 0.1 \text{ mm}$ to 1 mm as in table 6.3 wouldn't fit in a sub- $100 \mu\text{m}$ quadrupole; we will instead need to focus the beam through multiple progressively smaller quadrupole stages to reach sub-micron dimensions. We comment on how to do this (and how to build tiny quadrupoles) in section 6.5.1.

We can improve focus by increasing the trap voltage V_T , but only to a point: sufficiently high voltage will cause electrical breakdown, making the buffer gas into a conductive plasma²⁸. As described by the Paschen curve in figure 2.4, there is a maximum safe voltage below which breakdown never occurs. The exact voltage varies with gas, geometry, surface roughness and other conditions [138]; for this chapter we assume $V_T = 100 \text{ V}$ is always safe²⁹. Alternatively, we can use a low gas pressure (and trap size), on the left of the Paschen minimum, to increase the allowed voltage. Many particle accelerator quadrupoles use 0.01 Torr to 0.1 Torr pressures to reach voltages as high as $V_T = 1 \text{ kV}$ to 10 kV [360][355][357][361][362].

²⁷Approximately. The beam is somewhat Gaussian and subject to some other effects (section 6.3.3).

²⁸Which will distort the electric field, short-circuit electrodes, and generally stop focusing from working.

²⁹We further assume 200 V ($V_T = 100 \text{ V}$ plus 100 V for axial acceleration) is safe in section 6.4.

What pressure should the buffer gas be? There is an optimal value. Besides electrical breakdown, at low pressures damping takes longer than necessary (as described by the damping time constant in chapter 4); high pressures give slower axial movement (section 6.4) and reduced micromotion for lower ponderomotive focusing force [355][317]. The gas specifics and exact damping equation can vary so long as the damping is predictable³⁰. Our simulations generally use 0.01 Torr to 10 Torr argon in quadrupoles around 100 mm long.

Decreasing the temperature T improves resolution. Some particle accelerator RFQ beam coolers use liquid nitrogen to reach $T = 77$ K (vs. 298 K room temperature) [363][362][364].

What about our wide range of particle sizes: 350% variation, according to table 6.3? It turns out we can probably focus everything at once without worrying about chromatic aberration! All particles will be damped to $1k_B T$ radial thermal motion³¹ then stay at a constant minimum diameter which, according to equation 6.6, will only scale with \sqrt{m} so the mass variation merely doubles the beam diameter.

Particle charge should be as high as possible for better focusing (and higher axial velocity in section 6.4), though this results in higher space charge effects (section 6.3.3). If we can vary particle charge based on size (thus mass), as chapter 5 suggests may occur when charging to a fixed ionization energy, we would reduce mass/charge ratio variation.

We should also note that while simulating quadrupole traps is straightforward, simulating Brownian motion (see chapter 4), while feasible via statistical methods [215][216][365], is not. We did not have time to verify a numerical Brownian simulation for our large nanoparticles at intermediate pressures and so did without. This should not change our conclusions.

6.3.3 Additional Limits to Quadrupole Radial Focusing

We now have a tractable approach to radially focus particles—quadrupoles with buffer gas—and are ready to tackle the final problem of axial velocity control. But before we switch discussion from radial to axial particle movement, there are several more³² radial effects we should mention: space charge, RF heating, and beam expansion outside the trap due to thermal energy. These are all minor but will still affect the ultimate focusing performance.

Space Charge

A beam of nanoparticles contains many particles, and since all these particles have a positive charge, they will repel each other and make the beam wider, reducing printing resolution. This effect is called space charge and limits the number of particles in any given beam. Space charge limits are also a large concern in particle accelerators and electron and ion beam tools. In these systems, the Child-Langmuir law [296] gives the maximum density of charges that can be moved axially through a region with a given voltage. But we would like to consider radial forces for the moment, so we will need to make a different calculation.

³⁰Small quadrupoles can be smaller than the gas mean free path, so quantization effects may appear.

³¹This is sometimes called thermalization and is roughly why any damping method is called cooling, though it would be heating if the particles started with a lower velocity.

³²Even more effects exist (e.g., electrical noise). See [366] for a review in trapped-ion quantum computing.

Define the number flux N' as the number of nanoparticles per second moving through the beam cross-section (N' is fixed by the volumetric flux Q and particle diameter d_p). When N' is small (as an extreme, $N' = 1 \text{ s}^{-1}$), particles are so far apart that space charge effects are negligible and we can achieve the high resolution of table 6.4 without trouble. But if N' is sufficiently large, space charge pushes particles out radially.

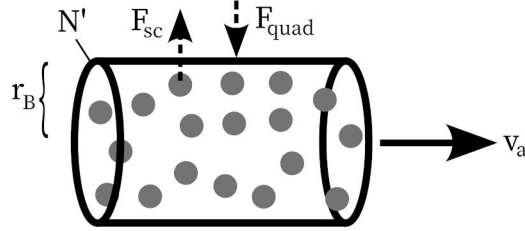


Figure 6.8: Cartoon of the space charge effect. Electrically charged nanoparticles in the same beam repel each other with force F_{SC} to make the beam wider (in addition to Brownian motion), opposing the quadrupole trap ponderomotive force F_{quad} that makes the beam more narrow. A total rate of N' particles, each with charge q , move through the beam cross-section (radius r_B or diameter $d_B = 2r_B$) at axial velocity v_a .

We can roughly approximate³³ the effect of space charge on radial focusing in a quadrupole as follows [367][360]: compare the quadrupole potential (equation 6.5) to a repulsive potential from the beam. Approximate the beam as uniform positive charge density within a cylinder of radius $r_B = d_B/2$. Since N' is the number of particles per time with charge q moving through the cylinder cross-section at velocity v_a , the linear charge density of the cylinder is qN'/v_a (units C m^{-1}). The electric field \vec{E} (pointing radially outward) of this cylinder and corresponding potential energy U_{SC} from $q\vec{E} = -\nabla U_{SC}$ (setting $U_{SC}(0) = 0$) are

$$|\vec{E}(r)| \approx \begin{cases} \frac{qN'r}{2\pi\epsilon_0 v_a r_B^2} & r \leq r_B \\ \frac{qN'}{2\pi\epsilon_0 v_a r} & r > r_B \end{cases} \quad \text{and} \quad U_{SC}(r) \approx \begin{cases} -\frac{q^2 N' r^2}{4\pi\epsilon_0 v_a r_B^2} & r \leq r_B \\ -\frac{q^2 N'}{2\pi\epsilon_0 v_a} \left(\ln\left(\frac{r}{r_B}\right) + \frac{1}{2} \right) & r > r_B \end{cases} \quad (6.7)$$

for radial distance r from the beam center. Particles are pushed away from the beam center via the electric field (i.e., they fall down the potential U_{SC}). The beam is stable when this potential U_{SC} is less than the quadrupole pseudopotential $\tilde{U}_T(r)$ (equation 6.5) in the same way we derived equation 6.6 (but ignoring³⁴ Brownian motion).

$$\tilde{U}_T(r) > U_{SC}(r) \quad \text{so} \quad \frac{qV_T r^2}{8R_T^2} > \frac{q^2 N' r^2}{4\pi\epsilon_0 v_a r_B^2} \quad (6.8)$$

³³More accuracy could be obtained via particle simulation, modeling the beam with Poisson's equation.

³⁴This is valid when space charge is a larger effect than Brownian motion; the exact boundary for N' we find will be a slight overestimate of the maximum charge a beam can fit.

Rearranging this equation, we find the maximum number flux N' that fits in a beam (that also satisfies equation 6.6) of diameter $d_B = 2r_B$ with quadrupole trap voltage V_T , axial velocity v_a , particle charge q , quadrupole trap radius R_T , and vacuum permittivity ϵ_0 :

$$N' < \frac{V_T \pi \epsilon_0 v_a d_B^2}{8qR_T^2}. \quad (6.9)$$

For example, a beam of diameter $d_B = 1 \mu\text{m}$ and $v_a = 1000 \text{ m s}^{-1}$ focused by a trap with $V_T = 100 \text{ V}$ and $R_T = 5 \mu\text{m}$ can move a maximum of $N'_{max} \approx 8.7 \times 10^{10}$ singly-charged ($q = 1e$) particles s^{-1} , which is a current of about 14 nA. We discuss the ramifications of this space charge limit in section 6.5.3, where it is often the largest constraint on print speed at high resolutions giving an incentive to use particles of higher mass and lower charge.

RF Heating

Our approximation of a quadrupole as a quadratic potential well for particles has some limits, and these differences can affect particle motion, typically increasing the beam diameter.

Recall the quadrupole trap works (in appendices A and B) by creating an oscillating electric field. A particle experiences quick oscillations that we call micromotion, and asymmetry in the field during micromotion is what provides the average ponderomotive force that makes the particle act as if it were in a quadratic potential well. This micromotion itself slightly increases the beam diameter³⁵, but in addition to this, disturbing the particle from an ideal micromotion trajectory modifies the resulting ponderomotive force which can then be nonconservative and add kinetic energy. RF heating is any such effect³⁶.

RF heating can happen in many ways. See [323] for an excellent review, or [368][369][365][370][371]. Collisions with gas molecules, for example, disturb particle motion and adjust their micromotion. We can likely neglect single collisions as our nanoparticles are significantly heavier than the surrounding gas molecules, but the collective behavior (which produces the drag we use) is statistically nontrivial [365]. Another source of RF heating is multiple nanoparticles repelling each other³⁷. This makes nanoparticles rest at a nonzero radial position, where they have nonzero micromotion. Finally, particles entering or leaving a quadrupole out of sync with its oscillations will be deflected in some direction (which is arguably RF heating); they might only experience half of a micromotion cycle. All these RF heating effects can be modeled with particle trajectory computer simulations.

Beam Expansion from Thermal Velocity

Our last consideration is what happens when a focused beam of particles leaves a quadrupole, because there must be some distance between the quadrupole and the substrate we wish to print particles onto. While in the quadrupole, particles stay within a constant beam diameter d_B but have radial energy $1k_B T$. As soon as the particles leave the trap at axial velocity v_a ,

³⁵Increase in beam diameter due to expected micromotion oscillations is not usually considered RF heating.

³⁶This occurs in any RF ion trap (see appendix A), hence the name.

³⁷This is what causes space charge repulsion, can also be called intra-beam scattering [372], and can distribute particles radially by mass/charge ratio [326].

the particles will also move outward radially, expanding the beam³⁸. We assume L is small and v_a high so drag is negligible. The mean radial velocity v_r from $kT = \frac{1}{2}mv_r^2$ is

$$v_r = \sqrt{\frac{2k_B T}{m}} \quad (6.10)$$

so the beam forms half-angle $\theta \approx v_r/v_a$. If the beam had original diameter d_{B1} (perhaps d_{Bquad} from equation 6.6) and travels axial distance L , the final beam diameter d_{B2} is

$$d_{B2} \approx d_{B1} + 2\theta L \approx d_{B1} + 2v_r \frac{L}{v_a} \approx d_{B1} + 2\frac{L}{v_a} \sqrt{\frac{2k_B T}{m}}. \quad (6.11)$$

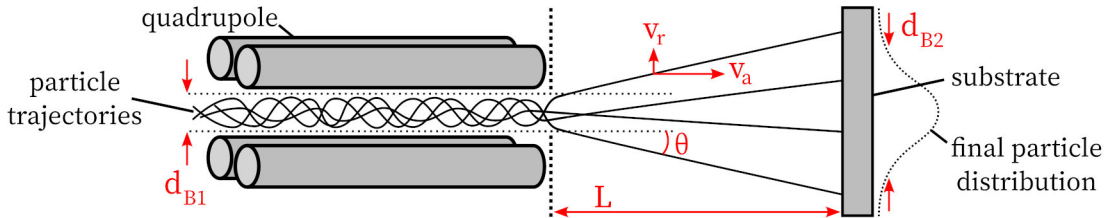


Figure 6.9: Illustration of beam expansion when particles (moving left to right) leave a quadrupole (or pinhole [214]). Particles have nonzero radial energy, so they move outward with no more quadrupole to confine them. The final beam distribution is roughly Gaussian.

	1 nm	10 nm	100 nm
v_r	41.9 m s^{-1}	1.32 m s^{-1}	0.0419 m s^{-1}
θ (1000 m s^{-1})	2.4° (41.9 mrad)	0.0759° (1.32 mrad)	0.0024° (0.0419 mrad)

Table 6.5: Mean radial velocity v_r of nanoparticles leaving a quadrupole at $298 \text{ K} = 25^\circ \text{C}$ and corresponding beam half-angles for $v_a = 1000 \text{ m s}^{-1}$, assuming density of copper. These tiny angles give low emittance so the ion optics of section 6.3.1 might actually be useful.

As a result of this effect, we may need to place the output of a quadrupole focusing mechanism close to the substrate (see section 6.5.1). For example: if 10 nm particles travel with an axial velocity $v_a = 100 \text{ m s}^{-1}$, then printed spot diameter increases $2v_r/v_a * 1 \mu\text{m} = 26 \text{ nm}$ for each micrometer of distance L from the substrate; at 1000 m s^{-1} this is only 2.6 nm. Achieving high resolution $< 1 \mu\text{m}$ probably requires putting the quadrupole exit within tens of microns of the substrate. Fortunately, this is feasible: machine tools and XYZ stages easily maintain position within $10 \mu\text{m}$. Quadrupole focusing, as in table 6.4, is the bigger limit.

Alternatively, note the beam exiting the quadrupole can have low emittance (see table 6.5), so we might allow the beam to travel a long L while expanding, then use standard ion optics (e.g., an Einzel lens) to focus it back over a similarly long³⁹ L if we can achieve sufficiently low chromatic aberration. We make some remarks in section 6.5.1.

³⁸This derivation also appears (with experimental confirmation) in [214] for aerodynamic lenses and supersonic gas jets [325], and as an upper limit for brightness of electron sources at some temperature [296][373].

³⁹This is how SEMs and FIBs can place their electron and ion optics far from a substrate.

6.4 Axial Acceleration

We are halfway to solving the particle focusing problem of section 6.1. We found a way to radially focus nanoparticles to small sub-1 μm areas by using quadrupole traps with buffer gas cooling, but also found we will need to somehow keep particles moving in the axial direction without being stopped by the buffer gas. Furthermore, in order to control printed material quality (see chapter 3), we want to set the axial speed of the particles when they impact the substrate to some adjustable value we can choose within $v_a = 100 \text{ m s}^{-1}$ to 3000 m s^{-1} .

A solution exists. We will be able to control particle axial speed, i.e., accelerate particles to a desired velocity. The fundamental trick we will use is that quadrupoles only control particle motion in the radial direction; axial movement is separate and can be controlled with its own electric field. We will first present a relatively simple approach (DC acceleration) and its limits then discuss a more advanced axial acceleration system (a linac).

6.4.1 DC Acceleration

The easiest method to make particles continue to move axially (instead of being slowed and stopped by gas damping) is to apply a DC⁴⁰ field in the axial direction, resulting in the basic 1D electrostatic movement discussed in section 6.2.

The most straightforward way to achieve this is to divide the quadrupole electrodes into axial segments onto which are applied the oscillating voltages required for the quadrupole plus a DC bias voltage that increases in the axial direction. The oscillating voltage component creates a quadrupole pseudopotential and the DC bias voltages create an axial field; they add together by superposition (the electric field is linear in voltage). Particles are now focused radially by the quadrupole with gas damping and also accelerated axially.

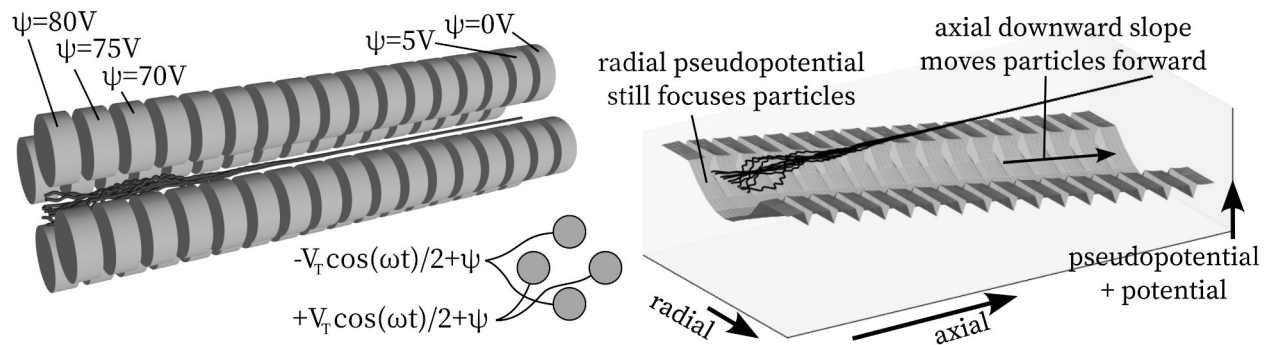


Figure 6.10: Left: we can take the quadrupole of section 6.3.2 and figure 6.6 and apply an axial electric field by segmenting the electrodes and applying an increasing DC bias ψ to each set (here, an additional 5 V per segment). Right: The resulting potential and pseudopotential field the particle moves in is a quadratic well that slopes down in the axial direction.

⁴⁰By DC for “direct current” we mean an electric field or voltage is time-invariant, as in any ion optics in section 6.3.1, as opposed to, e.g., the oscillating-in-time electric field of a quadrupole trap.

Particle trajectory simulations show this works. Particles have damped radial motion but keep moving in the axial direction, eventually producing a narrow beam with the diameter d_{Bquad} we computed in equation 6.6. We have successfully made a highly focused beam!

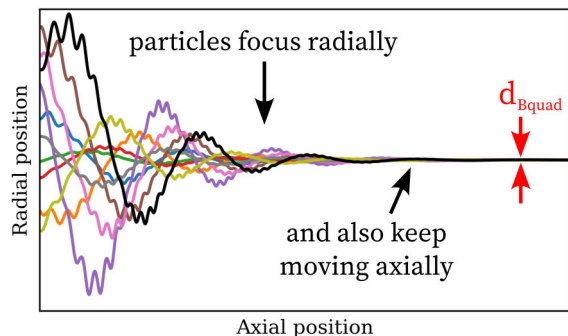


Figure 6.11: Trajectories of particles in a quadrupole with buffer gas, which focuses them radially, and DC acceleration, which keeps them moving in the axial direction. We have successfully made a focused beam! This continues figure 6.7 (and in fact uses an identical simulation save slightly higher pressure and more particles for visualization). The final beam diameter should be d_{Bquad} from equation 6.6 but, as briefly mentioned in section 6.3.2, the simulation results are slightly better than this since we only simulate drag and not Brownian motion. The general behavior is realistic.

This is not a new idea. Axial DC fields, both with and without a quadrupole, are common: they are the most basic way to move particles electrostatically (see section 6.2).

Any quadrupole using a buffer gas will run into the same axial slowing issue and solution. Using segmented electrodes to simultaneously create a radial quadrupole field and axial DC field is common practice in particle accelerator RFQ beam coolers [317][354][374][375][324][356][357][376] and mass spectrometry linear quadrupole traps [328][377]. There are also ways⁴¹ to create the axial field without segmenting the quadrupole, reducing the number of electrodes: the quadrupole electrodes can be tapered and slanted [379][328][380] or crosscut and twisted [364], or additional DC-only electrodes added around or between the quadrupole electrodes [381][382][362][378], though this distorts the quadrupole field [328][378].

Axial fields are also used without a quadrupole when focusing is not required. Applications include (see also chapter 3) ionized cluster beam deposition (ICBD) [178][47] which prints nanoparticles over a wide area instead of in a focused beam, ion optics for SEMs, FIBs, and ion implantation, micrometeoroid impact studies [198][199], and electrostatic precipitators [102]. Axial electric fields have been proposed to further accelerate particles in cold spray and aerosol deposition⁴² [98][383][384]. We should also mention ion mobility spectrometry [210][385][386] which moves molecules in an axial DC field in buffer gas (sometimes with a radial RF trap, but a simpler ring design, similar to the ion funnels we will mention in section 6.5.1, instead of a quadrupole as it does not need to minimize beam diameter).

⁴¹Confusingly, some of these nonsegmented geometries are sometimes called Linacs [328][378] with no relation to the generic linear accelerator linac as used in particle accelerators and section 6.4.2.

⁴²This increases particle impact velocity but does not solve the Brownian focusing limit from chapter 4.

We can analyze DC axial acceleration as follows.

First, without gas drag, an axial field of total voltage V will accelerate a particle of mass m and charge q from zero to a speed of $v_a = \sqrt{2qV/m}$ (from $\text{KE} = qV = \frac{1}{2}mv_a^2$); it adds qV kinetic energy (this is why the volt is a joule per coulomb). This happens no matter how long the field is. If we made an axial field without a quadrupole by taking just two of the three rings of an Einzel lens (section 6.3.1)—an “immersion lens”—whether the two ring electrodes are 100 μm or 100 mm long does not matter (as long as gas drag is negligible); the particle will reach the same speed as it travels through.

This speed increase from a gas-drag-free axial field varies with the square root of particle mass and charge. The square root means this is less sensitive than radially focusing with other ion optics (which depends directly on the mass/charge ratio). This limited chromatic aberration means we might find DC axial acceleration useful (if still imperfect) for our wide range of particle parameters if there is ever low gas pressure and we can use a high enough voltage: a 10 nm $q = 10e$ copper particle needs a high 1460 V to reach 1000 m s^{-1} .

A particle with gas drag in an axial field acts slightly differently: it will try to increase its speed as before, but because the gas drag force increases with velocity, it turns out particles will accelerate up to some steady-state drift velocity⁴³, and this drift velocity depends on the electric field (the voltage per distance), not the voltage itself. If the particle has viscous damping coefficient β giving drag force $F_{drag} = -\beta v_a$ (see chapter 4) and is pulled forward by an axial electric field E as $F_{field} = qE$, it will slow down or speed up until reaching drift velocity $v_{a,drift}$ defined by

$$F_{field} = qE = \beta v_{a,drift} = -F_{drag} \quad \text{so} \quad v_{a,drift} = \frac{q}{\beta} E = K \cdot E \quad (6.12)$$

where we define the electrical mobility⁴⁴ $K = q/\beta$ [102][205][211]. We can expand β using our Epstein drag equation 4.7 to see

$$v_{a,drift} = \frac{q}{\beta} E = \frac{12}{8 + \pi\varphi} \sqrt{\frac{k_B T}{2\pi m_g}} \frac{q}{P d_p^2} \cdot E \quad (6.13)$$

where P is the pressure, m_g is the gas molecular mass, $\varphi \approx 0.9$, and d_p is particle diameter. Because the mass of the particle varies with diameter cubed ($m = \rho\pi d_p^3/6$ where ρ is density), this steady-state velocity scales with $m^{-2/3}$, which means there is slightly more chromatic aberration than the $\sqrt{1/m} = m^{-1/2}$ scaling of gas-free acceleration. Furthermore, a particle only reaches this velocity if the field E is sustained over a long enough distance (roughly the gas stopping distance, equation 4.14), which requires high voltage V over long distance L for $E = V/L$ (at shorter distances, the particle accelerates similar to the no-drag case).

Gas breakdown usually limits the maximum voltage we can use to around 100 V (see section 6.3.2), thus limiting maximum electric field and drift velocity. We can compute the resulting possible drift velocities for particles of our range of sizes to see what might be practical.

⁴³This is similar to the terminal velocity of falling objects on Earth or electron drift velocity.

⁴⁴Electrical mobility is a crucial parameter in ion mobility spectrometry, where it is used to precisely differentiate molecules in a different way than the mass/charge ratio in mass spectrometry [210][385].

	1 nm	10 nm	100 nm
100 V, 0 Torr	2610 m s ⁻¹	82.6 m s ⁻¹	2.61 m s ⁻¹
100 V / 100 mm, 0.01 Torr	(13 200 m s ⁻¹)	(132 m s ⁻¹)	1.32 m s ⁻¹
100 V / 100 mm, 0.1 Torr	1320 m s ⁻¹	13.2 m s ⁻¹	0.132 m s ⁻¹
100 V / 100 mm, 1 Torr	132 m s ⁻¹	1.32 m s ⁻¹	0.0132 m s ⁻¹
100 V / 100 mm, 10 Torr	13.2 m s ⁻¹	0.132 m s ⁻¹	0.001 32 m s ⁻¹

Table 6.6: Top row: velocities of singly-charged Cu particles of the indicated diameters from a 100 V field (note this is similar to table 6.2). Bottom rows: drift velocities of the same particles in a field of 100 V applied over a 100 mm distance ($E = 1 \text{ V mm}^{-1}$); parentheses note a longer distance (and thus higher voltage) is required for the particle to reach that drift velocity. Most velocities are below our desired 100 m s^{-1} to 3000 m s^{-1} velocities but particles with higher charge q have proportionally higher drift velocities. In the top row, velocities vary with $\sqrt{m} \propto d_p^{3/2}$, and in the bottom row by $m^{2/3} \propto d_p^2$.

As shown in table 6.6, axial DC acceleration in gas cannot quite reach the 100 m s^{-1} to 3000 m s^{-1} velocities we want for most particles when allowing only 100 V. Other applications that use axial fields in gas typically accept this: particle accelerator RFQ beam coolers [374][376][362][364] and ion mobility spectrometry⁴⁵ use small fields (1 V to 200 V per 100 mm), because they only need nonzero (if low) velocity. If we want high velocities, we must use higher voltages, probably in vacuum. SEMs or ICB and similar [47][199] use high voltage ($> 1 \text{ kV}$) by working in high vacuum and chromatic aberration is either minimal (if all particles, e.g., electrons, are the same mass and charge) or ignored.

So DC axial acceleration through a quadrupole as in figure 6.10 works but is limited to low axial speeds. We could achieve high-speed impact velocities by accelerating in vacuum. But if we want very precise impact velocities that do not vary with particle size at all, we will need to use something more than a single axial DC field.

6.4.2 Linacs and Controlled Motion

There is a trick that could let us solve two problems simultaneously. At the cost of extra complexity, we could accelerate particles of different masses to the same velocity, and we could also reach higher velocities in a gas than with a simple axial DC field.

The trick is to start with segmented electrodes as in figure 6.10 but instead of applying a simple voltage gradient, we sinusoidally vary the voltage in the axial direction, making a number of “buckets” in the electrostatic potential. Background gas damping makes particles fall into these buckets much as it works for the quadrupole (section 6.3.2). We move the buckets along the axial direction (making the sinusoid a traveling wave) by changing voltages on each of the segmented electrodes, and the particles move with them. If we construct this correctly, all particles move as “bunches” inside the buckets precisely at the speed of the linac with no chromatic aberration. This is a linear accelerator, or linac.

⁴⁵Ion mobility spectrometry is interesting as it encourages chromatic aberration; that is how it works.

A linac can accelerate particles to higher velocities than a single DC field for the same voltage because as the field shifts, a particle that has already been accelerated by voltage V can be pushed again by the same voltage, even though that voltage didn't change in magnitude (only position). In high-energy physics, this is how particle accelerators can reach ridiculously high particle impact energies⁴⁶ (though our linac is different by including buffer gas).

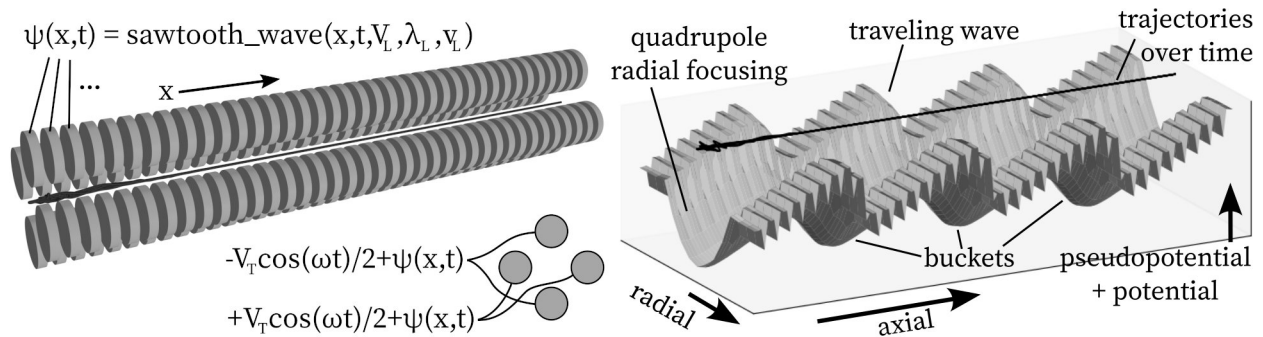


Figure 6.12: Beginning with a segmented quadrupole as in figure 6.10, instead of applying a smoothly increasing DC potential (in addition to quadrupole oscillations), use a wave of peak-to-peak amplitude V_L and wavelength λ_L (a sinusoid works, but a sawtooth wave with steeper slope is ideal) that travels in the axial direction at velocity v_L . This creates discrete buckets of electrostatic potential that particles fall into via buffer gas damping. As the buckets move at axial velocity v_L , the particles move with them at that velocity.

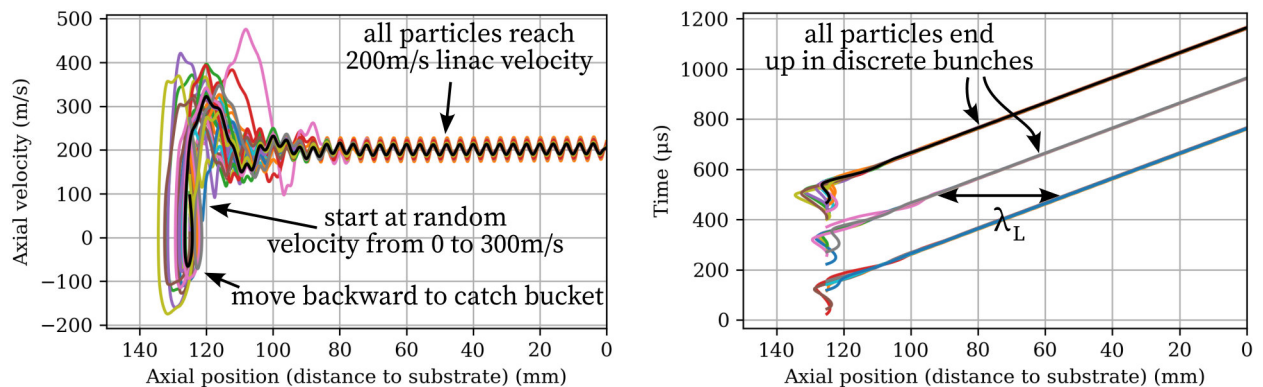


Figure 6.13: The linac works in simulation! These are trajectories of 4 nm to 6 nm Cu $q = 5e$ particles in a linac, beginning at axial position 125 mm with random velocities 0 m s^{-1} to 300 m s^{-1} and times (with respect to linac phase), and all eventually reach the steady-state $v_L = 200 \text{ meter/s}$ velocity of a linac with $V_L = 100 \text{ V}$, $\lambda_L = 40 \text{ mm}$, and 4 mm electrode pitch (and 100 Pa buffer gas) while forming bunches. The steady-state velocity oscillates due to the segmented electrodes. The particle drift velocity if the 100 V were applied over 100 mm is only 35 m s^{-1} ; this linac lets them achieve speeds over 5 times higher.

⁴⁶These can reach TeV particle kinetic energies without a teravolt DC voltage, which is impractical.

To analyze the linac, consider the potential particles feel in the axial direction. Let the linac have peak-to-peak voltage V_L , wavelength λ_L , and velocity v_L . The linac creates the axial potential energy surface $U_L(x, t)$ where x is distance in the axial direction and t is time. Let p_L be the distance between linac electrodes (the pitch); we must have $p_L < \lambda_L/2$ by the Nyquist theorem, and preferably $p_L < \lambda_L/4$. Let E_{Lmax} be the maximum electric field (because the electrodes are discretized, E_{Lmax} varies between V_L/p_L and $V_L/2p_L$ throughout a linac cycle). Let the particles have some mass m , diameter d_p , and charge q , and let the background buffer gas have pressure P (and temperature T , gas molecule mass m_g).

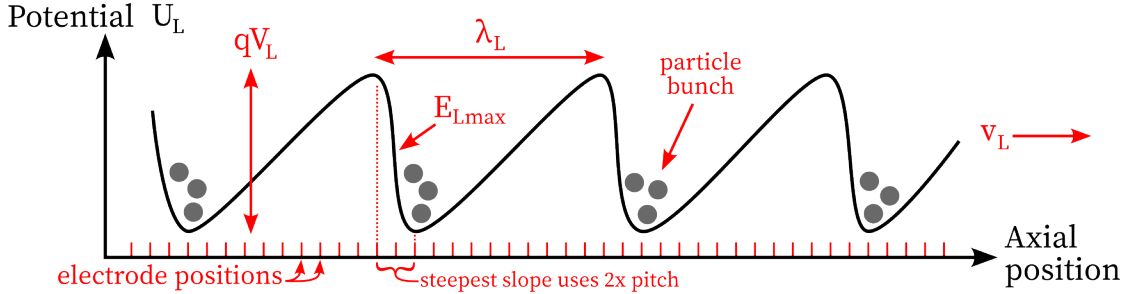


Figure 6.14: An annotated diagram of the linac potential waveform. This is a traveling wave of height $U_L = qV_L$, wavelength λ_L , and velocity v_L , created by electrodes at discrete positions. To maximize the force pushing particles to the right, we maximize the steepness of the left side of the well, which we do by making a sawtooth wave instead of simple sinusoid. Electrode discretization means it is more reliable to form the slope from twice the electrode pitch instead of over one. A beam separates into groups of particles, called bunches.

The behavior of our linac is somewhat complex and unique (particle accelerator linacs typically operate without buffer gas and with beam acceleration, not at constant velocity), but initial analysis and simulations lead us to hypothesize it can be roughly⁴⁷ described with the following three nondimensional parameters, which we name A_L , B_L , and C_L .

First, note that particles are pushed along by the linac with a maximum force of qE_{Lmax} and also experience gas drag; they will move as long as the former is greater than the latter. This is the same setup as drift velocity in section 6.4.1. We can express this with nondimensional parameter A_L , the ratio of maximum axial electrostatic force to gas drag at linac velocity v_L , and say that a linac and particle function as long as $A_L > 1$.

$$A_L > 1 \quad \text{where} \quad A_L = \frac{qE_{Lmax}}{\beta v_L} = \frac{qE_{Lmax}}{v_L} \cdot \left[\frac{8 + \pi\varphi}{12} \sqrt{\frac{2\pi m_g}{k_B T}} P d_p^2 \right]^{-1} \quad (6.14)$$

If $A_L < 1$, then the linac force is insufficient to move the particle at the linac velocity, and the particle will never move with the linac. It will instead be briefly accelerated by one side of a linac well as it passes, then decelerated by the other, resulting in oscillatory movement and minimal net velocity. Fortunately, A_L can be made arbitrarily high by minimizing the

⁴⁷We suspect this is close but not quite a complete parametrization; we leave confirmation to future work.

electrode pitch to maximize E_{Lmax} (though this requires more electrodes) and by minimizing pressure (though this increases C_L below and also quadrupole focusing time).

We can use A_L to see how fast a linac can be. From table 6.6, find a maximum particle drift velocity in an electric field of 100 V/100 mm, then note that increasing the field to E_{Lmax} in a linac will scale the velocity proportionally. For example, a singly-charged 10 nm particle has a drift velocity of only 13.2 m s^{-1} in a 100 V / 100 mm field at 0.1 Torr but can move 100x faster at 1320 m s^{-1} if the field is applied over only 1 mm. This is close to reaching the upper half of the 100 m s^{-1} to 3000 m s^{-1} impact velocity range we want.

However, there is a second more subtle requirement that applies to only a subset of particles. If a particle is already within the potential well of a linac at the correct velocity, the A_L parameter is sufficient to describe its behavior. But a particle at a different velocity, or not in phase with the linac, will skip between potential wells until it slows down and is kept within a bucket by gas damping, and careful analysis shows this is only possible if a single linac bucket has enough potential energy to accelerate the particle from zero to linac velocity⁴⁸. We define the second nondimensional parameter B_L to be the ratio of potential energy of a single linac well (the particle charge times linac amplitude) to the kinetic energy of a particle traveling at linac velocity. This is often a stricter limit than A_L .

$$B_L > 1 \quad \text{where} \quad B_L = \frac{2qV_L}{mv_L^2}. \quad (6.15)$$

	$q = 1e$	$q = 2e$	$q = 5e$	$q = 10e$	$q = 20e$
1 nm	2610 m s^{-1}	3700 m s^{-1}	-	-	-
10 nm	82.6 m s^{-1}	117 m s^{-1}	185 m s^{-1}	261 m s^{-1}	370 m s^{-1}
100 nm	2.61 m s^{-1}	3.7 m s^{-1}	5.84 m s^{-1}	8.26 m s^{-1}	11.7 m s^{-1}

Table 6.7: The maximum velocities of linacs that accept all input particles of some mass and charge ($B_L > 1$) at $V_L = 100 \text{ V}$, assuming copper. Small particles have a maximum charge; see chapter 5. This is one of the major restrictions to how good a linac can be: even if reaching higher velocities is possible according to the A_L parameter, such a linac would require incoming particles to be presorted into bunches, which is tricky to implement.

This parameter is somewhat optional for a linac depending on desired behavior. Assuming $A_L > 1$ (or else nothing works): when $B_L \gg 1$, all particles no matter their initial conditions will eventually travel with the linac (for gas drag will bring any particle to zero velocity, from where the potential well is strong enough to accelerate it). When $B_L < 1$, particles in an increasingly smaller window of initial parameters will travel with the linac (but, importantly, the well of a linac can still provide enough energy to speed a slightly slower particle up to

⁴⁸This is approximately because gas drag will slow a particle of any initial velocity to between 0 and v_L , at which point if a particle isn't caught by the crest of one bucket, it slips to the next bucket where it is pushed backward an equal amount by the opposite side, making it oscillate back and forth with little net motion. It can be helpful to analyze this in a reference frame moving at velocity v_L .

linac velocity). This means it is possible to create a linac that moves at higher velocities ($B_L < 1$ and $A_L > 1$) if particles are pre-bunched and fed to the linac at the right time.

We define the final linac parameter C_L to be the ratio of total linac length L to the stopping distance S of a particle in buffer gas (equation 4.14) at linac velocity v_L .

$$C_L \gg 1 \quad \text{where} \quad C_L = \frac{L}{S} = \frac{L}{\tau v_L} = \frac{L\beta}{mv_L} \quad (6.16)$$

When C_L is high (perhaps $C_L > 3$), gas drag has time to make particles reach steady state equilibrium with the linac, making it work as desired according to A_L and B_L parameters. But when C_L is low (perhaps $C_L < 3$), gas drag will not have time to equilibrate particle motion to the linac, so final particle velocities will be far from steady-state (i.e., potentially an unexpected wide range of velocities). This mainly determines linac length.

What can we conclude from this?

It seems like a linac does what we want, allowing us to axially move particles with a range of mass/charge ratios to a very specific (possibly adjustable) velocity v_L we choose. This can reach higher velocities than simple DC acceleration, which is helpful since DC acceleration’s drift velocity was a bit low for us. However, it is not a panacea: table 6.7 indicates that high-velocity linacs (perhaps 1000 m s^{-1} to 3000 m s^{-1}) require careful particle control, and the requirement to separate a particle beam into bunches will also reduce the total particles throughput which we will see strongly limits printing speed (section 6.5.3). Whether a linac is worthwhile depends on the circumstance.

Although our linac differs from standard particle accelerator linacs⁴⁹ [296], it is not entirely dissimilar to existing ideas. Particle accelerator RFQ beam coolers can often apply configurable DC biases to their segmented quadrupole electrodes, and they use this (a “buncher”) to make bunches of particles [357][364][362][356][387]. Traveling wave ion mobility spectrometry uses buffer gas with a very similar axial field to our linac [388][389] but operates in the $A_L < 1$ regime specifically so different size particles travel at different velocities (see [390] for experimental measurements showing the $A_L \approx 1$ boundary).

There is one more use for these techniques: a linac⁵⁰ can precisely move particles at slower speeds, possibly as a better-controlled alternative to the gas drag particle transport methods we studied in chapter 4. Using traveling waves to move charged particles has been suggested as an “electric curtain” [391][392][393] for purposes including cleaning dust off solar panels [394]. This (when more controlled) is also the standard approach to moving particles around trapped-ion quantum computers [395][396][397][398], and particles can be moved not only in a single line but through junctions [399][400][401][402][403], allowing particles to traverse a 2D (or 3D [404]) grid. This has also been used to move molecules for ion mobility spectrometry [390][405][406][407][408][409][169]. In other words, electrostatic manipulation can be used for general handling and sorting of particles⁵¹, not just for focusing and acceleration.

⁴⁹Though some similarities exist: linacs in vacuum still have phase stability; particles stay in buckets [296]. It is also possible to accelerate nanoparticles with such a high-vacuum linac [157].

⁵⁰We could also use the ponderomotive force in the axial direction, but the complexity is unnecessary.

⁵¹This might be useful for switching between different materials while printing.

6.5 Complete Electrostatic Focusing Systems

At long last (over 20 pages later!) we finally have everything we need to solve the focusing problem posed in section 6.1. Recall our goal is to move charged nanoparticles, which begin with some initial positions and velocities, onto a substrate in a narrow beam (near $1\ \mu\text{m}$ wide) and at high impact velocities ($100\ \text{m s}^{-1}$ to $3000\ \text{m s}^{-1}$), as quantified in tables 6.1 and 6.3. If we accomplish this, we will have found the last part of a printer hopefully capable of printing useful multimaterial nanoscale semiconductor devices.

In section 6.5.1, we will describe and simulate an example system capable of printing $10\ \text{nm}$ particles with $< 5\ \mu\text{m}$ resolution at $> 1000\ \text{m s}^{-1}$ and make some notes on how it would be physically constructed and how resolution could be improved to $< 1\ \mu\text{m}$ or better. We will follow this with more general remarks on printing particles electrostatically.

6.5.1 A Proof-of-Concept Focusing System and Beyond

There are multiple ways to combine our previously-discussed electrostatic manipulation components to solve the focusing problem, but to give a concrete working example we designed a particularly minimal and straightforward configuration. We focus particles in a quadrupole with buffer gas as per section 6.3.2, but since a single quadrupole is insufficient to focus all the way (see table 6.4), we add a second quadrupole to further focus the output of the first. To move particles axially, we choose to use segmented quadrupoles with DC fields (section 6.4.1) because a linac (section 6.4.2) is tricky to implement, then accelerate particles to high velocities right before impact with the substrate via an extremely high DC field.

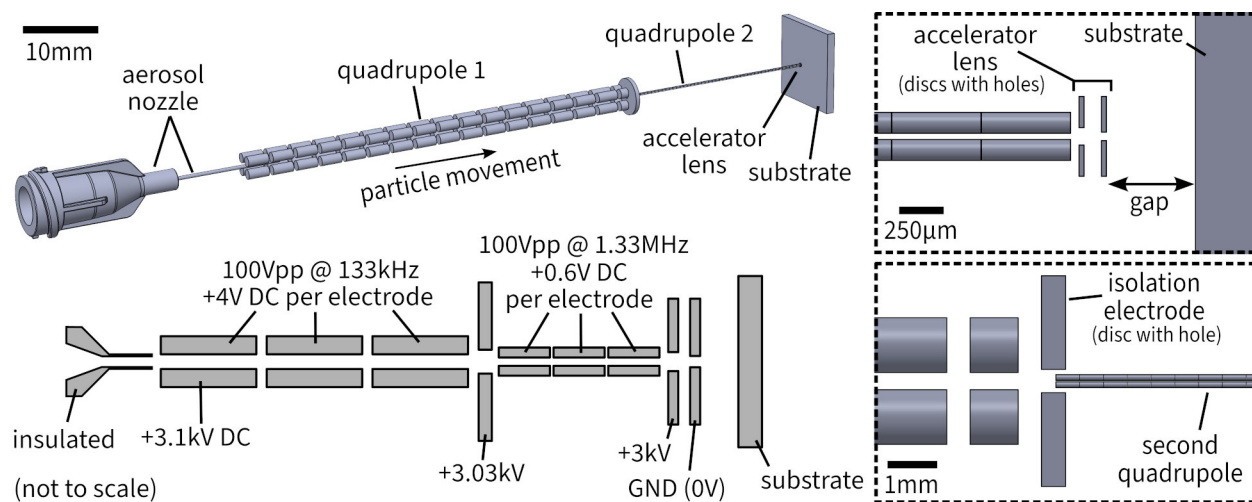


Figure 6.15: A (simulated) working electrostatic focusing system that prints $10\ \text{nm}$ $q = +10e$ nanoparticles with $< 5\ \mu\text{m}$ resolution at $> 1000\ \text{m s}^{-1}$. If built, this could be inserted into an existing aerosol deposition system (figure 6.18). Bottom left: a schematic (not to scale) of the system, which has two quadrupoles and a DC accelerating lens just before the substrate. Top left: a 3D render (to scale) of the system. Top right: close-up cross-section of geometry near substrate. Bottom right: close-up of junction between quadrupoles.

The resulting structure is extremely compact: only 75 mm long and below 5 mm in diameter. Particles can be injected via aerosol nozzle (another 25 mm long). The main trick this design uses is allowing low particle velocities in the quadrupoles to maximize focusing time while minimizing pressure, then using high voltage (avoiding breakdown via low pressure and small size) to accelerate particles right before impact with a simple DC accelerator lens. This lens is subject to the emittance theorem but only accelerates axially without focus, avoiding issues. We accept the chromatic aberration (velocity variation). The particles travel 0.5 mm between the final lens and substrate (making resolution only $1.3\ \mu\text{m}$ worse by equation 6.11).

We designed each quadrupole by choosing their voltage V_T and initial particle beam radius then making the trap radius R_T slightly larger. This combined with particle characteristics determines trap frequency (equation A.6) and minimum beam diameter (equation 6.6). We used a frequency 1.6 times minimum to allow a range of particles (8 nm to 12 nm) at some resolution cost. We chose buffer gas pressures⁵² high enough to focus quickly yet low enough (< 1 Torr) to allow high voltage acceleration without breakdown. Segmented electrodes apply an axial field high enough such that the particle stopping distance is longer than the junction between quadrupoles. An isolation electrode between the two quadrupoles prevents their waveforms interfering with each other. We ended up with the following parameters:

	Quadrupole 1	Quadrupole 2
Quadrupole radius R_T	0.5 mm	50 μm
Quadrupole length L_T	50 mm	25 mm
Voltage V_T	100 V	100 V
Frequency $f = \omega/2\pi$	133 kHz	1.33 MHz
DC acceleration voltage V_{DC}	64 V (over 50 mm)	30 V (over 25 mm)
Buffer gas pressure P (argon)	0.5 Torr	0.4 Torr
Drift velocity $v_{a,drift}$	34 m s^{-1}	40 m s^{-1}
Stopping distance S	15.5 mm ($v_0 = 200\ \text{m s}^{-1}$)	3.3 mm ($v_0 = 34\ \text{m s}^{-1}$)
Input beam diameter d_B	0.21 mm	23 μm (quad 1 output)
Output beam diameter d_{Bquad}	23 μm	2.3 μm

Table 6.8: Operating parameters of the two segmented quadrupoles. Calculated for 10 nm $q = +10e$ copper particles (with $f = 1.6f_{min}$ to allow 8 nm to 12 nm particles).

After focusing, the particles accelerate through two electrodes (an immersion lens) with a 3 kV DC voltage chosen to reach $> 1000\ \text{m s}^{-1}$ as approximated by $v_a = \sqrt{2qV/m}$ (section 6.4.1). Building this requires avoiding gas breakdown due to high voltage (section 6.3.2), but our 0.4 Torr pressure and the 100 μm electrode separation can probably suffice⁵³ (table 2.4). To avoid having to charge the substrate (section 6.3), the final electrode is grounded and the quadrupoles are raised to progressively higher voltages. The input aerosol nozzle can be electrically insulated, moving particles into the quadrupole via drag even when the main printer chamber is grounded. There would also be a cylindrical shield (not shown) around the entire focusing mechanism to prevent gas breakdown around its outside.

⁵²The 0.5 vs. 0.4 Torr pressure difference is unnecessary but demos differential pumping (chapter 4).

⁵³[355] confirmed 10 kV across a 150 μm gap between steel electrodes at < 0.5 Torr can avoid breakdown.

To demonstrate functionality, we used SIMION (section 6.3) to simulate motion of 8 nm to 12 nm particles through the focusing system (without Brownian motion; see section 6.3.2. Our conclusions should be unaffected). Due to software limitations, we simulated the two quadrupoles separately then merged the results to create the following graphs.

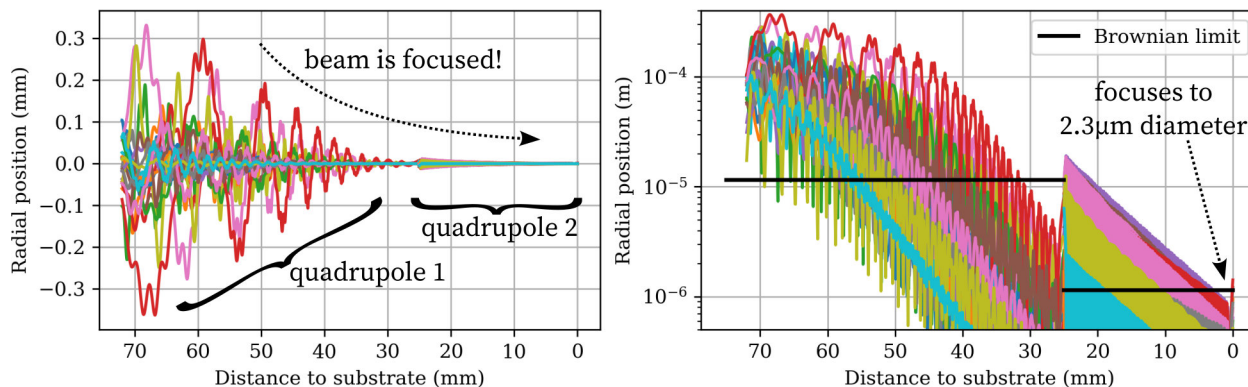


Figure 6.16: Left: nanoparticle radial positions as they are focused while moving toward the substrate. When entering a quadrupole and before focusing, note the beams briefly expand (beyond the simulation starting diameters of 0.21 mm and 23 μm from table 6.8) due to radial velocity and RF heating (section 6.3.3). Right: the same graph with a logarithmic scale. The Brownian limit is the realistic final beam diameter given by equation 6.6; our simulation unrealistically does better but would match this if simulating Brownian motion.

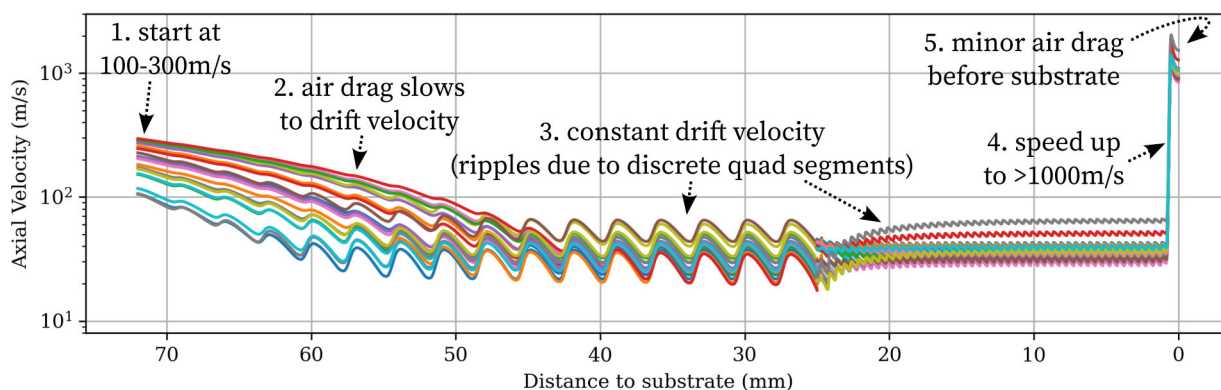


Figure 6.17: Axial velocity of particles as they move toward the substrate. They begin at the 100 m s^{-1} to 300 m s^{-1} we estimate our aerosol nozzle outputs (see chapter 4) but are quickly slowed down by air drag until DC acceleration plus drag (section 6.4.1) moves them at constant slow velocity through the quadrupoles. The final acceleration is nearly instantaneous and lets particles reach 1000 m s^{-1} to 2000 m s^{-1} (depending on mass/charge ratio—this is the chromatic aberration that a linac can improve upon). Finally, particles slow down slightly due to drag while traversing the gap before hitting the substrate (assuming 0.4 Torr). This could be reduced by minimizing the distance to or pressure at the substrate.

These simulations confirm the system works like we expect! In the radial direction, particles are focused by the first quadrupole, then focused further by the second. The final diameter of the particle beam is less than $5\ \mu\text{m}$ wide. Axially, particles reach a slow $40\ \text{m s}^{-1}$ drift velocity as they move through the quadrupoles then are accelerated to over $1000\ \text{m s}^{-1}$. Experimental confirmation will have to wait, as previously noted, until we have built a nanoparticle charger (see chapter 5). But a complete nanoparticle printing system should be straightforward to construct: we simply add our focusing system into our aerosol printer from chapter 4.

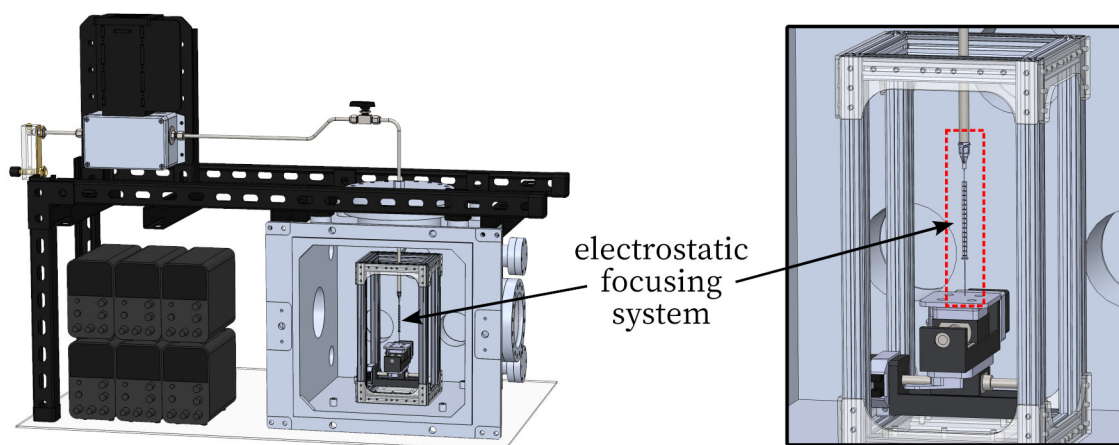


Figure 6.18: Left: render (not yet physically built) of what a complete nanoparticle printer with electrostatic focusing might look like. This is the aerosol printer of chapter 4, but as proposed in section 6.1, we have moved the aerosol nozzle away from the substrate to add our proof-of-concept focusing system. The only major missing component is a nanoparticle charger, which could be included as noted in chapter 5. Right: zoomed-in view.

Implementation Concerns

How can we manufacture the focusing system, given that it has extremely tiny electrodes and complex electrical waveforms (figure 6.15)? Regarding the mechanical construction, the smallest quadrupole has electrodes about $100\ \mu\text{m}$ wide. If they are made rectangular instead of perfectly round (which can work; see appendix A), the electrodes could be traces on stacked printed circuit boards (PCBs); this works for other ion traps [410][411][408][409][412]. Alternatively, microfabrication MEMS techniques⁵⁴ can be used to build these electrodes; this too is somewhat common⁵⁵ [415][416][417][414][418][419]. A final (amazing) option is to realize the very device we are designing is capable of printing multimaterial structures at this size scale: we could use one nanoparticle printer to make parts [420] for another!

As for the electrical circuitry, our challenge is to apply hundred-volt waveforms to electrodes, which act as small capacitors (our quadrupole electrodes are low picofarads while significantly larger ion traps might have nanofarads of capacitance). The waveforms are

⁵⁴I (the author) previously built a MEMS device of similar $100\times 10\ \text{mm}$ size for an unrelated project [15].

⁵⁵This is how the trapped ion quantum computers mentioned in appendix A are built [413][414].

sinusoids for the quadrupoles (where frequencies, typically 1 kHz to 10 MHz, depend on trap geometry and need to be adjusted further to suit different particle mass/charge ratios (section 6.3.2 and equation A.6), plus a DC potential (for DC acceleration, section 6.4.1) or possibly even a sawtooth wave for a linac (section 6.4.2). Many quadrupoles in the literature only require a single-frequency sinusoid (“RF” for radio frequency) with DC bias, which is most easily achieved with a resonant LC circuit to generate RF⁵⁶ while the DC bias is provided either by applying the RF to one pair of quadrupole electrodes and the DC to the other [424] or by combining the DC and RF with capacitive or inductive coupling [376][357][364][411]. An interesting alternative is to drive quadrupoles with a rectangular wave with precisely-controlled duty cycle [425][375][426][427]. This is called a digital ion trap. The electronics (fast high-voltage switches) can be simpler and easier to adjust than an LC resonator [428][429][430][431][432]. The performance can be comparable to a sinusoid-driven quadrupole [356][433] though the analysis is slightly more complicated [434][435][436].

For our electronics, because our analysis so far has used sinusoids, we made a preliminary investigation of circuits to generate adjustable-frequency sinusoids (via arbitrary waveform generation) in appendix C with promising results. It seems feasible to build cheap circuits that will generate arbitrary trap frequencies with DC offsets (or linac waveforms), which may be useful when printing nanoparticles of different sizes and charges. We also discussed the tens of electrodes that might be required⁵⁷. See appendix C for more detail.

This is a point worth repeating: by adjusting the trap frequency and DC acceleration voltage, the same focusing system should be able to handle a range of particle mass/charge ratios (one at a time). The focusing (equation 6.6) is somewhat independent of particle mass/charge so long as the frequency (equation A.6) is set correctly. This means we should be able to print multiple materials sequentially (as we did in chapter 4) without major problems.

Further Improvements

Although we’ve shown a way to print particles at $< 5 \mu\text{m}$ resolution with velocities spread between 1000 m s^{-1} to 2000 m s^{-1} , this is not quite as good as the specifications we originally hoped for in tables 6.1 and 6.3 (namely, $< 1 \mu\text{m}$ resolution and velocities with only $\pm 10\%$ variation). But we suspect reaching (and exceeding) these specifications is possible.

Improving resolution is most easily done by making a smaller quadrupole (perhaps a third stage) or raising quadrupole voltage, ultimately limited by equation 6.6 (table 6.4)—which suggests the theoretical possibility of sub-100 nm resolutions, at which point the finite size of the nanoparticles starts to be a limit to resolution! It is also possible that an Einzel lens, though not extremely effective due to chromatic aberration, still helps a small amount (perhaps we use the accelerating lens to focus slightly). Given how close we are already ($< 5 \mu\text{m}$) and the lack of fundamental barriers, we suspect sub-1 μm can be obtained without

⁵⁶Microfabrication plasma tools rely on similar resonant circuitry to generate RF signals, but typically at higher voltage and power specifically to generate a plasma via gas breakdown (unlike us) [421][422]. This is often at 13.56 MHz within an ISM frequency band so legal RF emission regulations are less strict, but some tools (e.g., pulsed DC sputtering) use lower kilohertz frequencies [423].

⁵⁷Our example system of figure 6.15 has 256 separate quadrupole electrodes, though since the two diagonals of a quadrupole are symmetric only $256/2 = 128$ separate signals are required.

too much more effort (in fact, if layers are printed with a 10:1 width:height aspect ratio as in chapter 4, we can print sub-micron layer thicknesses already). Reaching 100 nm is more difficult but surprisingly not out of the question.

We might add other electrostatic manipulation methods. Velocity variance can be reduced⁵⁸ with a linac. It might be possible to combine the multiple quadrupoles by tapering them if their different frequencies can be reconciled; tapered non-quadrupole ring geometries exist as ion funnels [218][412][411][437][432]. We could consider reducing the buffer gas throughout the focusing system (via differential pumping) to allow higher voltages at its end.

Better computer simulation may help design these improved focusing systems. Our own simulation neglected Brownian motion, modeled each quadrupole separately, and ignored space charge. While we think our analysis, which instead relied on analytical approximations, is generally correct, a better simulation could model the Brownian-dependent output beam diameter to confirm printing resolution. Even more useful would be computer optimization of electrode geometry [305][403][401] which can find ways to deform electrodes to improve performance (tapered quadrupole ends might better capture incoming particles [364]). Finally, a boundary element method simulation may be more accurate than the finite difference method SIMION uses [438][439].

In conclusion: it seems likely electrostatic focusing will work well, which means a complete multimaterial nanoscale printer is feasible! Our proof-of-concept electrostatic focusing system already definitively beats aerosol deposition, which cannot simultaneously reach high resolutions and high speeds, especially for smaller nanoparticles (see section 4.2.1). We are ready to make some final notes on electrostatic printing in general.

6.5.2 Managing Deposited Charge

There is an issue with electrostatic particle printing we have neglected to mention so far. When a charged particle is printed on a substrate, because like charges repel, it will deflect additional particles from being printed there. This will decrease resolution or, in the extreme, might even prevent new particles from sticking at all, stopping the print.

We know this will be a problem because it occurs elsewhere. This has been studied directly [290], was used (to beneficial effect) to pattern charged nanoparticles with an insulating mask [63][68], might occur inside aerosol tubing (chapter 4), and is a known effect in scanning electron microscopy and lithography where electrons build up on insulating surfaces and repel further electrons [440], decreasing image resolution (or they attract positively-charged nanoparticles as xerography [69]). It is also known that in ion traps (like ours), charge tends to build up on any insulating surface and deflect particle trajectories, so we should build our focusing system with only conductive exposed surfaces [416][415][441].

The easiest solution would be for the substrate (and the part we are printing) to be conductive so electrons can move through it to neutralize built-up charge. However, we are very explicitly

⁵⁸A simple mechanical mechanism [159][152] or electrostatic field (Wien filter) can filter particles by velocity, but this wastes particles just like an aperture does to improve position resolution.

hoping to print electrical circuits, which need insulation between conductors, and MOSFET transistors, which have charge-sensitive insulators⁵⁹. We need a more general approach.

The ultimate solution may be to actively neutralize charges⁶⁰ as they are printed. Reviewing the charging methods listed in chapter 5, note electrons can be generated⁶¹ with field or thermionic emission then impacted into nanoparticles after focusing and either before or after collision with the substrate. This is especially elegant as electrons are attracted to the positively-charged particles. This can occur in the gap between focusing system and substrate (0.5 mm long in our example system), which can be at sufficiently low pressure to allow electron travel. This may require careful engineering but seems physically feasible.

6.5.3 Printing Speed Limits

So far we have discussed almost exclusively the problem of moving nanoparticles with high resolution and velocity so we can make semiconductor devices. But there is another practical limit: how fast is printing? A slow fabrication process might be uneconomical even if it is otherwise easier than microfabrication. For example, focused ion beam induced deposition (FIBID, chapter 1 and section 6.5.4) is so slow that it is used only in rare circumstances.

It is easy to compute a maximum limit on printing speed that depends little on the other complexities we just discussed (or even electrostatic vs. aerosol focusing).

To calculate a maximum printing speed, the crucial realization is that particles can impact the substrate at up to a maximum velocity (as according to chapter 3, higher velocities will vaporize a particle and leave an impact crater instead of the desired deposition), and this applies a speed limit to everything else.

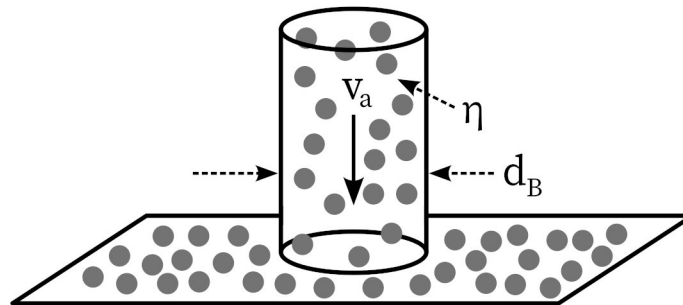


Figure 6.19: A cartoon illustrating a particles in a beam of diameter d_B being printed onto a substrate. The particles move at velocity v_a and fill a fraction η of the beam volume.

Consider a focused nanoparticle beam of diameter d_B impacting a substrate, which is scanned in the XY plane to produce a pattern. d_B is limited because we want the printer to have high resolution (for example, printing a $1\ \mu\text{m}$ wide line requires $d_B \leq 1\ \mu\text{m}$). The particles

⁵⁹Charges trapped in the gate oxide of a MOSFET during fabrication change its threshold voltage [1].

⁶⁰For prior art, see [177] which neutralizes argon clusters via diffusion (dis)charging.

⁶¹We might use a MEMS electron source to fit in the small gap before the substrate [442][443].

travel at velocity v_a , which chapter 3 suggests is at most 1000 m s^{-1} to 3000 m s^{-1} . Finally, particles in the beam⁶² don't touch; they fill some fraction of the beam volume for which we use the variable η (an efficiency). The maximum ($\eta = 1 = 100\%$) means there is no space between particles and the beam is a solid cylinder, which doesn't work, of course. It is not immediately clear what a reasonable upper bound to η should be⁶³, but if we choose 0.1%, we can compute a possible upper value for print speed. Calculate the volume of material printed onto the substrate per unit time, the volumetric flux Q , to be

$$Q = \frac{\eta v_a \pi d_B^2}{4}. \quad (6.17)$$

For example, printing with $d_B = 1 \mu\text{m}$ resolution, $v_a = 1000 \text{ m s}^{-1}$, and our hypothetical $\eta = 0.001$ deposits $Q = 7.9 \times 10^5 \mu\text{m}^3/\text{s}$. If we tried to print an integrated circuit with $10 \times 10 \times 0.01 \text{ mm}$ volume⁶⁴, the total print time is $1273 \text{ s} = 21 \text{ min}$. Printing with a smaller 100 nm beam is much slower: $Q = 7900 \mu\text{m}^3/\text{s}$, so that chip would take 35 hours to print. Contemporary state-of-the-art CPU, GPU, and memory chips have 10 nm features requiring another 100x time increase and months per chip, which seems impractical.

But this used a hypothetical value for η . How close to this can we actually get?

We previously calculated two other speed limits we can compare against: the rate we can produce nanoparticles and the space charge limit to fitting particles in a beam.

In chapter 2 (and confirmed in chapter 4), we found we could make particles at 0.6 mg h^{-1} to 6 mg h^{-1} , which is a volumetric flux (for copper) of $Q = 1.9 \times 10^4 \mu\text{m}^3/\text{s}$ to $1.9 \times 10^5 \mu\text{m}^3/\text{s}$, which is similar to Q with our hypothetical $\eta = 0.001 = 0.1\%$. We can make slightly faster nanoparticle sources (e.g., by combining multiple), so it seems nanoparticle generation will not be a strong limit to print speed⁶⁵, at least at these small resolutions.

Space charge limits (section 6.3.3) are stricter. Equation 6.9 approximates the number flux N' (particles per second) of particles with charge q that can be contained at velocity v_a in beam diameter d_B in a quadrupole of voltage V_T and radius R_T . We can use this to calculate the volumetric flux limit due to space charge Q_{SC} for particles with diameter d_p as

$$Q_{SC} = N' \cdot \frac{4}{3} \pi \left(\frac{d_p}{2} \right)^3 < \frac{V_T \pi \epsilon_0 v_a d_B^2}{8qR_T^2} \cdot \frac{\pi d_p^3}{6}. \quad (6.18)$$

This volumetric flux scales with the cube of particle diameter, which is the quantitative explanation for why using large nanoparticles (and low charge) instead of single atoms as first described in chapter 2 makes printing faster: we print more atoms per unit charge

⁶²Notice we're printing many small particles—billions per second—randomly inside a larger beam. This is because the nanoparticle size (1 nm to 50 nm diameter) is much smaller than the resolution we can place them with (perhaps $1 \mu\text{m}$), but it is also convenient because it allows us to treat the entire process statistically. This helps when, for example, nanoparticles have some variance in diameter and charge.

⁶³Randomly tightly packed spherical particles fill about $\eta = 64\%$ of a volume [444], but the movement of particles during focusing probably requires η to be much lower (say, $< 1\%$).

⁶⁴As noted in chapter 2, this is typical. Chips made with the SkyWater SKY130 130 nm process are $12 \mu\text{m}$ of transistors and wiring atop a silicon substrate [139], and most chips are several millimeters on a side.

⁶⁵This means we can afford to filter nanoparticles to reduce size variation as proposed in chapter 2.

(see table 2.1). For a specific value, our example focusing system in section 6.5.1 has (in the second quadrupole⁶⁶) $d_B = 5\ \mu\text{m}$, $V_T = 100\ \text{V}$, $R_T = 50\ \mu\text{m}$, $v_a = 40\ \text{m s}^{-1}$, $q = 10e$, and $d_p = 10\ \text{nm}$, giving $Q_{SC} = 45\ \mu\text{m}^3/\text{s}$ (and $\eta = 5.8 \times 10^{-8}$). This is very slow: that $10 \times 10 \times 0.01\ \text{mm}$ example chip would take two thirds of a year to print! A straight line $5\ \mu\text{m}$ wide and $500\ \text{nm}$ tall would be printed at only $20\ \mu\text{m s}^{-1}$. This is on the edge of impracticality. It is immediately apparent that space charge is likely the greatest limit to print speed.

We can increase the speed to reach reasonable rates as follows. First, we could consider using larger nanoparticles. Since $Q_{SC} \propto d_p^3$, doubling nanoparticle diameter to $20\ \text{nm}$ gets us 8x faster speed (though we need to carefully consider drift velocity and the final acceleration voltage); reducing particle charge q helps but not as much and makes focusing worse. We can also consider increasing particle velocity through the quadrupoles (perhaps with a linac, though this makes space charge worse; in a linac particles occupy the same radial distance as a continuous beam but only in discrete axial bunches), or optimizing quadrupole electrode radius R_T and increasing voltage V_T .

(We could also consider neutralizing the space charge (though the complexity means we will leave it to future work) [445][446][447][448][449] by engineering a situation where free negative charges coexist in the same area as our positive nanoparticles. This is most common in particle accelerators where an oppositely-charged background plasma offsets the space charge of a beam [296]. Alternatively, there has also been work on trapping (appendix A) and focusing neutral atoms [450][451][452].)

Another promising method is to actively vary the beam diameter d_B to print small features with high resolution but larger features more quickly with lower resolution, much like the front-end-of-line (FEOL) vs. back-end-of-line (BEOL) divide in microfabricated chips.

Finally, we could consider having multiple focusing systems printing particles in parallel⁶⁷. We could fit an array of tens of our example focusing system over a $10 \times 10\ \text{mm}$ chip, although this proportionally increases engineering complexity.

Each of these methods—larger particles, resolution variation, and parallelism—can add an order of magnitude improvement in speed. Together, we think it is possible to bring the total realistic volumetric flux back up to at least $5 \times 10^4\ \mu\text{m}^3/\text{s}$, which prints our test chip in 6 hours. This is reasonable and comparable to how long macroscale plastic and metal 3D printers take to make objects. Still, speed issues will always be significant, and slower speeds at higher resolutions might limit us to large-feature-size chips (see also section 7.2.2).

Again: speed limits mean we can probably only print simple low-resolution chips, and each will take hours to days.

⁶⁶The Child-Langmuir law [296] says particles of mass m and charge q accelerated from rest by a voltage V across distance L can create a maximum current density J (units A/m^2) of $J = 4/9 \cdot \sqrt{2q/m} \cdot \epsilon_0 V^{3/2} / L^2$. In our proposed system, this applies to the final accelerating lens but is less strict than radial space charge. It does not apply to drift motion in the quadrupoles, for which future work should derive a similar relation.

⁶⁷Massively parallel electron beam lithography systems do exist and are used commercially to make EUV lithography masks (IMS sells a tool with 262144 separate beams [453]); the company Multibeam is commercializing a multi-column e-beam tool [454]. Multi-beam FIB has been considered but is tricky [455].

6.5.4 Is it Possible to Do Better?

Before finishing this chapter, we can check our work against existing electrostatic particle manipulation systems to help determine whether even faster and higher-resolution printing might be possible (or to confirm we have started to run against fundamental limits).

First we should compare our methods to focused beam tools, which work on similar principles. As briefly mentioned in chapter 1, this includes scanning electron microscopes (SEMs), which use beams of electrons, and focused ion beam (FIB) tools, which use positively-charged single atoms. Much like we do, these tools create charged particles than focus them with emittance-limited ion optics to affect a surface. Thorough study has found their resolutions are limited⁶⁸ usually around 1 nm to 10 nm by emittance, geometrical aberrations (including spherical aberration and astigmatism), chromatic aberrations, space charge effects, diffraction⁶⁹, and system imperfections [296][304][457]. We have already accounted for these for nanoparticles; our previous analyses appear to be sufficiently complete and we cannot do much better.

To achieve their highest resolutions, FIBs and SEMs use bright (equation 6.3) particle sources [458][459][456], preferably with low temperature⁷⁰ (equation 6.11). The majority of FIBs are somewhat limited in the materials their sources provide: most use a liquid metal ion source (LMIS) [304][464][465][466] that typically makes a high-velocity beam of gallium ions (Ga^+). This Ga^+ beam can etch material or its impact energy can induce material deposition from a precursor gas that floats around the substrate [457][75][467] (“focused ion beam induced deposition”, “FIBID” [75] or “FIB-CVD” [467]). This can only print limited materials (mainly Pt, W, and SiO_2 , but with Ga and C impurities [75]; not semiconductors). Our quadrupole setup could be called a high-brightness low-velocity multimaterial nanoparticle source.

Though uncommon, a FIB system can print its ions directly on a surface [468][469], like our printing but with atoms instead of nanoparticles. This needs a different ion source (e.g., Au instead of Ga) and the relatively slow impact velocity⁷¹ makes it hard to focus [445][470][471]. Several prototypes printed lines of material [471][472][473] (including sub-micron resolution [470][472] and multimaterial printing [474]) and were explicitly proposed⁷² for direct-write microfabrication [473][472][470], but it was concluded that space charge limits meant the process would be impractically slow [445][475][473] ([473][445][476] suggest print rates of $Q = 1 \mu\text{m}^3/\text{s}$ and below). Today, this exists with wide beams as ion beam deposition (IBD) [477][478], while simpler FIBID (with Ga^+) found a niche for sample analysis despite similar slow speeds [476]. Our nanoparticle printing process is extremely similar to these approaches but, as shown in section 6.5.3, the use of nanoparticles instead of single atoms lets us print orders of magnitude faster, which is just barely enough to make the method practical.

We can now place our electrostatic nanoparticle printing method relative to other particle methods, FIB and aerosol deposition, to find it averages out the pros and cons of both. We may have found the Pareto-optimal regime for semiconductor device manufacturing.

⁶⁸These limits can be elegantly graphed as curves on a beam angle vs. area (emittance) plot [313][456].

⁶⁹Negligible for us; the deBroglie wavelength of a 1000 m s^{-1} 10 nm Cu particle is only $1.4 \times 10^{-16} \text{ m}$.

⁷⁰Recent work studied laser-cooled ion sources [460][456] or cooled single atoms [80][461][462][463].

⁷¹Below about $50 \text{ eV} \approx 10000 \text{ m s}^{-1}$, since higher velocities etch instead of deposit (see chapter 3).

⁷²First proposed perhaps by Feynman [16], who also explicitly called out space charge as a possible issue.

	Direct FIB	Nanoparticle printing	Aerosol deposition
Resolution d_B	< 100 nm	1 μm	> 10 μm
Particle impact velocity v_a	> 10 000 m s^{-1}	1000 m s^{-1}	< 500 m s^{-1}
Volumetric print speed Q	< 1 $\mu\text{m}^3/\text{s}$	$1 \times 10^5 \mu\text{m}^3/\text{s}$	$\gg 1 \times 10^5 \mu\text{m}^3/\text{s}$

Table 6.9: The (very approximate) specifications of our proposed electrostatic nanoparticle printing method compared to direct FIB deposition and aerosol deposition. Of the three, nanoparticle printing is the only one with resolution, impact velocity (chapter 3), and print speed (section 6.5.3) simultaneously suitable for semiconductor device fabrication.

This implies we may be close to the limits of not only electrostatic beam focusing but of any method that prints a beam of particles. And there are other reasons to suspect we can't do much better: for example, small particles (adatoms) can move around on the surface after impact (see chapter 3), making resolution likely at best on the order of 10 nm [43][171]. The fundamental limit becomes surface chemical reactions⁷³ (driven by kT thermal energy). We might hypothesize that manufacturing with even smaller resolutions approaching the atomic scale starts to require either lower temperatures or materials with more precisely arranged chemical (covalent) bonds, as done in synthetic chemistry and DNA nanotechnology.

To achieve higher manufacturing performance, future work might consider totally different approaches than particle beams. Standard microfabrication technically counts (though it has its own limits), or we could combine techniques ([480][481] propose aerosol deposition followed by FIB milling to increase resolution). More universally, recall that when discussing nanoparticle manipulation methods in chapter 3, we disregarded direct mechanical/chemical atomic-scale manipulation due to its complexity which makes engineering difficult. But this still holds promise⁷⁴, and if any system eventually supersedes both nanoparticle printing and microfabrication, this is likely where we would find it.

That is the end of this chapter and our analysis of electrostatic particle manipulation.

It seems electrostatic nanoparticle printing is likely to work. We proposed a concrete design and are ready to build a working implementation given a nanoparticle charger (chapter 5), after which many iterative improvements are available to increase performance (particularly resolution and speed)—and if there's one thing the microfabrication industry is good at, it's progressively improving a technology to its theoretical limits⁷⁵.

So we now finally have a nanoscale printer as proposed in chapter 1. But is it good enough to matter? Would this printing process achieve our goals of improving on microfabrication's speed, cost, or complexity? We will answer this at last in chapter 7.

⁷³Photolithography also starts hitting limits near 10 nm due to photoresist molecular structure [479].

⁷⁴This is roughly how biology works (in addition to all chemistry, of course).

⁷⁵Keeping Moore's law [6] alive for sixty years by consistently improving photolithography and other microfabrication tooling to astounding levels is one of humanity's greatest technical accomplishments.

Chapter 7

Future Work and Implications

We've proposed a solution to our original problem: how to manufacture electrical devices more easily than with microfabrication. We found a new way to print multiple semiconductor materials by manipulating nanoparticles, and we know how to achieve nanoscale resolution via electrostatics. But did it work? Did we actually improve upon microfabrication?

7.1 Remaining Steps to Print a Transistor

We should first ask if nanoparticle printing can compare with microfabrication at all, and to do so we can consider the quintessential microfabricated device: the transistor. Can we print a transistor? We weren't quite able to in this dissertation, but we're probably close.

Recall this dissertation covered many subtopics, each progressing toward our ultimate goal. To understand this progress, we can draw out what we accomplished and what future steps are required to make a transistor.

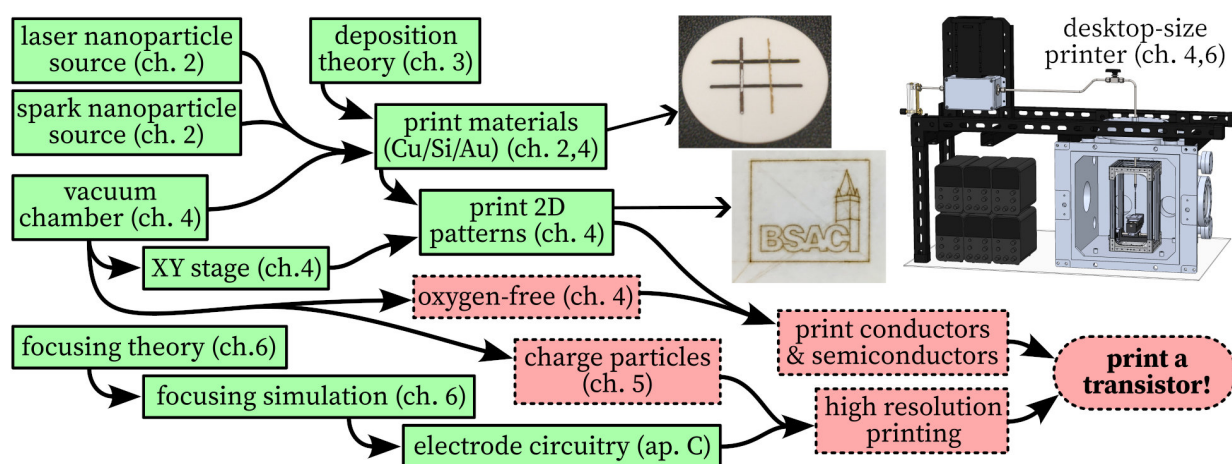


Figure 7.1: A dependency graph of what was accomplished in this dissertation (green, solid) and what tasks remain (red, dashed) before manufacturing standard semiconductor devices.

In the end, we made a number of important nontrivial advances but there are still several (small) steps left before we can print a transistor, though we think it is achievable.

In chapter 1, we made the simplification that transistors and other devices require multiple materials, each of precise atomic composition, combined with high $1\ \mu\text{m}$ resolution. With the hypothesis that printing nanoparticles might achieve these requirements, we experimentally demonstrated multimaterial printing in chapters 2 and 4. Our use of aerosol focusing limited both resolution and material properties—chapter 3 suggested higher impact velocities were needed for materials to have electrically-useful crystalline structures. This inspired chapters 5 and 6, where we proposed an electrostatic focusing mechanism capable of both high $< 5\ \mu\text{m}$ printing resolution and also the high $1000\ \text{m s}^{-1}$ velocity we required with the theoretical possibility of future improvement. But along the way, we ran into two roadblocks:

- **Oxygen:** Residual oxygen inside the vacuum chamber stuck to nanoparticles, reacting with conductors and semiconductors to instead make insulators (e.g., Si became SiO_2). As discussed in section 4.3.3, this is a well-known effect easily solved with a better (albeit expensive) vacuum chamber.
- **Charging:** The methods of electrostatically moving particles to high resolution and velocity that we found in chapter 6 required the particles to be electrically charged. We were unable to build a UV charger in chapter 5, but it seems likely a future attempt can succeed; prior art already exists (section 5.4).

These two problems should be solvable with engineering effort. They are not fundamental limits, merely temporary slowdowns we did not have the time or funding to pursue within this dissertation. However, as a result of these problems, the most interesting electronic device we experimentally demonstrated was merely a barely conductive gold trace in section 4.3.3. Printing other conductive metals or semiconductors requires solving the oxidation issue, and printing materials with useful atomic structures and thus electrical properties requires solving charging to get high particle impact velocities.

But once these problems are solved, building a transistor might be as simple as printing layers of doped silicon, insulators, and metal wiring as in figure 1.1. In reality, since the atomic structure of printed materials varies with deposition conditions, experimentation is likely required to find what particle velocities and other conditions result in electrical properties suitable for a transistor—but this seems feasible, given prior art in chapter 3 was able to build semiconductor ohmic contacts and PN junctions [171][172][47].

We can now put this entire dissertation into perspective: we proposed a single tool, a desktop-size printer, to (sometimes) replace microfabrication. We are not the first to discuss such a paradigm—direct-write printing of semiconductors [19] has been proposed many times via aerosol deposition [60] or FIB [445][473]—but no other method has worked. Our approach might become the first to simultaneously achieve the high resolution, print speed, and material capability needed to make many semiconductor devices. This may be the first complete roadmap to general-purpose¹ nanoscale device manufacturing using similar materials but methods separate from standard microfabrication. But is this new method useful?

¹Not including niche applications such as wide-area printing of polymer solar cells [482].

7.2 What if it Works?

Suppose future work follows through with the above roadmap and we obtain a functional nanoparticle printer that can make semiconductor devices. Does this matter?

Our original motivation for this project was improving on the high difficulty, cost, and time of microfabrication. While quantifying difficulty is somewhat subjective (though we posit using only a single tool removes much of the complexity of normal microfabrication), cost and time are quite computable as follows.

We will find nanoparticle printing might make prototyping of simple semiconductor devices significantly faster and cheaper, though microfabrication is still easily superior for mass production or high performance applications (such as computer CPUs and memory).

7.2.1 Cost Comparison

Although money is a very noisy metric, it can give a useful approximation of the overall difficulty of a manufacturing process, accounting for all materials, equipment, time, energy, labor, space, and other resources involved. How might the monetary cost of nanoparticle printing compare to microfabrication?

Item	Cost	Note
vacuum pump	\$3k	prices vary widely
vacuum chamber	\$15k	often custom-made
pulsed laser	\$3k	have recently decreased in price
tubing & fittings	\$3k	expensive to meet high-vacuum requirements
gas flow (MFCs, filters)	\$3k	
XY stage	\$5k	a DIY stage can fall below \$1000 [483]
electrode circuitry	\$1k	custom (e.g., appendix C)
material targets	\$1k	at most
computer	\$1k	for XY stage and system control
miscellaneous	\$5k	to reach a round number
Total	\$40k	approximately; can vary significantly

Table 7.1: Rough estimates for the components of a nanoparticle printer if purchased new. Actual price may vary significantly. The components in this dissertation were obtained used for perhaps 10x less, and certain additional components (e.g., a turbopump, loadlock, and integrated metrology equipment), if added, might increase the price up to 10x.

Both microfabrication and nanoparticle printing have two main costs: the manufacturing equipment (which is typically very expensive) and the materials the equipment makes chips out of. The materials are relatively cheap since chips and other semiconductor devices are physically very small, so in both cases the capital cost of the manufacturing equipment, amortized over all chips it builds, would be the majority of a single chip's cost.

Nanoparticle printing, unlike microfabrication, uses only a single vacuum chamber and may be able to do without a cleanroom or postprocessing steps². The equipment cost is relatively low: merely the cost of a single printer, which we can estimate by summing its individual components in table 7.1 as below \$100k.

Microfabrication equipment (as per section 1.1) consists of tens of separate tools, kept in a dust-free cleanroom, and the infrastructure to power them and safely handle large quantities of chemicals. This is much more complex to set up than a single printer. We can graph the historical cost of microfabrication fabs to find even minimal fabs³ are multimillion dollar investments, one or two orders of magnitude more than a nanoparticle printer.

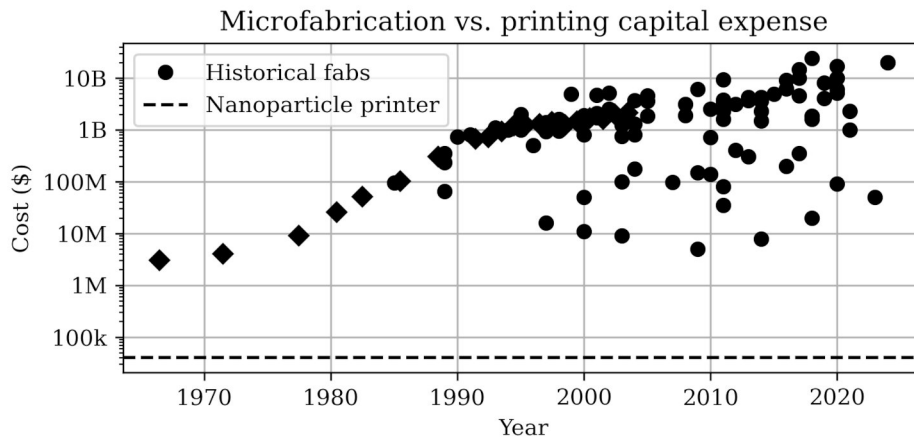


Figure 7.2: Some historical microfabrication fab costs from [9] (diamonds) and [484] (circles). Higher end fabs became more expensive over time to include tooling for higher performance chips, though they also increased throughput (via larger wafers [9]) so total cost per chip would not increase too much. The best comparison for nanoparticle printing are the cheapest earliest fabs at several million dollars—which we have still beat handily.

So if we want a minimal system capable of any semiconductor manufacturing whatsoever, a nanoparticle printer would be by far the cheapest option to build. But if our goal is to mass produce large numbers of chips, these results change.

Once the manufacturing equipment exists, we estimated a nanoparticle printer would take hours to days to print single chips (section 6.5.3), which is hundreds to thousands of chips per year. A \$40k printer cost amortized over several years might result in a cost per chip of \$100 or similar. This only works for chips that are simple or printed with relatively low resolution; modern CPUs are likely infeasible (see section 7.2.2).

Microfabrication, on the other hand, regularly makes sub-\$1 integrated circuits (as well as hundred-dollar CPUs). Even though a large fab is more expensive, it can make such high

²Annealing or release etch steps may be useful, but we’ll ignore those for simplicity.

³The data of figure 7.2 is subject to selection bias: cheaper fabs are less likely to be tracked. However, we can estimate the cost of cheap fabs by noting each needs tens of pieces of equipment, each of which is often in the same \$10k–\$100k price range as our nanoparticle printer, and thereby reach the same conclusion.

quantities of chips that, when amortized, the cost per chip is lower than printing—but only with a certain extremely important caveat. Microfabrication can only mass produce identical chips. It makes thousands or millions of copies of the same thing.

Specifically, whenever a microfabrication fab receives a blueprint for a new chip, it must prepare the fab for that specific design (including making photolithography masks), which takes nontrivial time and cost (masks can be thousands to millions of dollars, and the first wafers might be done in weeks to months). It runs the planar fabrication process on hundreds or thousands of silicon wafers, each of which contains hundreds of chips (see section 1.1). Each new chip design must pay for the fab preparation plus hundred-chip wafers, so getting a fab to make only a single chip from that design is inefficient and expensive even if the original fab equipment costs were already amortized out (compared to printing, which can easily make each chip unique).

How much are these per-design microfabrication costs? Definitive minimum prices are hard to come by. Commercial fabs tend to keep information private (fabs often require customers to sign a nondisclosure agreement covering fab details, for example [485]). Some information is publicly available from multi-project wafer (MPW) services, which are middleman companies that combine multiple smaller chip designs together before sending the result to a fab, which reduces the cost per design and is intended for prototyping. These are generally the cheapest ways to manufacture a chip in low volumes.

Fab	Min. cost	Min. qty.	Lead time	Tapeouts per year
GlobalFoundries 130nm	\$44900	50 chips	5 months	2
TSMC 65nm	\$4700		3 months	6–10
TSMC 28nm	\$11100		3 months	4
UMC 40N (40nm)	\$103000	90 chips	4.5 months	5
UMC L180 (180nm)	\$19900	50 chips		2
IHP SG13S (130nm)	\$5300	40 chips	6 months	3
X-Fab XT018 (180nm)	\$6100	50 chips	7 months	2–5
SkyWater SKY130 (130nm)	\$3500	25 chips	5 months	4

Table 7.2: Approximate minimum cost, time, and availability of some microfabrication fab processes via MPW services. These numbers are not accurate enough to compare fabs and are only intended to indicate order-of-magnitude similarities. Each fab process accepts new designs (“tapeouts”) only several times per year and returns a minimum number of chips at some cost after some lead time. Data is combined from [486][487][488][489][490] using the cheapest advertised prices among all MPW services. This does not account for the additional cost of EDA chip design software, which often far exceeds \$100k per year.

We can see the minimum cost to get chips of a new design is in the thousands of dollars, though this typically provides 10–100 chips, nearing the \$100 per chip cost of nanoparticle printing (making these chips in larger volumes would lower the price further). Note this does not include difficulties communicating with the fabs (nondisclosure agreements and expensive design software) or the long lead time required to make chips (discussed in section 7.2.2), but

chips are fabricated with minimum feature sizes of 180 nm or below, much better than the 1 μm resolution nanoparticle printing might easily reach, which means the microfabricated transistors will generally be faster and draw less power.

Using this data and assuming microfabricated chips can cost as little as \$1 each when a million or more are made, we can draw the following approximate graph of the cost required to make a given number of chips of a new design.

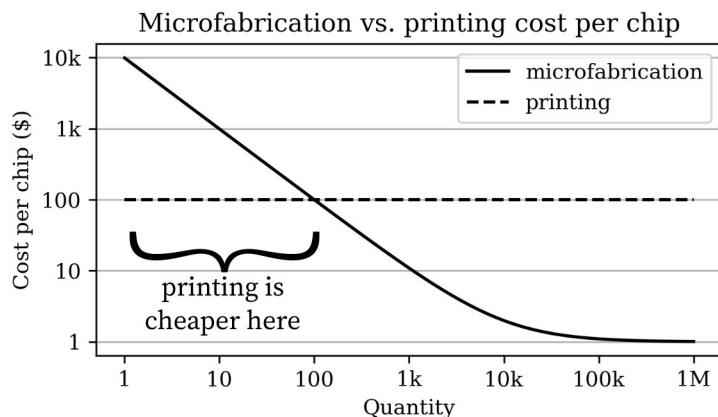


Figure 7.3: Very approximate cost per chip to produce a given quantity of a new chip design, including amortized equipment capital expenses. The decrease in microfabrication costs is due to amortizing additional design-specific costs such as mask making. From this figure we see that nanoparticle printing may be most useful for small quantities of chips (below about 100). Many more advanced fab processes (say, for CPUs) are much more expensive.

It appears nanoparticle printing will likely be cheaper whenever only a low quantity of some chip design (below about 100) is required; microfabrication becomes cheaper (with higher chip quality) for higher quantities⁴. This suggests printing might be suitable for research and prototyping applications, which typically use only these low chip volumes (and in section 7.2.2 we will see printing lead time is much faster, which is also helpful for prototyping), as opposed to more generic integrated circuits which are built millions at a time and sold worldwide over multiple years.

We can also consider different kinds of chips.

Most of our discussion in this section applies to integrated circuits (ICs), which are purely electrical circuits. Most chips are ICs, and fabs specialize in these by standardizing a certain sequence of fabrication steps, after which customer designs simply change the arrangement of transistors made with that standardized process on a chip. But as stated in Chapter 1, integrated circuits are not the only thing microfabrication makes. Another (albeit smaller) category is microelectromechanical systems (MEMS), which are small mechanical devices and sensors (including inkjet printheads, cell phone RF filters, microphones, and more).

⁴This is the same effect observed between plastic 3D printing, which makes single parts one at a time, and plastic injection molding, which has significant setup (mold making) costs but can then produce thousands of parts more cheaply on average.

Although MEMS devices are generally mass-produced and roughly follow the same economics as ICs, the development of a new MEMS device is much more painful. Microfabrication fabs that make ICs with a standardized process are reliable, so a chip designer can often simulate a design then have it made successfully by a fab on only the first or second attempt. On the other hand, each MEMS device typically uses a different fabrication process (to make different material layers or make them different thicknesses, for example), so fabs cannot standardize processes⁵. Developing a new MEMS device requires both designing the chip and also completely changing the sequence of microfabrication steps, which can take a dedicated engineer months of testing due to microfabrication’s complexity (so this also requires physical access to a fab). The excellent book [491] on MEMS development estimates the cost of a new MEMS device as follows, and we see nanoparticle printing might again be useful for prototyping.

Development stage	Minimum cost	Time
Proof-of-concept prototype	\$500k	1 year
Advanced prototypes	\$1.5M	1.2 years
Foundry feasibility	\$1M	0.8 years
Foundry pilot production	\$1M	1 year
Total	\$4M	4 years

Table 7.3: Total cost (tools and labor) and time for developing a MEMS device with standard microfabrication, copied from [491]. This includes not only the MEMS fabrication but also chip characterization and testing, and is significantly higher than building an IC. Nanoparticle printing might be able to replace the proof-of-concept prototype stage.

Finally, we should mention several other ongoing attempts to make microfabrication easier, cheaper, and faster. Pragmatic Semiconductor [492], InchFab (MEMS) [493], Atomic Semi [494], and Minimal Fab [495] are all small organizations that appear⁶ to be building microfabrication fabs while attempting to reduce the equipment capital cost by making smaller tools⁷ and reduce the per-design cost and time by using smaller wafers and fewer microfabrication steps. We applaud these efforts and look forward to their hopeful success, but it is possible that since they still rely on the multiple-tool planar process microfabrication paradigm, their total improvements will be limited (compared to, for example, the large turnaround time improvements from nanoparticle printing we discuss in section 7.2.2).

In conclusion, there do indeed seem to be situations in which nanoparticle printing can be cheaper than microfabrication. This is mainly the case when only a small number of chips (1–100) of some new design are required, and we should also stress that printed chips will likely be lower quality than microfabrication, unable to make certain complex chips (e.g., computer CPUs). All this suggests printing may be useful for research and prototyping.

⁵With the notable historic exception of the PolyMUMPs standardized MEMS process, which to the best of our knowledge was never responsible for a significant fraction of worldwide MEMS fabrication.

⁶As best as we can determine from publicly available information. These organizations are all relatively new and might not have settled on a particular commercial strategy yet.

⁷Several excellent custom-built microfabrication tools proposed for InchFab are [421][422][496].

7.2.2 Time Comparison

Besides cost, another important parameter of a manufacturing process is how long it takes. Here, too, nanoparticle printing and microfabrication differ greatly.

Consider the time after a new chip design has begun manufacturing. Some number of chips will be made after a certain amount of time (in manufacturing, the number of things made is typically called the “volume” as in “high volume manufacturing”).

A nanoparticle printer should be straightforward. In section 6.5.3, we calculated one can probably make several simple chips per day. This can continue indefinitely.

Microfabrication is more complicated: it takes several months to prepare a fab for a new design and complete the first batch of wafers (from section 7.2.1 and especially table 7.2, which adds the additional constraint that new designs are only accepted every few months). Afterward, more wafers can be produced extremely quickly. As noted in section 1.1, a wafer actually takes weeks to months to be manufactured, but making multiple chips per wafer and running multiple wafers at different steps in parallel allows a very high total rate. A large modern fab can produce thousands of wafers per month, each with hundreds of chips.

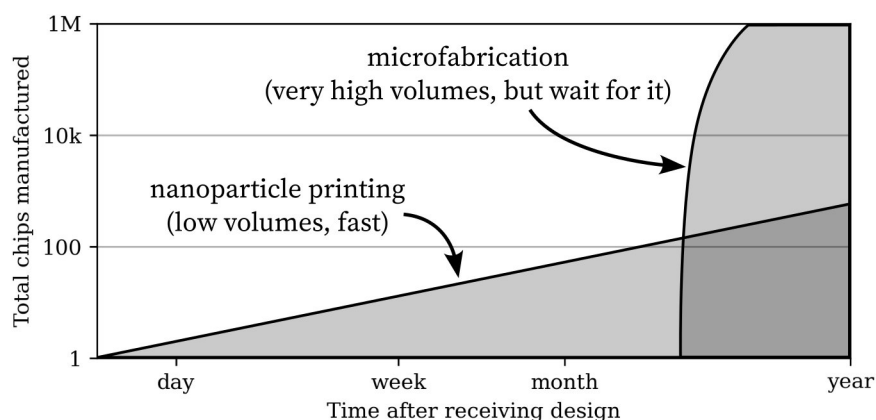


Figure 7.4: Another way nanoparticle printing significantly differs from microfabrication. Printing can make a single chip within a day and continue producing chips at a constant rate. Microfabrication requires several months to get started, but then (if desired) can produce large numbers of chips very quickly.

We see a nanoparticle printer might be useful whenever turnaround times of a month or less are required: in other words, research and prototyping applications⁸—again! By sheer fortunate coincidence, nanoparticle printing is doubly beneficial (cost and turnaround time) for research applications, and the break-even point with microfabrication is once again near the 100-chip mark. By analogy to macroscopic manufacturing methods (such as 3D printing and laser cutting, which similarly produce low volumes of parts quickly), this might justify calling nanoparticle printing a rapid prototyping technique.

⁸A chip might be manufactured, tested, tweaked, and a new version manufactured, repeating as desired.

There is another speed-related effect worth consideration. We have claimed several times (e.g., section 6.5.3) that nanoparticle printing can only make “simple” chips, not large modern chips like CPUs, GPUs, and memory. What does that mean, and why is that?

Although all semiconductor devices are made by arranging materials in different 3D patterns (see chapter 1), some patterns are much more complicated and thus harder to make than others. A solar cell or LED is just several uniform layers of material, while a computer CPU has thousands to billions of tiny transistors. Call these “simple” and “complex”.

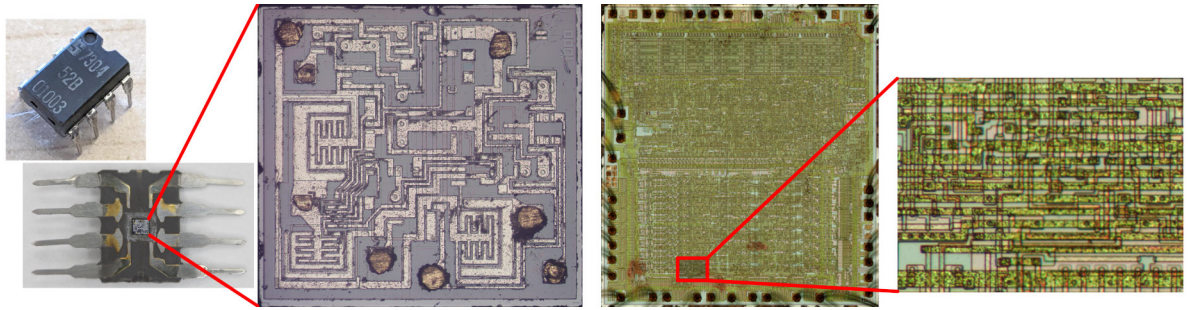


Figure 7.5: Examples of chip complexity. Top-down images of chips (see figure 1.1) are from the excellent [497][498][499]. Left: a simple 1.2 mm wide chip with about 25 transistors and other components (an early 555 timer IC). Right: a complex 10 mm wide chip with about 4500 transistors (the MOS 6502, the CPU of the the Atari 2600, Apple II, Commodore 64, and other historical computers). The right chip has significantly higher complexity (and modern computer CPUs, with billions of transistors in the same space, have vastly more).

We might quantify complexity by taking a digital picture (a square grid of pixels) of the chip and counting how many pixels we needed to accurately describe it. A blank square needs only one pixel. We could pixelate the left chip of figure 7.5 to a 250x250 pixel grid without losing fundamental details, but the right chip needs at least 5000x5000 pixels or its tiny wires blur together. Because chips are actually several layers stacked in 3D, we use the term voxel (a 3D pixel). The number of voxels in a chip is a way to measure its complexity⁹.

This finally lets us describe what we mean. Microfabrication cares little about complexity¹⁰ because photolithography (section 1.1) makes all features of a 2D layer on a chip at once in parallel, but nanoparticle printing has to put down each voxel one at a time. In section 6.5.3 we hypothesized a fast nanoparticle printer might print material at up to $5 \times 10^4 \mu\text{m}^3/\text{s}$ (varying with resolution) with 1 μm resolution, which is (very approximately) 5×10^4 voxels/s. This cannot print the trillions of voxels required for a modern CPU in a reasonable amount of time. Nanoparticle printing is best suited for printing simple chips.

⁹An improved metric accounting for varying feature sizes might use the size in bits of a compressed image, i.e., the information entropy. The corresponding manufacturing metric is the information transfer rate to the substrate. [500][501][502][503][504][505] compare resolution vs. speed of other manufacturing methods.

¹⁰As long as photolithography resolution and yield suffice. Incidentally, Moore’s law [6], which is typically explained as photolithography improvements making more complex chips possible, does not describe simpler things like solar cells (for which smaller size isn’t an improvement as they need the area to collect sunlight), or even MEMS, for which more general microfabrication improvements (materials, etc.) matter more.

7.2.3 Efficiency and Environmental Impact

Nanoparticle printing might have an additional significant advantage over microfabrication: extreme space, material, and energy efficiency. For example, a microfabrication fab needs a warehouse-sized cleanroom with tens of tools while a printer could fit on a desktop.

The nanoparticle printing process requires as input only electricity, an inert gas for particle flow, and the target materials, and only outputs printed chips, exhaust gas¹¹, and waste heat. Contrast this to microfabrication [7][8], which in addition to a high power draw requires photoresist, wet developing and removal chemicals [506][507], hazardous process gases, and water for wafer cleaning between steps; the output is additional hazardous liquid and gas byproducts that must be properly cared for¹². Of a chip's entire lifetime, its manufacturing has the greatest impact to assorted worldwide systems and environments [509][510][511][512], so improving manufacturing efficiency¹³ and reducing byproducts is useful.

We quantified printer power consumption by measuring electricity use of our chapter 4 printer and adding the hypothetical power draw of a nanoparticle charger UV lamp (chapter 5) and a drive circuit (appendix C) for an electrostatic focusing system.

Component	Power draw (W)
Edwards R8 vacuum pump	800
Edwards APG-M-NW16 vacuum gauge	1
xTool 1064nm laser	10
XY stage (custom)	24
UV lamp	4
40-output electrode drive circuit	400
Laptop computer	20
Total	1300

Table 7.4: Electrical power draw of assorted parts of a nanoparticle printer. The vacuum pump (high vacuum not included here) draws 60% of the power and the electrode circuitry is known to be inefficient; future work can likely reduce power use much further.

The total 1300 W power draw of the printer is small enough it can be supplied by a single standard 120 V 15 A North American NEMA 5-15 mains outlet. It appears we can bring fabrication energy requirements¹⁴ (at least for simple chips) down from the industrial scale to a desktop tool capable of running in any standard workshop¹⁵.

This suggests nanoparticle printing is ideal for distributed onsite manufacturing of chips—which (yet again!) may make it an excellent fit for research and prototyping.

¹¹Possibly with some nanoparticles, which can be filtered out and the gas fed back to the input.

¹²Insufficient chemical containment at early Silicon Valley fabs created groundwater contamination and human health hazards that had to be cleaned up decades later [508].

¹³An interesting calculation for future work is the theoretical minimum energy required to assemble a chip.

¹⁴Though average energy use per chip may be similar to microfabrication, for chips made by which [513] found a surprisingly constant 1.5 kWh/cm², about what printing needs for an hour-long print job.

¹⁵Or perhaps a space station? Sending a fragile microfabrication fab to orbit would be much harder.

7.3 What Printing Can't Do

We should emphasize: **printing will not replace microfabrication** (save in very limited circumstances). If we took our results from this dissertation, built a full nanoparticle printer (section 7.1) and improved it to its theoretical limits (section 6.5.3), it would not change the majority of the microfabrication industry, instead assisting only simple and low-volume research applications. But that does not mean these improvements are unimportant.

Throughout this dissertation, the new nanoparticle printing method we proposed does indeed seem to be easier, cheaper, and faster than microfabrication in some ways, achieving the goals we set out to reach in chapter 1. It is easier as measured by complexity and equipment cost, cheaper in low volumes, and has faster turnaround times.

On the other hand, printing is worse than microfabrication in that it cannot make complex chips (modern CPUs) and is slower and more expensive for mass production. The majority of the microfabrication industry is exactly these chips (precisely because mass production lets this part of the industry scale to high volumes) and would be unchanged by printing.

Printing may be useful in circumstances when low volumes, fast turnaround times, and simplicity are more important than chip complexity or mass production. Examples include research and prototyping of new MEMS devices, small analog circuits, and sensors—most university research, for example, only needs several copies of a given chip. Another promising possibility is making minimal chips affordable, easy, and fast enough for education: creating simple chips may be the best way to teach students semiconductor device design.

There may also be times when printing and microfabrication are used together. A printed chip might be subsequently postprocessed with a microfabrication-style anneal or release etch (for MEMS), or even combined with techniques like spatial ALD (section 1.2.4) to print more uniform thin films than nanoparticles can manage by themselves. Likewise, microfabrication prototyping fabs, where many engineers constantly develop new semiconductor devices, may benefit from the addition of a nanoparticle printer.

So, while microfabrication will remain the only practical method to make computers in the foreseeable decades, nanoparticle printing may open new avenues of rapid prototyping, finally increasing the accessibility of semiconductor manufacturing to match its ubiquitous use in our contemporary world. We think that's a future worth aiming for.

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Appendix A

Ion Traps and Quadrupoles

In chapter 6 we discussed the motion of charged nanoparticles in electric fields in vacuum then introduced certain static electric fields with useful properties (e.g., Einzel lenses focus particle beams). But something was missing at first: there was no way¹ to force (or “trap”) a particle to stay still (levitate), even though it sounds like an easy thing to do.

It turns out trapping particles is fundamentally impossible with electric fields that do not change over time. This is called Earnshaw’s theorem [514]. But as we will shortly discover, trapping is possible if we allowing electric fields to oscillate with time, and this is widely used in multiple areas of study [293]. We will introduce these ideas, especially linear quadrupole traps, so that we can use them in chapter 6 (specifically starting in section 6.3.2).

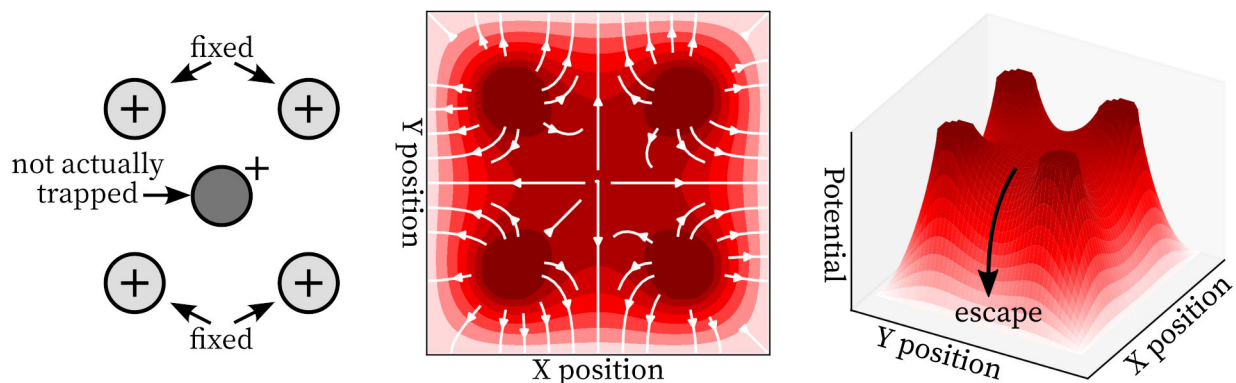


Figure A.1: An example of Earnshaw’s theorem. Left: consider a positively charged particle between four infinitely long positively charged circular rods in a 2D plane. Charges repel each other, so one’s intuition might expect the particle would be trapped in the middle, but in fact there is always a direction the particle is pushed in until it is far away (middle and right figures); when centered between the rods it is only in unstable equilibrium. The same occurs in any arrangement of electrodes/fixed charges (e.g., at the vertices of a tetrahedron).

¹At least without tracking the particle and changing the field to compensate, which is often impractical.

Earnshaw’s theorem can be quickly proved as follows: consider a time-invariant electric field. At any location the field satisfies Gauss’s law by having zero divergence (Laplace’s equation), which means the field is either perfectly flat or has decreasing potential in some direction.

We can avoid Earnshaw’s theorem and levitate particles by allowing the electric field to change with time² in a way that uses a particle’s inertia to prevent its escape. To do this we use the ponderomotive force, which we describe and prove in detail in appendix B.

The ponderomotive force (appendix B) is an emergent effect that occurs as follows. Suppose a point particle of mass m and charge q at position \vec{x} placed in a time-oscillating electric field of the form $\vec{E}(t, \vec{x}) = \vec{E}_0(\vec{x}) \cdot \cos(\omega t)$. The particle will vibrate back and forth slightly (“micromotion”) but, on average, will feel a net force

$$\vec{F}(\vec{x}) = -\frac{q^2}{4m\omega^2} \nabla \left(|\vec{E}_0(\vec{x})|^2 \right) \quad (\text{A.1})$$

as long as the oscillation angular frequency ω is sufficiently large (as noted in appendix B, ω has units rad s^{-1} ; most applications use frequency $f = \omega/2\pi$). That is, the particle will be moved toward regions of lower electric field magnitude, which is always away from any electrodes (with varying voltages generating the oscillating field). Furthermore, this average behavior is conservative, meaning the particle moves as if it is in a potential just like a static electric field—this is extremely elegant.

Given this trick, our setup of figure A.1 can actually work as we intuitively expect if, instead of putting each of our four fixed electrodes at a single charge or voltage, we apply the correct oscillating voltages. Specifically, the lower left and upper right (diagonal) electrodes should have the same voltage changing sinusoidally with time, and the lower right and upper left (the other diagonal) need the same voltage but offset 180° in time—that is, if one diagonal electrode set has a positive voltage, the other diagonal has a negative, and vice-versa. The only remaining requirement is the oscillation frequency is above a certain minimum. A charged particle now experiences a force toward the center of the electrode array.

These sorts of structures are called “ion traps” as they confine charged particles (including atomic ions) to a fixed location. Sometimes they are called “RF traps” due to the oscillation at radio frequencies (kilohertz to megahertz), and sometimes “Paul traps” after Wolfgang Paul who won the 1989 Physics Nobel [321] with Dehmelt [515] for developing them.

It is easy to make ion traps in many shapes; almost any electrode arrangement can work. However, the most common [293] ion trap shape is the “quadrupole”, which has four electrodes like we previously considered (albeit ideally hyperbolas instead of circles). Quadrupole traps are the only ion trap geometry with a tractable exact particle motion equation [293], are the simplest to build, and also provide the strongest trapping force³.

We will review the full analytical theory of quadrupole traps—which are also what we use in chapter 6—then make some remarks about other trap geometries.

²Or by other methods, e.g., adding magnetic fields, which we briefly discuss at the end of this appendix.

³See our notes on multipole traps also at the end of this appendix.

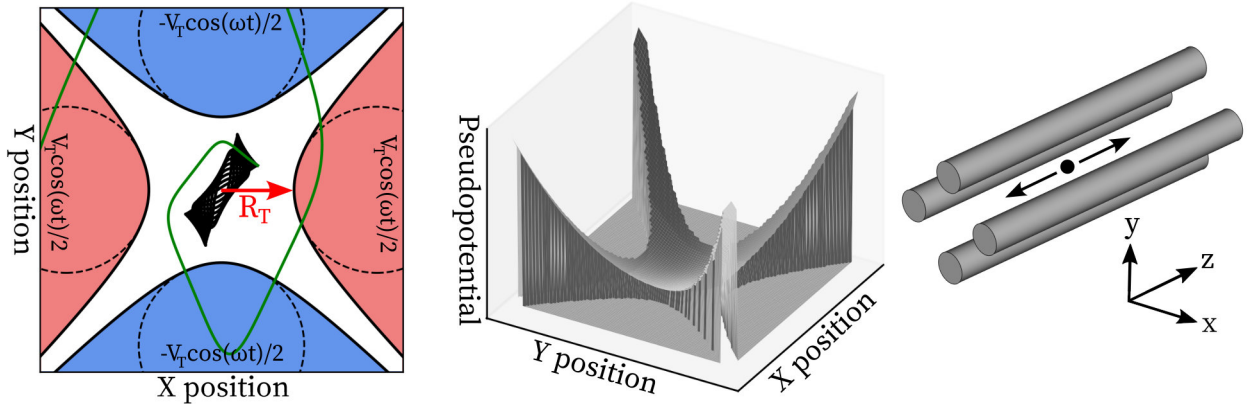


Figure A.2: Left: a 2D quadrupole ion trap made by four electrodes (two red, two blue) with corresponding oscillating voltages. At any one time, two are positive and the other two are negative. The electrodes are hyperbolas for an ideal quadrupole but can be approximated by circles [516][517]. We call the distance from trap center to the nearest electrode R_T . Some particles (black line) oscillate but are trapped between the electrodes; others (green line) move sufficiently far that they hit an electrode and are lost. Center: the average force stably trapped particles feel is a 2D quadratic potential well; we derive this in equation A.9. Right: extending this into 3D traps a particle between rod electrodes. The particle can move back and forth freely with no force or friction.

An ideal 2D quadrupole trap [293][515][321] is made from four hyperbolic electrodes⁴ placed together as in figure A.2, fairly similar to figure A.1. Put two electrodes on the x axis and two on the y ; the two x electrodes will always have the same voltage and similar for y . The distance from the trap center (the coordinate system origin) is R_T , and the electrodes are defined by $R_T^2 = \pm(x^2 - y^2)$.

To operate the trap, apply oscillating voltage $V_T \cos(\omega t)/2$ to one pair of electrodes (where V_T is a voltage, ω is an angular frequency, and t is time) and $-V_T \cos(\omega t)/2$ to the other (note this means the maximum total voltage difference between electrodes is V_T)⁵. This generates an electric field \vec{E} inside the trap (between the electrodes) of

$$\vec{E}(x, y) = -\frac{V_T}{R_T^2} \cos(\omega t) \begin{bmatrix} x \\ -y \end{bmatrix} \quad (\text{A.2})$$

which has electric potential energy U_T (with $q\vec{E} = -\nabla U_T$) of

$$U_T(x, y) = \frac{qV_T}{2R_T^2} (x^2 - y^2) \cos(\omega t). \quad (\text{A.3})$$

⁴Since hyperbolas are hard to manufacture, the electrodes can be approximated well with circular electrodes of radius $1.14r_0$ [516][517][518] with centers at coordinates $(R_0 + 1.14r_0, 0)$, etc.

⁵Analysis of quadrupoles sometimes instead uses $V_0 = V_T/2$.

To analyze particle motion inside the trap, we could directly apply our ponderomotive force analysis (equation A.1) to equation A.2. We will do so momentarily. However, of all ion traps the quadrupole is notable in that it is possible to analyze exact particle trajectories without the ponderomotive approximation [358], so we will do that first.

So consider a particle of mass m and charge q moving $x(t)$ according to the simplified Lorentz force $\vec{F} = q\vec{E}$ (see section 6.2) and $\vec{F} = m\vec{a}$. An examination of equation A.2 reveals the electric field is independent in the x and y directions—this is why the quadrupole is simple enough to analyze—so we only have to write the equation of motion in the x direction; the particle will independently move in the y direction similarly:

$$\frac{d^2x}{dt^2} = -\frac{qV_T}{mR_T^2} \cos(\omega t) x. \quad (\text{A.4})$$

This is a Mathieu differential equation; these occur in many areas of physics⁶. The solution trajectories (which are generally periodic oscillations) are known [520] but too complex to write here. But there is another useful way to analyze a Mathieu system: it turns out trajectories have one of two behaviors. Either trajectories will remain within some finite value (are “stable”, i.e., our trapped particle will always stay trapped, close to the origin), or trajectories will grow until particles exit the trap (as in figure A.2).

To see this stability behavior, we need to rewrite equation A.4 in a standard form. To help, we will modify our conditions by adding a DC bias V'_T to the electrodes (the two x electrode voltages increase by $V'_T/2$ and the y decrease by $V'_T/2$). We don’t usually want this save in quadrupole mass spectrometry [359], but it’s useful for illustration. Equation A.4 becomes $\frac{d^2x}{dt^2} = -q/(mR_T^2) [V'_T + V_T \cos(\omega t)] \cdot x$. This matches the standard [520][521] Mathieu form

$$\frac{d^2w}{du^2} + [a_m - 2q_m \cos(2u)] w = 0 \quad (\text{A.5})$$

when $w = x$, $u = t \cdot \omega/2$, $a_m = (4qV'_T)/(mR_T^2\omega^2)$, and $q_m = (2qV_T)/(mR_T^2\omega^2)$. A thorough analysis of Mathieu equations [520] shows trajectories are either stable or unstable depending on the nondimensional parameters a_m and q_m in a surprisingly complex way, which we graph in figure A.3 (an Ince-Strutt diagram). For our purposes, we mainly care about the case when $V'_T = 0$ and thus $a_m = 0$, at which point the particle trajectory is stable when $q_m < 0.91$ (approximately), with little regard for its initial conditions.

Ion traps (and the ponderomotive force in general) only work when the voltage oscillation frequency ω is sufficiently high (as noted in appendix B); that is the case here. We can rewrite the Mathieu stability criterion $q_m < 0.91$ to get the minimum angular frequency ω :

$$\omega > \sqrt{\frac{2qV_T}{0.91mR_T^2}} \approx \sqrt{\frac{2qV_T}{mR_T^2}}. \quad (\text{A.6})$$

⁶For example, the Mathieu equation describes Kapitza’s pendulum, the effect that an inverted pendulum can be stable when oscillated vertically [519].

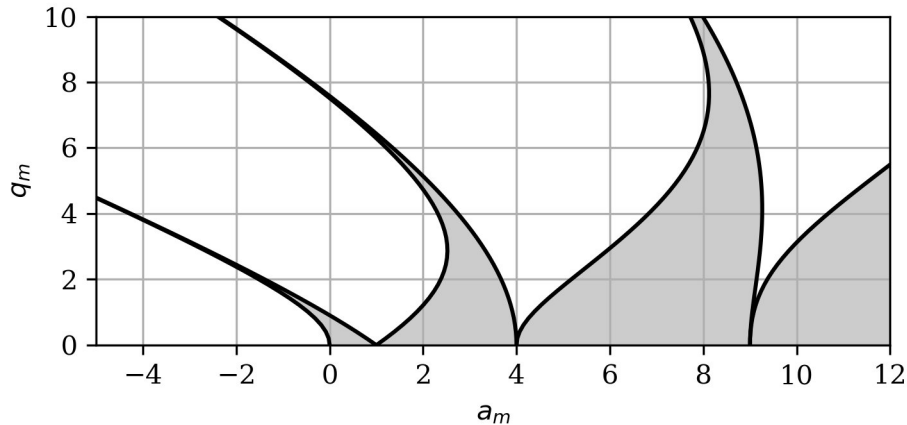


Figure A.3: The Ince-Strutt diagram [520][519][359]. The solutions to a Mathieu equation with parameters a_m and q_m are stable inside the regions shaded gray; otherwise, trajectories grow to infinity over time. The graph is symmetric about $q_m = 0$. We are mainly concerned with the region $a_m = 0$, for which stability occurs when $q_m < 0.91$ (approximately). This complexity of this graph is why finding the minimum frequency ω for an ion trap is hard.

This is about as much useful information as we’re going to get out of the Mathieu equation. Equation A.6 describing the minimum frequency will be very useful (and is more accurate than our approximation of equation B.14 in appendix B), however, so we will briefly try to wrap more intuition around it. The frequency is important because, again, once trap geometry and voltage are fixed, the relationship between frequency ω and particle mass/charge ratio m/q determines whether the particle is stably trapped, and how strongly.

To build intuition, consider the relationship between the minimum frequency ω and the mass m of the particle (keeping charge q constant for illustration). In the normal case when the quadrupole electrodes have no DC bias ($V_T' = 0$ and $a_m = 0$), another way of stating $q_m < 0.91$ is that all particles above a certain mass will be trapped. Smaller particles will accelerate too quickly and leave the trap before voltages can oscillate to pull them back.

On the other hand, if some DC bias V_T' is applied to the electrodes, figure A.3 suggests there are regions ($a_m < 0$)⁷ where larger particles are unstable. This is because, as particle size increases for fixed ω , the trap force is weaker and eventually small enough that the Earnshaw’s theorem effect from the DC bias will move the particle out of the trap.

Quadrupole mass spectrometers work by taking advantage of this Mathieu stability criterion with combined lowpass and highpass effects [359]. Careful selection of voltages V_T and V_T' and frequency ω means particles within only a small (adjustable!) range of mass/charge ratios will be trapped and can be measured⁸.

⁷This is asymmetrical because we’re only considering one direction of motion (x or y). When the DC bias V_T' is applied to the electrodes, Earnshaw escapes are only in one of these directions; the other is stable.

⁸In chapter 6 we will want to use parameters (e.g., $V_T' = 0$) that trap a wider range of particles, though we might consider using this effect to filter nanoparticles by size; see chapter 2 for other filter methods.

It is probably clear that this exact Mathieu approach to analyzing quadrupole motion is complicated. Fortunately, we have a much easier way to understand and approximate the behavior of a quadrupole trap (or any other ion trap, even when the exact solution is unavailable): we apply the aforementioned ponderomotive force (still from appendix B).

Again, the ponderomotive effect is that a particle feels an average force away from strong oscillating electric fields. We can apply equation A.1 to equation A.2 to find the ponderomotive force \vec{F} felt by a particle in a quadrupole trap:

$$\vec{F} = -\frac{q^2 V_T^2}{2m\omega^2 R_T^4} \begin{bmatrix} x \\ y \end{bmatrix}. \quad (\text{A.7})$$

That is, a particle will feel an average force toward the center of the trap (which is why the trap works). This force is conservative, i.e., it is as if the particle were trapped in a potential field—the “pseudopotential”—with potential energy \tilde{U}_T (as $\vec{F} = q\vec{E} = -\nabla\tilde{U}_T$)

$$\tilde{U}_T(r) = \frac{q^2 V_T^2 r^2}{4m\omega^2 R_T^4} \quad (\text{A.8})$$

where we have defined $r = \sqrt{x^2 + y^2}$ as the distance of the particle from the trap center. This is a radially symmetric 2D quadratic potential well, as shown in figure A.2! The behavior of a particle is now easy to reason about: if its initial position and kinetic energy are enough to stay within the well, it will stay trapped, merely oscillating within it over time (with angular frequency $\omega q_m/\sqrt{8}$ and amplitude X_P). Of course, ponderomotive micromotion is overlaid on top with frequency ω and, via equation B.5, amplitude $q_m X_P/2$.

Finally, suppose we have particles with a range of mass/charge ratios. These can be captured in the same trap if the frequency is sufficiently high. Find this frequency using equation A.6 for the lightest particles (smallest mass/charge ratio m_0/q_0). We can combine this with equation A.8 to rewrite the pseudopotential energy (at that optimal frequency) for any particle with mass/charge ratio m/q as

$$\tilde{U}_T(r) \approx \frac{qV_T r^2}{8R_T^2} \cdot \frac{q}{q_0} \cdot \frac{m_0}{m}. \quad (\text{A.9})$$

which now acts just like a normal electrostatic potential that scales with charge and voltage. Particles with $m/q > m_0/q_0$ will see proportionally smaller potential energies, and particles with $m/q < m_0/q_0$ escape the trap and are lost (by construction). This equation will be useful for us given the wide range of nanoparticle sizes we expect to use.

All this is enough to design the ion optics we use in chapter 6. We are done with analysis, though there are other minor effects we will discuss when relevant (e.g., the micromotion of the ponderomotive force can make it difficult to bring particle positions and velocities to exactly zero at the trap center, an effect called RF heating we bring up in section 6.3.3).

However, we think it is worth briefly mentioning alternative traps beyond quadrupoles.

RF ion traps are easy to design: simply place an oscillating⁹ electric field between electrodes, and particles are trapped at regions of minimum electric field (“RF nulls”). This simplicity has allowed ion traps to find use in many subjects. Besides their use in mass spectrometry as quadrupoles [358] and related shapes (e.g., Kingdon trap geometries [522]), ion traps can be used in particle accelerators (see section 6.3.2) or trapped-ion quantum computing, in which ions are cooled to their quantum ground state (which requires careful study of noise [366]). This also uses a clever trick: the trap electrodes can all be placed on the same surface (a planar ion trap [395][396][523][413][409]), making it easy to microfabricate complex traps with multiple sections that particles can be moved between [416], though the trap depth is about 100x lower than a quadrupole of similar dimensions and voltage [524][525].

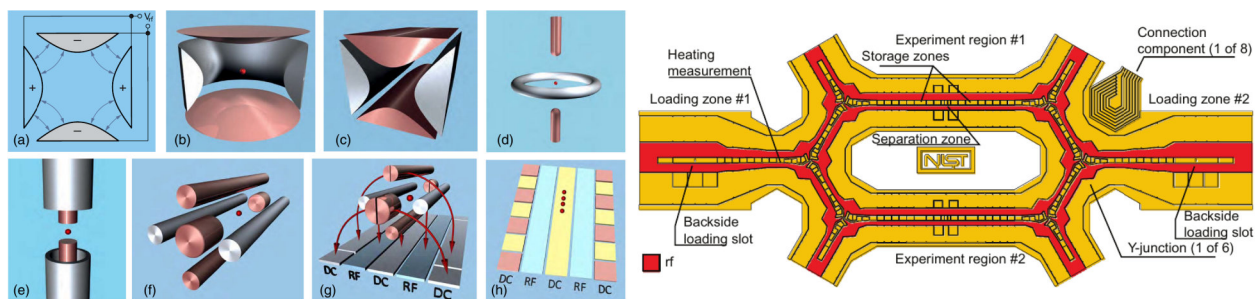


Figure A.4: Left: some other RF ion trap geometries, from [366]. The same quadrupole potential can be rotated to trap a particle at a point, or the electrodes can be a different shape. The electrodes can even be placed on a single planar surface, forming a particle trap just above it. Right: top view of a 5 mm wide planar ion trap separated into many segments demonstrating techniques for future trapped-ion quantum computers. Atomic ions could be levitated and moved around these tracks or through the three-way junctions [396].

Given the huge design space, it is worthwhile to ask if there are optimal trap shapes. One way to analyze this is to realize that no matter the electrode geometry, the potential at the center of a trap can be written as a multipole expansion: a linear combination of dipole, quadrupole, hexapole, and higher-order fields. The quadrupole field has the steepest center (which is what we want in chapter 6, so we use quadrupole electrodes¹⁰). Higher-order “multipoles”, made with 6, 8, or other even numbers of electrodes, have a steeper edges and a flatter trap center, which can be useful if low RF heating is preferable at the expense of position resolution or for trapping multiple ions of significantly different masses [293].

It is also possible to build traps with magnetic fields. A “Penning trap” confines charged particles with only a DC electrostatic and magnetic field [321]. If a particle has a magnetic moment it can be trapped by certain magnetic fields even if it has no electric charge [321]. Microfabricated magnetic traps exist [526], and sufficiently good magnetic traps are used to store antimatter [527][528][529].

In short: electromagnetic particle traps have significant variety.

⁹It is also possible to use square waves instead of sinusoids; see digital ion traps in section 6.5.1.

¹⁰Using concave arc electrodes instead of convex hyperbolas or circular rods can give a slightly higher quadrupole component plus higher-order multipole factors with the same trap radius and voltage [355].

Appendix B

The Ponderomotive Force

In this appendix we derive and explain the ponderomotive force, which is the effect that a charged mass placed into an oscillating electric field feels an average force in the direction of lower electric field magnitude. This is a fundamental part of RF ion traps.

Specifically, we will see that a point particle of mass m and charge q at position \vec{x} placed in a time-oscillating electric field of the form $\vec{E}(t, \vec{x}) = \vec{E}_0(\vec{x}) \cdot \cos(\omega t)$ experiences the time-averaged (for time periods much larger than $1/\omega$) net force

$$\vec{F}(\vec{x}) = -\frac{q^2}{4m\omega^2} \nabla \left(|\vec{E}_0(\vec{x})|^2 \right). \quad (\text{B.1})$$

This effect is elegant and notable as follows:

- Because this force is the gradient of a continuous function (namely, $\frac{q^2}{4m\omega^2} |\vec{E}_0(\vec{x})|^2$), it is conservative, and that function acts like a potential energy function, exactly analogous to the regular Lorentz force being conservative for a static electric potential. Incidentally, we call this potential of the ponderomotive force the “pseudopotential”. The behavior of particles under a ponderomotive force is easily intuited by imagining classical motion through the potential energy landscape of the pseudopotential.
- By electric field superposition, this oscillating electric field may be combined with additional DC and AC fields and their effect on particle motion evaluated separately as if there were no difference between an electrostatic potential and pseudopotential.
- The ponderomotive force acts equally (as a time-averaged force) on negatively and positively charged particles.
- The ponderomotive force is not subject to Earnshaw’s theorem and thus allows simple stable electrostatic levitation (as used in ion traps).
- The ponderomotive force is stronger at slower oscillation frequencies ω . However, this also causes stronger unwanted particle movements (which we call “micromotion”) and for any given application there is a limit beyond which the micromotion becomes too large. Thus there is usually a finite optimal value for ω .

We will first attempt to build an intuition for how the ponderomotive force works by considering one-dimensional motion of a particle in an electric field as in the following figure:

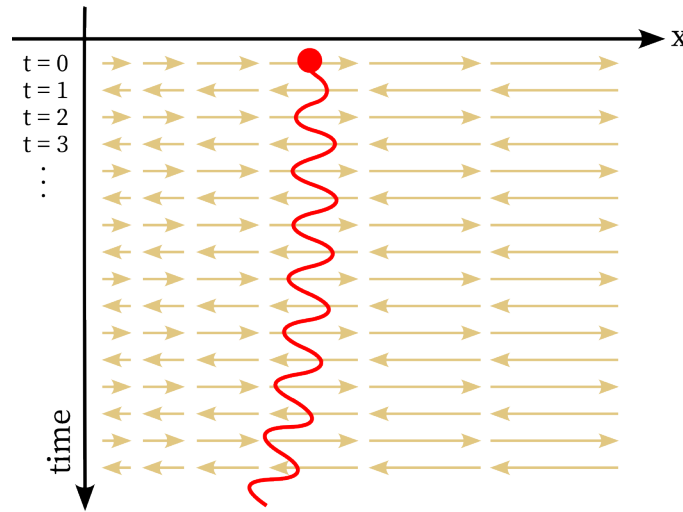


Figure B.1: A figure to guide ponderomotive force intuition.

The electric field, shown in yellow, oscillates sinusoidally with time and always has increasing magnitude toward the right-hand side of this one-dimensional world.

Consider the motion of a positively charged particle (the red circle) in this field. At time $t = 0$, the electric field points to the right, and so the particle begins to move in that direction. At $t = 1$, this is reversed, so the particle slows and then starts moving to the left instead. Repeat over time, and the particle oscillates around its average position. This is the “micromotion” mentioned earlier.

If the electric field had constant magnitude everywhere, this is all that would happen. However, the electric field is stronger to the right and, importantly, the particle oscillation is in phase with the electric field. In the 50% of the time the particle is further to the right of its average position, the stronger electric field there is pointing toward the left, and in the half of the time the particle is to the left, the electric field points to the right but is weaker. As a result, there is a force imbalance: the particle experiences slightly more force toward the left, and slowly moves, on average, in that direction. This is the ponderomotive force.

Now let’s formalize this.

Consider a particle of mass m in a 1D rapidly oscillating force field $qE_0(x) \cos(\omega t)$, where $qE_0(x)$ is the force on the particle at position x , t is time, and ω is angular frequency (note many engineering applications prefer a frequency f with $\omega = 2\pi f$).

Assume the particle motion $x(t)$ has slow/large (ponderomotive, also called “secular”, movement) and fast/small (micromotion) components $x_s(t)$ and $x_f(t)$, respectively:

$$x(t) = x_s(t) + x_f(t). \tag{B.2}$$

Our goal is to find $x_s(t)$. From $F = qE_0(x) \cos(\omega t) = ma$, we can find $a = \frac{d^2x}{dt^2}$:

$$\frac{d^2x}{dt^2} = \frac{d^2x_s}{dt^2} + \frac{d^2x_f}{dt^2} = \frac{qE_0(x_s + x_f)}{m} \cos(\omega t). \quad (\text{B.3})$$

We will first approximate $x_f(t)$ as follows. Assume $qE_0(x_s + x_f) \approx qE_0(x_s)$, i.e., the micromotion oscillation amplitude is small compared to the distance over which the electric field varies, and further assume the micromotion is significantly faster than ponderomotive movement so we can consider a short amount of time in which $\frac{d^2x_s}{dt^2} \approx 0$ but $\frac{d^2x_f}{dt^2} > 0$. Then at any given such moment,

$$\frac{d^2x_f}{dt^2} \approx \frac{qE_0(x_s) \cos(\omega t)}{m} \quad (\text{B.4})$$

and

$$x_f(t) \approx -\frac{qE_0(x_s) \cos(\omega t)}{m\omega^2}. \quad (\text{B.5})$$

We see the fast micromotion $x_f(t)$ is periodic with amplitude proportional to force, as we would intuitively expect. Calculation of $x_s(t)$, the net movement due to ponderomotive force, is more involved because we now have to consider variation in $E_0(x)$ combined with $x_f(t)$. Start again from equation B.3, but this time approximate the electric field $E_0(x)$ as varying linearly around x_s :

$$\frac{d^2x_s}{dt^2} + \frac{d^2x_f}{dt^2} \approx \frac{1}{m} \left(qE_0(x_s) + x_f \cdot q \frac{dE_0}{dx}(x_s) \right) \cos(\omega t). \quad (\text{B.6})$$

Substituting in our approximation B.5 for $x_f(t)$:

$$\frac{d^2x_s}{dt^2} + \frac{qE_0(x_s) \cos(\omega t)}{m} \approx \frac{1}{m} \left(qE_0(x_s) - \frac{qE_0(x_s) \cos(\omega t)}{m\omega^2} \cdot q \frac{dE_0}{dx}(x_s) \right) \cos(\omega t) \quad (\text{B.7})$$

which simplifies to

$$\frac{d^2x_s}{dt^2} \approx -\frac{qE_0(x_s)}{m^2\omega^2} \cdot q \frac{dE_0}{dx}(x_s) \cdot \cos^2(\omega t). \quad (\text{B.8})$$

Note we were able to combine the $\cos(\omega t)$ frequency of micromotion with the $\cos(\omega t)$ frequency of electric field variation to get a factor of $\cos^2(\omega t)$. We can average this out over time ($\cos^2(\omega t) \rightarrow 1/2$) to find

$$\frac{d^2x_s}{dt^2} \approx -\frac{qE_0(x_s)}{2m^2\omega^2} \cdot q \frac{dE_0}{dx}(x_s) = -\frac{q^2}{4m^2\omega^2} \cdot \frac{d}{dx} (|E_0(x_s)|^2). \quad (\text{B.9})$$

Using $F = ma$ where $a = \frac{d^2x_s}{dt^2}$, we then obtain the expected 1D ponderomotive force

$$F(x_s) \approx -\frac{q^2}{4m\omega^2} \cdot \frac{d}{dx} (|E_0(x_s)|^2). \quad (\text{B.10})$$

This derivation is now complete. This same derivation is straightforward to repeat in the multidimensional case, giving the promised result

$$\vec{F}(\vec{x}_s) \approx -\frac{q^2}{4m\omega^2} \nabla (|\vec{E}_0(\vec{x}_s)|^2). \quad (\text{B.11})$$

This force, as previously mentioned, is the gradient of a scalar function which can be treated as a potential energy U where $\vec{F} = -\nabla U$. This pseudopotential is

$$U(\vec{x}_s) \approx \frac{q^2}{4m\omega^2} |\vec{E}_0(\vec{x}_s)|^2. \quad (\text{B.12})$$

Now recall our derivation assumed the micromotion is small, which holds so long as the field oscillation frequency ω is sufficiently high. What is the minimum value of ω that works?

A general calculation of the precise minimum frequency ω_{min} is nontrivial [293] (for an example, see the Mathieu stability criterion for quadrupole electrodes in Appendix A), but we can approximate it¹ as follows. Suppose we want the peak-to-peak micromotion amplitude to be less than some distance L (for example, the distance between electrodes generating the electric field). Then, using equation B.5, we can write

$$L \approx \frac{2qE_0}{m\omega_{min}^2}, \quad (\text{B.13})$$

or

$$\omega_{min} \approx \sqrt{\frac{2qE_0}{mL}}. \quad (\text{B.14})$$

This equation is limited because it assumes a constant electric field magnitude E_0 when, by premise, the electric field will have varying magnitude. However, setting E_0 to the average or maximum electric field observed over the area of L should suffice for approximating micromotion amplitude to within an order of magnitude, and this can be refined later with numerical simulation. Defining $f_{min} = \omega_{min}/2\pi$, our nanoparticle ion traps typically² have $1 \text{ kHz} < f_{min} < 1 \text{ MHz}$.

Finally, a historical note: the basic derivation here is well-known and was used while developing the first ion traps and mass spectrometers, e.g., by Dehmelt [515]. Also, the fundamental physics holds not just for electric fields but for any force field [530].

¹For discussion and comparison of several other methods to approximate where motion is stable, see [293], which prefers the conservative criterion $\omega_{min} \approx \text{sqrt}((2q|\nabla\vec{E}_0|)/(0.3m))$ with the same dimensions as ours.

²Example: +10 charge 10 nm dia. Cu particles in a 100 V and 1 mm field have $f_{min} = 42 \text{ kHz}$.

Appendix C

High Voltage Waveform Generator

In chapter 6, we discovered that some methods of electrostatically focusing nanoparticles need a complicated voltage waveform applied to each of tens of electrodes (a segmented quadrupole). Although there were some alternative electrode geometries with simpler waveform requirements, these complex setups were easier to analyze and might sometimes give superior results. In this appendix, we build a proof-of-concept circuit to show creating these waveforms (and thus our complicated focusing mechanisms) would be feasible¹.

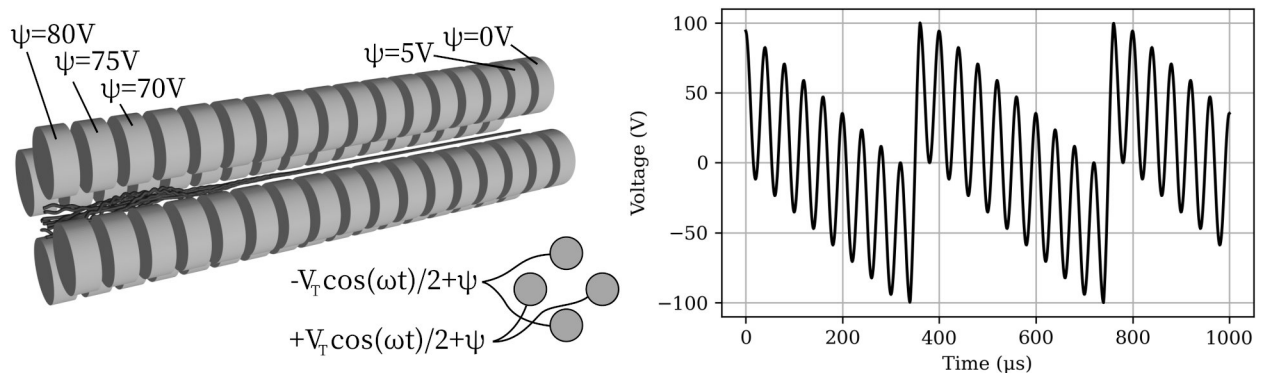


Figure C.1: Left: an example 17-segment quadrupole (section 6.4.1), where each of $17 \cdot 2 = 34$ electrode pairs needs a waveform consisting of a sine wave (with adjustable frequency ω) plus DC bias ψ . Right: one of the more extreme possibilities is to replace the DC bias with a sawtooth wave to make this into a linac (section 6.4.2), giving the displayed waveform.

We require a circuit that can achieve the following:

- Create a time-varying voltage with up to 200 V amplitude (limited by gas breakdown), preferably ± 100 V centered around zero (so particles don't feel a net force toward the outer vacuum chamber, which is grounded).

¹As noted in chapter 6, we didn't physically build a complete electrostatic particle manipulation system because we lacked a working nanoparticle charger from chapter 5, but we should be able to in the future.

- This voltage needs to have a sinusoidal component to drive a quadrupole with a frequency 1 kHz to at least 1 MHz (table 6.4) adjustable in real time to handle particles of different mass/charge ratios. It should also be able to add a DC bias (again adjustable) and, if we need to build a linac, also superimpose a sawtooth wave (with maximum frequency component 1 kHz to 1 MHz defining the linac velocity).
- The voltage needs to be applied to metal electrodes in a vacuum chamber, which generally act as small capacitors probably in the 10 pF range. The possibility of gas breakdown suggests the circuit should tolerate temporary output short circuits.
- And since the waveforms on any two electrodes may not correlate (especially with both quadrupole and linac), we need an individual waveform for each of tens of electrodes.

This circuit is rather difficult to build due to the combination of high 1 MHz frequency and high 200 V voltage, let alone the requirement it be adjustable in real time with nonsinusoidal components (a DC bias or sawtooth wave) or the need to create tens of similar waveforms. The only simplifying factors are that the load is very small (10 pF) and simulations suggested high voltage output resolution is not necessary (5 bits = 32 voltage levels is more than enough; see also digital ion traps in section 6.5.1).

Again, there may be simpler ways to build a particle focusing system (see section 6.5.1 for thoughts on different electrodes, waveforms, and circuits), but if we can build a circuit that satisfies our complex requirements here, it would also suffice to power any simpler mechanism we want, so we decided to proceed.

This circuit is a high voltage and frequency arbitrary waveform generator. These do already exist for several purposes, but no existing solution is perfect for us. Available opamps cannot simultaneously output the high voltages and frequencies we require. Examples include the ADHV4702 [531], OPA462 [532], and HV264 [533], which can respectively reach ± 110 V, ± 90 V, and 215 V, but only up to about 10 kHz to 30 kHz. Driver circuits for piezoelectric or ultrasound actuators (which are also small capacitive loads) also achieve our voltage specifications but only up to low kilohertz frequencies [534][535][536]. Speeds > 10 MHz are possible when constructed via custom integrated circuits [537][538], but this is generally not feasible given the cost of custom ICs (see chapter 7)². Other amplifiers built from discrete components can reach 500 V at 5 MHz [539][540], but the required circuits are fairly complicated and sometimes use specialized components (e.g., vacuum tubes [539]). Off-the-shelf amplifiers capable of ± 150 V signals from DC to 5 MHz are available from [541], but at \$2500 each, tens of these cost more than the rest of a nanoparticle printer combined.

This prior art suggests our circuit is possible but difficult to build. To demonstrate it could be cheap enough while driving tens of electrodes, we will have to design our own.

Safety note: These circuits can use somewhat high voltages and somewhat high power, enough to potentially cause electrical injuries. Caution was taken during assembling and testing. We ran only minimal experiments with loose cables to show basic functionality; further development would warrant building a robust enclosure for the system.

²The point of this dissertation is making such custom integrated circuits feasible; it might someday be.

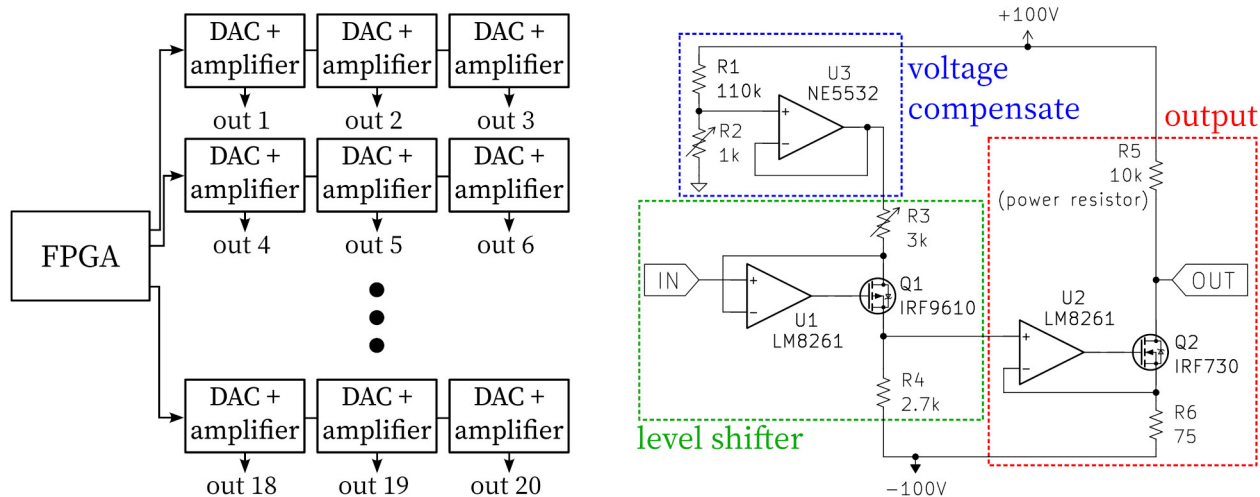


Figure C.2: Left: proposed system architecture. An FPGA sends digital signals to multiple boards, each with DAC and high voltage amplifier. Right: (simplified) high voltage amplifier. A class-A amplifier (“output”) amplifies an incoming signal shifted to the low supply rail (“level shifter”). A “voltage compensate” circuit allows the high supply rail voltage to vary without affecting output gain. Resistors R2 and R3 calibrate the output DC bias and gain.

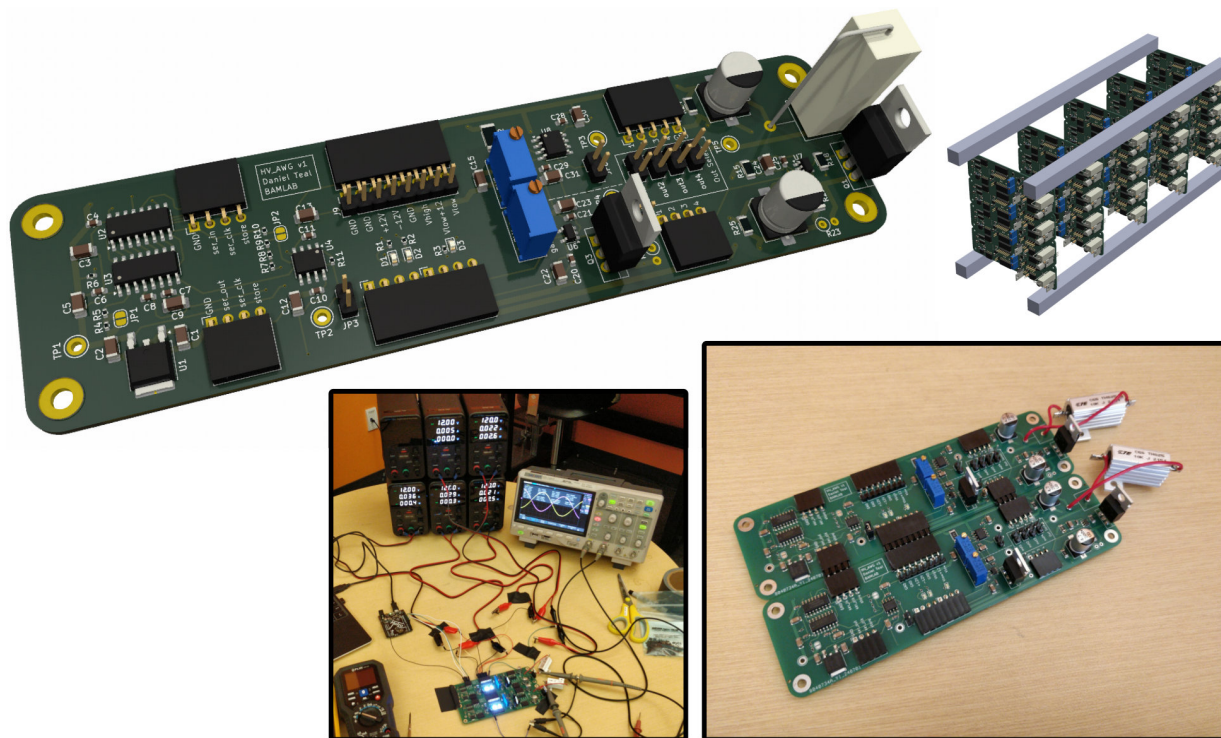


Figure C.3: Clockwise from top left: a 3D render of the DAC + amplifier board, a concept render of a multiboard array, two assembled and daisy-chained boards, and the daisy-chained boards generating ± 120 V (240 Vpp) 20 Hz sinusoids, confirming basic functionality.

To demonstrate how a system with tens of output waveforms might be built, we chose an architecture where a single FPGA would provide signals to drive tens of boards (figure C.2), each containing a DAC and high voltage amplifier. The amplifier circuit was as shown in figure C.2. We chose a class A amplifier circuit topology as (though inefficient³) it is simple, predictable, and can be built from a single off-the-shelf high voltage NMOS MOSFET. To create a bipolar signal, we floated the class A amplifier to a negative voltage supply rail ($< -100\text{ V}$), then used current to transfer the input signal from near ground to the negative voltage rail⁴. Finally, a voltage compensation circuit adjusted the bias and gain to make the output independent to the high rail voltage. All power rails were provided from external supplies and shared between boards to reduce size, cost, and inefficiency.

We designed a PCB with a serial data circuit, DAC, and the high voltage amplifier⁵. These boards were designed to be daisy-chained together and arrayed en masse in a single enclosure (see figure C.3), where the class-A amplifier MOSFETs and power resistors could be attached to a heatsink if desired. We built and tested two of these PCBs (figure C.3) and confirmed their basic functionality. All circuit components are off-the-shelf, cheap, and have high availability. The total part and assembly cost of a single board is about \$25 (two orders of magnitude less than the previously-mentioned off-the-shelf amplifier [541]), making an array of tens of electrodes economically feasible. Finally, we confirmed our system could generate high voltage high frequency⁶ signals by connecting an Agilent 33210A signal generator (providing a $\pm 1\text{ V}$ (2 Vpp) wave) to a high voltage amplifier (bypassing the DAC for simplicity) and generating the frequency response plot in figure C.4.

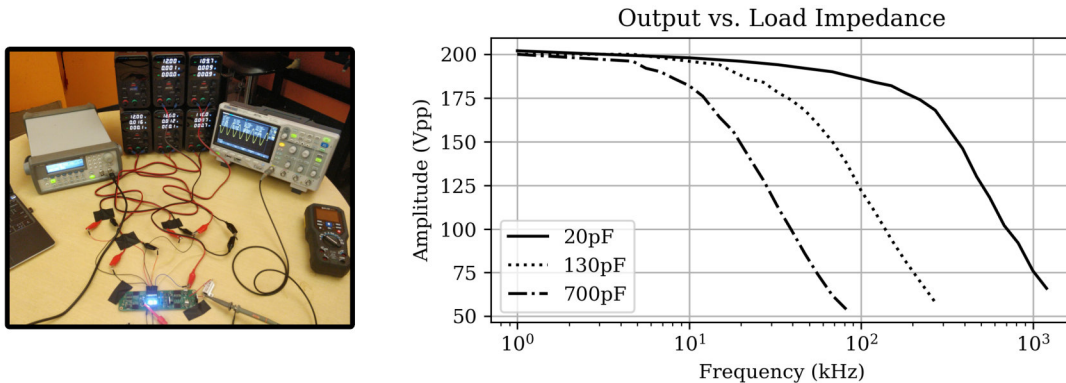


Figure C.4: Left: high frequency test setup with external signal input to amplifier. Right: Frequency response of the high voltage amplifier circuit with several capacitive loads.

We can conclude it seems possible to affordably construct a high voltage, high frequency, multi-output signal generator that meets our requirements, and constructing the full system can be done when ready for experimental tests. Driving circuitry is likely not the limit to nanoparticle printer feasibility.

³A single amplifier drew up to 10 W; efficiency (vs. CV^2f capacitor power draw) varied $\approx 0.01\%$ to 10%.

⁴We chose not to use feedback from the amplifier output to input to avoid phase delay problems.

⁵This could be simplified by putting all electronics on a smaller board, possibly inside the vacuum chamber to minimize parasitic capacitive load [424], or ultimately on a custom integrated circuit [542].

⁶Higher frequencies are achievable by decreasing the value of power resistor R5 in figure C.2.