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Mathematical Studies of Electrostatic Free Energies



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# Mathematical Studies of Electrostatic Free Energies

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in

Mathematics

by

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2019

The dissertation of Benjamin Ciotti is approved, and it is acceptable in quality and form for publication on microfilm:

Chair

University of California San Diego

2019

DEDICATION

To my parents, Paul and Holly Ciotti

# EPIGRAPH

*Things should be as simple as possible, but not simpler.*

—Albert Einstein

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ABSTRACT OF THE DISSERTATION

**Mathematical Studies of Electrostatic Free Energies**

by

Benjamin Ciotti

Doctor of Philosophy in Mathematics

University of California San Diego, 2019

Professor Bo Li, Chair

Motivated by biological models of solvation, this dissertation consists of analysis of models of electrostatic free energy of charged systems that incorporate both continuum and discrete idealizations of charges.

Discrete models of charge can yield vastly divergent results than the corresponding continuum models for systems with a small number of particles, but will be shown in Chapter 2 to be asymptotically equivalent in the large particle number limit. In Section 2.1 the energy of a given continuum charge distribution is shown to be representable as a limit of approximating discrete charge distributions by way of properties of harmonic functions and Riemann sum approximations. In Section 2.2 the problem is reversed in that a given sequence of collections of point charges is shown to have a limiting continuum charge density with the same limiting

electrostatic energy.

Motivated by application to a minimization problem common in molecular modelling, potential theory, and fluid mechanics, Chapter 3 details a delicate multi-scale construction to generalize the results of Chapter 2 to more general measures, requiring the further development of the theory of Radon measures and their Fourier transforms, facilitated by a gradient flow evolution of the domain.

The analysis of Chapter 4 concerns a hybrid model of solvation that incorporates statistical mechanics and the classical Coulomb energy of a system, allowing for both continuous and discrete distributions of charge whose equilibrium configuration is described by the Poisson–Boltzmann Equation. Motivated by application to optimization, a modified free energy functional is constructed by way of a Legendre transform and is shown to be equivalent.

Despite the long history of competition between these models, a precise treatment of the question has never been addressed, to this author's knowledge. This work is significant in bridging the gap between scales, and furthermore has application to a wide variety of physical and biological modelling problems.

# Chapter 1

# Introduction

Electrostatics is the branch of physics concerned with time-independent distributions of electric charge and the corresponding fields, potentials and energies. It is fundamental and serves as the first chapter in many introductory textbooks on the topic of electricity and magnetism. The implications and applications of electrostatics are numerous and far-reaching, coming to bear on biophysics, physical chemistry, solid state physics, nanophysics, optics, chemical engineering, and materials science. A survey of the *Journal of Electrostatics* will reveal applications as varied as drug design, ceramics, turbine generators, induction heating systems, chipsets, cell phones, transmission lines, and antennae. Electrostatics plays an important role in the distribution of ions in a solution surrounding charged macromolecules, hence the application to molecular modelling which can be used to study lipid bilayers, proteins, and DNA, and are useful in drug design and cancer research.

At the core of electrostatics is *Coulomb's law*, which states [30] that the force between two small charged bodies separated by a distance that is large compared to their internal breadth should be

- repulsive between like charges, and attractive between unlike charges;

- directly proportional to the charge of the bodies; and

- inversely proportional to the square of the distance between them.

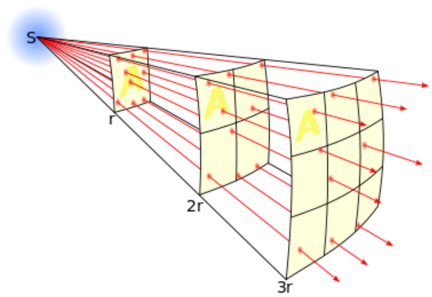


Figure 1.1: Field line flux per unit area decreasing with the inverse square of distance

Coulomb's law is one of the four Maxwell's equations that comprise the basis of classical electromagnetic theory. While it is derivable from quantum electrodynamics, the intuition that electric field lines should decrease in density with the inverse square of distance seems physically plausible from the standpoint that the flux of field lines through a surface bounding the object should be conserved, as seen in Figure 1. The inverse-square relation was initially determined in experimental work by Coulomb, Cavendish, and Priestly dating to the late 1700's [70], and has been repeatedly confirmed to greater orders of accuracy as technology has improved, but there is now a theoretical basis in relativistic quantum mechanics from which Coulomb's law can be derived as a consequence of the massless nature of the photon, the carrier of electromagnetic force. The inverse square law notably appears as well in Newton's law of gravitation. It has thus been the focus of much mathematical analysis, and has spurred the development of rich and varied mathematical subfields, including partial differential equations, harmonic analysis, potential theory, and geometric measure theory, all of which come to bear on this dissertation.

To be precise, suppose we have a pair of small, spherical charged particles

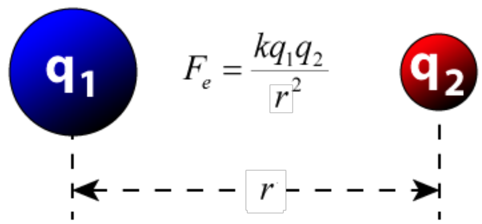


Figure 1.2: Coulomb's Law for the force between charged particles

whose centers are a distance $r$ apart, and with charges represented by real numbers $q_1$ and $q_2$ (cf. Figure 1). Then the electric force on $q_2$ due to $q_1$ will be

$$\frac{kq_1q_2}{r^2},$$

in a direction opposite to that of the location of charge $q_1$ [70, 30]. Note that, in accordance with Newton's 3rd Law, the force on $q_1$ due to $q_2$ is equal and opposite to that on $q_2$ due to $q_1$. By integrating this force along a path starting infinitely far away, we find

$$\frac{kq_1}{r}$$

is the energy per unit charge required to bring $q_2$ to this position, and is referred to as the *potential* due to $q_1$. The constant $k$ varies with the unit system being used, and shall be hereafter normalized to 1. By the principle of linear superposition, if we have a set of discrete charges $q_1, \ldots, q_n$, at respective positions $x_1, \ldots, x_n$ in space, then the potential at a point $x$ in space due to $q_1, \ldots, q_n$ is

$$\sum_{i=1}^{n} \frac{q_i}{|x - x_i|},$$

and represents the energy required to bring a unit charge in from infinitely far away to position $x$ while holding all the other charges fixed. If we imagine assembling this configuration of charges by sequentially bringing in each charge from a distance infinitely far away while holding the previously assembled charges fixed, we arrive at an expression [70, 30] for the energy required to do so:

$$\sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{q_iq_j}{|x_i-x_j|}.$$

This can be written more symmetrically as

$$\frac{1}{2}\sum_{i\neq j}\frac{q_iq_j}{|x_i-x_j|}.$$

The factor of 1/2 compensates for double counting pairs of interactions, but is inconsequential for the purposes of this dissertation and will be dropped, and we henceforth regard

$$\sum_{i\neq j}\frac{q_iq_j}{|x_i-x_j|} \tag{1.0.1}$$

as the *discrete energy* of the configuration (or "distribution") of charges $q_1,\ldots,q_n$ at respective positions $x_1,\ldots,x_n$.

No reference is made here to the size or shape of the charges, or what is meant by their position. A natural choice would be their center of mass (or charge, rather). For radially symmetric distributions, this is the same as their center. As specified in the statement of Coulomb's law, their breadth (or "diameter") should be small compared to the inter–particle distances. In the limit that the particle diameter decreases to 0, the charges are idealized as points. A famous result which shall be re–proven in this paper is Newton's theorem, which states that the interaction energy between non-overlapping radially symmetric charge distributions is the same as that between two point charges positioned at the respective centers and comprising the same charge.

The practice of idealizing particles as point charges (or masses) is common in physics and engineering, due to the ease and intuition with which the models can be understood and implemented, owing to the reduction in degrees of freedom. It is understood that such an idealization is a physical impossibility and leads to mathematical singularities (to which a considerable portion of this dissertation is devoted to addressing). This can be seen readily from the equations, for example, if one imagines assembling a unit point charge by bringing two half charges together to the same point – the energy required would be infinite. If this is not convincing, one can calculate the energy of a uniformly charged ball of unit charge and radius $R$. A simple calculation yields the energy of this charge configuration to be $.6R^{-1}$, which diverges as $R$ tends to 0.

The usual carrier of charge in practice is the electron, and modern estimates for the radius of the electron put it at roughly (with within a few orders of magnitude) $10^{-20}$ meters [15], suggesting the point charge idealization to be reasonable on a wide range of length scales, including those relevant to biology[1]. Accordingly, biological systems will tend to have a large number of particles, on the order of $10^{23}$. This is far more than is reasonable for any computation that makes use of equation (1.0.1), and it becomes reasonable if not necessary to formulate models in terms of a charge *density*.

The concept of density is not always well–defined. The familiar definition of the density of a quantity is the amount per unit volume. But this definition has an inherent length scale involved. For in the case of particle density, for example, the definition breaks down at extreme scales. From a faraway perspective, the density of almost any earthly quantity is negligible. While at the scale of atomic radii, the density of nearly any substance outside a black hole will be zero almost everywhere,

[1]To put this into perspective, the diameter of a human cell is approximately $10^{-5}$ meters.

except inside an atomic nuclei, where it will be approximately equal to that of a black hole, roughly $10^{18}$ kg/m$^3$ [35]. Yet no one will deny the utility of density calculations in most practical applications, including biological models.

Thus we consider a density $\rho$ as a function from $\mathbb{R}^3$ to $\mathbb{R}$ satisfying that $\int_V \rho dx$ should approximate the charge in a volume $V$. Then the potential $U$ due to this distribution of charge is given by

$$U(x) = \int \frac{\rho(y)dy}{|x-y|}, \tag{1.0.2}$$

and the energy of the distribution $\rho$ is

$$\frac{1}{2}\int U(x)\rho(x)dx,$$

which can be written more symmetrically as

$$\frac{1}{2}\int\int \frac{\rho(x)\rho(y)}{|x-y|}dydx.$$

As in (1.0.1) we disregard the prefactor of 1/2 that accounts for double–counting of pairs of interactions, and regard

$$E[\rho] = \int\int \frac{\rho(x)\rho(y)}{|x-y|}dydx, \tag{1.0.3}$$

to be the *continuum energy* of $\rho$, when this expression is makes sense (which will be discussed shortly).

These expressions for the potential and the energy are believable extensions of the discrete forms, by way of Riemann sum approximations of the integrals. But the integrand is unbounded due to the singularity of the Coulomb potential, so the analysis must be done with care. Even the existence and well-definedness of the expression (1.0.3) is non-trivial and must be addressed.

The function $U(x)$ defined in (1.0.2) is well known as the solution to Poisson's equation with zero boundary conditions at infinity:

$$\begin{cases} \Delta\psi = -\rho \quad \text{in } \mathbb{R}^3, \\ \psi(\infty) = 0, \end{cases}$$

[26, 22] and is the cornerstone of the theory of elliptic PDE. Solutions are well-behaved in charge-free regions, where they satisfy several properties such as harmonicity, regularity, the maximum principle and the mean value property.

One issue manifestly apparent is the discrepancy between the discrete energy (1.0.1) and the continuum energy (1.0.3). As we will show in the appendix, the continuum energy is never negative but the discrete energy can be, for example in the case of a positive and negative charge. So clearly they are not equal, even if it were possible to conceive of a way to represent a point charge with a continuous distribution.

The discrepancy lies in the infinite self energy of point charges. These are excluded, for obvious reasons, from the discrete formulation via the "$i \neq j$" condition. No such restriction exists for the continuum energy. In fact, even if we did exclude the set of points $\{(x, y) \in \mathbb{R}^3 \times \mathbb{R}^3 : x = y\}$, the continuum energy would not change since that is a set of measure zero in $\mathbb{R}^6$.

But perhaps, with an appropriate scaling, they approach a common value in the limit that the number of particles gets very large, lending validation to the practice of employing density calculations. This is the central problem of this dissertation, and shall be addressed directly in Chapter 2. Chapter 3 generalizes results of

Chapter 2 to charge distributions concentrated on lower dimensional surfaces, with a goal of applying the results to a minimization problem common in electrostatics and molecular modelling. Chapter 4 is independent but related, and analyzes an alternative approach to models of electrostatics in statistical mechanics by way of Legendre transforms.

In Section 2.1, we wish to express the energy of a given smooth and bounded charge density $\rho$ on a bounded Lipschitz domain $\Omega$ as a limit of discrete energies. This is achieved via a careful Reimann sum approximation of the integral (1.0.3). The unbounded integrand necessitates a delicate analysis. Key will be the harmonicity and local integrability of the Coulomb potential, which allow us to establish bounds on the discrete energy in terms of the continuum energy.

In Section 2.2, the problem is a reversal, in a sense, of that of the previous section. Rather than starting with a fixed charge density, we assume the existence of a sequence of discrete charge densities. Then under a geometric assumptions on their distribution, a subsequence will converge to a charge distribution whose density is continuous with respect to Lebesgue measure in $\mathbb{R}^3$. We heavily employ the technique of convolution, which for two functions $f$ and $g$ from $\mathbb{R}^3$ to $\mathbb{R}$ is given by

$$(f * g)(x) = \int f(x-y)g(y)dy,$$

*when this makes sense.* This definition can be extended to measures, and has the beneficial property that $f * g$ inherits the nicest regularity of either $f$ or $g$. We typically choose $f$ to be smooth, compactly supported in the unit ball, radially symmetric, nonnegative, and of unit mass, in which case the convolution (or mollification) of $g$ by $f$ is akin to an averaging procedure, with $f$ being the weighting. In this sense, the mollification of a discrete charge distribution is a good approximation to the density, yielding the approximate number of particles in a volume at a given length scale. We can adjust this length scale by defining rescaled mollifier $f_\lambda(x) = \lambda^{-3} f(x/\lambda)$. Then $\int f dx = \int f_\lambda dx$, so the mass is preserved, but is highly concentrated for small $\lambda$ since the support of $f_\lambda$ is contained in a ball of radius $\lambda$. By employing the Banach–Alaoglu Theorem to guarantee the existence of a vaguely convergent subsequence, we can extract a limit and demonstrate it has the desired properties.

In Chapter 3 we are required to further develop the theory of Radon measures as distributions of charge. A useful property of Radon measures is that they are exactly dual to the space of continuous functions vanishing at infinity. Although the vanishing at infinity condition is actually not much needed for our purposes, as all measures we consider will be supported in the closure of a bounded domain $\Omega$.

The set of Radon measures is large enough to include delta functions as well as Lebesgue measure and measures whose Radon–Nikodym density with respect to the Lebesgue measure are given by any integrable function. They can also be considered as distributions, which are often called "generalized functions" and are dual to $C_c^\infty$, the space of compactly supported, infinitely differentiable functions. The theory of distributions was largely developed to handle delta functions and their derivatives. Since we will not be concerned with derivatives of charge densities, we will not be concerned with this generalization, and will largely confine our discussions to the language of measures. This has the advantage of staying dual to $C_0(\mathbb{R}^n)$ as opposed to $C_c^\infty(\mathbb{R}^n)$.

In order to fully utilize the theory of energies of Radon measures, we develop some Fourier analysis, as detailed in the Appendix, and briefly summarized here.

The Fourier transform of a compactly supported signed Radon measure is $\mu$ is

$$\widehat{\mu}(k) := \int e^{-ik\cdot x} d\mu(x).$$

$\widehat{\mu}$ is bounded and continuous, although rarely of compact support. Loosely speaking, Fourier transforms interchange decay for regularity. In this dissertation, almost all distributions considered will have compact support, so their transforms will all be quite smooth but will also have low regularity. Consider, e.g., the Fourier transform of a delta function $\delta_{x_0}$:

$$\widehat{\delta_{x_0}}(k) = e^{-ik\cdot x_0},$$

which is infinitely differentiable but has no decay.

By extending the theory to tempered distributions, we can define the Fourier transform of the Coulomb potential: If $v(x) = 1/|x|$ for $x \in \mathbb{R}^3$, then we have the "equality"

$$\widehat{v}(k) = \frac{4\pi}{|k|^2}$$

holding in a weak sense, which allows us to express the electrostatic energy of a signed Radon measure in terms of its Fourier transform via

$$\iint \frac{d\mu(x)d\mu(y)}{|x-y|} = \int \frac{|\widehat{\mu}(x)|^2}{2\pi^2|x|^2} dx. \tag{1.0.4}$$

Much of the difficulty in analyzing electrostatic energies of distributions of point charges is due to the infinities involved, such as the infinite self-energy of a point charge. But these need not be the only infinities. It is also possible to have finite, compactly supported charge distributions that are not point charges but still have infinite energy. For example, the energy of a unit charge supported on the thin “wire” comprising the line segment from (0,0,0) to (1,0,0) in $\mathbb{R}^3$ has infinite energy, as will any charge distribution supported on a set of Hausdorff dimension 1 or less [51]. On the other hand, it is a simple exercise in calculus to show that a normalized uniform measure on the surface of a sphere of radius $R$ has finite energy $.5R^{-1}$, implying that measures need not be absolutely continuous with respect to Lebesgue measure in order to have finite energy. Conversely, a charge distribution that is absolutely continuous with respect to Lebesgue measure need not be of finite energy, e.g., a measure whose Lebesgue density is equal to $|x|^{-5/2}$ in a neighborhood of the origin.

The collection of subsets of $\mathbb{R}^3$ satisfying the property that any nonzero measure supported on them has infinite energy are exactly the sets of capacity 0, where the capacity of a measurable set $A \subset \mathbb{R}^3$ is defined by

$$C(A) := \left( \inf\{ \iint \frac{d\mu(x)d\mu(y)}{|x-y|} : \mu \text{ is a Borel probability measure supported on } A\} \right)^{-1}.$$

The mathematical theory of capacitance (with its generalizations of the definition given above) is rich in its own right. While the results contained in this dissertation do not directly address questions of capacity, it will be useful to occasionally reference this definition.

In [9], Capet and Friesecke consider a system of fixed, hard spheres enclosing positive charges that are themselves surrounded by a sea of discrete negative charges, and they prove that in the large particle number limit there is a convergence of discrete particle densities and energies to a continuum limit, and that in the large particle asymptotic limit, the energy minimizing distribution of negative ions will uniformly cover the spheres of positive charge in such a way as to exactly neutralize their charge. By way of the concept of balayage which we describe in Section 3.3, a point charge at the center of a spherical volume from which other charges are excluded is equivalent to a surface charge uniformly distributed on the surface of the sphere, of total charge equal to that of the charge at the center. In light of (1.0.4), it is not surprising that the minimizing configuration is thus equivalent to a zero charge distribution.

In [59], Serfaty proves a similar but more generalized result relating convergence of the minima/minimizers of discrete energy functionals (of discrete probability measures) to a continuum energy functional, in the presence of an external potential which could itself describe the field of a fixed background charge density, a confining bounded domain, or other forces.

Both Friesecke and Serfaty rely upon the same delicate multiscale construction whereby densities are averaged at an intermediate mesoscale and discrete particle are placed on a finer microscale (or "interparticle distance"). And in both of their proofs, only discrete probability measures of the form

$$\frac{1}{n}\sum_{i=1}^{n}\delta_{x_i}$$

are considered, while in this dissertation their techniques are adapted to signed measures of the form

$$\frac{1}{n}\sum_{i=1}^{n}q_i\delta_{x_i}$$

for $-1 \leqslant q_i \leqslant 1$. This generalization of allowed charge "valences" is intended to model the physically plausible scenario that the domain in question should contain both negative and positive charges (or ions), possibly of differing valence (i.e. integer multiples of the fundamental charge of the electron). Moreover, the problem in this dissertation is not phrased as a minimization problem as in [9] and [59], although we do present an application to the minimization problem in Section 3.3.

Chapter 4 of this dissertation is independent of the others. It concerns models of solvation, which were the impetus for investigating electrostatics. Solvation is the study of solutes dissolved in a solvent. The solute typically consists of charged macromolecules, which interact with a dielectric solvent containing mobile ions. The typical quantities of interest include the concentrations of the various chemical species, the electric potential, the entropy, the shape of the solvent accessible surface, the temperature, the surface tension, and the pressure. The assumptions of statistical mechanics dictate that we assume the ions to be in a Boltzmann distribution, according to their electrostatic energy. This leads to the Poisson–Boltzmann (PB) equation:

$$\nabla \cdot \varepsilon \nabla \phi = -f - \sum_{i=1}^{M} c_i^{\infty} q_i e^{-\beta q_i \phi}. \tag{1.0.5}$$

Here $\phi$ the electrostatic potential, $\varepsilon$ the dielectric coefficient, $f$ a fixed charge distribution, $c_i^{\infty}$ the reference densities of the $i$th chemical species, $M$ the number of species, and $\beta$ the inverse thermal energy.

The PB equation can be obtained as the Euler–Lagrange equation of the PB functional

$$I[\phi] = \int_{\Omega} \left[ -\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - \beta^{-1} \sum_{i=1}^{M} c_i^{\infty} \left( e^{-\beta q_i \phi} - 1 \right) \right] dx.$$

However, such a PB functional is concave downward and maximized at its critical point, making it inconsistent in many applications where a macroscopic free-energy functional is minimized. In [48], Maggs proposed a Legendre transformed form of the electrostatic free-energy functional of all possible dielectric displacements. This new functional is convex and minimized at the displacement corresponding to the critical point of the PB functional, and the minimum value is exactly the equilibrium electrostatic free energy. In Chapter 4, we study mathematically the Legendre transformed electrostatic free-energy functionals and the related variational principles. We first prove that the PB functional and its Legendre transformed functional are equivalent. We then consider a phenomenological electrostatic free-energy functional that includes a higher-order gradient term, proposed by Bazant, Storey, and Kornyshev [3] to describe charge-charge correlations. For such a functional, we introduce the corresponding Legendre transformed functional and obtain the related equivalence. We further consider the case without ions. We show that the electrostatic energy functional is equivalent to a Legendre transformed energy functional with constraint, and prove the convergence of the Legendre transform of a perturbed electrostatic energy functional. Finally, we apply the Legendre transform to the dielectric boundary electrostatic free energy in molecular solvation.

# Chapter 2

# Passage from Discrete to Continuum Models

## 2.1 Continuum energy as the limit of discrete energies: The case of a given continuous charge density

Let $\Omega \subset \mathbb{R}^3$ be a bounded domain with a Lipschitz-continuous boundary $\partial\Omega$. Let $\rho \in C^1(\overline{\Omega})$ represent a charge density. The continuum electrostatic energy due to the charge density $\rho$ is given by

$$\int_\Omega \frac{1}{2}\rho\psi\,dx \qquad (2.1.1)$$

(see e.g., [30]). Here $\psi$ is the electrostatic potential, defined to be the unique weak solution to the boundary-value problem of Poisson's equation

$$\begin{cases} \Delta\psi = -\rho \quad \text{in } \mathbb{R}^3, \\ \psi(\infty) = 0, \end{cases}$$

where we set $\rho = 0$ in $\mathbb{R}^3 \backslash \overline{\Omega}$ and we assume a uniform dielectric coefficient taken to be the unity in certain units. One can verify (see e.g., p.23 in [22], Section 1.7 in [30]) that the unique solution $\psi$ is given by

$$\psi(x) = \frac{1}{4\pi} \int_\Omega \frac{\rho(y)}{|x-y|}\, dy \qquad \forall x \in \mathbb{R}^3.$$

This and (2.1.1) imply that

$$\frac{1}{8\pi} \iint\limits_{\Omega\times\Omega} \frac{\rho(x)\rho(y)}{|x-y|}\, dxdy \tag{2.1.2}$$

is the electrostatic energy of $\rho$. By the Fubini–Tonelli theorem (Theorem 2.39 in [25]), we also have

$$\frac{1}{8\pi} \iint\limits_{\Omega\times\Omega} \frac{\rho(x)\rho(y)}{|x-y|}\, dxdy = \frac{1}{8\pi} \int_\Omega \int_\Omega \frac{\rho(x)\rho(y)}{|x-y|}\, dxdy = \frac{1}{8\pi} \int_\Omega \int_\Omega \frac{\rho(x)\rho(y)}{|x-y|}\, dydx.$$

We now construct a sequence of sets of point charges by partitioning the domain $\Omega$ and approximating the continuous charge density $\rho$ with linear combinations of delta functions, and we define the corresponding discrete electrostatic energies using Coulomb's law. We call a class of finitely many subsets of $\Omega$ a *partition of* $\Omega$, if the following are satisfied:

(P1) Each of these subsets is a domain in $\mathbb{R}^3$ with a Lipschitz-continuous boundary;

(P2) These subsets are pairwise disjoint;

(P3) The union of the closures of these subdomains is $\overline{\Omega}$.

We call these subsets *cells* of the partition. For any partition $P$ of $\Omega$, we shall define the *size* of $P$ by

$$\|P\| = \max_{\omega \in P} \operatorname{diam}(\overline{\omega}).$$

Let $\{P^n\}_{n=1}^{\infty}$ be a sequence of partitions of $\overline{\Omega}$. We assume that there exist natural numbers $N_n \nearrow +\infty$ and real numbers $r_n \searrow 0$ such that, for each $n \geqslant 1$, $P^n$ consists of *regular cells* $\omega_i^n$ $(i = 1, \ldots, N_n)$ and irregular cells (which are the remaining cells, if any) satisfying the following two conditions:

- *The uniform size condition:* For each $n \geqslant 1$ and each $i$ $(1 \leqslant i \leqslant N_n)$, there exists $x_i^n \in \omega_i^n$ such that the open ball $B(x_i^n, r_n) \subseteq \omega_i^n$. Moreover,

$$\gamma := \inf_{n \geqslant 1} \inf_{1 \leqslant i \leqslant N_n} \frac{|B(x_i^n, r_n)|}{|\omega_i^n|} > 0; \tag{2.1.3}$$

- *The almost covering condition:* $\lim_{n\to\infty} \left|\overline{\Omega} \setminus \left(\cup_{i=1}^{N_n} \overline{\omega_i^n}\right)\right| = 0$.

Here and below, we denote by $|A|$ the Lebesgue measure of a Lebesgue-measurable set $A$ in a properly understood space $\mathbb{R}^d$. Note that, since $r_n \searrow 0$, the uniform size condition implies that

$$\lim_{n\to\infty} \|P^n\| = 0. \tag{2.1.4}$$

An example of a sequence of partitions $P^n$ $(n = 1, 2, \ldots)$ that satisfy these conditions can be constructed as follows; cf. Figure 2.1: Let $\Omega \subseteq \Pi_{\alpha=1}^3 (a_\alpha, b_\alpha)$ for some real numbers $a_\alpha$ and $b_\alpha$ with $a_\alpha < b_\alpha$ $(\alpha = 1, 2, 3)$. Set $L_\alpha = b_\alpha - a_\alpha$. For each integer $n \geqslant 1$, cover $\Pi_{\alpha=1}^3 (a_\alpha, b_\alpha)$ with a finite difference grid with grid cells $\Pi_{\alpha=1}^3 (a_\alpha, a_\alpha + (i_\alpha/n) L_\alpha)$ $(i_\alpha = 1, \ldots, n)$. The partition $P^n$ consists of all the

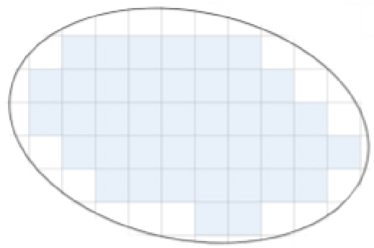

Figure 2.1: Example of regular cells

nonempty intersections of $\Omega$ and these grid cells. The regular cells of $P^n$ are those grid cells that are completely contained in $\Omega$, and the charge positions $x_i^n$ are the centers of those regular cells. The uniform size condition is satisfied with $r_n = \min_{\alpha=1,2,3} L_\alpha/(2n)$. Since the boundary $\partial\Omega$ is Lipschitz-continuous,

$$\lim_{\eta \to 0^+} |\{x \in \Omega : \mathrm{dist}\,(x, \partial\Omega) \leqslant \eta\}| = 0,$$

see, e.g., [39]. Therefore, the almost covering condition is satisfied.

Given a sequence of partitions $P^n$ of $\overline{\Omega}$ that satisfy the uniform size condition and the almost covering condition, with associated sequences $N_n \nearrow +\infty$, $r_n \searrow 0$, $\omega_i^n \in P^n$ and $x_i^n \in \omega_i^n$ $(i = 1, \ldots, N_n; n = 1, 2, \ldots)$ as above, we define the sequence of discrete charges $\{Q_i^n\}_{i=1}^{N_n}$ $(n = 1, 2, \ldots)$ by

$$Q_i^n = \rho(x_i^n)|\omega_i^n|, \qquad i = 1, \ldots, N_n;\ n = 1, 2, \ldots \tag{2.1.5}$$

By Coulomb's law [30],

$$\frac{1}{8\pi} \sum_{i,j=1, i\neq j}^{N_n} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|}. \tag{2.1.6}$$

is the corresponding sequence of the discrete electrostatic energies

The main result of this section is as follows;

**Theorem 2.1.1.**

$$\lim_{n\to\infty} \sum_{i,j=1, i\neq j}^{N_n} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|} = \iint\limits_{\Omega\times\Omega} \frac{\rho(x)\rho(y)}{|x-y|}\, dxdy. \tag{2.1.7}$$

We shall use two facts, stated below as lemmas, to prove the theorem. The first is the integrability of the function

$$f(x,y) := \frac{\rho(x)\rho(y)}{|x-y|} \qquad \forall x, y \in \Omega. \tag{2.1.8}$$

This will imply absolute continuity: the integral of $f$ is small over a set of small measure. The second is an identity connecting the discrete expression $1/|x_0 - y_0|$ for distinct points $x_0$, $y_0 \in R^3$, and an integral of $1/|x-y|$ against $x$ and $y$ over two disjoint balls in $\mathbb{R}^3$ centered at $x_0$ and $y_0$, respectively.

**Lemma 2.1.1.** *With $f$ defined as above we have that $f \in L^1(\Omega \times \Omega)$.*

*Proof.* Clearly, $f$ is Lebesgue-measurable. Let $R > 0$ be such that $\Omega \subset B(0,R)$. We have

$$\begin{aligned}
\iint\limits_{\Omega\times\Omega} |f(x,y)|\, dxdy &\leqslant \|\rho\|_\infty^2 \iint\limits_{\Omega\times\Omega} \frac{dxdy}{|x-y|} \\
&\leqslant \|\rho\|_\infty^2 \int_{B(0,R)} \left[ \iint_{B(0,R)} \frac{dx}{|x-y|} \right] dy \\
&\leqslant \|\rho\|_\infty^2 \int_{B(0,R)} \left[ \iint_{B(0,2R)} \frac{dx}{|x|} \right] dy \\
&= \|\rho\|_\infty^2 \int_{B(0,R)} \left[ 4\pi \int_0^{2R} \frac{1}{s} s^2 ds \right] dy \\
&= \frac{32}{3}\pi^2 R^5 \|\rho\|_\infty^2
\end{aligned}$$

$$< \infty,$$

as desired. $\square$

**Lemma 2.1.2.** *Suppose* $x_0$, $y_0 \in \mathbb{R}^3$ *and* $R$, $S > 0$ *satisfy* $B(x_0,R) \cap B(y_0,S) = \emptyset$, *then*

$$\frac{1}{|x_0 - y_0|} = \frac{1}{|B(x_0,R)|\,|B(y_0,S)|} \int_{B(x_0,R)} \int_{B(y_0,S)} \frac{1}{|x-y|}\, dydx$$

*Proof.* Note that $1/|z|$ is a harmonic function for $z \in \mathbb{R}^3 \backslash \{0\}$. Note also that $x \notin B(y_0,S)$ provided that $x \in B(x_0,R)$, since

$$|x - y_0| = |x - x_0 + x_0 - y_0| \geqslant |x_0 - y_0| - |x - x_0| > R + S - R = S.$$

We have now by the (volumetric) mean-value theorem for a harmonic function that

$$\begin{aligned}
\frac{1}{|x_0 - y_0|} &= \frac{1}{|B(x_0,R)|} \int_{B(x_0,R)} \frac{1}{|x - y_0|}\, dx \\
&= \frac{1}{|B(x_0,R)|} \int_{B(x_0,R)} \left[ \frac{1}{|B(y_0,S)|} \int_{B(y_0,S)} \frac{1}{|x-y|}\, dy \right] dx \\
&= \frac{1}{|B(x_0,R)|\,|B(y_0,S)|} \int_{B_R(x_0)} \int_{B_r(y_0)} \frac{1}{|x-y|}\, dydx,
\end{aligned}$$

completing the proof. $\square$

For convenience, we denote

$$E = \iint\limits_{\Omega\times\Omega} \frac{\rho(x)\rho(y)}{|x-y|}\, dxdy \qquad \text{and} \qquad E_n = \sum_{i,j=1, i\neq j}^{N_n} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|}. \tag{2.1.9}$$

By (2.1.2) and (2.1.6), we need to prove

$$\lim_{n\to\infty} E_n = E. \tag{2.1.10}$$

To do so, we shall decompose the continuum energy $E$ into three parts: $E^{\text{irreg}}$; $E^{\text{reg diag}}$; and $E^{\text{reg nondiag}}$. We also decompose accordingly the discrete energy $E_n$ into two parts: $E_n^{\text{reg diag}}$ and $E_n^{\text{reg nondiag}}$.

- The part $E^{\text{irreg}}$ is an integral related to irregular cells in a partition $P^n$, which converges to 0 as $n \to \infty$ by the almost covering condition and the absolute continuity of $f \in L^1(\Omega \times \Omega)$; cf. Lemma 2.1.1.

- The part $E^{\text{reg diag}}$ is an integral over a region of all the pairs of regular cells in $P^n$ that are inside a small neighborhood of the diagonal

$$D := \{(x, y) \in \Omega \times \Omega : x = y\}. \tag{2.1.11}$$

  This part is small, again due to the absolute continuity of $f$.

- The part $E_n^{\text{reg diag}}$ is the sum of those terms in the discrete energy $E_n$ that are related to pairs of regular cells in a small neighborhood along the diagonal $D$. This part is small for large $n$ by Lemma 2.1.2 and the absolute continuity of of $1/|x-y|$ (a special case of $f$ with $\rho \equiv 1$.)

- The difference between $E^{\text{reg nondiag}}$ and $E_n^{\text{reg nondiag}}$ is small for large $n$ due to the uniform continuity of $f$ off the diagonal and our definition of $Q_i^n$.

*Proof of Theorem 2.1.1. Step 1. Treatment of irregular cells.* For each $n \geqslant 1$, let us denote by $R_n$ and $I_n$ the class of all regular cells and irregular cells of the partition

$P^n$, and by $\cup R_n$ and $\cup I_n$ their unions, respectively. Since $f(x,y) = f(y,x)$, we have by (2.1.9) that

$$
\begin{aligned}
E &= \iint\limits_{\Omega\times\Omega} f(x,y)\,dxdy \\
&= \left(\int_{\cup R_n} + \int_{\cup I_n}\right)\left[\left(\int_{\cup R_n} + \int_{\cup I_n}\right) f(x,y)\,dx\right] dy \\
&= \int_{\cup R_n}\int_{\cup R_n} f(x,y)\,dxdy + \int_{\cup I_n}\int_{\cup I_n} f(x,y)\,dxdy + 2\int_{\cup I_n}\int_{\cup R_n} f(x,y)\,dxdy \\
&= \iint\limits_{\cup R_n\times\cup R_n} f(x,y)\,dxdy + \iint\limits_{\cup I_n\times\cup I_n} f(x,y)\,dxdy + 2\iint\limits_{\cup I_n\times\cup R_n} f(x,y)\,dxdy.
\end{aligned}
$$

It therefore follows from the almost covering condition $\lim_{n\to\infty}|\cup I_n| = 0$, which implies that $\lim_{n\to\infty}|\cup I_n \times \cup I_n| = 0$ and $\lim_{n\to\infty}|\cup I_n \times \cup R_n| = 0$, and the absolute continuity of $f$ that

$$
E = \lim_{n\to\infty} \iint\limits_{\cup R_n\times\cup R_n} f(x,y)\,dxdy. \tag{2.1.12}
$$

Let $\varepsilon > 0$. By (2.1.10) and (2.1.12), it suffices to show now that there exists a natural number $N$ such that

$$
\left| \iint\limits_{\cup R_n\times\cup R_n} f(x,y)\,dxdy - E_n \right| < \varepsilon. \tag{2.1.13}
$$

*Step 2. Treatment of pairs of regular cells in a small neighborhood of the diagonal $D$.* By the absolute continuity of $f(x,y)$ and that of $1/|x-y|$ (a special case of $f$ with $\rho \equiv 1$) on $\Omega\times\Omega$, there exists $\delta > 0$ such that for any measurable subset $A \subseteq \Omega\times\Omega$

$$
\iint\limits_A |f(x,y)|\,dxdy < \frac{\varepsilon}{3} \qquad \text{and} \qquad \iint\limits_A \frac{dxdy}{|x-y|} < \frac{\varepsilon\gamma^2}{3(\|\rho\|_\infty^2 + 1)} \qquad \text{if } |A| < \delta. \tag{2.1.14}
$$

Let $\eta > 0$ be such that

$$|D_{2\eta}| < \delta, \tag{2.1.15}$$

where

$$D_\alpha = \{(x,y) \in \Omega \times \Omega : \text{dist}\,((x,y), D) < \alpha\}$$

with $\alpha > 0$ is the $\alpha$-neighborhood of the diagonal $D$ defined in (2.1.11).

For each $n \geqslant 1$, let us denote

$$T_{n,\eta} = \{\omega_i^n \times \omega_j^n : \omega_i^n \text{ and } \omega_j^n \text{ are regular cells of } P^n,\ (\omega_i^n \times \omega_j^n) \cap D_\eta \neq \emptyset\},$$

$$S_{n,\eta} = \{\omega_i^n \times \omega_j^n : \omega_i^n \text{ and } \omega_j^n \text{ are regular cells of } P^n,\ (\omega_i^n \times \omega_j^n) \cap D_\eta = \emptyset\}.$$

Note that $S_{n,\eta}$ and $T_{n,\eta}$ are disjoint. Moreover,

$$\cup R_n \times \cup R_n = (\cup S_{n,\eta}) \cup (\cup T_{n,\eta}). \tag{2.1.16}$$

By the uniform size condition, thre exists $\tilde{N}$ such that the union of all

$$\cup T_{n,\eta} \subseteq D_{2\eta} \qquad \text{if } n \geqslant \tilde{N}. \tag{2.1.17}$$

This, together with (2.1.15) and (2.1.14), implies that

$$\iint\limits_{\cup T_{n,\eta}} |f(x,y)|\, dxdy < \frac{\varepsilon}{3} \qquad \text{and} \qquad \iint\limits_{\cup T_{n,\eta}} \frac{dxdy}{|x-y|} < \frac{\varepsilon\gamma^2}{3(\|\rho\|_\infty^2 + 1)} \qquad \text{if } n \geqslant \tilde{N}. \tag{2.1.18}$$

Now, let $\omega_i^n$ and $\omega_j^n$ be any pair of distinct regular cells in $T_{n,\eta}$. Then it follows from the definition of $Q_i^n$ and $Q_j^n$ (cf. (2.1.5)), Lemma 2.1.2, and the uniform size condition (cf. (2.1.3)) that

$$
\begin{aligned}
\frac{|Q_i^n Q_j^n|}{|x_i^n - x_j^n|} &= \frac{|\rho(x_i^n)\rho(x_j^n)|\,|\omega_i^n|\,|\omega_j^n|}{|x_i^n - x_j^n|} \\
&\leqslant \frac{\|\rho\|_\infty^2 |\omega_i^n|\,|\omega_j^n|}{|x_i^n - x_j^n|} \\
&= \frac{\|\rho\|_\infty^2 |\omega_i^n|\,|\omega_j^n|}{|B(x_i^n, r_n)|\,|B(x_j^n, r_n)|} \iint\limits_{B(x_i^n, r_n)\times B(x_j^n, r_n)} \frac{dxdy}{|x-y|} \\
&\leqslant \frac{\|\rho\|_\infty^2}{\gamma^2} \iint\limits_{\omega_i^n \times \omega_j^n} \frac{dxdy}{|x-y|} \qquad \text{if } n \geqslant \tilde{N}.
\end{aligned}
$$

This and the second inequality in (2.1.18) then imply that

$$
\left| \sum_{\omega_i^n \times \omega_j^n \in T_{n,\eta}, i \neq j} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|} \right| \leqslant \frac{\|\rho\|_\infty^2}{\gamma^2} \int_{\cup T_{n,\eta}} \frac{dxdy}{|x-y|} < \frac{\varepsilon}{3} \qquad \text{if } n \geqslant \tilde{N}. \tag{2.1.19}
$$

*Step 3. Treatment of pairs of regular cells away from the diagonal.* The uniform continuity of $f$ on $\overline{\Omega \times \Omega} \backslash D_\eta$ implies the existence of $\sigma > 0$ such that

$$
|f(x,y) - f(x',y')| < \frac{\varepsilon}{3|\Omega \times \Omega|} \qquad \text{if } |(x,y) - (x',y')| < \sigma. \tag{2.1.20}
$$

By (2.1.4), there exists a natural number $\hat{N}$ such that $\|P^n\| < \sigma$ if $n \geqslant \hat{N}$. Note that if $\omega_i^n \times \omega_j^n \in S_{n,\eta}$, then we must have $i \neq j$. Therefore, it follows from (2.1.5) and (2.1.20) that

$$
\begin{aligned}
&\left| \iint\limits_{\cup S_{n,\eta}} f(x,y)\, dxdy - \sum_{\omega_i^n \times \omega_j^n \in S_{n,\eta}} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|} \right| \\
&\qquad \leqslant \sum_{\omega_i^n \times \omega_j^n \in S_{n,\eta}} \iint\limits_{\omega_i^n \times \omega_j^n} \left| f(x,y) - f(x_i^n, x_j^n) \right| dxdy
\end{aligned}
$$

$$< \frac{\varepsilon}{3} \qquad \text{if } n \geqslant \hat{N}. \tag{2.1.21}$$

Finally, let $N = \max\{\tilde{N}, \hat{N}\}$. We have by (2.1.16), the first inequality in (2.1.18), (2.1.19), and (2.1.21) that

$$\begin{aligned}
\left| \iint\limits_{\cup R_n \times \cup R_n} f(x,y)\,dxdy - E_n \right| &\leqslant \iint\limits_{\cup T_{n,\eta}} |f(x,y)|\,dxdy + \left| \sum_{\omega_i^n \times \omega_j^n \in T_{n,\eta}, i \neq j} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|} \right| \\
&\quad + \left| \iint\limits_{\cup S_{n,\eta}} f(x,y)\,dxdy - \sum_{\omega_i^n \times \omega_j^n \in S_{n,\eta}} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|} \right| \\
&< \varepsilon \qquad \text{if } n \geqslant N,
\end{aligned}$$

leading to (2.1.13). □

## 2.2 Continuum energy as the limit of discrete energies: The case of a sequence of sets of point charges

Consider now a sequence of sets of point charges in our bounded domain $\Omega$ in $\mathbb{R}^3$. Each such set yields a discrete electrostatic energy. We shall furnish a continuum charge density as a limit (in an appropriate sense) of a sequence of the discrete particle densities, calculate its continuum energy, and show that to be the limit of corresponding discrete energies.

Let $N_n$ be a sequence of natural numbers increasing to $\infty$. For each $n \in \{1, 2, \ldots\}$, let $X_n = \{x_1^n, \ldots, x_{N_n}^n\} \subset \Omega$ be a set of $N_n$ discrete points in $\Omega$. To each $x_i^n$ we associate a partial charge $Q_i^n \in [-1, 1]$. The familiar discrete energy of this configuration of charges $Q_i^n$ at positions $x_i^n$ is given (up to a factor of $\frac{1}{2}$ or $\frac{1}{8\pi}$) by

$$\sum_{1\leqslant i,j\leqslant N_n, i\neq j} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|}.$$

In allowing the number of charges to increase to $\infty$, it will be natural to rescale our charges by a normalization factor of $1/N_n$. Thus we consider discrete charge distribution

$$\rho_n = \frac{1}{N_n}\sum_{i=1}^{N_n} Q_i^n \delta_{x_i^n},$$

which will be regarded as a signed Radon measure on $\mathbb{R}^3$, the space of which is dual to $C_0(\mathbb{R}^3)$, the completion of $C_c(\mathbb{R}^3)$ under the uniform norm. We accordingly define the discrete energy

$$E_d[\rho_n] = \frac{1}{N_n^2}\sum_{1\leqslant i,j\leqslant N_n, i\neq j} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|}.$$

If $\rho$ is a signed Radon measure with $d\rho = f dx$ for some $f \in L^\infty(\mathbb{R}^3)$ supported on $\overline{\Omega}$, then we define

$$E[\rho] = \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{d\rho(x)d\rho(y)}{|x-y|}.$$

The geometric assumption will be that, for each $n = 1, 2, ...$ there exists a radius $r_n > 0$ such that

(G1) $B_{r_n}(x_i^n) \subset \Omega$ for all $i = 1, \dots, N_n$,

(G2) $B_{r_n}(x_i^n) \cap B_{r_n}(x_j^n) = \emptyset$ holds for all $i, j = 1, \dots, N_n$ with $j \neq i$,

(G3) $\gamma := \inf_{n\geqslant 1} N_n |B_{r_n}| > 0$.

Note the boundedness of $\Omega$ and assumption (G2) imply that $r_n \to 0$ as $n \to \infty$.

**Theorem 2.2.1.** *There exists a subsequence of $\{\rho_n\}$, not relabeled, and a signed Radon measure $\rho$ on $\mathbb{R}^3$ that satisfy the following:*

*(1)* $\rho_n$ *converges vaguely to* $\rho$*;*

*(2) There exists* $f \in L^\infty(\mathbb{R}^3)$ *such that* $f = 0$ *a.e. on* $\overline{\Omega}^c$ *and* $d\rho = f dx$*;*

*(3)* $\lim_{n\to\infty} E_d[\rho_n] = E[\rho]$.

Here and below, $\nu_n \rightharpoonup \nu$ denotes vague convergence, and means

$$\int_{\mathbb{R}^3} g d\nu_n \to \int_{\mathbb{R}^3} g d\nu \qquad \forall\, g \in C_0(\mathbb{R}^3).$$

The proof of Theorem 2.2.1 consists of 4 steps.

Step 1. Show the existence of the limit $\rho$ and that $d\rho/dx = f \in L^\infty(\mathbb{R}^3)$.

Step 2. Use mollifiers to construct "smoothed out" densities $\rho_n * \varphi_\lambda$ with corresponding energies $E[\rho_n * \varphi_\lambda]$.

Step 3. Obtain three different energy approximations.

Step 4. Show convergence via an "epsilon over three"–type argument.

*Proof of Theorem 2.2.1: Step 1. Existence of a limiting Radon measure with a bounded density.* For a given signed measure $\nu$, the Hahn Decomposition Theorem (Theorem 3.3 of Folland [25]) gives that there exist disjoint measurable sets $P_\nu$ and $N_\nu$, the positive and negative sets for $\nu$ respectively, which are unique up to $\nu$–null sets and such that $\nu^+(\cdot) := \nu(\cdot \cap P_\nu)$ and $\nu^-(\cdot) := -\nu(\cdot \cap N_\nu)$ are (nonnegative) measures and $\nu = \nu^+ - \nu^-$.

The positive (respectively negative) sets for $\rho_n$ are exactly the locations of positive (respectively negative) charge i.e.

$$P_{\rho_n} = \{x_i^n : Q_i^n > 0, 1 \leqslant i \leqslant N_n\}, \qquad N_{\rho_n} = \{x_i^n : Q_i^n < 0, 1 \leqslant i \leqslant N_n\},$$

as $\rho_n$ is positive on any subset of $P_{\rho_n}$, negative on any subset of $N_{\rho_n}$, and null on $(P_{\rho_n} \cup N_{\rho_n})^c$. Letting $\nu^+$ and $\nu^-$ denote the positive and negative parts, respectively, of a given signed measure $\nu$, and $a^\pm = \max(\pm a, 0)$ for $a \in \mathbb{R}$, it follows that $\rho_n = \rho_n^+ - \rho_n^-$ is the Hahn decomposition of $\rho_n$ with

$$\rho_n^+ = \frac{1}{N_n} \sum_{i=1}^{N_n} Q_i^{n+} \delta_{x_i^n} \quad \text{and} \quad \rho_n^- = \frac{1}{N_n} \sum_{i=1}^{N_n} Q_i^{n-} \delta_{x_i^n},$$

and the total variation $|\rho_n| = \rho_n^+ + \rho_n^-$.

Since $|Q_i^n| \leqslant 1$ for all $i, n$, we have for $g \in C_0(\mathbb{R}^3)$ that

$$|\langle \rho_n^+, g \rangle| = \left| \frac{1}{N_n} \sum_{i=1}^{N_n} Q_i^{n+} g(x_i^n) \right| \leqslant \|g\|_\infty \qquad \text{for } n = 1, 2, \ldots$$

Similarly,

$$|\langle \rho_n^-, g \rangle| = \left| \frac{1}{N_n} \sum_{i=1}^{N_n} Q_i^{n-} g(x_i^n) \right| \leqslant \|g\|_\infty \qquad \text{for } n = 1, 2, \ldots$$

Since $\rho_n^+$ and $\rho_n^-$ are uniformly bounded linear functionals on separable space $C_0(\mathbb{R}^3)$, by Theorem 5.18 of Folland [25] they have vaguely convergent subsequences. By consecutively passing to such a subsequence, first for $\rho_n^+$ and then for $\rho_n^-$, we may assume without relabeling that

$$\rho_n^+ \rightharpoonup \rho' \quad \text{and} \quad \rho_n^- \rightharpoonup \rho''$$

for some (nonnegative) Radon measures $\rho', \rho''$ on $\mathbb{R}^3$. Setting $\rho := \rho' - \rho''$, we have

$$\rho_n = \rho_n^+ - \rho_n^- \rightharpoonup \rho. \tag{2.2.1}$$

We claim that

$$|\rho| \leqslant \rho' + \rho''. \tag{2.2.2}$$

The Hahn Decomposition for $\rho$ gives that there exist disjoint measurable sets $P_\rho$ and $N_\rho$ such that

$$\rho = \rho^+ - \rho^-$$

with

$$\rho^+(\cdot) = \rho(\cdot \cap P_\rho) \text{ and } \rho^-(\cdot) = -\rho(\cdot \cap N_\rho).$$

Then for measurable $A \subset \mathbb{R}^3$,

$$\rho^+(A) = \rho(A \cap P) = \rho'(A \cap P) - \rho''(A \cap P) \leqslant \rho'(A \cap P) \leqslant \rho'(A)$$

i.e., $\rho^+ \leqslant \rho'$. Similarly, $\rho^- \leqslant \rho''$. It follows that

$$|\rho_n| = \rho_n^+ + \rho_n^- \rightharpoonup \rho' + \rho'' \geqslant \rho^+ + \rho^- = |\rho|. \tag{2.2.3}$$

To show that $\rho$ has an $L^\infty$ Radon–Nikodym derivative with respect to the Lebesgue measure, we first establish a bound on $|\rho_n|(B_\lambda)$ for balls $B_\lambda$ of radius $\lambda$:

$$|\rho_n|(B_\lambda) \leqslant \frac{1}{N_n} \#\{i : x_i^n \in B_\lambda\}. \tag{2.2.4}$$

From volume considerations, we have that

$$\#\{i : x_i^n \in B_\lambda\} \leqslant \#\{i : B_{r_n}(x_i^n) \subset B_{\lambda + r_n}\} \leqslant \frac{|B_{\lambda + r_n}|}{|B_{r_n}|}, \tag{2.2.5}$$

since $B_{r_n}(x_i^n) \subset B_{\lambda + r_n}$ if $x_i^n \subset B_\lambda$, and $B_{r_n}(x_i^n) \cap B_{r_n}(x_j^n) = \emptyset$ if $i \neq j$. This, (2.2.4), and the definition of $\gamma$ imply that

$$|\rho_n|(B_\lambda) \leqslant \frac{|B_{\lambda+r_n}|}{N_n|B_{r_n}|} \leqslant \frac{1}{\gamma}|B_{\lambda+r_n}|. \tag{2.2.6}$$

This implies that

$$\liminf_n |\rho_n|(B) \leqslant \frac{1}{\gamma}|B| \tag{2.2.7}$$

for any ball $B \subset \mathbb{R}^3$.

Suppose $A \subset \mathbb{R}^3$ is bounded with $|A| = 0$. By Lemma 2.2.1 below, this implies that for any $\epsilon > 0$, there exist a countable collection of open balls $B_i$ covering $A$ with $\sum_i |B_i| < \epsilon$. If $O$ is an open set and Radon measures $\nu_n$ converge vaguely to $\nu$, then

$$\nu(O) \leqslant \liminf_n \nu_n(O)$$

by Theorem 1.24 in [50]. This, (2.2.3), and (2.2.7) give

$$|\rho|(B) \leqslant (\rho_\infty^+ + \rho_\infty^-)(B) \leqslant \liminf_n |\rho_n|(B) \leqslant \frac{1}{\gamma}|B| \tag{2.2.8}$$

for any open ball $B \in \mathbb{R}^3$. Thus

$$|\rho|(A) \leqslant |\rho|(\bigcup_i B_i) \leqslant \sum_i |\rho|(B_i) \leqslant \frac{1}{\gamma}\sum_i |B_i| < \frac{1}{\gamma}\epsilon. \tag{2.2.9}$$

It follows from the Radon–Nikodym Theorem (Theorem 3.8 in [25]) that

$$d\rho = f dx \tag{2.2.10}$$

for some $f \in L^1(\mathbb{R}^3)$. Moreover, the Lebesgue Differentiation Theorem (Theorem

3.21 in [25]) gives that

$$|f(x)| = \lim_{\lambda\to 0^+} \frac{1}{|B_\lambda|}\int_{B_\lambda(x)} |f(y)|dy \qquad \text{for almost every } x \in \mathbb{R}^3.$$

But using the fact that $d|\rho| = |f|dx$ (cf. Section 3.3 in [25]), we have

$$\begin{aligned}\frac{1}{|B_\lambda|}\int_{B_\lambda(x)} |f(y)|dy =& \frac{1}{|B_\lambda|}|\rho|(B_\lambda(x))\\ \leqslant& \frac{1}{|B_\lambda|}\liminf_n |\rho_n|(B_\lambda(x))\\ \leqslant& \frac{1}{\gamma},\end{aligned}$$

so $|f(x)| \leqslant 1/\gamma$ for almost every $x$, hence $f \in L^\infty(\mathbb{R}^3)$.

Since $|\rho|(O) \leqslant \liminf |\rho_n|(O) = 0$ for any open set $O \subset \overline{\Omega}^c$, the support of of $\rho$ is contained in $\overline{\Omega}$. Thus, after modifying $f$ on a set of measure 0 if necessary, we have

$$supp(f) \subset \overline{\Omega}. \tag{2.2.11}$$

*Step 2. Construction of coarse-grained densities and energies.* It is a standard result that for any signed Radon measure $\nu$ we have

$$\varphi_\lambda * \nu \rightharpoonup \nu \text{ as } \lambda \to 0^+,$$

where $\varphi \in C_c^\infty(\mathbb{R}^3)$ is nonnegative, radially symmetric, of unit mass, $supp(\varphi) \subset \overline{B_1(0)}$, and $\varphi_\lambda(x) = \lambda^{-3}\varphi(x/\lambda)$ (cf. Theorem 2.6 in Mattila [51]). That is,

$$\lim_{\lambda\to 0^+}\int_{\mathbb{R}^3} g(x)(\varphi_\lambda * \nu)(x)dx = \int_{\mathbb{R}^3} g(x)d\nu(x)$$

for all $g \in C_0(\mathbb{R}^3)$. Here the convolution

$$(\varphi * \nu)(x) = \int_{\mathbb{R}^3} \varphi(x-y) d\nu(y)$$

is a function from $\mathbb{R}^3$ to $\mathbb{R}$. As is typical in related texts, when there is no possibility of confusion we occasionally abuse notation by referring to $\varphi * \nu$ in place of the measure whose Radon–Nikodym density with respect to the Lebesgue measure is given by $\varphi * \nu$.

In particular we have

$$\rho_n * \varphi_\lambda \rightharpoonup \rho_n \text{ as } \lambda \to 0^+$$

for each fixed $n$, where

$$(\rho_n * \varphi_\lambda)(x) = \frac{1}{N_n} \sum_{i=1}^{N_n} Q_i^n \varphi_\lambda(x - x_i^n).$$

And since $\varphi_\lambda(\cdot - x) \in C_c^\infty(\mathbb{R}^3)$, we have the pointwise convergence

$$\lim_{n\to\infty} (\rho_n * \varphi_\lambda)(x) = (\rho * \varphi_\lambda)(x) \qquad \text{for all } x \in \mathbb{R}^3, \tag{2.2.12}$$

by the definition of vague convergence.

Having smoothed the densities by mollifying with $\varphi_\lambda$, we have well-defined energies

$$E[\rho_n * \varphi_\lambda] = \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\rho_n * \varphi_\lambda)(x)(\rho_n * \varphi_\lambda)(y) dx dy}{|x-y|} \tag{2.2.13}$$

and

$$E[\rho * \varphi_\lambda] = \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{(\rho * \varphi_\lambda)(x)(\rho * \varphi_\lambda)(y) dx dy}{|x-y|}. \tag{2.2.14}$$

We then have

$$\begin{aligned} &|E_d[\rho_n] - E[\rho]| \leqslant \\ &|E_d[\rho_n] - E[\rho_n * \varphi_\lambda]| + |E[\rho_n * \varphi_\lambda] - E[\rho * \varphi_\lambda]| + |E[\rho * \varphi_\lambda] - E[\rho]|, \end{aligned} \tag{2.2.15}$$

and the strategy that follows will be to show each of these terms gets small.

*Step 3. Energy estimates on the three terms of* (2.2.15). For the first term we need the following claim: For all $\lambda > 0$ there exists $\tilde{N} = \tilde{N}(\lambda)$ such that

$$|E_d[\rho_n] - E[\rho_n * \varphi_\lambda]| \leqslant C\left(\lambda^2 + \frac{1}{N_n \lambda}\right) \qquad \text{if } n \geqslant \tilde{N}(\lambda), \tag{2.2.16}$$

where $C$ is a constant independent of $n$ and $\lambda$.

*Step 3a. Proof of the inequality* (2.2.16). Defining $\vartheta := \varphi * \varphi$, we have that $\vartheta \in C_c^\infty(\mathbb{R}^3)$ is supported inside $B_2(0)$. Setting $\vartheta_\lambda(x) := \lambda^{-3}\vartheta(x/\lambda)$, the following properties for all $\lambda > 0$:

- $\vartheta_\lambda \geqslant 0$;
- $\vartheta_\lambda = \varphi_\lambda * \varphi_\lambda$ (via the change of variables $y \mapsto \lambda y$);
- $\int_{\mathbb{R}^3} \vartheta_\lambda(x) dx = \int_{\mathbb{R}^3} \varphi_\lambda(x) dx \cdot \int_{\mathbb{R}^3} \varphi_\lambda(x) dx = 1 \cdot 1 = 1$;
- $\vartheta_\lambda$ is radially symmetric (via the change of variables $x \mapsto Rx$, with $R$ a rotation, and using the radial symmetry of $\varphi_\lambda$).

Then using the Fubini–Tonelli Theorem, the local integrability of $1/|x-y|$, and the fact that $\rho_n * \varphi_\lambda \in L^\infty$,

$$\begin{aligned}
E[\rho_n * \varphi_\lambda] &= \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\rho_n * \varphi_\lambda)(x)(\rho_n * \varphi_\lambda)(y)}{|x-y|} dxdy \\
&= \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{1}{|x-y|} \left[\frac{1}{N_n}\sum_{i=1}^{N_n} Q_i^n \varphi_\lambda(x-x_i^n)\right]\left[\frac{1}{N_n}\sum_{j=1}^{N_n} Q_j^n \varphi_\lambda(y-x_j^n)\right] dxdy \\
&= \frac{1}{N_n^2}\sum_{1\leqslant i,j\leqslant N_n} Q_i^n Q_j^n \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_\lambda(x-x_i^n)\varphi_\lambda(y-x_j^n)}{|x-y|} dxdy.
\end{aligned}$$

Making the change of variables $y \mapsto y + x_j^n$ gives

$$E[\rho_n * \varphi_\lambda] = \frac{1}{N_n^2}\sum_{1\leqslant i,j\leqslant N_n} Q_i^n Q_j^n \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\varphi_\lambda(x-x_n^i)\varphi_\lambda(y)}{|x-y-x_j^n|} dxdy,$$

and the further change $x \mapsto y - x + x_i^n$ gives

$$\begin{aligned}
E[\rho_n * \varphi_\lambda] &= \frac{1}{N_n^2}\sum_{1\leqslant i,j\leqslant N_n} Q_i^n Q_j^n \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\varphi_\lambda(y-x)\varphi_\lambda(y)}{|x_i^n - x_j^n - x|} dxdy \\
&= \frac{1}{N_n^2}\sum_{1\leqslant i,j\leqslant N_n} Q_i^n Q_j^n \int_{\mathbb{R}^3} \frac{1}{|x_i^n - x_j^n - x|}\left[\int_{\mathbb{R}^3} \varphi_\lambda(y-x)\varphi_\lambda(y)dy\right] dx \\
&= \frac{1}{N_n^2}\sum_{1\leqslant i,j\leqslant N_n} Q_i^n Q_j^n \int_{\mathbb{R}^3} \frac{\vartheta_\lambda(x)}{|x_i^n - x_j^n - x|} dx. \qquad (2.2.17)
\end{aligned}$$

Since $\int_{\mathbb{R}^3} \vartheta_\lambda(x)dx = 1$, the difference in energies is

$$\begin{aligned}
&E_d[\rho_n] - E[\rho_n * \varphi_\lambda] \\
&= \frac{1}{N_n^2}\sum_{1\leqslant i,j\leqslant N_n, i\neq j} Q_i^n Q_j^n \frac{1}{|x_i^n - x_j^n|} \\
&\quad - \frac{1}{N_n^2}\sum_{1\leqslant i,j\leqslant N_n} Q_i^n Q_j^n \int_{\mathbb{R}^3} \frac{\vartheta_\lambda(x)dx}{|x_i^n - x_j^n - x|}
\end{aligned}$$

$$= \frac{1}{N_n^2} \sum_{1 \leqslant i,j \leqslant N_n, i \neq j} Q_i^n Q_j^n \int_{\mathbb{R}^3} \left[ \frac{1}{|x_i^n - x_j^n|} - \frac{1}{|x_i^n - x_j^n - x|} \right] \vartheta_\lambda(x) dx$$
$$- \frac{1}{N_n^2} \sum_{i=1}^{N_n} (Q_i^n)^2 \int_{\mathbb{R}^3} \vartheta_\lambda(x) \frac{1}{|x|} dx.$$

The integral in the last term $\int_{\mathbb{R}^3} \vartheta_\lambda(x) \frac{1}{|x|} dx = c/\lambda$, where

$$c := \int_{\mathbb{R}^3} \vartheta(x) \frac{1}{|x|} dx = \int_{\mathbb{R}^3} (\varphi * \varphi)(x) \frac{1}{|x|} dx > 0 \tag{2.2.18}$$

depends only on $\varphi$ and is finite by the local integrability of $1/|x|$, hence the self-energy terms are bounded by

$$\frac{1}{N_n^2} \sum_{i=1}^{N_n} (Q_i^n)^2 \frac{c}{\lambda} \leqslant \frac{c}{N_n \lambda}.$$

This leaves the main term:

$$\frac{1}{N_n^2} \sum_{1 \leqslant i,j \leqslant N_n, i \neq j} Q_i^n Q_j^n \int_{\mathbb{R}^3} \left[ \frac{1}{|x_i^n - x_j^n|} - \frac{1}{|x_i^n - x_j^n - x|} \right] \vartheta_\lambda(x) dx,$$

which is split into two parts. If $|x_i^n - x_j^n| > 2\lambda$, then by Newton's Theorem (Theorem A.1.1), the interaction energy is the same as that between two discrete charges, and the terms cancel out. Combining this fact with the estimate

$$\left| \frac{1}{|x_i^n - x_j^n|} - \frac{1}{|x_i^n - x_j^n - x|} \right| \leqslant \frac{|x|}{|x_i^n - x_j^n| |x_i^n - x_j^n - x|}$$

gives that

$$\left| \frac{1}{N_n^2} \sum_{i \neq j} Q_i^n Q_j^n \int_{\mathbb{R}^3} \left[ \frac{1}{|x_i^n - x_j^n|} - \frac{1}{|x_i^n - x_j^n - x|} \right] \vartheta_\lambda(x) dx \right|$$
$$\leqslant \frac{1}{N_n^2} \sum_{i,j: 0 < |x_i^n - x_j^n| \leqslant 2\lambda} \frac{1}{|x_i^n - x_j^n|} \int_{\mathbb{R}^3} \frac{|x| \vartheta_\lambda(x)}{|x_i^n - x_j^n - x|} dx.$$

By the mean value property, if $i \neq j$ then

$$\frac{1}{|x_i^n - x_j^n|} = \frac{1}{(\frac{4}{3}\pi r_n^3)} \int_{B_{r_n}(x_j^n)} \frac{dy}{|x_i^n - y|}.$$

Since the $B_{r_n}(x_i^n)$ are pairwise disjoint, we have

$$\begin{aligned}
\sum_{i,j:0<|x_i^n - x_j^n|\leqslant 2\lambda} \frac{1}{|x_i^n - x_j^n|} =& \sum_i \sum_{j:0<|x_i^n - x_j^n|\leqslant 2\lambda} \frac{1}{(\frac{4}{3}\pi r_n^3)} \int_{B_{r_n}(x_j^n)} \frac{dy}{|x_i^n - y|} \\
\leqslant& \sum_i \frac{C}{r_n^3} \int_{B_{2\lambda + r_n}(0)} \frac{dy}{|y|} \\
\leqslant& C N_n \frac{(2\lambda + r_n)^2}{r_n^3} \\
\leqslant& C N_n \left( \frac{\lambda^2}{r_n^3} + \frac{1}{r_n} \right).
\end{aligned}$$

Using (A.1.2),

$$\begin{aligned}
\int_{\mathbb{R}^3} \frac{|x|\vartheta_\lambda(x)dx}{|x_i^n - x_j^n - x|} =& \int_{\mathbb{R}^3} \min\left( \frac{1}{|x|}, \frac{1}{|x_i^n - x_j^n|} \right) |x|\vartheta_\lambda(x)dx \\
\leqslant& \int_{\mathbb{R}^3} \frac{1}{|x|} |x|\vartheta_\lambda(x)dx \\
=& \int_{\mathbb{R}^3} \vartheta_\lambda(x)dx \\
=& 1.
\end{aligned}$$

Thus

$$\begin{aligned}
&\left| \frac{1}{N_n^2} \sum_{i,j:0<|x_i^n - x_j^n|\leqslant 2\lambda} \frac{Q_i^n Q_j^n}{|x_i^n - x_j^n|} \int_{\mathbb{R}^3} \frac{|x|\vartheta_\lambda(x)}{|x_i^n - x_j^n - x|} dx \right| \\
&\qquad\qquad \leqslant \frac{C}{N_n} \left( \frac{\lambda^2}{r_n^3} + \frac{1}{r_n} \right).
\end{aligned} \tag{2.2.19}$$

Since $r_n \searrow 0$, choose $\tilde{N} = \tilde{N}(\lambda)$ such that $n > \tilde{N}$ implies $r_n \leqslant \lambda$. Then combining

(2.2.19) with the estimate bounding the self energy term by $c/N_n\lambda$, we have

$$|E_d[\rho_n] - E[\rho_n * \varphi_\lambda]| \leqslant C\left(\frac{\lambda^2}{N_n r_n^3} + \frac{1}{N_n\lambda}\right) \qquad \text{for } n \geqslant \tilde{N}.$$

Applying the uniform size condition that $N_n r_n^3$ is bounded below by a positive constant, we get the result (2.2.16).

*Step 3b. We show that for any* $\lambda > 0$, $\lim_{n\to\infty} E[\rho_n * \varphi_\lambda] = E[\rho * \varphi_\lambda]$: Since

$$\begin{aligned} |\rho_n * \varphi_\lambda(x)| = &\left|\frac{1}{N_n}\sum_{i=1}^{N_n} Q_i^n \varphi_\lambda(x - x_i^n)\right| \leqslant \frac{1}{N_n}\sum_{i=1}^{N_n} |Q_i^n| \|\varphi_\lambda\|_\infty \\ \leqslant &\|\varphi_\lambda\|_\infty = \lambda^{-3}\|\varphi\|_\infty, \end{aligned}$$

for fixed $\lambda$ the $\rho_n * \varphi_\lambda$ are uniformly bounded in $n, x$. It was also shown previously that $1/|x-y|$ is locally integrable on $\mathbb{R}^6$. Thus, $(\rho_n * \varphi_\lambda)(x)(\rho_n * \varphi_\lambda)(y)/|x-y|$ is bounded by $(\lambda^{-3}\|\varphi\|_\infty)^2/|x-y|$, which is locally integrable, so by (2.2.12) and the dominated convergence theorem,

$$\lim_{n\to\infty} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\rho_n * \varphi_\lambda)(x)(\rho_n * \varphi_\lambda)(y)dxdy}{|x-y|} = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\rho * \varphi_\lambda)(x)(\rho * \varphi_\lambda)(y)dxdy}{|x-y|},$$

i.e.,

$$\lim_{n\to\infty} E[\rho_n * \varphi_\lambda] = E[\rho * \varphi_\lambda]. \tag{2.2.20}$$

*Step 3c. We show* $\lim_{\lambda\to 0^+} E[\rho * \varphi_\lambda] = E[\rho]$. We have

$$E[\rho * \varphi_\lambda] = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{(\rho * \varphi_\lambda)(x)(\rho * \varphi_\lambda)(y)}{|x-y|}dxdy$$

$$
\begin{aligned}
&= \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{1}{|x-y|}\left[\int_{\mathbb{R}^3}\varphi_\lambda(x-x')d\rho(x')\right]\left[\int_{\mathbb{R}^3}\varphi_\lambda(y-y')d\rho(y')\right]dxdy \\
&= \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{1}{|x-y|}\left[\int_{\mathbb{R}^3}\varphi_\lambda(x-x')f(x')dx'\right]\left[\int_{\mathbb{R}^3}\varphi_\lambda(y-y')f(y')dy'\right]dxdy \\
&= \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \left[\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_\lambda(x-x')\varphi_\lambda(y-y')f(x')f(y')}{|x-y|}dx'dy'\right]dxdy \\
&= \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \left[\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_\lambda(x-x')\varphi_\lambda(y-y')}{|x-y|}dxdy\right]f(x')f(y')dx'dy'.
\end{aligned}
$$

by the Fubini–Tonelli Theorem. In Theorem A.1.2 it is shown that if radially symmetric nonnegative $\phi \in L^1$ is unit mass, then

$$
\int_{\mathbb{R}^3}\frac{\phi(x)dx}{|x-y|} \leqslant \frac{1}{|y|}.
$$

It follows that

$$
\begin{aligned}
\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_\lambda(x-x')\varphi_\lambda(y-y')dxdy}{|x-y|} &= \int_{\mathbb{R}^3}\varphi_\lambda(y-y')\left[\int_{R^3}\frac{\varphi_\lambda(x-x')dx}{|x-y|}\right]dy \\
&= \int_{\mathbb{R}^3}\varphi_\lambda(y-y')\left[\int_{R^3}\frac{\varphi_\lambda(x)dx}{|x-(y-x')|}\right]dy \\
&\leqslant \int_{\mathbb{R}^3}\frac{\varphi_\lambda(y-y')}{|y-x'|}dy \\
&= \int_{\mathbb{R}^3}\frac{\varphi_\lambda(y)}{|y-(x'-y')|}dy \\
&\leqslant \frac{1}{|x'-y'|}. \qquad (2.2.21)
\end{aligned}
$$

Thus we get that

$$
\left|\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_\lambda(x-x')\varphi_\lambda(y-y')dx'dy'}{|x'-y'|}f(x)f(y)\right| \leqslant \frac{|f(x)||f(y)|}{|x-y|}. \qquad (2.2.22)
$$

Similar to the calculation leading to (2.2.17), we can write

$$\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_\lambda(x-x')\varphi_\lambda(y-y')dxdy}{|x-y|} = \int_{\mathbb{R}^3} \frac{\vartheta_\lambda(z)dz}{|x'-y'-z|}.$$

Since $\vartheta$ is radially symmetric, nonnegative, and of unit mass, $\vartheta_\lambda$ forms an approximate identity as $\lambda \to 0$, i.e.,

$$\lim_{\lambda\to 0} \int_{\mathbb{R}^3} g(x)\vartheta_\lambda(x)dx = g(0)$$

for all $g$ in $C_0(\mathbb{R}^3)$. In particular, if $x \neq y$ and if $\phi(\cdot)$ is equal to $1/|x-y-\cdot|$ multiplied by a smooth cutoff function equal to 1 in a neighborhood of the origin and supported in a ball of radius less than $|x-y|$, we get that

$$\int_{\mathbb{R}^3} \frac{\vartheta_\lambda(z)dz}{|x-y-z|} \to \frac{1}{|x-y|} \text{ as } \lambda \to 0^+,$$

i.e.,

$$\lim_{\lambda\to 0^+} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_\lambda(x-x')\varphi_\lambda(y-y')dx'dy'}{|x'-y'|} = \frac{1}{|x-y|}. \tag{2.2.23}$$

for $x \neq y$. This convergence still holds if we allow $x$ to equal $y$ (so $1/|x-y| = +\infty$) but this is immaterial as the diagonal $\{(x,y) \in \mathbb{R}^3 \times \mathbb{R}^3 : x = y\}$ is measure zero in $\mathbb{R}^6$.

Apply the dominated convergence theorem in conjunction with (2.2.22) and (2.2.23) and dominating function $\|f\|_\infty^2/|x-y| \in L^1_{loc}(\mathbb{R}^3 \times \mathbb{R}^3)$ to get

$$\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \left[ \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_\lambda(x-x')\varphi_\lambda(y-y')}{|x'-y'|} dx'dy' \right] f(x)f(y)dxdy \to \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{f(x)f(y)}{|x-y|} dxdy$$

as $\lambda \to 0^+$, i.e.,

$$\lim_{\lambda \to 0^+} E[\rho * \varphi_\lambda] = E[\rho]. \tag{2.2.24}$$

*Step 4. Convergence of the energies.* Given $\epsilon > 0$, first select $\lambda$ small enough that $|E[\rho * \varphi_\lambda] - E[\rho]| < \epsilon/2$, *and* $C\lambda^2 < \epsilon/2$, where the constant $C$ is that from the estimate (2.2.16) that

$$|E_d[\rho_n] - E[\rho_n * \varphi_\lambda]| \leqslant C\left(\lambda^2 + \frac{1}{N_n \lambda}\right).$$

Then

$$\begin{aligned}
|E_d[\rho_n] - E[\rho]| &\leqslant |E_d[\rho_n] - E[\rho_n * \varphi_\lambda]| + |E[\rho_n * \varphi_\lambda] - E[\rho * \varphi_\lambda]| \\
&\quad + |E[\rho * \varphi_\lambda] - E[\rho]| \\
&\leqslant \frac{\epsilon}{2} + \frac{C}{N_n \lambda} + |E[\rho_n * \varphi_\lambda] - E[\rho * \varphi_\lambda]| + \frac{\epsilon}{2}.
\end{aligned}$$

Letting $n$ tend to infinity, we have

$$\lim_n \frac{C}{N_n \lambda} = 0 \quad \text{and} \quad \lim_n |E[\rho_n * \varphi_\lambda] - E[\rho * \varphi_\lambda]| = 0,$$

so

$$\limsup_{n \to \infty} |E_d[\rho_n] - E[\rho]| \leqslant \epsilon.$$

Since $\epsilon > 0$ was arbitrary, we must have

$$\limsup_n |E_d[\rho_n] - E[\rho]| = 0,$$

hence

$$\lim_{n} |E_d[\rho_n] - E[\rho]| = 0,$$

and the theorem is proved. $\square$

The various convergences are summarized in the following diagrams:

$$
\begin{array}{ccc}
E[\rho_n * \varphi_\lambda] & \to_n & E[\rho * \varphi_\lambda] \\
 & & \downarrow_\lambda \\
E_d[\rho_n] & \to_n & E[\rho]
\end{array}
\qquad\qquad
\begin{array}{ccc}
\rho_n * \varphi_\lambda & \to_n & \rho * \varphi_\lambda \\
\downharpoonleft_\lambda & & \downharpoonleft_\lambda \\
\rho_n & \rightharpoonup_n & \rho
\end{array}
$$

**Lemma 2.2.1.** *If $A \subset \mathbb{R}^3$ is a bounded set of Lebesgue measure $0$, then for all $\epsilon > 0$ there exists a countable collection of open balls $B_i$ covering $A$ with $\sum_i |B_i| < \epsilon$.*

*Proof.* By Theorem 2.40 in Folland [25], there exists an open set $O$ containing $A$ with $|O| < \epsilon/5$. By Lemma 2.43 in Folland [25], $O$ is a countable union of cubes (i.e. products of intervals of equal length) $Q_i$ with disjoint interiors $\mathring{Q}_i$. Since

$$\bigcup_i \mathring{Q}_i \subset O,$$

we have

$$\sum_i |\mathring{Q}_i| \leqslant |O| < \epsilon/5.$$

Enclose each $Q_i$ in an open ball $B_i$ of radius equal to the side length of $Q_i$, so $|B_i| = \frac{4\pi}{3}|Q_i| < 5|Q_i|$. Then

$$O \subset \bigcup_i Q_i \subset \bigcup_i B_i,$$

and hence

$$\sum_i |B_i| < \sum_i 5|Q_i| = 5\sum_i |\mathring{Q}_i| < \epsilon. \qquad \square$$

## 2.3 Non-uniqueness of the limit of a sequence of sets of point charges

The non-uniqueness of the limit of the of the sequence of sets of point charges holds true in general, even if additional assumptions are imposed upon the sets, as the following counterexamples will demonstrate. Retaining the notation of the prvious section, $\Omega$ is a smooth, bounded domain in $\mathbb{R}^3$, and $X_n = \{x_1^n, \ldots, x_{N_n}^n\}$ is a collection of distinct points in $\Omega$.

*Claim*: Even if $X_n \subset X_{n+1}$ holds for $n = 1, 2, \ldots$, the corresponding sequence of rescaled discrete charge distributions

$$\rho_n = \frac{1}{N_n} \sum_{i=1}^{N_n} \delta_{x_i^n}$$

representing unit charges (i.e. electrons) at positions $x_1^n, \ldots, x_{N_n}^n$ need not have a *unique* limit.

Consider a partition of $\Omega$ into two components $A$ and $B$ with nonempty interiors and having boundary of measure 0. Let $Y_n = (2^{-n}\mathbb{Z}^3) \cap \Omega$. Then $Y_n \subset Y_{n+1}$, and $Y_{n+1}$ has $2^3 = 8$ times the point density as does $Y_n$. Define

$$X_n = \begin{cases} (Y_n \cap B) \cup (Y_{n+1} \cap A) & \text{for } n \text{ even,} \\ (Y_n \cap A) \cup (Y_{n+1} \cap B) & \text{for } n \text{ odd.} \end{cases}$$

Then $X_n \subset X_{n+1}$, and letting $N_n$ be the number of points in $X_n$, we set $\rho_n = \frac{1}{N_n} \sum_{x_i \in X_n} \delta_{x_i}$.

$X_n$ is uniformly distributed on $A$, and uniformly distributed on $B$, but has eight times as many points per unit volume in one than the other, hence eight times the density. Then in the limit we will have

$$\mu_{2n} \rightharpoonup 8\rho_0\chi_A + \rho_0\chi_B,$$

where $\rho_0$ is a constant to be determined, and $\chi_A$ is the indicator function of the set $A$. Normalizing the total mass to 1 gives

$$1 = 8\rho_0|A| + \rho_0|B| = 8\rho_0|A| + \rho_0(|\Omega| - |A|) = \rho_0(7|A| + |\Omega|),$$

so

$$\rho_0 = \frac{1}{7|A| + |\Omega|},$$

and

$$\mu_{2n} \rightharpoonup \frac{8}{7|A| + |\Omega|}\chi_A + \frac{1}{7|A| + |\Omega|}\chi_B.$$

Similarly,

$$\mu_{2n+1} \rightharpoonup \frac{1}{7|B| + |\Omega|}\chi_A + \frac{8}{7|B| + |\Omega|}\chi_B.$$

Thus, we get two different subsequential limits of the densities. Moreover, the corresponding energies are different as well, in general.

We demonstrate this with a specific example: Let $\Omega = \{x \in \mathbb{R}^3 : |x| < 2\}$, and set $A = \{x \in \mathbb{R}^3 : |x| \leqslant 1\}$ and $B = \{x \in \mathbb{R}^3 : 1 < |x| < 2\}$. After much calculation, we find the normalized limiting densities and energies:

$$\mu_{2n} \rightharpoonup \mu_{even} := \frac{8 \cdot 3}{15 \cdot 4\pi}\chi_A + \frac{3}{15 \cdot 4\pi}\chi_B$$

and

$$\mu_{2n+1} \rightharpoonup \mu_{odd} := \frac{3}{57 \cdot 4\pi}\chi_A + \frac{8 \cdot 3}{57 \cdot 4\pi}\chi_B,$$

with corresponding energies

$$E[\mu_{even}] = \frac{59}{150} \approx .393 \quad \text{and} \quad E[\mu_{odd}] = \frac{313}{1083} \approx .289.$$

The result is in agreement with the intuition that the distribution with the higher concentration of charge closer together should have the higher energy. It also follows from the results of this chapter that the discrete energies corresponding to $\mu_{2n}$ and $\mu_{2n+1}$ converge to $E[\mu_{even}]$ and $E[\mu_{odd}]$, respectively.

# Chapter 3

# Extensions to Radon measures

## 3.1 Introduction

The principal of energy minimization is abundant in nature. Given a conducting material (a medium in which charges can move) in the presence of an external electric field, the charges in the conductor will align themselves so as to minimize the energy of the configuration. Any higher energy states are non-equilibrium states or at best unstable, and will quickly tend to a local minimum of the energy. Earnshaw's theorem [19] states that charges cannot be held in equilibrium by electrostatic forces alone. This is reflected in the concept of capacity, whereby the charge in a conducting material accumulates on the surface and is representable as a surface charge density.

In the case of collection of positive charges confined to a conductor, discrete charges will repel each other onto the surface of the conductor. More to the point from a biological perspective is the case of a fixed, charged macromolecule surrounded by ions. Here the ions may be positively or negatively charged or a mixture of both, and are subject to an external electric field emitted by the fixed charges. In a physical situation, there will be other contributions to the energy, such as van der Waals forces, pressure, and entropy, and these must be accounted for. In this section we consider only the classical Coulomb force, and suppose the charges to be confined to a fixed domain $\Omega$, effectively introducing an insurmountable force to be present against charges that push against the boundary of the domain. In Chapter 4 we address contributions from additional forces.

The theory of balayage dictates that for the purposes of charges contained in a conducting medium, the field due to an external source of charge is equivalent to that produced by a surface charge on the boundary of the conductor. This is the motivation for extending our results of Chapter 2 to charge distributions that are concentrated on lower dimensional objects such as surfaces. Such distributions are no longer absolutely continuous with respect to three–dimensional Lebesgue measure, but can be represented in full generality by signed Radon measures.

The results of Section 2.1 demonstrated that continuously differentiable distributions of charge $\rho$ could be approximated by discrete distributions such that the discrete energies converge to the energy of the continuous distribution. With a modification of the argument, this can be shown to hold for compactly supported $\rho \in L^\infty(\mathbb{R}^3)$, provided we continue to accept

$$E[\rho] := \iint \frac{d\rho(x)d\rho(y)}{|x-y|}$$

as the definition of the energy of $\rho$. From Lemma 2.1.1, this is well–defined for compactly supported $\rho \in L^\infty(\mathbb{R}^3)$. In this chapter we show that results of Chapter 2 can be generalized to arbitrary signed Radon measures supported on $\overline{\Omega}$, for which $L^\infty$ densities are a special case. Following this we demonstrate an application of these results to a problem of minimization in the presence of an external field.

## 3.2 Extension to signed Radon measures

Let $\Omega \subset \mathbb{R}^3$ be a bounded domain with $C^2$ boundary. As before, we let $\mathcal{M}$ be the set of signed Radon measures supported on $\overline{\Omega}$ with total variation less than or equal to one. Let $\mu \in \mathcal{M}$ be such that

$$\iint \frac{d\mu^+(x)d\mu^-(y)}{|x-y|} < \infty,$$

where $\mu = \mu^+ - \mu^-$ is the Jordan decomposition of $\mu$ in to positive measures $\mu^+$ and $\mu^-$, and define

$$E[\mu] = E[\mu^+] + E[\mu^-] - 2E[\mu^+, \mu^-], \tag{3.2.1}$$

where

$$E[\alpha, \beta] := \iint \frac{d\alpha(x)d\beta(y)}{|x-y|} \tag{3.2.2}$$

for positive Radon measures $\alpha$ and $\beta$, and we write

$$E[\alpha] := E[\alpha, \alpha].$$

If $E[\mu^+]$ and $E[\mu^-]$ are finite, then

$$E[\mu^+, \mu^-] \leqslant \sqrt{E[\mu^+]E[\mu^-]} < \infty$$

by Corollary B.2.3, so $E[\mu] \in (-\infty, \infty]$.

Note that in most literature relevant to the problem (e.g., [37, 51, 9]), the authors avoid the issue of well–definedness of the Coulomb energy by restricting to nonnegative measures or to measures with finite energy.

Interestingly, there is an alternate formulation for the energy of a signed

Radon measure of compact support in terms of its Fourier transform which has the benefit of *always* being defined, and which agrees with $E[\mu]$ whenever $E[\mu]$ is defined. This is proved in Theorem B.2.4 of Appendix B, in which we derive properties of Fourier transforms of Radon measures and apply them to energy integrals.

A discrete charge density is a signed Radon measure of the form $\mu = \sum_{i=1}^{n} q_i \delta_{x_i}$, with $x_1, \ldots, x_n \in \mathbb{R}^3$ distinct, and $q_1, \ldots, q_n \in \mathbb{R}$, and for which the discrete energy is

$$E_d[\mu] = \sum_{i \neq j} \frac{q_i q_j}{|x_i - x_j|}.$$

Note this is not the same as $E[\mu]$, which would be undefined or at best infinite for non-zero discrete measures $\mu$. Denoting the "diagonal" terms by

$$D := \{(x, x) \in \mathbb{R}^3 \times \mathbb{R}^3\},$$

we have

$$E_d[\mu] = \int_{\mathbb{R}^3 \times \mathbb{R}^3 \setminus D} \frac{d(\mu \times \mu)(x, y)}{|x - y|},$$

which is $E[\mu]$ excepting the infinite self–energy terms comprising the diagonal $D$.

In this dissertation we are concerned with physically plausible charge distributions, which are comprised of electrons or other ions, and for which there is an upper bound on the amount of charge a single particle can carry, such as the maximum valence of any ion in the system we are considering. Normalizing this maximum to 1 and renormalizing our densities by particle number, we restrict ourselves to consideration of discrete charge densities in the admissible set

$$\mathcal{A} := \left\{ \mu = \frac{1}{N} \sum_{i=1}^{N} q_i \delta_{x_i} : N \in \mathbb{N}, \{q_i\}_{i=1}^{N} \subset [-1, 1],\ \{x_i\}_{i=1}^{N} \subset \overline{\Omega} \text{ distinct} \right\}.$$

We continue the convention of identifying $\mu$ with $f$ when $\mu$ is absolutely continuous with respect to Lebesgue and $d\mu = f dx$.

The main result of this section is as follows:

**Theorem 3.2.1.** *For $\mu \in \mathcal{M}$ with $E[|\mu|] < \infty$, there exists a sequence of discrete charge distributions $\mu_n \in \mathcal{A}$ such that*

1. $\mu_n \rightharpoonup \mu$ *as* $n \to \infty$,
2. $E_d[\mu_n] \to E[\mu]$ *as* $n \to \infty$.

Note that by preceding remarks, the requirement that $E[|\mu|] < \infty$ is equivalent to the requirement that $E[\mu]$ be defined and finite.

The proof consists of a careful multiscale construction, and is preceded by a reduction to the case that $\mu$ is compactly supported inside $\Omega$ and has $C^1$ density with respect to Lebesgue measure, which we justify with two lemmas. Here and throughout this dissertation, *supp*$(\mu)$ denotes the support of a signed measure (or function) $\mu$, and is defined as the smallest closed set for which $\mu$ is null (or zero, respectively) on its complement.

**Lemma 3.2.1.** *Given $\mu \in \mathcal{M}$ with $E[|\mu|] < \infty$, there exist a sequence of measures $\nu_k \in \mathcal{M}$ satisfying*

1. *supp*$(\nu_k) \subset \Omega$,
2. $\nu_k \rightharpoonup \mu$ *as* $k \to \infty$,
3. $E[\nu_k] \to E[\mu]$ *as* $k \to \infty$.

*Proof.* Define the signed distance function

$$d(x) = \begin{cases} \min\{|x-y| : y \in \partial\Omega\} & x \in \overline{\Omega}, \\ -\min\{|x-y| : y \in \partial\Omega\} & x \in \mathbb{R}^3 \backslash \overline{\Omega}. \end{cases}$$

For $r > 0$, set $T_r := \{x \in \overline{\Omega} : d(x) < r\}$. There exists $\delta > 0$ such that

- $d$ is twice continuously differentiable on $T_\delta$; and
- for every $x \in T_\delta$ there exists a unique $x' \in \partial\Omega$ such that $|x - x'| = d(x)$

(see Theorem 3 in [36]). Applying the triangle inequality to nearby points $x$ and $y$ in $T_\delta$ give that $|\nabla d| \leqslant 1$ in $T_\delta$. Choosing $x \in T_\delta$ and $x' \in \partial\Omega$ such that $d(x) = |x - x'|$ and considering points on the straight line segment connecting $x$ and $x'$, one finds that $|\nabla d| = 1$ on $T_\delta$. Since $\partial\Omega$ is the level set $\{d = 0\}$, $\nabla d$ is the normal to $\partial\Omega$, and is oriented toward the interior of $\Omega$ as defined.

Let $\xi$ be a smooth cutoff function that is equal to one on $T_{\delta/2}$ and supported in $T_\delta$, and let $\tilde{d}(x) = d(x)\xi(x)$. Since $\nabla\tilde{d}$ is the inward pointing normal vector on $\partial\Omega$, the flow on $\mathbb{R}^3$ of the ODE

$$\tfrac{d}{dt}X = \nabla\tilde{d}(X) \tag{3.2.3}$$

is "inward" to $\Omega$ along $\partial\Omega$. Since $\tilde{d} \in C_c^2(\mathbb{R}^3)$, $\nabla\tilde{d}$ is Lipschitz, say with Lipschitz constant

$$L := \sup_{x \neq y} \frac{|\nabla\tilde{d}(x) - \nabla\tilde{d}(y)|}{|x - y|}.$$

The fundamental theorem of ODE (see e.g., Section 17.1 in [67]) gives that there exists a time interval $[-\tau, \tau]$ on which the flow exists and is unique. Let $\Phi_t$ be the associated flow map taking $x \in \mathbb{R}^3$ to its position at time $t \in [-\tau, \tau]$ under the flow (3.2.3). Then

$$\frac{d}{dt}\Phi_t(x) = \nabla\tilde{d}(\Phi_t(x)) \text{ and } \Phi_0(x) = x$$

for all $x \in \mathbb{R}^3$ and $t \in [-\tau, \tau]$, so for $x, y \in \mathbb{R}^3$ and $t \in [0, \tau]$ we have

$$\Phi_t(x) - \Phi_t(y) = x - y + \int_0^t \left[\nabla\tilde{d}(\Phi_s(x)) - \nabla\tilde{d}(\Phi_s(y))\right] ds,$$

so

$$\begin{aligned} |\Phi_t(x) - \Phi_t(y)| &\leqslant |x - y| + \int_0^t \left|\nabla\tilde{d}(\Phi_s(x)) - \nabla\tilde{d}(\Phi_s(y))\right| ds \\ &\leqslant |x - y| + \int_0^t L\,|\Phi_s(x) - \Phi_s(y)|\, ds. \end{aligned}$$

By Gronwall's Inequality (see e.g., Section 17.3 in [67]), this gives

$$|\Phi_t(x) - \Phi_t(y)| \leqslant e^{Lt}|x - y| \tag{3.2.4}$$

for all $t \in [0, \tau]$ and $x, y \in \mathbb{R}^3$.

Similarly, for $t \in [0, \tau]$ we have

$$\begin{aligned} |\Phi_{-t}(x) - \Phi_{-t}(y)| &= \left|x - y + \int_0^{-t} \left[\nabla\tilde{d}(\Phi_s(x)) - \nabla\tilde{d}(\Phi_s(y))\right] ds\right| \\ &= \left|x - y - \int_{-t}^0 \left[\nabla\tilde{d}(\Phi_s(x)) - \nabla\tilde{d}(\Phi_s(y))\right] ds\right| \\ &\leqslant |x - y| + \int_{-t}^0 L\,|\Phi_s(x) - \Phi_s(y)|\, ds. \end{aligned}$$

Gronwall's Inequality then gives

$$|\Phi_{-t}(x) - \Phi_{-t}(y)| \leqslant e^{Lt}|x - y| \tag{3.2.5}$$

for $x, y \in \mathbb{R}^3$ and $t \in [0, \tau]$. By uniqueness, $\Phi_t$ is one–to–one and $\Phi_{-t}(\Phi_t(x)) = x$, so replacing $x$ and $y$ in (3.2.5) by $\Phi_t(x)$ and $\Phi_t(y)$, respectively, gives

$$|x - y| \leqslant e^{Lt}|\Phi_t(x) - \Phi_t(y)|,$$

which combined with (3.2.4) gives

$$e^{-Lt}|x - y| \leqslant |\Phi_t(x) - \Phi_t(y)| \leqslant e^{Lt}|x - y| \tag{3.2.6}$$

for all $t \in [0, \tau]$ and $x, y \in \mathbb{R}^3$.

Define the push–forward measures $\Phi_t \# \mu$ by

$$\Phi_t \# \mu(A) = \mu(\Phi_t^{-1}(A)). \tag{3.2.7}$$

Since $\nabla \tilde{d}$ is the inward normal along $\partial\Omega$, $\Phi_t(\overline{\Omega})$ is contained in $\Omega$ for $t \in (0, \tau]$. But $\Phi_t(\overline{\Omega})$ is compact since $\Phi_t(\cdot)$ is a homeomorphism, so

$$supp(\Phi_t \# \mu) \subset \Omega \quad \text{for } t \in (0, \tau]. \tag{3.2.8}$$

If $\mu = \mu|_P - \mu|_N$ is the Hahn decomposition of $\mu$, then $|\mu| = \mu|_P + \mu|_N$, and a straightforward calculation shows

$$\Phi_t \# \mu = (\Phi_t \# \mu)|_{\Phi_t(P)} - (\Phi_t \# \mu)|_{\Phi_t(N)}$$

to be the Hahn decomposition of $\Phi_t \# \mu$, so

$$|\Phi_t \# \mu| = (\Phi_t \# \mu)|_{\Phi_t(P)} + (\Phi_t \# \mu)|_{\Phi_t(N)}. \tag{3.2.9}$$

Theorem 3.6.1 in [6] states that given measurable spaces $X$ and $Y$, signed measure

$\mu$ on $X$, and measurable mapping $f : X \to Y$, a measurable function $g$ on $Y$ is integrable with respect to the pushforward measure $f\#\mu$ if and only if the composition $g \circ f$ is integrable with respect to $\mu$, in which case

$$\int_Y g\, d(f\#\mu) = \int_X g \circ f\, d\mu. \tag{3.2.10}$$

Writing $\chi_A$ for the indicator function of a set $A \subset \mathbb{R}^3$, (3.2.9) and (3.2.10) give

$$\begin{aligned}
\|\Phi_t\#\mu\| &= \int_{\mathbb{R}^3} d|\Phi_t\#\mu| \\
&= \int_{\mathbb{R}^3} d(\Phi_t\#\mu)|_{\Phi_t(P)} + \int_{\mathbb{R}^3} d(\Phi_t\#\mu)|_{\Phi_t(N)} \\
&= \int_{\mathbb{R}^3} \chi_{\Phi_t(P)}(x) d(\Phi_t\#\mu)(x) + \int_{\mathbb{R}^3} \chi_{\Phi_t(N)}(x) d(\Phi_t\#\mu)(x) \\
&= \int_{\mathbb{R}^3} \chi_{\Phi_t(P)}(\Phi_t(x)) d\mu(x) + \int_{\mathbb{R}^3} \chi_{\Phi_t(N)}(\Phi_t(x)) d\mu(x) \\
&= \int_{\mathbb{R}^3} \chi_P(x) d\mu(x) + \int_{\mathbb{R}^3} \chi_N(x) d\mu(x) \\
&= \int_{\mathbb{R}^3} d\mu|_P + \int_{\mathbb{R}^3} d\mu|_N \\
&= \int_{\mathbb{R}^3} d|\mu| \\
&= \|\mu\|.
\end{aligned} \tag{3.2.11}$$

From (3.2.8) and (3.2.11), it follows that

$$\Phi_t\#\mu \in \mathcal{M}. \tag{3.2.12}$$

To establish vague convergence, let $g \in C_0(\mathbb{R}^3)$, and apply the change of variables formula (3.2.10):

$$\int_{\mathbb{R}^3} gd(\Phi_t\#\mu) - \int_{\mathbb{R}^3} gd\mu = \int_{\mathbb{R}^3} g\circ\Phi_t d\mu - \int_{\mathbb{R}^3} gd\mu = \int_{\mathbb{R}^3} [g(\Phi_t(x)) - g(x)]d\mu(x).$$

Since

$$\Phi_t(x) = x + \int_0^t \nabla\tilde{d}(\Phi_s(x))ds,$$

we find that $|\Phi_t(x) - x| \leqslant t\|\nabla\tilde{d}\,\|_\infty$ holds for $t \in [0,\tau]$. Given $\epsilon > 0$, there exists $\delta > 0$ such that $|g(x) - g(y)| < \epsilon$ holds for all $x, y \in \mathbb{R}^3$ such that $|x - y| < \delta$. Then for $0 \leqslant t < \delta/\|\nabla\tilde{d}\,\|_\infty$, we get

$$|g(\Phi_t(x)) - g(x)| < \epsilon,$$

so

$$\left|\int_{\mathbb{R}^3} gd(\Phi_t\#\mu) - \int_{\mathbb{R}^3} gd\mu\right| \leqslant \epsilon\int_{\mathbb{R}^3} d|\mu| \leqslant \epsilon,$$

proving that

$$\Phi_t\#\mu \rightharpoonup \mu \qquad \text{as} \quad t \to 0^+. \tag{3.2.13}$$

Since

$$e^{-Lt}|x-y| \leqslant |\Phi_t(x) - \Phi_t(y)| \leqslant e^{Lt}|x-y| \tag{3.2.14}$$

holds for all $t \in [0,\tau]$ and $x, y \in \mathbb{R}^3$, we get

$$\frac{e^{-Lt}}{|x-y|} \leqslant \frac{1}{|\Phi_t(x) - \Phi_t(y)|} \leqslant \frac{e^{Lt}}{|x-y|}.$$

Hence,

$$\left|\frac{1}{|\Phi_t(x) - \Phi_t(y)|} - \frac{1}{|x-y|}\right| \leqslant \frac{(e^{Lt}-1)}{|x-y|}. \tag{3.2.15}$$

From the change of variables formula (3.2.10), we find that

$$E[\Phi_t\#\mu] = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{d\mu(x)d\mu(y)}{|\Phi_t(x) - \Phi_t(y)|}.$$

Using (3.2.15), it follows that

$$|E[\Phi_t\#\mu] - E[\mu]| \leqslant (e^{Lt} - 1)E[|\mu|],$$

hence

$$E[\Phi_t\#\mu] \to E[\mu] \quad \text{as } t \to 0^+. \tag{3.2.16}$$

For for $k > 1/\tau$, we set $\nu_k := \Phi_{\frac{1}{k}}\#\mu$ and by (3.2.8), (3.2.12), (3.2.13) and (3.2.16), the lemma is proved. □

**Lemma 3.2.2.** *For $\mu \in \mathcal{M}$ with $E[|\mu|] < \infty$ and supp$(\mu) \subset \Omega$, there exists a sequence of signed measures $\nu_k \in \mathcal{M}$ such that*

1. *$\nu_k$ is absolutely continuous with respect to Lebesgue measure with $C^1$ density,*
2. *supp$(\nu_k) \subset \Omega$,*
3. *$\nu_k \rightharpoonup \mu$ as $k \to \infty$,*
4. *$E[\nu_k] \to E[\mu]$ as $k \to \infty$.*

*Proof.* Let $\varphi \in C_c^1(\mathbb{R}^3)$ be a mollifier, i.e., $\varphi$ is radially symmetric, compactly supported in $B_1(0)$, nonnegative, and of unit mass. For $\lambda > 0$ we set $\varphi_\lambda(x) = \lambda^{-3}\varphi(x/\lambda)$. Recall the convolution $(\varphi * \mu)(\cdot)$ is the function (or measure, whose density with respect to Lebesgue measure is) $\int_{\mathbb{R}^3} \varphi(\cdot - y)d\mu(y)$. We have from standard results on convolutions (see e.g., Section 9.1 in [25]) that

- $\varphi_\lambda * \mu$ (regarded as a function) is $C^1$,
- $\varphi_\lambda * \mu \rightharpoonup \mu$ as $\lambda \to 0^+$,
- $supp(\varphi_\lambda * \mu) \subset supp(\mu) + supp(\varphi_\lambda)$.

Since $supp(\varphi_\lambda) \subset B_\lambda(0)$, there exists $\lambda_0 = \lambda_0(\mu)$ such that $supp(\varphi_\lambda * \mu) \subset \Omega$ for $\lambda < \lambda_0$. From Theorem B.2.4,

$$E[\mu] = (2\pi)^{-3} \int_{\mathbb{R}^3} \frac{4\pi |\widehat{\mu}|^2}{|k|^2} dk.$$

Similarly, we also have for $\lambda > 0$ that

$$E[\varphi_\lambda * \mu] = (2\pi)^{-3} \int_{\mathbb{R}^3} \frac{4\pi |\widehat{\varphi_\lambda * \mu}|^2}{|k|^2} dk = (2\pi)^{-3} \int_{\mathbb{R}^3} \frac{4\pi |\widehat{\varphi_\lambda}|^2 |\widehat{\mu}|^2}{|k|^2} dk.$$

But $|\widehat{\varphi_\lambda}| \leqslant 1$, and $|\widehat{\varphi_\lambda}| \to 1$ as $\lambda \to 0$. Hence by the dominated convergence theorem,

$$E[\varphi_\lambda * \mu] \to E[\mu]$$

as $\lambda \to 0^+$. Then for $k > 1/\lambda_0$, $\nu_k := \varphi_{1/k} * \mu$ will suffice.

□

*Proof of theorem 3.2.1. Step 1. Reduction to the case of compactly supported $C^1$ densities.* Since $C(\overline{\Omega})$ is separable, the closed unit ball in $C(\overline{\Omega})^*$ is metrizable with respect to the vague (or weak*, equivalently) topology (cf. Lemma 3.101 in [47]). But $C(\overline{\Omega})^*$ is isometrically isomorphic to the set of signed Radon measures on $\overline{\Omega}$ by Theorem 7.18 in [25]. By identifying measures on $\overline{\Omega}$ with their zero extensions to $\mathbb{R}^3$, we find the closed unit ball of the set of signed Radon measures on $\overline{\Omega}$ to be isometrically isomorphic to $\mathcal{M}$, hence $\mathcal{M}$ is metrizable (with respect to vague convergence), say with metric $D$.

Now for $k \in \mathbb{N}$, we choose $\nu_k \in \mathcal{M}$ such that

- $\nu_k$ is compactly supported in $\Omega$,
- $\nu_k$ has $C^1$ density with respect to Lebesgue measure on $\mathbb{R}^3$,
- $D(\nu_k, \mu) < \frac{1}{k}$,
- $|E[\nu_k] - E[\mu]| < \frac{1}{k}$.

Suppose we can show the theorem for $\mu \in \mathcal{M}$ with $C^1$ density and $supp(\mu) \subset \Omega$. Then for each $\nu_k$ we can find a sequence $\mu'_n(\nu_k) \in \mathcal{A}$, $n = 1, 2 \ldots$, such that

- $\mu'_n(\nu_k) \rightharpoonup \nu_k$ as $n \to \infty$,
- $E_d[\mu'_n(\nu_k)] \to E[\nu_k]$ as $n \to \infty$.

Then for each $k = 1, 2, \ldots$, we choose $n_k \in \mathbb{N}$ such that

- $n_k$ is increasing with $k$,
- $D(\mu'_{n_k}(\nu_k), \nu_k) < 1/k$,
- $|E_d[\mu'_{n_k}(\nu_k)] - E[\nu_k]| < 1/k$.

Then $\mu_k := \mu'_{n_k}(\nu_k)$ is a discrete charge distribution in $\mathcal{A}$ that satisfies

$$D(\mu_k, \mu) = D(\mu'_{n_k}(\nu_k), \mu) \leqslant D(\mu'_{n_k}(\nu_k), \nu_k) + D(\nu_k, \mu) \leqslant 2/k,$$

so $\mu_k$ converges vaguely to $\mu$ as $k \to \infty$, and moreover,

$$|E_d[\mu_k] - E[\mu]| = \left|E_d[\mu'_{n_k}(\nu_k)] - E[\mu]\right|$$

$$\leqslant \left|E_d[\mu'_{n_k}(\nu_k)] - E[\nu_k]\right| + |E[\nu_k] - E[\mu]|$$
$$\leqslant 2/k,$$

so $E_d[\mu_k]$ converges to $E[\mu]$ as $k \to \infty$.

*Step 2. Construction of discrete densities.* It remains to prove the theorem for the case that $\mu \in \mathcal{M}$ with $C^1$ density and $supp(\mu) \subset \Omega$. The techniques of Chapter 2 will not suffice due to the unboundedness of $\mu$ with respect to Lebesgue density, so we implement a technical multiscale construction comparable to that in [9]. In this construction we will partition the region $\Omega$ at different scales: a mesoscale $h_n$ describing the cell width upon which the averaging procedure used to define density will take place, and a microscale $a_n$ characterizing the interparticle distances. Crucial will be how the various scales transform with the number of particles. If $N_n$ is the number of particles, then for the microscale, we will require that $a_n^3 \sim 1/N_n$, for this will enforce a "volume filling" property of the sets of point charges similar to the geometric properties enforced in Chapter 2. For the mesoscale, we will need the number of particles per mescoscale cell to increase without bound, necessitating a scaling law of $h_n^s \sim 1/N_n$ for some $s > 3$. For concreteness, we let $s = 4$, and to ensure that all lengths divide each other evenly, we partition $\Omega$ into diadic length boxes. With $a_n^3$ and $h_n^4$ both scaling as a power of 2 representing inverse particle number $1/N_n$, we set $N_n = 2^{12n}$ as a natural choice relative to which all other relative scales involved are made apparent.

Proceeding, we may assume that $d\mu = \rho dx$, with $\rho \in C^1(\mathbb{R}^3)$ and $supp(\mu) \subset \Omega$.

Cover $supp(\mu)$ by $m_0$ disjoint cubes contained in $\Omega$ of side length $h_0 = 2^{n_0}$ for $n_0 \in \mathbb{Z}$. Further subdivide these into smaller disjoint cubes $C_i$ of side length

$$h_n = h_0/8^n.$$

Then

$$supp(\mu) \subset \bigcup_{i=1}^{m_n} C_i \subset \Omega,$$

where

$$m_n = m_0(h_0/h)^3 = m_0 2^{9n} \tag{3.2.17}$$

is the number of smaller cubes. We set the number of particles of $\mu_n$ to be

$$N_n = 2^{12n}. \tag{3.2.18}$$

Recalling $\|\mu\|$ to denote the total variation norm of $\mu$, we select $l_i \in \mathbb{N} = \{0, 1, \ldots\}$ such that

$$\left| l_i - \frac{N_n|\mu|(C_i)}{\|\mu\|} \right| \leqslant 1 \tag{3.2.19}$$

and

$$\sum_{i=1}^{m_n} l_i = N_n. \tag{3.2.20}$$

$l_i$ is the number of particles to be placed in cube $C_i$, and $l_i/N_n$ approximates the fraction of total charge of $|\mu|$ that is contained in $C_i$ by choosing $l_i$ to be one of the two closest integers to $N_n|\mu|(C_i)/\|\mu\|$ in such a way that

$$\sum_i l_i = \sum_i \frac{N_n|\mu|(C_i)}{\|\mu\|} = N_n.$$

The $l_i$ charges to be placed in $C_i$ (with positions $x_j^i$ to be specified shortly) are each assigned a charge

$$q_i := \frac{\mu(C_i)\|\mu\|}{|\mu|(C_i)}. \tag{3.2.21}$$

Observe that $|q_i| \leqslant 1$, and our discrete density on $C_i$ will be

$$\mu_n|_{C_i} = \frac{1}{N_n} \sum_{j=1}^{l_i} q_i \delta_{x_j^i}. \tag{3.2.22}$$

Let $k_0 \in \mathbb{Z}$ be such that $2^{3k_0+2} \geqslant \|\rho\|_\infty / \|\mu\|$, and set $a_n := 2^{-4n-k_0-1}$ to be our interparticle distance. From (3.2.19) we have

$$\begin{aligned} l_i &\leqslant \frac{N_n |\mu|(C_i)}{\|\mu\|} + 1 \\ &\leqslant \frac{2^{12n} \|\rho\|_\infty h_n^3}{\|\mu\|} + 1 \\ &= \frac{2^{12n} \|\rho\|_\infty 2^{3n_0 - 9n}}{\|\mu\|} + 1 \\ &\leqslant 2^{12n + 3k_0 + 2 + 3n_0 - 9n} + 1 \\ &= 2^{3n + 3k_0 + 3n_0 + 2} + 1. \end{aligned}$$

Then for $n \geqslant -n_0 - k_0$ ($n_0$ and $k_0$ being two integer constants depending only on $\mu$) we have $l_i \leqslant 2^{3n+3k_0+3n_0+3}$, so

$$\left(\frac{h_n}{a_n}\right)^3 = \left(\frac{2^{n_0 - 3n}}{2^{-4n-k_0-1}}\right)^3 = 2^{3n+3k_0+3n_0+3} \geqslant l_i$$

for all $i = 1, \ldots, m_n$. Thus it makes sense to place $x_1^i, \ldots, x_{l_i}^i$ in distinct points of $a_n \mathbb{Z}^3 \cap C_i$ and define

$$\mu_n := \frac{1}{N_n} \sum_{i=1}^{m_n} \sum_{j=1}^{l_i} q_i \delta_{x_j^i}. \tag{3.2.23}$$

Observe that

$$\|\mu_n\| = \frac{1}{N_n} \sum_i l_i |q_i| \leqslant \frac{1}{N_n} \sum_i l_i = 1.$$

Having constructed our discrete density, we are ready to show the two convergences.

*Step 3. Vague convergence.* Let $g \in C_0(\mathbb{R}^3)$ and $c_i$ be the center of cube $C_i$. Then

$$\begin{aligned}\int_{\mathbb{R}^3} g d\mu_n - \int_{\mathbb{R}^3} g d\mu &= \sum_i \int_{C_i} [g(x) - g(c_i)] d\mu_n(x) \\ &\quad + \sum_i g(c_i) \left( \int_{C_i} d\mu_n(x) - \int_{C_i} d\mu(x) \right) \\ &\quad + \sum_i \int_{C_i} [g(c_i) - g(x)] d\mu(x),\end{aligned}$$

so

$$\begin{aligned}\left| \int_{\mathbb{R}^3} g d\mu_n - \int_{\mathbb{R}^3} g d\mu \right| &\leqslant \sum_i \int_{C_i} |g(x) - g(c_i)| d|\mu_n|(x) + \sum_i g(c_i) |\mu_n(C_i) - \mu(C_i)| \\ &\quad + \sum_i \int_{C_i} |g(x) - g(c_i)| d|\mu|(x) \\ &\leqslant \max_i \max_{x \in C_i} |g(x) - g(c_i)| \|\mu_n\| + \|g\|_\infty \sum_i |\mu_n(C_i) - \mu(C_i)| \\ &\quad + \max_i \max_{x \in C_i} |g(x) - g(c_i)| \|\mu\| \\ &\leqslant \max_i \max_{x \in C_i} |g(x) - g(c_i)| + m_n \|g\|_\infty \max_i |\mu_n(C_i) - \mu(C_i)| \\ &\quad + \max_i \max_{x \in C_i} |g(x) - g(c_i)|.\end{aligned}$$

The first and last terms go to 0 as $n \to \infty$ since $g$ is continuous and the diameter of each $C_i$ goes to 0 as $n \to \infty$.

For the middle term, we need the fact that (3.2.19), (3.2.21), and (3.2.22) imply that

$$|\mu_n(C_i) - \mu(C_i)| \leqslant \frac{1}{N_n} \tag{3.2.24}$$

holds for all $i = 1, \ldots, N_n$. Then

$$m_n \|g\|_\infty \max_i |\mu_n(C_i) - \mu(C_i)| \leqslant \frac{m_n}{N_n} \|g\|_\infty = m_0 \|g\|_\infty 2^{-3n},$$

which goes to 0 in the limit $n \to \infty$. This establishes the vague convergence of $\mu_n$ to $\mu$.

*Step 4. Energy convergence.* Let $\{x_k : k = 1, \ldots, N_n\}$ be a re–enumeration of $\{x_j^i : j = 1, \ldots, m_n, i = 1, \ldots, l_i\}$, so

$$\mu_n = \frac{1}{N_n} \sum_{k=1}^{N_n} q_k \delta_{x_k}.$$

Denote Coulomb potential $v(x) := \frac{1}{|x|}$, and for $\alpha > 0$, define cutoff Coulomb potential

$$v_\alpha(x) := \begin{cases} \frac{1}{|x|} & |x| \geqslant \alpha, \\ \frac{1}{\alpha} & |x| < \alpha. \end{cases}$$

Then

$$\begin{aligned}
E_d[\mu_n] - E[\mu] &= \iint\limits_{(\mathbb{R}^3 \times \mathbb{R}^3) \setminus D} \frac{d\mu_n(x) d\mu_n(y)}{|x-y|} - \iint\limits_{(\mathbb{R}^3 \times \mathbb{R}^3)} \frac{d\mu(x) d\mu(y)}{|x-y|} \\
&= \iint\limits_{(\mathbb{R}^3 \times \mathbb{R}^3) \setminus D} v(x-y) d\mu_n(x) d\mu_n(y) - \iint\limits_{(\mathbb{R}^3 \times \mathbb{R}^3)} v(x-y) d\mu(x) d\mu(y) \\
&= \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} v_\alpha(x-y) \Big( d\mu_n(x) d\mu_n(y) - d\mu(x) d\mu(y) \Big) \\
&\quad - \iint\limits_{D} v_\alpha(x-y) d\mu_n(x) d\mu_n(y)
\end{aligned}$$

$$+ \iint\limits_{(\mathbb{R}^3\times\mathbb{R}^3)\setminus D} \Big(\frac{1}{|x-y|} - v_\alpha(x-y)\Big) d\mu_n(x)d\mu_n(y)$$
$$- \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \Big(\frac{1}{|x-y|} - v_\alpha(x-y)\Big) d\mu(x)d\mu(y).$$

The first term goes to 0 as $n \to \infty$ since $\mu_n \times \mu_n \rightharpoonup \mu \times \mu$ and $v_\alpha$ is continuous.

The second term equals $\frac{1}{\alpha N_n^2}\sum_{k=1}^{N_n} q_k^2$ and is bounded in absolute value by $1/N_n\alpha$, which goes to 0 in the limit $n \to \infty$.

The fourth term is the negative of

$$\iint\limits_{|x-y|<\alpha} \frac{d\mu(x)d\mu(y)}{|x-y|},$$

and is bounded in absolute value by

$$\|\rho\|_\infty^2 \iint\limits_{(x,y)\in\overline{\Omega}\times\overline{\Omega},|x-y|<\alpha} \frac{dxdy}{|x-y|},$$

which can be made arbitrarily small for small $\alpha$ by the local integrability of $v$ (see Lemma 2.1.1).

Using Lemma 2.1.2, the third term is equal to

$$\frac{1}{N_n^2} \sum_{k,l:0<|x_k-x_l|<\alpha} \frac{q_k q_l}{|x_k-x_l|}$$
$$= \frac{1}{N_n^2|B_{a_n}|^2} \sum_{k,l:0<|x_k-x_l|<\alpha} q_k q_l \int_{B_{a_n}(x_k)} \int_{B_{a_n}(x_l)} \frac{1}{|x-y|} dxdy.$$

But $N_n|B_{a_n}| = 2^{12n}4\pi a^3/3 = \pi 2^{-3k_0-1}/3 =: C$ is constant, so the above expression is bounded in absolute value by

$$C^2 \iint_{(x,y)\in\overline{\Omega}\times\overline{\Omega},|x-y|<\alpha+a_n} \frac{dxdy}{|x-y|},$$

which converges as $n \to \infty$ to

$$C^2 \iint_{(x,y)\in\overline{\Omega}\times\overline{\Omega},|x-y|<\alpha} \frac{dxdy}{|x-y|},$$

which can be made arbitrarily small for small $\alpha$.

Thus we have shown that $E_d[\mu_n] \to E[\mu]$ as $n \to \infty$. □

## 3.3 Application to minimization in the presence of an external field

Let $\Omega \subset \mathbb{R}^3$ be a bounded domain with $C^2$ boundary, and suppose a signed Radon measure $\nu$ to be a fixed external charge density of total charge $\|\nu\| \leqslant 1$ that is compactly supported outside $\overline{\Omega}$. Consider the problem of minimizing the energy of of the combined distribution of charge $\mu + \nu$, where $\mu$ is allowed to vary over the set $\mathcal{M}$ of charge distributions (signed Radon measures) supported on $\overline{\Omega}$ of total charge (total variation) bounded by 1. This could apply, for example, to an implicit–solvent model in which $\Omega$ is the solvent region, $\nu$ represents fixed solute charges, and $\mu$ the distribution of ions in the solvent (cf. [64, 14, 27, 65, 41, 66, 18, 23, 53, 58, 10, 11, 71]).

Recall from (3.2.2) the mutual energy of (nonnegative) Radon measures, which is extended to signed Radon measures $\mu_1$ and $\mu_2$ with respective Jordan decompositions $\mu_1 = \mu_1^+ - \mu_1^-$, $\mu_2 = \mu_2^+ - \mu_2^-$, as

$$E[\mu_1, \mu_2] = E[\mu_1^+, \mu_2^+] + E[\mu_1^-, \mu_2^-] - E[\mu_1^+, \mu_2^-] - E[\mu_1^-, \mu_2^+], \tag{3.3.1}$$

provided this expression does not consist of infinities of opposite sign.

Then if it is defined, the electrostatic energy of our combined system is

$$E[\mu + \nu] = E[\mu] + 2E[\mu, \nu] + E[\nu].$$

$E[\nu]$ is the energy of the fixed charge distribution and is not assumed to be finite or even defined, but since it is constant, it can be disregarded for the purpose of minimization. It will be shown shortly that $E[\mu, \nu]$ is well defined for all $\mu \in \mathcal{M}$. Thus we are left with the problem of minimizing $E[\mu] + 2E[\mu, \nu]$ over $\mu \in \mathcal{M}$. Define functional $J : \mathcal{M} \to \mathbb{R} \cup \{\pm\infty\}$ by

$$J[\mu] := \begin{cases} E[\mu] + 2E[\mu, \nu] & \text{if } E[|\mu|] < \infty \\ \infty & \text{otherwise,} \end{cases}$$

and our minimization problem becomes the problem of finding $\underline{\mu} \in \mathcal{M}$ such that

$$J[\underline{\mu}] = \inf_{\mu \in \mathcal{M}} J[\mu]. \tag{3.3.2}$$

Likewise, we can consider discrete charge distributions in

$$\mathcal{A} = \left\{ \frac{1}{N} \sum_{i=1}^{N} q_i \delta_{x_i} \in \mathcal{M} : N \in \mathbb{N}, \{q_i\}_{i=1}^N \subset [-1, 1],\ \{x_i\}_{i=1}^N \subset \overline{\Omega} \text{ distinct} \right\}$$

with discrete energy functional $J_d : \mathcal{A} \to \mathbb{R} \cup \{\pm\infty\}$ given by

$$J_d[\mu] := E_d[\mu] + 2E[\mu, \nu].$$

Write

$$U^\nu(x) = \int_{\mathbb{R}^3} \frac{d\nu(y)}{|x-y|}$$

for the potential due to $\nu$. Since $\nu$ is compactly supported in $\overline{\Omega}^c$, there exists $r > 0$ such that $|x - y| > r$ for all $x \in \overline{\Omega}$ and $y \in supp(\nu)$. Then for $x, z \in \overline{\Omega}$,

$$|U^\nu(x) - U^\nu(z)| = \left| \int_{\mathbb{R}^3} \frac{d\nu(y)}{|x-y|} - \int_{\mathbb{R}^3} \frac{d\nu(y)}{|z-y|} \right| \leqslant \int_{\mathbb{R}^3} \frac{|x-z| d|\nu|(y)}{|x-y||z-y|}$$

$$\leqslant |x-z| \frac{\|\nu\|}{r^2},$$

so $U^\nu$ is Lipschitz continuous on $\overline{\Omega}$. Thus we find that $E[\mu,\nu] = \int U^\nu d\mu$ is well–defined and finite for all $\mu \in \mathcal{M}$. Then for $x \in \overline{\Omega}$ we find that

$$|U^\nu(x)| = \left| \int_{\mathbb{R}^3} \frac{d\nu(y)}{|x-y|} \right| \leqslant \int_{\mathbb{R}^3} \frac{d|\nu|(y)}{|x-y|} \leqslant \int_{\mathbb{R}^3} \frac{d|\nu|(y)}{r} = \frac{\|\nu\|}{r}, \tag{3.3.3}$$

so $U^\nu$ is bounded by $\|\nu\|/r$ on $\overline{\Omega}$, so for $\mu \in \mathcal{M}$ we find that

$$|E[\mu,\nu]| = \left| \int_{\mathbb{R}^3} U^\nu(x) d\mu(x) \right| \leqslant \int_{\mathbb{R}^3} |U^\nu(x)|\, d|\mu|(x) \leqslant \frac{\|\mu\|\|\nu\|}{r}.$$

**Theorem 3.3.1.** *Let $\Omega, \nu, J, J_d$ be as defined above.*

*(1) There exists a unique solution $\underline{\mu} \in \mathcal{M}$ to the minimization problem* (3.3.2), *and moreover, the support of $\underline{\mu}$ is contained in $\partial\Omega$.*

*(2) There exists a sequence of measures $\mu_n \in \mathcal{A}$ such that*

*(a)* $\mu_n \rightharpoonup \underline{\mu}$ *as* $n \to \infty$*,*

*(b)* $J_d[\mu_n] \to J[\underline{\mu}]$ *as* $n \to \infty$*.*

*(3) If* $\varepsilon > 0$ *is given, then the sequence* $\mu_n$ *may be constructed so as to have the support of* $\mu_n$ *contained in an* $\varepsilon$*–neighborhood of* $\partial\Omega$ *for all* $n$*.*

Here an "$\varepsilon$–neighborhood" of a set $A$ refers to

$$\bigcup_{y \in A} B_\varepsilon(y) = \{x : |x - y| < \varepsilon \text{ for some } y \in A\}.$$

*Proof.* Observe that an arbitrary $C^2$ domain $G \subset \mathbb{R}^3$ satisfies an exterior cone condition: every point $x \in \partial G$ is accessible from outside of $G$ by a finite cone that does not otherwise intersect $\overline{G}$. Then given any signed Radon measure $\alpha$ supported on $G$, there exists a new signed measure $\alpha'$ supported on $\partial G$ such that

$$U^{\alpha'}(x) = U^{\alpha}(x) \qquad \text{for all } x \notin G,$$

by Theorem 4.3 in [37]. Moreover, we have that $\|\alpha'\| \leqslant \|\alpha\|$, by Theorem 4.1 in [37].

Applying this to the present problem with $G = \mathbb{R}^3 \backslash \overline{\Omega}$, we have that there exists a signed Radon measure $\nu'$ supported on $\partial\Omega$ such that $\|\nu'\| \leqslant \|\nu\|$ (so $\nu' \in \mathcal{M}$) and $U^{\nu'} = U^{\nu}$ on $\overline{\Omega}$. Furthermore, we find by Corollary 2 to Theorem 4.6 in [37] that the induced measure $\nu'$ is unique, by the boundedness of $U^{\nu}$ on $\overline{\Omega}$ (cf. (3.3.3)). Then $E[\mu, \nu] = E[\mu, \nu']$, and while $E[\nu]$ may not be finite or even defined, we have that

$$E[\nu'] = \int_{\mathbb{R}^3} U^{\nu'} d\nu' = \int_{\mathbb{R}^3} U^{\nu} d\nu' = \iint\limits_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{d\nu(x) d\nu'(y)}{|x - y|} \leqslant \frac{\|\nu'\| \|\nu\|}{r} \leqslant \frac{1}{r} < \infty.$$

Thus, for $\mu \in \mathcal{M}$ with $E[|\mu|] < \infty$ we have that

$$E[\mu] + 2E[\mu, \nu] = E[\mu] + 2E[\mu, \nu'] + E[\nu'] - E[\nu'] = E[\mu + \nu'] - E[\nu']$$

so

$$J[\mu] = E[\mu + \nu'] - E[\nu']. \tag{3.3.4}$$

But

$$E[\mu + \nu'] = (2\pi)^{-3} \int_{\mathbb{R}^3} \frac{4\pi}{|k|^2} |\widehat{\mu} + \widehat{\nu'}|^2 dk$$

by Theorem B.2.4. Observe that if $\alpha$ is any signed Radon measure of compact support, then $\widehat{\alpha}$ is bounded and continuous, and

$$\int_{\mathbb{R}^3} \frac{|\widehat{\alpha}|^2}{|k|^2} dk = 0 \iff \widehat{\alpha} \equiv 0 \iff \alpha \text{ is the zero measure},$$

by uniqueness of the Fourier transform. Then we see that $J$ is uniquely minimized at $\underline{\mu} = -\nu' \in \mathcal{M}$, establishing (1). Note the minimum is then given by

$$J[-\nu'] = -E[\nu'].$$

Now that we have identified our minimizer of the continuum energy functional $J[\cdot]$, we can apply Theorem 3.2.1 of the previous section to yield a sequence of discrete charge distributions $\mu_n \in \mathcal{A}$ such that

- $\mu_n \rightharpoonup -\nu'$ as $n \to \infty$,
- $E_d[\mu_n] \to E[-\nu']$ as $n \to \infty$.

Since $U^\nu$ is continuous on $\overline{\Omega}$, we find that

$$\lim_{n\to\infty} E[\mu_n,\nu] = \lim_{n\to\infty}\int_\Omega U^\nu d\mu_n = -\int_\Omega U^\nu d\nu' = -\int_\Omega U^{\nu'} d\nu' = -E[\nu'],$$

so

$$\lim_{n\to\infty} J_d[\mu_n] = \lim_{n\to\infty}\Big(E_d[\mu_n] + 2E[\mu_n,\nu]\Big) = E[-\nu'] - 2E[\nu']$$
$$= E[\nu'] - 2E[\nu'] = -E[\nu'] = J[-\nu'] = \inf_{\mu\in\mathcal{M}} J[\mu],$$

establishing (2).

To show that our discrete densities may be assumed to be contained in an arbitrarily small neighborhood of $\partial\Omega$, refer to lemmas 3.2.1 and 3.2.2, which were used in the construction of the approximating discrete measures of Theorem 3.2.1. Recalling the notation of the lemmas, we had

- $d(x) = \min_{y\in\partial\Omega} |x-y|$ for $x \in \overline{\Omega}$,
- flow map $\Phi_t$ taking points to their position after time $t$ under the flow (3.2.3),
- smooth, nonnegative, radially symmetric unit mass mollifier $\varphi_\lambda$ compactly supported in $B_\lambda(0)$.

As shown in Lemma 3.2.1, the flow map $\Phi_t$ smoothly flows points on $\partial\Omega$ with velocity given by the inward normal vector, and there exists a $\delta > 0$ such that all points in $\{x \in \overline{\Omega} : d(x) < \delta\}$ flow with unit speed. Then for $0 \leqslant t < \delta$, we will have

$$\Phi_t(\partial\Omega) \subset \{x \in \overline{\Omega} : d(x) < t\}.$$

But

$$supp(\varphi_\lambda * \Phi_t\#\nu') \subset \bigcup_{y\in supp(\Phi_t\#\nu')} B_\lambda(y),$$

so $\varphi_\lambda * \Phi_t\#\nu'$ will be supported in a $\lambda$–neighborhood of a $t$–neighborhood of $\partial\Omega$. Hence, given any $\varepsilon > 0$, we can choose $t < \varepsilon/3$ and $\lambda < \varepsilon/3$ so

$$supp(\varphi_\lambda * \Phi_t\#\nu') \subset \{x \in \overline{\Omega} : d(x) < 2\varepsilon/3\}.$$

Referring now to the construction of the discrete densities in Step 2 of Theorem 3.2.1, we can choose the support of the discrete densities to be contained in an arbitrarily small neighborhood of the support of the smooth densities which they are approximating, hence they may be assumed to be contained in $\{x \in \overline{\Omega} : d(x) < \varepsilon\}$, establishing (3). $\square$

# Chapter 4

# Legendre Transforms

## 4.1 Introduction

We consider an ionic solution that consists of $M$ ionic species together with solvent and that occupies a bounded region $\Omega \subseteq \mathbb{R}^3$. A commonly used electrostatic free-energy functional, often termed the Poisson–Boltzmann (PB) electrostatic free-energy functional, takes the form [55, 63, 27, 10, 41, 24, 2, 14]

$$I[\phi] = \int_\Omega \left[ -\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) \right] dx. \tag{4.1.1}$$

Here, $\phi : \Omega \to \mathbb{R}$ is any possible electrostatic potential, $\varepsilon : \Omega \to \mathbb{R}$ is the dielectric coefficient that can vary spatially in the region $\Omega$, and $f : \Omega \to \mathbb{R}$ is the density of fixed charges. In the classical PB theory, the function $B : \mathbb{R} \to \mathbb{R}$ is given by

$$B(\phi) = \beta^{-1} \sum_{i=1}^{M} c_i^\infty \left( e^{-\beta q_i \phi} - 1 \right), \tag{4.1.2}$$

where $\beta = (k_{\mathrm{B}}T)^{-1}$ with $k_{\mathrm{B}}$ the Boltzmann constant and $T$ the absolute temperature, $c_i^\infty$ is the bulk concentration of the $i$th ionic species, and $q_i = Z_i e$ is the charge of an ion in the $i$th ionic species with $Z_i$ the valence of such an ion and $e$ the elementary charge. Note that the function $B = B(s)$ is smooth and strictly convex, and is minimized at $s = 0$ under the usual assumption of charge neutrality: $B'(0) = \sum_{i=1}^M c_i^\infty q_i = 0$. The Euler–Lagrange equation of the functional $I = I[\phi]$ is

$$\nabla \cdot \varepsilon \nabla \phi - B'(\phi) = -f. \tag{4.1.3}$$

This is exactly the PB equation for the equilibrium electrostatic potential $\phi$. Moreover, the functional value $I[\phi]$ at this critical point $\phi$, which is the same as the maximum value of the functional $I$, is exactly the (macroscopic) electrostatic free energy.

The functional $I$ defined in (4.1.1) is an expression of the electrostatic free energy through the equilibrium electrostatic potential of an underlying ionic system. It can be derived from minimizing the following effective electrostatic free-energy functional of all the ionic concentrations $c_i : \Omega \to [0, \infty)$ $(1 \leqslant i \leqslant M)$ [55, 10, 41, 24]:

$$\begin{aligned} &F[c] \\ &= \int_\Omega \left\{ \frac{1}{2} \left( f + \sum_{i=1}^M q_i c_i \right) \phi + \beta^{-1} \sum_{i=1}^M c_i \left[ \ln \left( \Lambda^3 c_i \right) - 1 \right] - \sum_{i=1}^M \mu_i c_i - \beta^{-1} \sum_{i=1}^M c_i^\infty \right\} dx, \end{aligned} \tag{4.1.4}$$

where $c = (c_1, \ldots, c_M)$. (We define $s \ln s = 0$ for $s = 0$.) The first part of the free energy $F[c]$ is the electrostatic potential energy, where $f + \sum_{i=1}^M q_i c_i$ is the total charge density and $\phi : \Omega \to \mathbb{R}$ is the corresponding electrostatic potential defined as the solution to Poisson's equation

$$\nabla \cdot \varepsilon \nabla \phi = -\left( f + \sum_{i=1}^{M} q_i c_i \right), \tag{4.1.5}$$

together with some boundary conditions. The second part, where $\Lambda$ is the thermal de Broglie wavelength, is the entropy of the ions. The third part of the free energy $F[c]$ arises from the constraint of a fixed total number of ions in each ionic species. Here $\mu_i$ is the chemical potential for an ion of the $i$th species and is related to other parameters by $\mu_i = \beta^{-1} \ln(\Lambda^3 c_i^\infty)$ [10]. The last part of the free energy $F[c]$ is the ionic pressure. Note that the functional $F$ is strictly convex. The equilibrium ionic concentrations $c_i = c_i(x)$ $(1 \leqslant i \leqslant M)$, defined by the vanishing of the first variations $\delta_{c_i} F[c] = 0$ $(1 \leqslant i \leqslant M)$, and the corresponding equilibrium electrostatic potential $\phi$, satisfy the Boltzmann distributions $c_i(x) = c_i^\infty e^{-\beta q_i \phi(x)}$ for $x \in \Omega$ and $i = 1, \ldots, M$. These and Poisson's equation (4.1.5) lead to the PB equation (4.1.3), where

$$-B'(\phi) = \sum_{i=1}^{M} c_i^\infty q_i e^{-\beta q_i \phi} = \sum_{i=1}^{M} q_i c_i$$

is exactly the local density of the ionic charges. Moreover, the free energy $F$ is minimized at the equilibrium concentrations, and this minimum value is exactly $I[\phi]$, the (macroscopic) electrostatic free energy; see, e.g., [41, 55, 10] for more details.

We remark that the variational approach in the PB theory has been generalized to include the ionic size effect (or excluded volume effect); cf. [34, 7, 41, 40] and also [4, 20, 12, 8, 31, 32, 69, 46, 72, 33, 43, 21, 45]. Let us denote by $v_i$ the volume of an ion in the $i$th ionic species $(1 \leqslant i \leqslant M)$. Let us also denote by $c_0 = c_0(x)$ $(x \in \Omega)$ the local concentration of solvent molecules, and by $v_0$ the volume of a solvent molecule. Then $\sum_{i=0}^{M} v_i c_i(x) = 1$ for all $x \in \Omega$. This means that the solvent concentration is determined by all the ionic concentrations. The generalized, size-modified electrostatic free-energy functional of all the ionic concentrations is the same as the functional $F[c]$ defined in (4.1.4), except that the entropy integrand term (i.e., the logarithmic term in the integrand) is replaced by $\beta^{-1} \sum_{i=0}^{M} \left[ c_i \ln(v_i c_i) - 1 \right]$, where the sum starts from $i = 0$ [34, 7, 40]. The new functional is strictly convex and admits a unique set of free-energy minimizing concentrations that are determined by the equilibrium conditions (i.e., the vanishing of first variations) [41, 40, 43]:

$$\frac{v_i}{v_0} \ln(v_0 c_0) - \ln(v_i c_i) = \beta \left( q_i \phi - \mu_i \right) \qquad \text{in } \Omega, \quad i = 1, \dots, M, \tag{4.1.6}$$

where $\phi$ is the corresponding electrostatic potential. This set of nonlinear algebraic equations determine uniquely the generalized Boltzmann distributions $c_i = c_i(\phi)$ $(i = 1, \dots, M)$. If all $v_i$ $(i = 0, 1, \dots, M)$ are the same, say, $v_i = v$, then such distributions are given by

$$c_i = \frac{c_i^\infty e^{-\beta q_i \phi}}{1 + \sum_{j=1}^{M} v c_j^\infty \left( e^{-\beta q_j \phi} - 1 \right)} \qquad \text{in } \Omega, \quad i = 1, \dots, M, \tag{4.1.7}$$

where $c_i^\infty = v^{-1} e^{\beta \mu_i} / (1 + \sum_{j=1}^{M} e^{\beta \mu_j})$ $(i = 1, \dots, M)$. If the sizes are nonuniform, then explicit formulas of Boltzmann distributions $c_i = c_i(\phi)$ $(i = 1, \dots, M)$ seem unavailable. (Numerically, one can minimize the free-energy functional of concentrations using Poisson's equation (4.1.5) as a constraint; cf. [72]. Alternatively, one can obtain such distributions by solving numerically the system of equations (4.1.6) for a set of values of $\phi$.) In any case (with or without the size effect included, and uniform or nonuniform size when the size effect is included), the minimum electrostatic free energy can be written in terms of the electrostatic potential $\phi$ as in (4.1.1), where the function $B : \mathbb{R} \to \mathbb{R}$ is defined by

$$-B'(\phi) = \sum_{i=1}^{M} q_i c_i(\phi) \qquad \text{and} \qquad B(0) = 0, \tag{4.1.8}$$

The condition of the charge neutrality is now $B'(0) = 0$. It is shown in [40] that $B$ is smooth, strictly convex, and minimized uniquely at 0. The generalized PB equation has exactly the same form as in (4.1.3).

An advantage of the PB theory (classical or size-modified) is that once the equilibrium potential $\phi$ is determined by solving the PB equation, all the ionic concentrations are also known. However, the fact that the critical point $\phi$ *maximizes* the functional $I$ defined in (4.1.1), due to the negative quadratic term in the functional, makes it inconsistent to couple the PB electrostatic free energy with other macroscopic energies, such as the surface energy of a dielectric boundary, that are often minimized to yield a stable equilibrium state. Naturally, one tries to construct a free-energy functional that is satisfactory in several ways. First, such a functional should have a unique minimizer and the corresponding minimum value should be the exact (macroscopic) electrostatic free energy. Second, the minimizer should satisfy the PB equation. It turns out that this is impossible as shown in [10].

To see the idea, let us only consider the case in which there are no mobile ionic charges; and hence set the $B$-term to be 0. The electrostatic energy is given by

$$E = \int_{\Omega} \frac{1}{2} f \phi \, dx, \tag{4.1.9}$$

where $\phi$ is the solution to Poisson's equation

$$\nabla \cdot \varepsilon \nabla \phi = -f, \tag{4.1.10}$$

together with some boundary conditions. Using this equation, we have by integration by parts that

$$\begin{aligned} E &= \int_\Omega \left( f\phi - \frac{1}{2} f\phi \right) dx \\ &= \int_\Omega \left[ f\phi + \frac{1}{2} (\nabla \cdot \varepsilon \nabla \phi)\phi \right] dx \\ &= \int_\Omega \left( f\phi - \frac{\varepsilon}{2} |\nabla \phi|^2 \right) dx + \text{ some boundary terms.} \end{aligned}$$

If the region $\Omega$ is large enough, with its boundary far away from the support of $f$ (the closure of the set of points where $f$ is not zero), then the boundary terms are small and can be neglected. This derivation shows how the negative quadratic term appears. Now the electrostatic potential $\phi$, the solution to Poisson's equation (4.1.10), maximizes this functional (without the boundary terms). One may try the following functional:

$$\int_\Omega \left( a|\nabla \phi|^2 + b\phi \right) dx,$$

for some $a$ and $b$ that can depend on $f$ and $\varepsilon$ but not on $\phi$. If the functional is minimized at some $\phi$ that solves Poisson's equation and the minimum value is the same as (4.1.9), then the only choice of $a$ and $b$ is that $a = -\varepsilon/2$ and $b = f$; cf. [10].

To resolve the issue of concavity of the PB free-energy functional, Maggs [48] constructed a Legendre transformed electrostatic free-energy functional of all possible electrostatic displacements $D : \Omega \to \mathbb{R}^3$ :

$$D \mapsto \int_\Omega \left[ \frac{1}{2\varepsilon} |D|^2 + B^*(f - \nabla \cdot D) \right] dx. \qquad (4.1.11)$$

Here $B^*$ is the Legendre transform of the function $B$. Indeed, the dielectric displacement is related to the electrostatic potential $\phi$ by $D = -\varepsilon \nabla \phi$. This allows us to rewrite

$$-\frac{\varepsilon}{2}|\nabla\phi|^2 = \frac{1}{2\varepsilon}|D|^2 + D\cdot\nabla\phi.$$

With this and an integration by parts, we can then rewrite the original PB functional (4.1.1) into

$$\begin{aligned}&\int_\Omega \left[-\frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi - B(\phi)\right] dx\\ &\qquad = \int_\Omega \left[\frac{1}{2\varepsilon}|D|^2 + (f-\nabla\cdot D)\phi - B(\phi)\right] dx + \text{boundary term.}\end{aligned}$$

Now, the terms $(f-\nabla\cdot D)\phi - B(\phi)$ are related to the Legendre transform of the convex function $B$ evaluated at $f-\nabla\cdot D$. Therefore, it is natural to construct the functional (4.1.11) [48]. Pujos and Maggs [54] applied this approach to develop models for computer simulations of fluctuations in ionic solution. Maggs and Podgornik [49] and Blossey, Maggs, and Podgornik [5] have also used the Legendre transformed functional to study the asymmetric steric effect and correlations in electrostatic interactions.

We recall that the Legendre transform $h^*:\mathbb{R}\to\mathbb{R}\cup\{+\infty\}$ for a given function $h:\mathbb{R}\to\mathbb{R}$ is defined by [56, 73]

$$h^*(\xi) = \sup_{s\in\mathbb{R}}\left[s\xi - h(s)\right] \qquad \forall\xi\in\mathbb{R}.$$

If $h$ is smooth, strictly convex, and minimized at some critical point, then $h^*:\mathbb{R}\to\mathbb{R}$ is also smooth and strictly convex, and we have the equivalences

$$h^*(\xi) = s^*\xi - h(s^*) \iff h'(s^*) = \xi \iff {h^*}'(\xi) = s^*. \tag{4.1.12}$$

In this chapter, we study mathematically Maggs' Legendre transformed functional with extension to several cases and with application to dielectric boundary implicit-solvent models for the solvation of charged molecules.

(1) We give a rigorous proof of the equivalence of the Legendre transformed functional (cf. (4.1.11)) and the original PB functional (cf. (4.1.1)). This means in particular that the minimizing displacement field $D$ of the Legendre transformed functional is exactly the one that corresponds to the maximizing potential $\phi$ of the PB functional: $D = -\varepsilon\nabla\phi$. We also derive the interface conditions for the equilibrium displacement for the case with a dielectric boundary.

(2) We study a phenomenological free-energy functional that includes higher-order gradients of the electrostatic potential, proposed by Bazant, Storey, and Kornyshev [3] for describing charge-charge correlations. In a simple setting (e.g., without the surface charges), this functional can be written as

$$\phi \mapsto \int_\Omega \left[ -\frac{\varepsilon}{2} \left( |\nabla\phi|^2 + l_c^2 |\Delta\phi|^2 \right) + f\phi - B(\phi) \right] dx,$$

where $l_c > 0$ is the (constant) correlation length. We shall introduce a corresponding Legendre transformed functional and prove that these functionals are equivalent.

(3) We consider the case where there are no mobile ions in an underlying electrostatic system. The electrostatic energy of such a system is the same as (4.1.1) except the $B$-term is not included. This setting is simpler but is in fact more subtle to understand, as the Legendre transform of the zero function is $+\infty$ everywhere except at 0. We shall first show that the electrostatic energy functional is equivalent to the Legendre transformed functional

$$D \mapsto \int_\Omega \frac{1}{2\varepsilon} |D|^2 dx \tag{4.1.13}$$

that is to be minimized over the class of displacements $D$ such that $\nabla \cdot D = f$ in $\Omega$. Following the suggestion in [48], we also consider a perturbed electrostatic energy functional

$$I_\mu[\phi] = \int_\Omega \left[ -\frac{\varepsilon}{2}|\nabla \phi|^2 + f\phi - \frac{\mu}{2}|\phi|^2 \right] dx,$$

where $\mu > 0$ is a small parameter. We apply the Legendre transform to this functional, and prove that the minimizing displacement and minimum value of the transformed energy converge as $\mu \to 0$ to the displacement of the maximizing electrostatic potential and maximum value of the original, unperturbed functional.

(4) We consider the dielectric boundary electrostatic free-energy functional in the implicit-solvent model for the solvation of charged molecules [71, 42, 17, 18]

$$I_\Gamma[\phi] = \int_\Omega \left[ -\frac{\varepsilon_\Gamma}{2}|\nabla \phi|^2 + f\phi - \chi_+ B(\phi) \right] dx.$$

Here, $\Gamma$ is the dielectric boundary—an interface that separates a solute region (i.e., the region of charged molecules) $\Omega_-$ from the solvent (e.g., salted water) region $\Omega_+$ in which there are mobile ions, $f$ represents the fixed charges of solute atoms, and $\chi_+ = \chi_{\Omega_+}$ is the characteristic function of the solvent region. The dielectric coefficient $\varepsilon_\Gamma$ is a constant in $\Omega_-$ and another constant in $\Omega_+$. The term $\chi_+ B(\phi)$ results from a usual assumption in the implicit-solvent modeling that the mobile ions do not penetrate into the solute region. Based on our analysis of the corresponding Legendre transform of the integrand of $I_\Gamma[\phi]$, we propose to use the same Legendre transformed electrostatic free-energy functional (4.1.11) but identify the admissible electrostatic displacements to be those vector fields $D : \Omega \to \mathbb{R}^3$ such that $\nabla \cdot D = f$ in $\Omega_-$. With such a setting, we again prove the equivalence of the two free-energy functionals.

## 4.2 Equivalence of two free-energy functionals

Let $\Omega$ be a bounded domain in $\mathbb{R}^3$ with a $C^2$ boundary $\partial\Omega$, $f \in L^2(\Omega)$, and $g \in W^{1,\infty}(\Omega)$. (We use standard notations of Lebesgue and Sobolev spaces as in [1, 26].) Denote

$$H^1_g(\Omega) = \left\{ u \in H^1(\Omega) : u = g \text{ on } \partial\Omega \right\}.$$

Here and below, the boundary values are understood in the sense of trace [1, 26]. Let $\varepsilon \in L^\infty(\Omega)$ be such that $\varepsilon_{\min} \leqslant \varepsilon(x) \leqslant \varepsilon_{\max}$ for all $x \in \Omega$, where $\varepsilon_{\min}$ and $\varepsilon_{\max}$ are two positive constants. Let $B \in C^3(\mathbb{R})$ be such that

(1) $B$ is strictly convex in $\mathbb{R}$;

(2) $B$ is minimized at 0 with minimum value $B(0) = 0$; and

(3) $B(\pm\infty) = \infty$, and either $B'(\pm\infty) = \pm\infty$ or $B'$ is bounded.

In the classical PB theory, the function $B$ is given in (4.1.2), and hence $B'(\pm\infty) = \pm\infty$. In the size-modified PB theory, it is shown in [40] that $B'$ is bounded. Note that the Legendre transform $B^* : \mathbb{R} \to \mathbb{R}$ is a strictly convex and $C^2$ function. In particular, $B^*(0) = 0$, since $B'(0) = 0$. We define $I : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$ by (4.1.1). Note that $I[\phi] < \infty$ for any $\phi \in H^1_g(\Omega)$.

**Theorem 4.2.1.** *The functional $I : H^1_g \to \mathbb{R} \cup \{-\infty\}$ has a unique maximizer $\phi_B \in H^1_g(\Omega)$ and the maximum value is finite. Moreover, $\phi_B$ is the unique weak solution to the boundary-value problem of PB equation*

$$\int_\Omega [\varepsilon \nabla \phi_B \cdot \nabla \eta + B'(\phi_B)\eta]\, dx = \int_\Omega f\eta\, dx \qquad \forall \eta \in H^1_0(\Omega), \tag{4.2.1}$$

*and* $\phi_B \in L^\infty(\Omega)$.

*Proof.* For the classical PB functional where the function $B$ is given in (4.1.2), this is similar to the proof of Theorem 2.1 in [42]. For the size-modified PB functional, where $B$ is given by (4.1.7) or implicitly by (4.1.8), this is similar to the proof of Theorem 5.1 in [40], where the fact that $\phi_B \in L^\infty(\Omega)$ is a direct consequence of the PB equation and regularity theory (e.g., Chapter 8 in [26]). $\square$

We denote

$$H(\mathrm{div}, \Omega) = \left\{ D \in \left[L^2(\Omega)\right]^3 : \nabla \cdot D \in L^2(\Omega) \right\},$$

where the divergence $\nabla \cdot D$ is defined in the weak sense:

$$\int_\Omega \nabla \cdot D \, \eta \, dx = -\int_\Omega D \cdot \nabla \eta \, dx \qquad \forall \eta \in H_0^1(\Omega). \tag{4.2.2}$$

We recall that $H(\mathrm{div}, \Omega)$ is a Hilbert space with the inner product [68]

$$\langle D, G \rangle = \int_\Omega \left[ D \cdot G + (\nabla \cdot D)(\nabla \cdot G) \right] dx \qquad \forall D, G \in H(\mathrm{div}, \Omega).$$

If $D \in H(\mathrm{div}, \Omega)$, then the trace $D \cdot n : \partial\Omega \to \mathbb{R}$ is in $L^2(\partial\Omega)$, where $n$ is the unit exterior normal at the boundary $\partial\Omega$, and

$$\int_\Omega (\nabla \cdot D) \, \eta \, dx = -\int_\Omega D \cdot \nabla \eta \, dx + \int_{\partial\Omega} (D \cdot n) \, \eta \, dS \qquad \forall \eta \in H^1(\Omega); \tag{4.2.3}$$

see [68]. We define $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ by

$$J[D] = \int_\Omega \left[ \frac{1}{2\varepsilon} |D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS. \tag{4.2.4}$$

Note that we have an additional boundary integral term in this functional, compared with the functional defined in (4.1.11). Formal calculations show that the Euler–Lagrange equation for the functional $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ is

$$\frac{D}{\varepsilon} + \nabla(B^{*\prime}(f - \nabla \cdot D)) = 0 \qquad \text{in } \Omega. \tag{4.2.5}$$

Let us denote

$$H_0(\mathrm{div}, \Omega) = \{D \in H(\mathrm{div}, \Omega) : D \cdot n = 0 \text{ on } \partial\Omega\}.$$

(Note that this is not the subspace of $H(\mathrm{div}, \Omega)$ that consists of divergence-free vector fields. The subscript 0 here indicates a vanishing normal component of the vector field on the boundary.) We call $D \in H(\mathrm{div}, \Omega)$ a weak solution to the Euler–Lagrange equation (4.2.5), if

$$\int_\Omega \left[ \frac{D \cdot G}{\varepsilon} - B^{*\prime}(f - \nabla \cdot D)(\nabla \cdot G) \right] dx = 0 \qquad \forall G \in H_0(\mathrm{div}, \Omega). \tag{4.2.6}$$

The following theorem indicates that the PB electrostatic free-energy functional $I$ defined in (4.1.1) and its Legendre transformed free-energy functional $J$ defined in (4.2.4) are equivalent:

**Theorem 4.2.2.** *We have*

$$I[\phi] \leqslant J[D] \qquad \forall \phi \in H_g^1(\Omega) \quad \forall D \in H(\mathrm{div}, \Omega). \tag{4.2.7}$$

*Moreover, if $\phi_B \in H_g^1(\Omega)$ is the unique maximizer of $I : H_g^1(\Omega) \to \mathbb{R} \cup \{-\infty\}$ and*

$D_B = -\varepsilon \nabla \phi_B$, *then* $D_B \in H(\mathrm{div}, \Omega)$ *and*

$$I[\phi_B] = \max_{\phi \in H_g^1(\Omega)} I[\phi] = \min_{D \in H(\mathrm{div},\Omega)} J[D] = J[D_B]. \tag{4.2.8}$$

*In particular,* $D_B$ *is the unique minimizer of* $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ *with a finite minimum value, and* $D_B$ *is also the unique weak solution to boundary-value problem of the Euler–Lagrange equation for the functional* $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$

$$\frac{D}{\varepsilon} + \nabla(B^{*\prime}(f - \nabla \cdot D)) = 0 \qquad \text{in } \Omega, \tag{4.2.9}$$

$$B^{*\prime}(f - \nabla \cdot D) = g \qquad \text{on } \partial\Omega. \tag{4.2.10}$$

We note that the inequality (4.2.7) shows that the functional of two-variable $(\phi, D)$ derived in [48] (cf. Eq. (17) there) is convex in $D$ and concave in $\phi$. We also note that, if $D = D_B$, then the Euler–Lagrange equation (4.2.9) is just the constitutive relation $D_B = -\varepsilon \nabla \phi_B$, and the boundary condition (4.2.10) is just the boundary condition for $\phi_B$: $\phi_B = g$ on $\partial\Omega$.

*Proof of Theorem 4.2.2.* Let $\phi \in H_g^1(\Omega)$ and $D \in H(\mathrm{div}, \Omega)$. By the definition of the Legendre transform and integration by parts, we obtain

$$\begin{aligned}
I[\phi] &= \int_\Omega \left[ -\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) \right] dx \\
&\leqslant \int_\Omega \left[ -\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) + \frac{1}{2\varepsilon} |D + \varepsilon \nabla \phi|^2 \right] dx \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon} |D|^2 + f\phi - B(\phi) + D \cdot \nabla \phi \right] dx \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon} |D|^2 + (f - \nabla \cdot D)\phi - B(\phi) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&\leqslant \int_\Omega \left[ \frac{1}{2\varepsilon} |D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS
\end{aligned}$$

$$= J[D]. \tag{4.2.11}$$

This proves (4.2.7).

Now let $\phi_B \in H_g^1(\Omega)$ be the unique maximizer of $I$ over $H_g^1(\Omega)$ and let $D_B = -\varepsilon\nabla\phi_B$. Clearly, $D_B \in [L^2(\Omega)]^3$. By (4.2.1) and (4.2.2), $\nabla\cdot D_B = f - B'(\phi_B) \in L^2(\Omega)$. Hence $D_B \in H(\mathrm{div}, \Omega)$. Moreover,

$$f - \nabla \cdot D_B = B'(\phi_B) \in H^1(\Omega). \tag{4.2.12}$$

This and (4.1.12) imply that

$$B^*(f - \nabla \cdot D_B) = (f - \nabla \cdot D_B)\phi_B - B(\phi_B) \qquad \text{a.e. } \Omega, \tag{4.2.13}$$

$$B^{*\prime}(f - \nabla \cdot D_B) = \phi_B \qquad \text{a.e. } \Omega. \tag{4.2.14}$$

Repeating similar steps in (4.2.11) above, we have then by (4.2.13) that

$$\begin{aligned}
I[\phi_B] &= \int_\Omega \left[ -\frac{\varepsilon}{2}|\nabla\phi_B|^2 + f\phi_B - B(\phi_B) \right] dx \\
&= \int_\Omega \left[ -\frac{\varepsilon}{2}|\nabla\phi_B|^2 + f\phi_B - B(\phi_B) + \frac{1}{2\varepsilon}|D_B + \varepsilon\nabla\phi_B|^2 \right] dx \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon}|D_B|^2 + f\phi_B - B(\phi_B) + D \cdot \nabla\phi_B \right] dx \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon}|D_B|^2 + (f - \nabla \cdot D_B)\phi_B - B(\phi_B) \right] dx + \int_{\partial\Omega} g D_B \cdot n \, dS \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon}|D_B|^2 + B^*(f - \nabla \cdot D_B) \right] dx + \int_{\partial\Omega} g D_B \cdot n \, dS \\
&= J[D_B]. 
\end{aligned} \tag{4.2.15}$$

By (4.2.11) and (4.2.15), we have for any $D \in H(\mathrm{div}, \Omega)$ that $J[D_B] = I[\phi_B] \leqslant J[D]$. This implies (4.2.8), and $D_B$ minimizes $J$ over $H(\mathrm{div}, \Omega)$. Since the Legendre transform takes convex functions to convex functions, the uniqueness of minimizer of $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ follows from the strict convexity of $J$. Clearly, the minimum value $J[D_B]$ is finite.

By Theorem 4.2.1, $\phi_B \in H^1(\Omega) \cap L^\infty(\Omega)$; and hence, by (4.2.12), $f - \nabla \cdot D_B \in H^1(\Omega) \cap L^\infty(\Omega)$. Consequently, for any $G \in [C^1(\overline{\Omega})]^3 \subset H(\mathrm{div}, \Omega)$, we conclude from that fact that $\delta J[D_B][G] := (d/dt)|_{t=0} J[D_B + tG] = 0$, and from the dominated convergence theorem allowing the exchange of the limit and integration that

$$\delta J[D_B][G] = \int_\Omega \left[ \frac{D_B \cdot G}{\varepsilon} + B^{*\prime}(f - \nabla \cdot D_B)(-\nabla \cdot G) \right] dx + \int_{\partial\Omega} gG \cdot n \, dS = 0. \tag{4.2.16}$$

By (4.2.14), $B^{*\prime}(f - \nabla \cdot D_B) = \phi_B \in H^1(\Omega) \cap L^\infty(\Omega)$. Note that $[C^1(\overline{\Omega})]^3$ is dense in $H(\mathrm{div}, \Omega)$. It then follows that (4.2.16) holds true for any $G \in H(\mathrm{div}, \Omega)$. In particular, (4.2.6) is true for any $G \in H_0(\mathrm{div}, \Omega)$, implying that that $D_B$ is a weak solution to (4.2.9). It follows from (4.2.3) and (4.2.16) with $G \in H(\mathrm{div}, \Omega)$ that

$$\int_\Omega \left[ \frac{D_B}{\varepsilon} + \nabla \left( B^{*\prime}(f - \nabla \cdot D_B) \right) \right] \cdot G \, dx + \int_{\partial\Omega} \left[ g - B^{*\prime}(f - \nabla \cdot D_B) \right] G \cdot n \, dS = 0. \tag{4.2.17}$$

By choosing $G \in H_0(\mathrm{div}, \Omega)$, we obtain (4.2.9) with $D = D_B$. The two equations (4.2.9) and (4.2.17) then imply that the second integral in (4.2.17) vanishes for any $G \in H(\mathrm{div}, \Omega)$. This leads to (4.2.10) with $D = D_B$. The uniqueness of the weak solution follows from the strict convexity of $B^*$ and a usual argument; cf. e.g., the proof of Theorem 2.1 in [42]. $\square$

Let us denote

$$W = \{D \in H(\mathrm{div}, \Omega) : \text{ there exists } \phi \in H^1(\Omega) \text{ such that } D = -\varepsilon \nabla \phi\}.$$

Clearly, this is a linear subspace of $H(\mathrm{div}, \Omega)$. The following is a direct consequence of Theorem 4.2.2:

**Corollary 4.2.1.** *Let $D_B$ be the minimizer of the functional $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ as stated in Theorem 4.2.2. Then, $D_B \in W$ and*

$$J[D_B] = \min_{D \in H(\mathrm{div},\Omega)} J[D] = \min_{D \in W} J[D].$$

We now consider the dielectric boundary problem and the interface conditions for the minimizer of the Legendre transformed functional. Let $\Gamma$ be a $C^2$, closed surface such that $\Gamma \subset \Omega$. Denote $\Omega_-$ the interior of $\Gamma$ and $\Omega_+ = \Omega \setminus \overline{\Omega_-}$. So, both $\Omega_-$ and $\Omega_+$ are bounded open sets in $\mathbb{R}^3$, and $\Omega = \Omega_- \cup \Omega_+ \cup \Gamma$. We assume now that the dielectric coefficient is given by

$$\varepsilon(x) = \varepsilon_\Gamma(x) = \begin{cases} \varepsilon_- & \text{if } x \in \Omega_-, \\ \varepsilon_+ & \text{if } x \in \Omega_+, \end{cases} \tag{4.2.18}$$

where $\varepsilon_-$ and $\varepsilon_+$ are two distinct positive numbers. We denote by $[\![u]\!] = u|_{\Omega_+} - u|_{\Omega_-}$ the jump across $\Gamma$ of a function $u : \Omega \to \mathbb{R}$ from $\Omega_+$ to $\Omega_-$. We also denote by $n$ the unit normal at $\Gamma$ pointing from $\Omega_-$ to $\Omega_+$. Since the piecewise constant function $\varepsilon \in L^\infty(\Omega)$, Theorem 4.2.2 still holds true. It follows from routine calculations [41, 42] that the maximizer $\phi_B \in H^1_g(\Omega)$ of $I : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$ is characterized by the following set of equations:

$$
\begin{cases}
\varepsilon_- \Delta \phi_B - B'(\phi_B) = -f & \text{in } \Omega_-, \\
\varepsilon_+ \Delta \phi_B - B'(\phi_B) = -f & \text{in } \Omega_+, \\
[\![\phi_B]\!] = 0 \quad \text{and} \quad [\![\varepsilon_\Gamma \nabla \phi_B \cdot n]\!] = 0 & \text{on } \Gamma, \\
\phi_B = g & \text{on } \partial\Omega.
\end{cases}
\tag{4.2.19}
$$

In particular, $\phi_B|_{\Omega_\pm} \in H^2(\Omega_\pm)$. The spaces $H^2(\Omega_\pm)$ can be replaced by $H^3(\Omega_\pm)$ if $f \in H^1(\Omega)$.

The following theorem provides a similar set of conditions that characterize the minimizer $D_B$ of the Legendre transformed functional $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ :

**Theorem 4.2.3.** *Assume $f \in H^1(\Omega)$. Let $D \in [L^2(\Omega)]^3$ be such that $D|_{\Omega_-} \in [H^2(\Omega_-)]^3$ and $D|_{\Omega_+} \in [H^2(\Omega_+)]^3$. Then $D = D_B \in H(\mathrm{div}, \Omega)$ (the unique minimizer of $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ as in Theorem 4.2.2) if and only if $D$ satisfies the following set of equations:*

$$
\begin{cases}
\dfrac{D}{\varepsilon_-} + \nabla \left( B^{*\prime}(f - \nabla \cdot D) \right) = 0 & \textit{in } \Omega_-, \\
\dfrac{D}{\varepsilon_+} + \nabla \left( B^{*\prime}(f - \nabla \cdot D) \right) = 0 & \textit{in } \Omega_+, \\
[\![D \cdot n]\!] = 0 \quad \textit{and} \quad [\![\nabla \cdot D]\!] = 0 & \textit{on } \Gamma, \\
B^{*\prime}(f - \nabla \cdot D) = g & \textit{on } \partial\Omega.
\end{cases}
\tag{4.2.20}
$$

We note that, if $D = D_B$, the unique minimizer of $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$, then $D = -\varepsilon_\Gamma \nabla \phi_B$ with $\phi_B$ the unique maximizer of $I : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$. Consequently, the first interface condition $[\![D \cdot n]\!] = 0$ on $\Gamma$ in (4.2.20) is exactly the second interface condition $[\![\varepsilon_\Gamma \nabla \phi_B \cdot n]\!] = 0$ on $\Gamma$ in (4.2.19); and, as shown below in the proof of Theorem 4.2.3, the second interface condition $[\![\nabla \cdot D]\!] = 0$ on $\Gamma$ in

(4.2.20) is exactly the first interface condition $[\![\phi_B]\!] = 0$ on $\Gamma$ in (4.2.19). Moreover, the last equations in (4.2.20) and (4.2.19) are exactly the same.

*Proof of Theorem 4.2.3.* Clearly, the minimizer $D_B = -\varepsilon_\Gamma \nabla \phi_B \in [L^2(\Omega)]^3$, where $\phi_B \in H^1_g(\Omega)$ is the maximizer of $I : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$. Moreover, by the regularity of $\phi_B$, we have $D_B|_{\Omega_\pm} \in [H^2(\Omega_\pm)]^3$. It follows from (4.2.16), the divergence theorem, and the fact that the unit normal $n$ points from $\Omega_-$ to $\Omega_+$ that

$$
\begin{aligned}
0 &= \delta J[D_B][G] && (4.2.21)\\
&= \int_{\Omega_-} \left[ \frac{D_B \cdot G}{\varepsilon} + B^{*\prime}(f - \nabla \cdot D_B)(-\nabla \cdot G) \right] dx \\
&\quad + \int_{\Omega_+} \left[ \frac{D_B \cdot G}{\varepsilon} + B^{*\prime}(f - \nabla \cdot D_B)(-\nabla \cdot G) \right] dx + \int_{\partial\Omega} gG \cdot n \, dS \\
&= \int_{\Omega_-} \left[ \frac{D_B}{\varepsilon} + \nabla \left( B^{*\prime}(f - \nabla \cdot D_B) \right) \right] \cdot G \, dx \\
&\quad + \int_{\Omega_+} \left[ \frac{D_B}{\varepsilon} + \nabla \left( B^{*\prime}(f - \nabla \cdot D_B) \right) \right] \cdot G \, dx + \int_\Gamma [\![B^{*\prime}(f - \nabla \cdot D_B)]\!] G \cdot n \, dS \\
&\quad + \int_{\partial\Omega} \left[ g - B^{*\prime}(f - \nabla \cdot D_B) \right] G \cdot n \, dS \qquad \forall G \in H(\mathrm{div}, \Omega). && (4.2.22)
\end{aligned}
$$

Choosing $G$ with its support inside $\Omega_+$ and $\Omega_-$ implies the first two equations in (4.2.20), respectively. As a result, the above equation is reduced to the one without any volume integrals. Choosing $G$ supported inside $\Omega$ implies that $[\![B^{*\prime}(f - \nabla \cdot D_B)]\!] = 0$, which further implies that $[\![\nabla \cdot D_B]\!] = 0$ on $\Gamma$, since $B^{*\prime}$ is a strictly monotonic function and the trace of $f \in H^1(\Omega)$ on $\Gamma$ is well defined. The above equation is then further reduced to the one with the right-hand side being only the integral over $\partial\Omega$. This then finally leads to the boundary condition in the last equation of (4.2.20). The first interface condition $[\![D_B \cdot n]\!] = 0$ follows from the relation $D_B = -\varepsilon_\Gamma \nabla \phi_B$ and the continuity $[\![\varepsilon_\Gamma \nabla \phi_B \cdot n]\!] = 0$ on $\Gamma$ in (4.2.19).

Assume now $D \in [L^2(\Omega)]^3$ with $D|_{\Omega_\pm} \in [H^2(\Omega_\pm)]^3$. Define $q \in L^2(\Omega)$ by

$q = \nabla \cdot D$ in $\Omega_- \cup \Omega_+$. Since $[\![D \cdot n]\!] = 0$ on $\Gamma$ and $n$ points from $\Omega_-$ to $\Omega_+$,

$$
\begin{aligned}
\int_\Omega qu\,dx &= \int_{\Omega_-} (\nabla \cdot D)u\,dx + \int_{\Omega_+} (\nabla \cdot D)u\,dx \\
&= -\int_{\Omega_-} D \cdot \nabla u\,dx - \int_{\Omega_+} D \cdot \nabla u\,dx - \int_\Gamma [\![D \cdot n]\!] u\,dS \\
&= -\int_\Omega D \cdot \nabla u\,dx \qquad \forall u \in H_0^1(\Omega).
\end{aligned}
$$

Hence, $q = \nabla \cdot D$ and $D \in H(\mathrm{div}, \Omega)$. If $D$ also satisfies (4.2.20), then we have by the similar calculations as before (cf. (4.2.16) and (4.2.21)) that $\delta J[D][G] = 0$ for all $G \in H(\mathrm{div}, \Omega)$. Since $J$ is strictly convex, $D$ is the unique minimizer of $J$, and hence $D = D_B$. □

## 4.3 The case with a higher-order gradient term

In this (and only in this) section, we shall assume that $\varepsilon$ is a constant for simplicity. We also assume that the boundary of $\Omega$, and the function $f$ and $g$ on $\Omega$ are all sufficiently smooth so that the solution to an underlying boundary-value problem of partial differential equation is regular enough. Let $\sigma > 0$ be a constant. We define

$$H_g^2(\Omega) = \{\phi \in H^2(\Omega) : \phi = g \text{ and } \partial_n \phi = \partial_n g \text{ on } \partial\Omega\},$$

and $\hat{I} : H_g^2(\Omega) \to \mathbb{R} \cup \{-\infty\}$ by [3]

$$\hat{I}[\phi] = \int_\Omega \left[ -\frac{\sigma}{2}(\Delta\phi)^2 - \frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi - B(\phi) \right] dx.$$

Here the higher-order gradient term $-(\sigma/2)|\Delta\phi|^2$ describes the ion-ion correlation with $\sqrt{\sigma/\varepsilon}$ the correlation length [3]. This functional is the same as the phenomenological electrostatic free-energy functional proposed in [3] except we drop the surface charge term for simplicity. By formal calculations, the Euler–Lagrange equation of the functional $\widehat{I}$ is

$$\sigma\Delta^2\phi - \varepsilon\Delta\phi + B'(\phi) = f \qquad \text{in } \Omega.$$

A function $\phi \in H^2_g(\Omega)$ is a weak solution to this equation if

$$\int_\Omega \left[\sigma\Delta\phi\Delta\eta + \varepsilon\nabla\phi\cdot\nabla\eta + B'(\phi)\eta\right]\, dx = \int_\Omega f\eta\, dx \qquad \forall \eta \in H^2_0(\Omega). \tag{4.3.1}$$

**Theorem 4.3.1.** *There exists a unique $\hat{\phi} \in H^2_g(\Omega)$ such that*

$$\hat{I}[\hat{\phi}] = \max_{\phi\in H^2_g(\Omega)} \hat{I}[\phi]$$

*with a finite maximum value. Moreover, $\hat{\phi}$ is the unique weak solution to the boundary-value problem*

$$\sigma\Delta^2\phi - \varepsilon\Delta\phi + B'(\phi) = f \qquad \textit{in } \Omega, \tag{4.3.2}$$

$$\phi = g \quad \textit{and} \quad \partial_n\phi = \partial_n g \qquad \textit{on } \partial\Omega. \tag{4.3.3}$$

*Proof.* We consider equivalently the minimization of the functional $-\hat{I}$. Note that $u \mapsto \|\Delta u\|_{L^2(\Omega)}$ is a norm of $H^2_0(\Omega)$ that is equivalent to the $H^2(\Omega)$-norm. Therefore, since $B \geqslant 0$, there exist constants $C_1 > 0$ and $C_2 \geqslant 0$ such that

$$-\hat{I}[u] \geqslant C_1\|u\|^2_{H^2(\Omega)} - C_2 \qquad \forall u \in H^2_g(\Omega). \tag{4.3.4}$$

Now, let $\alpha = \inf_{\phi\in H^2_g(\Omega)}(-\hat{I})[\phi] > -\infty$. Clearly, $\alpha \leqslant (-\hat{I})[g] < \infty$ and hence $\alpha$ is finite. Let $\phi_j \in H^2_g(\Omega)$ $(j = 1, 2, \dots)$ be such that $(-\hat{I})[\phi_j] \to \alpha$. Then, it follows from (4.3.4) that $\{\phi_j\}$ is bounded in $H^2(\Omega)$. Since $H^2(\Omega)$ is a Hilbert space and can be compactly embedded into $H^1(\Omega)$ and $C(\overline{\Omega})$, there exists a subsequence, not relabeled, of $\{\phi_j\}$ that converges weakly in $H^2(\Omega)$, strongly in $H^1(\Omega)$, and uniformly on $\overline{\Omega}$ to some $\hat{\phi} \in H^2(\Omega)$. Since $H^2_g(\Omega)$ is convex and closed in $H^2(\Omega)$ by the trace theorem [22, 26], it is weakly closed in $H^2_g(\Omega)$. Hence $\hat{\phi} \in H^2_g(\Omega)$. Clearly, $-\hat{I}$ is strictly convex. Moreover, it is continuous with respect to the strong convergence of $H^2(\Omega)$. Therefore, $-\hat{I}$ is weakly lower-semicontinuous, and hence $\liminf_{j\to\infty}(-\hat{I})[\phi_j] \geqslant (-\hat{I})[\hat{\phi}]$. This implies that $(-\hat{I})[\hat{\phi}] = \alpha$ and that $\hat{\phi}$ is a minimizer of $-\hat{I}$ over $H^2_g(\Omega)$. The uniqueness of such a minimizer is a consequence of the strict convexity of the functional $-\hat{I}$. Finally, noting that $\hat{\phi} \in C(\overline{\Omega})$, we obtain (4.3.1), with $\hat{\phi}$ replacing $\phi$, by routine calculations; hence $\hat{\phi} \in H^2_g(\Omega)$ is a weak solution to the boundary-value problem (4.3.2) and (4.3.3). The uniqueness of such a weak solution again follows from the strict convexity of the functional $-\hat{I}$. $\square$

We define

$$H^2(\mathrm{div}, \Omega) = \{D \in [H^2(\Omega)]^3 : \nabla \cdot D \in H^2(\Omega)\}.$$

Note that if $D \in H^2(\mathrm{div}, \Omega)$ then

$$\int_\Omega \Delta(\nabla \cdot D)\,\eta\,dx = -\int_\Omega \nabla(\nabla \cdot D)\cdot\nabla\eta\,dx + \int_{\partial\Omega} \partial_n(\nabla \cdot D)\,\eta\,dS \qquad \forall \eta \in H^1(\Omega).$$

We define the Legendre transformed functional $\hat{J} : H^2(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ of the functional $\hat{I} : H^2_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$ by

$$\hat{J}[D] = \int_\Omega \left[ \frac{1}{2\varepsilon}|D|^2 + \frac{\sigma}{2\varepsilon}|\nabla \cdot D|^2 + B^*\left(f - \nabla \cdot D + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot D)\right)\right] dx$$

$$+\int_{\partial\Omega}\left\{\left[D\cdot n-\frac{\sigma}{\varepsilon}\partial_n(\nabla\cdot D)\right]g+\frac{\sigma}{\varepsilon}(\nabla\cdot D)\partial_n g\right\}dS.$$

The following theorem is parallel to Theorem 4.2.2:

**Theorem 4.3.2.** *We have*

$$\hat{I}[\phi]\leqslant\hat{J}[D]\qquad\forall\phi\in H_g^2(\Omega)\quad\forall D\in H^2(\mathrm{div},\Omega).\tag{4.3.5}$$

*Moreover, if $\hat{\phi}\in H_g^2(\Omega)$ is the unique maximizer of $\hat{I}:H_g^2(\Omega)\to\mathbb{R}\cup\{-\infty\}$ and $\hat{D}=-\varepsilon\nabla\hat{\phi}$, then $\hat{D}\in H^2(\mathrm{div},\Omega)$ and*

$$\hat{I}[\hat{\phi}]=\max_{\phi\in H_g^2(\Omega)}\hat{I}[\phi]=\min_{D\in H^2(\mathrm{div},\Omega)}\hat{J}[D]=\hat{J}[\hat{D}].\tag{4.3.6}$$

*In particular, $\hat{D}$ is the unique minimizer of $\hat{J}:H^2(\mathrm{div},\Omega)\to\mathbb{R}\cup\{+\infty\}$ with a finite minimum value.*

*Proof.* Fix $\phi\in H_g^2(\Omega)$ and $D\in H^2(\mathrm{div},\Omega)$. We have by the definition of $\hat{I}[\phi]$ and $\hat{J}[D]$, integration by parts, and the fact that $\phi=g$ and $\partial_n\phi=\partial_n g$ on $\partial\Omega$ that

$$\begin{aligned}
\hat{I}[\phi]&=\int_\Omega\left[-\frac{\sigma}{2}(\Delta\phi)^2-\frac{\varepsilon}{2}|\nabla\phi|^2+f\phi-B(\phi)\right]dx\\
&\leqslant\int_\Omega\Big[-\frac{\sigma}{2}(\Delta\phi)^2-\frac{\varepsilon}{2}|\nabla\phi|^2+f\phi-B(\phi)+\frac{\sigma}{2\varepsilon^2}|\nabla\cdot D+\varepsilon\Delta\phi|^2\\
&\qquad+\frac{1}{2\varepsilon}|D+\varepsilon\nabla\phi|^2\Big]dx\\
&=\int_\Omega\left[\frac{\sigma}{2\varepsilon^2}|\nabla\cdot D|^2+\frac{1}{2\varepsilon}|D|^2+f\phi-B(\phi)+\frac{\sigma}{\varepsilon}(\nabla\cdot D)\Delta\phi+D\cdot\nabla\phi\right]dx\\
&=\int_\Omega\left[\frac{\sigma}{2\varepsilon^2}|\nabla\cdot D|^2+\frac{1}{2\varepsilon}|D|^2+f\phi-B(\phi)-\frac{\sigma}{\varepsilon}\nabla(\nabla\cdot D)\cdot\nabla\phi-(\nabla\cdot D)\phi\right]dx\\
&\qquad+\int_{\partial\Omega}\left[\frac{\sigma}{\varepsilon}(\nabla\cdot D)\partial_n g+(D\cdot n)g\right]dS\\
&=\int_\Omega\left[\frac{\sigma}{2\varepsilon^2}|\nabla\cdot D|^2+\frac{1}{2\varepsilon}|D|^2+\phi\left(f-\nabla\cdot D+\frac{\sigma}{\varepsilon}\Delta(\nabla\cdot D)\right)-B(\phi)\right]dx
\end{aligned}$$

$$
\begin{aligned}
&\quad + \int_{\partial\Omega} \left[ \frac{\sigma}{\varepsilon}(\nabla \cdot D)\partial_n g + (D \cdot n)g - \frac{\sigma}{\varepsilon}\partial_n(\nabla \cdot D)g \right] dS \\
&\leqslant \int_\Omega \left[ \frac{1}{2\varepsilon}|D|^2 + \frac{\sigma}{2\varepsilon^2}|\nabla \cdot D|^2 + B^* \left( f - \nabla \cdot D + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot D) \right) \right] dx \\
&\quad + \int_{\partial\Omega} \left\{ \left[ D \cdot n - \frac{\sigma}{\varepsilon}\partial_n(\nabla \cdot D) \right] g + \frac{\sigma}{\varepsilon}(\nabla \cdot D)\partial_n g \right\} dS. \\
&= \hat{J}[D]. \qquad (4.3.7)
\end{aligned}
$$

This proves (4.3.5).

Now let $\hat{\phi} \in H_g^2(\Omega)$ be the unique maximizer of $\hat{I}$ over $H_g^2(\Omega)$ and let $\hat{D} = -\varepsilon\nabla\hat{\phi}$. Since $\hat{\phi}$ satisfies (4.3.2) and all $\Omega$, $f$, and $g$ are sufficiently smooth, we have $\hat{\phi} \in H^3(\Omega)$ and $\Delta\hat{\phi} \in H^2(\Omega)$. These imply that $\hat{D} \in H^2(\mathrm{div}, \Omega)$. Moreover, by (4.3.2) again, we have

$$
f - \nabla \cdot \hat{D} + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot \hat{D}) = B'(\hat{\phi}) \qquad \text{a.e. } \Omega. \qquad (4.3.8)
$$

This and (4.1.12) imply that

$$
B^* \left( f - \nabla \cdot \hat{D} + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot \hat{D}) \right) = \hat{\phi} \left( f - \nabla \cdot \hat{D} + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot \hat{D} \right) - B(\hat{\phi}) \qquad \text{a.e. } \Omega. \qquad (4.3.9)
$$

Repeating (4.3.7) above with $\hat{\phi}$ and $\hat{D}$ replacing $\phi$ and $D$, respectively, noting that the two inequalities are in fact equalities in this case, we then obtain $\hat{I}[\hat{\phi}] = \hat{J}[\hat{D}]$. This implies (4.3.6). Hence $\hat{D}$ minimizes $\hat{J}$ over $H^2(\mathrm{div}, \Omega)$. Since the Legendre transform takes convex functions to convex functions, the uniqueness of the minimizer of $\hat{J} : H^2(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ follows from the strict convexity of $\hat{J}$. Clearly, the minimum value $\hat{J}[\hat{D}]$ is finite. □

## 4.4 The case without ions

We define $I_0 : H_g^1(\Omega) \to \mathbb{R}$ by

$$I_0[\phi] = \int_\Omega \left( -\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi \right) dx \qquad \forall \phi \in H_g^1(\Omega). \tag{4.4.1}$$

This functional is the same as $I[\phi]$ with $B(\phi)$ replaced by the 0 function. Let us denote by $B_0$ the 0 function, i.e., $B_0(s) = 0$ for all $s \in \mathbb{R}$. As in the previous case, we define $\tilde{J}_0 : H(\text{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ by

$$\tilde{J}_0[D] = \int_\Omega \left[ \frac{1}{2\varepsilon} |D|^2 + B_0^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} gD \cdot n \, dS \qquad \forall D \in H(\text{div}, \Omega).$$

However, by the definition of Legendre transform, $B_0^*(\xi) = \infty$ if $\xi \neq 0$ and $B_0^*(0) = 0$. Hence, $\tilde{J}_0[D] = +\infty$ for all $D \in H(\text{div}, \Omega)$ except those that satisfy $\nabla \cdot D = f$ a.e. in $\Omega$. We therefore consider the following constrained variational problem: Minimize the functional $J_0 : H(\text{div}_f, \Omega) \to \mathbb{R}$, defined by

$$J_0[D] = \int_\Omega \frac{1}{2\varepsilon} |D|^2 dx + \int_{\partial\Omega} gD \cdot n \, dS \qquad \forall D \in H(\text{div}_\text{f}, \Omega),$$

where

$$H(\text{div}_\text{f}, \Omega) = \{\text{D} \in \text{H}(\text{div}, \Omega) : \nabla \cdot \text{D} = \text{f a.e. } \Omega\}.$$

Note that $J_0$ differs from the functional defined in (4.1.13) by the boundary integral term.

We recall that there exists a unique $\phi_0 \in H_g^1(\Omega)$ that maximizes $I_0$ over $H_g^1(\Omega)$, and the maximizer $\phi_0$ is the unique weak solution to $\nabla \cdot \varepsilon \nabla \phi_0 = -f$ in $\Omega$ and $\phi_0 = g$ on $\partial\Omega$; cf. [22, 26, 41].

**Theorem 4.4.1.** *We have*

$$I_0[\phi] \leqslant J_0[D] \qquad \forall \phi \in H_g^1(\Omega) \quad \forall D \in H(\mathrm{div}_\mathrm{f}, \Omega). \tag{4.4.2}$$

*Moreover, if* $\phi_0 \in H_g^1(\Omega)$ *is the unique maximizer of* $I_0 : H_g^1(\Omega) \to \mathbb{R}$ *and* $D_0 = -\varepsilon \nabla \phi_0$*, then* $D_0 \in H(\mathrm{div}_\mathrm{f}, \Omega)$ *and*

$$J_0[D_0] = \min_{D \in H(\mathrm{div}_\mathrm{f}, \Omega)} J[D] = \max_{\phi \in H_g^1(\Omega)} I_0[\phi] = I_0[\phi_0]. \tag{4.4.3}$$

*In particular,* $D_0$ *is the unique minimizer of* $J_0 : H(\mathrm{div}_\mathrm{f}, \Omega) \to \mathbb{R}$ *and the minimum value is finite.*

*Proof.* Let $\phi \in H_g^1(\Omega)$ and $D \in H(\mathrm{div}_\mathrm{f}, \Omega)$. Similar to the proof of (4.2.11) but with the fact that $\nabla \cdot D = f$ a.e. in $\Omega$, we have

$$\begin{aligned}
I_0[\phi] &= \int_\Omega \left( -\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi \right) dx \\
&\leqslant \int_\Omega \left( -\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi + \frac{1}{2\varepsilon} |D + \varepsilon \nabla \phi|^2 \right) dx \\
&= \int_\Omega \left( \frac{1}{2\varepsilon} |D|^2 + f\phi + D \cdot \nabla \phi \right) dx \\
&= \int_\Omega \frac{1}{2\varepsilon} |D|^2 dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&= J_0[D].
\end{aligned}$$

This proves (4.4.2). Clearly, $D_0 \in H(\mathrm{div}_\mathrm{f}, \Omega)$, since $\phi_0$ is the weak solution to $\nabla \cdot \varepsilon \nabla \phi_0 = -f$. To prove (4.4.3), we notice that the above inequality is in fact an equality if we replace $\phi$ by $\phi_0$ and $D$ by $D_0$, respectively. This equality and (4.4.2) then lead to (4.4.3). Now (4.4.3) implies that $D_0$ is a minimizer of $J_0$ over $H(\mathrm{div}_\mathrm{f}, \Omega)$. It is the unique minimizer, since $J_0$ is convex. $\square$

We now consider a different approach as suggested in [48]. We approximate the functional $I_0$ by $I_\mu : H_g^1(\Omega) \to \mathbb{R}$ with $\mu > 0$, defined by

$$I_\mu[\phi] = \int_\Omega \left( -\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - \frac{\mu}{2}\phi^2 \right) dx \qquad \forall \phi \in H_g^1(\Omega). \tag{4.4.4}$$

For any $\mu > 0$, let us define $B_\mu : \mathbb{R} \to \mathbb{R}$ by $B_\mu(s) = \mu s^2/2$. It is easy to verify that the Legendre transform of $B_\mu$ is given by $B_\mu^*(\xi) = \xi^2/2\mu$ for any $\xi \in \mathbb{R}$. Correspondingly, for each $\mu > 0$, we define the Legendre transformed functional $J_\mu : H(\mathrm{div}, \Omega) \to \mathbb{R}$ by

$$J_\mu[D] = \int_\Omega \left( \frac{1}{2\varepsilon} |D|^2 + \frac{1}{2\mu} |f - \nabla \cdot D|^2 \right) dx + \int_{\partial\Omega} gD \cdot n \, dS \qquad \forall D \in H(\mathrm{div}, \Omega).$$

**Theorem 4.4.2.** (1) *For each $\mu \geqslant 0$, there exists a unique $\phi_\mu \in H_g^1(\Omega)$ that maximizes $I_\mu : H_g^1(\Omega) \to \mathbb{R}$ and that is also the unique weak solution to the boundary-value problem*

$$\begin{cases} \nabla \cdot \varepsilon \nabla \phi_\mu - \mu \phi_\mu = -f & \text{in } \Omega, \\ \phi_\mu = g & \text{on } \partial\Omega. \end{cases} \tag{4.4.5}$$

(2) *We have for any $\mu > 0$ that*

$$I_\mu[\phi] \leqslant J_\mu[D] \qquad \forall \phi \in H_g^1(\Omega) \quad \forall D \in H(\mathrm{div}, \Omega). \tag{4.4.6}$$

*Let $\phi_\mu$ be the maximizer of $I_\mu : H_g^1(\Omega) \to \mathbb{R}$ and $D_\mu = -\varepsilon \nabla \phi_\mu$ ($\mu \geqslant 0$). Then we have for any $\mu > 0$ that*

$$I_\mu[\phi_\mu] = \max_{\phi \in H_g^1(\Omega)} I_\mu[\phi] = \min_{D \in H(\mathrm{div}, \Omega)} J_\mu[D] = J_\mu[D_\mu]. \tag{4.4.7}$$

*In particular, $D_\mu$ is the unique minimizer of $J_\mu : H(\mathrm{div}, \Omega) \to \mathbb{R}$.*

(3) *There exist constants $C > 0$ and $\mu_0 > 0$, depending only on $\Omega$, $f$, $g$, and $\varepsilon_{\min}$ and $\varepsilon_{\max}$, such that for all $\mu \in (0, \mu_0]$*

$$\|D_\mu - D_0\|_{L^2(\Omega)} \leqslant \varepsilon_{\max}\|\phi_\mu - \phi_0\|_{H^1(\Omega)} \leqslant C\mu, \tag{4.4.8}$$

$$|J_\mu[D_\mu] - I_0[\phi_0]| = |I_\mu[\phi_\mu] - I_0[\phi_0]| \leqslant C\mu. \tag{4.4.9}$$

*Proof.* (1) This part is standard; cf. [22, 26].

(2) The proof of this part is the same as that of Theorem 4.2.2 with $B_\mu$, $\phi_\mu$, and $D_\mu$ replacing $B$, $\phi_B$, and $D_B$, respectively.

(3) By (1), $\phi_\mu$ ($\mu > 0$) and $\phi_0$ satisfy

$$\int_\Omega (\varepsilon\nabla\phi_\mu \cdot \nabla\eta + \mu\phi_\mu\eta)\, dx = \int_\Omega f\eta\, dx \qquad \forall\eta \in H_0^1(\Omega), \tag{4.4.10}$$

$$\int_\Omega \varepsilon\nabla\phi_0 \cdot \nabla\eta\, dx = \int_\Omega f\eta\, dx \qquad \forall\eta \in H_0^1(\Omega), \tag{4.4.11}$$

respectively. Letting $\eta = \phi_\mu - \phi_0 \in H_0^1(\Omega)$ and subtracting (4.4.11) from (4.4.10), we get

$$\int_\Omega \varepsilon|\nabla\phi_\mu - \nabla\phi_0|^2 dx = -\mu\int_\Omega \phi_\mu(\phi_\mu - \phi_0)\, dx.$$

It then follows from Poincaré's inequality and the Cauchy–Schwarz inequality that

$$\|\phi_\mu - \phi_0\|^2_{H^1(\Omega)} \leqslant C\mu\|\phi_\mu\|_{L^2(\Omega)}\|\phi_\mu - \phi_0\|_{L^2(\Omega)}.$$

Here $C$ denotes a generic constant that only depends on $\Omega$, $f$, $g$, $\varepsilon_-$, and $\varepsilon_+$. Consequently,

$$\|\phi_\mu - \phi_0\|_{H^1(\Omega)} \leqslant C\mu\|\phi_\mu\|_{L^2(\Omega)} \leqslant C\mu\|\phi_\mu - \phi_0\|_{L^2(\Omega)} + C\mu\|\phi_0\|_{L^2(\Omega)}.$$

Note $\phi_0$ only depends on $\Omega$, $f$, $g$, $\varepsilon_-$, and $\varepsilon_+$. Hence, we obtain the second inequality in (4.4.8) for all $\mu \in (0, \mu_0]$ for some $\mu_0 > 0$ sufficiently small and depending only on $\Omega$, $f$, $g$, $\varepsilon_-$, and $\varepsilon_+$. The first inequality in (4.4.8) follows from $D_\mu = -\varepsilon\nabla\phi_\mu(\mu \geqslant 0)$ and $0 < \varepsilon_{\min} \leqslant \varepsilon \leqslant \varepsilon_{\max}$ in $\Omega$.

It now follows from the definition of $I_\mu$ (cf. (4.4.4)) and $I_0$ (cf. (4.4.1)), and (4.4.8) that for all $\mu \in (0, \mu_0]$

$$
\begin{aligned}
|I_\mu[\phi_\mu] - I_0[\phi_0]| &= \left| \int_\Omega \left[ -\frac{\varepsilon}{2} \left( |\nabla\phi_\mu|^2 - |\nabla\phi_0|^2 \right) + f(\phi_\mu - \phi_0) - \frac{\mu}{2}\phi_\mu^2 \right] dx \right| \\
&\leqslant \frac{\varepsilon_{\max}}{2} \|\nabla\phi_\mu - \nabla\phi_0\|_{L^2(\Omega)} \|\nabla\phi_\mu + \nabla\phi_0\|_{L^2(\Omega)} \\
&\qquad + \|f\|_{L^2(\Omega)} \|\phi_\mu - \phi_0\|_{L^2(\Omega)} + \frac{\mu}{2}\|\phi_\mu\|_{L^2(\Omega)}^2 \\
&\leqslant C\mu \left( \|\nabla\phi_\mu + \nabla\phi_0\|_{L^2(\Omega)} + 1 + \|\phi_\mu\|_{L^2(\Omega)}^2 \right) \\
&\leqslant C\mu \big( \|\nabla\phi_\mu - \nabla\phi_0\|_{L^2(\Omega)} + 2\|\nabla\phi_0\|_{L^2(\Omega)} + 1 \\
&\qquad + 2\|\phi_\mu - \phi_0\|_{L^2(\Omega)}^2 + 2\|\phi_0\|_{L^2(\Omega)}^2 \big) \\
&\leqslant C\mu \left( \mu + 2\mu^2 + 1 \right).
\end{aligned}
$$

This proves (4.4.9). □

## 4.5 Application to dielectric boundary implicit solvation

We now consider the dielectric boundary problem in molecular solvation. Let again $\Gamma$ be a $C^2$, closed surface such that $\Gamma \subset \Omega$. Denote $\Omega_-$ the interior of $\Gamma$ and $\Omega_+ = \Omega \backslash \overline{\Omega_-}$. So, $\Omega = \Omega_- \cup \Omega_+ \cup \Gamma$. Here, $\Omega_-$ and $\Omega_+$ are the solute and solvent regions, respectively, and $\Gamma$ is the dielectric boundary. As before, we denote by $n$

the unit normal at $\Gamma$ pointing from $\Omega_-$ to $\Omega_+$. The piecewise constant, dielectric coefficient $\varepsilon_\Gamma : \Omega \to \mathbb{R}$ is defined again in (4.2.18) with $\varepsilon_-$ and $\varepsilon_+$ two distinct positive constants. Denote again by $\chi_+$ the characteristic function of $\Omega_+$. We define $I_\Gamma : H^1_g(\Omega) \cup \{-\infty\}$ by

$$I_\Gamma[\phi] = \int_\Omega \left[ -\frac{\varepsilon_\Gamma}{2} |\nabla \phi|^2 + f\phi - \chi_+ B(\phi) \right] dx \qquad \forall \phi \in H^1_g(\Omega). \tag{4.5.1}$$

Clearly, $I[\phi] < \infty$ for any $\phi \in H^1_g(\Omega)$. We consider the maximization of the functional $I_\Gamma : H^1_g(\Omega) \cup \{-\infty\}$ and the boundary-value problem of the PB equation

$$\nabla \cdot \varepsilon_\Gamma \nabla \phi - \chi_+ B'(\phi) = -f \qquad \text{in } \Omega, \tag{4.5.2}$$

$$\phi = g \qquad \text{on } \partial\Omega. \tag{4.5.3}$$

The following theorem collects some useful results proved in [41, 42, 44, 13]:

**Theorem 4.5.1.** (1) *The functional $I_\Gamma : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$ has a unique* maximizer $\phi_\Gamma \in H^1_g(\Omega)$. *Moreover, the maximum value is finite, and*

$$\|\phi_\Gamma\|_{H^1(\Omega)} + \|\phi_\Gamma\|_{L^\infty(\Omega)} \leqslant C$$

*for some constant $C > 0$ depending on $\varepsilon_-$, $\varepsilon_+$, $f$, $g$, $B$, and $\Omega$ but not on $\Gamma$.*

(2) *The maximizer $\phi_\Gamma$ is the unique solution to the boundary-value problem of the PB equation* (4.5.2) *and* (4.5.3).

(3) *The boundary-value problem of the PB equation* (4.5.2) *and* (4.5.3) *is equivalent*

*to the elliptic interface problem*

$$
\begin{cases}
\varepsilon_-\Delta\phi = -f & \text{in } \Omega_-, \\
\varepsilon_+\Delta\phi - B'(\phi) = -f & \text{in } \Omega_+, \\
[\![\phi]\!] = [\![\varepsilon_\Gamma \nabla\phi \cdot n]\!] = 0 & \text{on } \Gamma, \\
\phi = g & \text{on } \partial\Omega.
\end{cases}
\tag{4.5.4}
$$

*In particular,* $\phi|_{\Omega_-} \in H^2(\Omega_-)$ *and* $\phi|_{\Omega_+} \in H^2(\Omega_+)$. *The spaces* $H^2(\Omega_-)$ *and* $H^2(\Omega_+)$ *can be replaced by* $H^3(\Omega_-)$ *and* $H^3(\Omega_+)$, *respectively, if* $f \in H^1(\Omega)$.

We now denote

$$V_\Gamma = \{D \in H(\mathrm{div}, \Omega) : \nabla \cdot D = f \text{ a.e. } \Omega_-\}$$

and define $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$ by

$$J_\Gamma[D] = \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma}|D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} gD \cdot n \, dS.$$

Note that $V_\Gamma$ is a convex subset of $H(\mathrm{div}, \Omega)$. Note also that $J_\Gamma[D]$ is the same as $J[D]$ defined in (4.2.4) (with $\varepsilon_\Gamma$ replacing $\varepsilon$). Here we use the subscript $\Gamma$ to indicate that $J_\Gamma$ is defined on $V_\Gamma$. It is clear that $J_\Gamma[D] > -\infty$ for any $D \in V_\Gamma$.

**Theorem 4.5.2.** *We have for any* $\phi \in H^1_g(\Omega)$ *and any* $D \in V_\Gamma$ *that* $I_\Gamma[\phi] \leqslant J_\Gamma[D]$. *If we denote* $\phi_\Gamma \in H^1_g(\Omega)$ *the unique maximizer of* $I_\Gamma : H^1_g(\Omega) \to \mathbb{R}$ *and* $D_\Gamma = -\varepsilon_\Gamma \nabla\phi_\Gamma$, *then* $D_\Gamma \in V_\Gamma$, *and* $D_\Gamma$ *is the unique minimizer of* $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$. *Moreover,*

$$J_\Gamma[D_\Gamma] = \min_{D \in V_\Gamma} J_\Gamma[D] = \max_{\phi \in H^1_g(\Omega)} I_\Gamma[\phi] = I_\Gamma[\phi_\Gamma]. \tag{4.5.5}$$

*Proof.* Let $\phi \in H^1_g(\Omega)$ and $D \in V_\Gamma$. Since $\nabla \cdot D = f$ in $\Omega_-$ and $B^*(0) = 0$, we have

$B^*(f - \nabla \cdot D) = 0$ a.e. $\Omega_-$. Therefore, by integration by parts, we obtain that

$$
\begin{aligned}
I_\Gamma[\phi] &= \int_\Omega \left[ -\frac{\varepsilon_\Gamma}{2} |\nabla \phi|^2 + f\phi - \chi_+ B(\phi) \right] dx \\
&\leqslant \int_\Omega \left[ -\frac{\varepsilon_\Gamma}{2} |\nabla \phi|^2 + f\phi - \chi_+ B(\phi) + \frac{1}{2\varepsilon_\Gamma} |D + \varepsilon_\Gamma \nabla \phi|^2 \right] dx \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D|^2 + f\phi - \chi_+ B(\phi) + D \cdot \nabla \phi \right] dx \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D|^2 + f\phi - \chi_+ B(\phi) - \phi \nabla \cdot D \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D|^2 + \chi_+ \left( \phi(f - \nabla \cdot D) - B(\phi) \right) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&\leqslant \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D|^2 + \chi_+ B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&= J_\Gamma[D]. \qquad (4.5.6)
\end{aligned}
$$

Let $\phi_\Gamma \in H^1_g(\Omega)$ be the unique maximizer of $I_\Gamma : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$ and $D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma \in [L^2(\Omega)]^3$. Since $\phi_\Gamma$ is the unique weak solution to the boundary-value problem of PB equation (4.5.2) and (4.5.3), we have by (4.5.2) that $\nabla \cdot D_\Gamma = f - \chi_+ B'(\phi_\Gamma) \in L^2(\Omega)$. Hence $D_\Gamma \in H(\mathrm{div}, \Omega)$. By the first equation in (4.5.4), $\nabla \cdot D_\Gamma = f$ a.e. $\Omega_-$. Hence, $D_\Gamma \in V_\Gamma$. By the second equation in (4.5.4), we have

$$B'(\phi_\Gamma) = f - \nabla \cdot D_\Gamma \qquad \text{in } \Omega_+. \qquad (4.5.7)$$

Consequently,

$$B^*(f - \nabla \cdot D_\Gamma) = \phi_\Gamma (f - \nabla \cdot D_\Gamma) - B(\phi_\Gamma) \qquad \text{in } \Omega_+.$$

Therefore, we can repeat those steps in (4.5.6) with $\phi_\Gamma$ and $D_\Gamma$ replacing $\phi$ and $D$, respectively, to get

$$
\begin{aligned}
I_\Gamma[\phi_\Gamma] &= \int_\Omega \left[ -\frac{\varepsilon_\Gamma}{2} |\nabla \phi_\Gamma|^2 + f\phi_\Gamma - \chi_+ B(\phi_\Gamma) \right] dx \\
&= \int_\Omega \left[ -\frac{\varepsilon_\Gamma}{2} |\nabla \phi_\Gamma|^2 + f\phi_\Gamma - \chi_+ B(\phi_\Gamma) + \frac{1}{2\varepsilon_\Gamma} |D_\Gamma + \varepsilon_\Gamma \nabla \phi_\Gamma|^2 \right] dx \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + f\phi_\Gamma - \chi_+ B(\phi_\Gamma) + D_\Gamma \cdot \nabla \phi_\Gamma \right] dx \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + f\phi_\Gamma - \chi_+ B(\phi_\Gamma) - \phi_\Gamma \nabla \cdot D_\Gamma \right] dx + \int_{\partial\Omega} g D_\Gamma \cdot n \, dS \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + \chi_+ \left( \phi_\Gamma (f - \nabla \cdot D_\Gamma) - B(\phi_\Gamma) \right) \right] dx + \int_{\partial\Omega} g D_\Gamma \cdot n \, dS \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + \chi_+ B^*(f - \nabla \cdot D_\Gamma) \right] dx + \int_{\partial\Omega} g D_\Gamma \cdot n \, dS \\
&= \int_\Omega \left[ \frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + B^*(f - \nabla \cdot D_\Gamma) \right] dx + \int_{\partial\Omega} g D_\Gamma \cdot n \, dS \\
&= J_\Gamma[D_\Gamma].
\end{aligned}
$$

This and (4.5.6), together with the fact that $\phi_\Gamma$ maximizes $I_\Gamma : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$, imply (4.5.5). The inequality (4.5.6) and (4.5.5) imply that $D_\Gamma$ minimizes $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{\infty\}$. This minimizer is unique since the functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{\infty\}$ is convex. $\square$

Denote

$$W_\Gamma = \{D \in V_\Gamma : \text{ there exists } \phi \in H^1(\Omega) \text{ such that } D = -\varepsilon_\Gamma \nabla \phi \text{ in } \Omega\}.$$

Clearly, $W_\Gamma$ is a convex subset of $V_\Gamma$. The following is a direct consequence of Theorem 4.5.2:

**Corollary 4.5.1.** *Let $D_\Gamma$ be the minimizer of the functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$ as* *stated in Theorem 4.5.2. Then,* $D_\Gamma \in W_\Gamma$ *and*

$$J_\Gamma[D_\Gamma] = \min_{D\in V_\Gamma} J[D] = \min_{D\in W_\Gamma} J[D].$$

The following theorem provides a set of conditions, similar to those in (4.5.4), that characterize the minimizer $D_\Gamma$ of the Legendre transformed functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$:

**Theorem 4.5.3.** *Assume* $f \in H^1(\Omega)$. *Let* $D \in [L^2(\Omega)]^3$ *be such that* $D|_{\Omega_-} \in [H^2(\Omega_-)]^3$ *and* $D|_{\Omega_+} \in [H^2(\Omega_+)]^3$, *and* $D = -\varepsilon_- \nabla \phi_-$ *in* $\Omega_-$ *for some* $\phi_- \in H^1(\Omega_-)$. *Then* $D = D_\Gamma \in V_\Gamma$ *(the unique minimizer of* $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$ *as in Theorem 4.5.2) if and only if* $D$ *satisfies the following set of equations:*

$$\begin{cases} \nabla \cdot D = f & \text{in } \Omega_-, \\ \dfrac{D}{\varepsilon_+} + \nabla \left( B^{*\prime}(f - \nabla \cdot D) \right) = 0 & \text{in } \Omega_+, \\ [\![ D \cdot n ]\!] = 0 & \text{on } \Gamma, \\ \dfrac{1}{\varepsilon_-} D|_{\Omega_-} \cdot \tau = -\partial_\tau \left( B^{*\prime}(f - \nabla \cdot D)|_{\Omega_+} \right) & \forall \text{ unit vector } \tau \text{ tangential to } \Gamma, \\ B^{*\prime}(f - \nabla \cdot D) = g & \text{on } \partial\Omega. \end{cases} \tag{4.5.8}$$

Several remarks are in order. First, if $D = D_\Gamma$, the unique minimizer of $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$, then $D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma$ with $\phi_\Gamma$ the unique maximizer of $I_\Gamma : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$. Consequently, as shown in the proof of the theorem, the equations in (4.5.8) are equivalent to those in (4.5.4). Second, the second interface condition (i.e., the fourth equation in (4.5.8)) is not the jump across $\Gamma$ of a very same quantity. This is because the $B$ part is only for the solvent region $\Omega_+$ as it models the ionic contribution. Therefore, the Legendre transform is only applied to part of the entire region $\Omega$. Finally, we require $D$ to be the gradient of a function in $\Omega_-$. Otherwise, the divergence-free vector field $D + \varepsilon_- \nabla \phi_\Gamma$ in $\Omega_-$ may be nonzero in $\Omega_-$. (It will be a curl of a vector field if $\Omega_-$ is simply connected.) Note the minimizer $D_\Gamma$ fulfills this requirement. Moreover, in terms of numerical implementation, solving the equation $\nabla \cdot D = f$ in $\Omega_-$ can be converted to solving a more well-defined equation $-\varepsilon_- \Delta \phi_- = f$ in $\Omega_-$.

*Proof of Theorem 4.5.3.* Clearly, the minimizer $D_\Gamma \in V_\Gamma$ of the functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$ satisfies $D_\Gamma \in [L^2(\Omega)]^3$. Since $D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma$ with $\phi_\Gamma$ the maximizer of $I_\Gamma : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$, we have by Theorem 4.5.1 that $D_\Gamma|_{\Omega_\pm} \in [H^2(\Omega_\pm)]^3$, and that clearly $D_\Gamma = -\varepsilon_- \nabla \phi_\Gamma$ in $\Omega_-$ with $\phi_\Gamma \in H^1(\Omega)$. We show that $D_\Gamma$ satisfies (4.5.8). The first equation in (4.5.8) with $D_\Gamma$ replacing $D$ follows from the definition of $V_\Gamma$ and the fact that $D_\Gamma \in V_\Gamma$. Note from (4.5.7) and (4.1.12) that

$$B^{*\prime}(f - \nabla \cdot D_\Gamma) = \phi_\Gamma \qquad \text{in } \Omega_+. \tag{4.5.9}$$

This and the relation $D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma$ imply the second equation in (4.5.8) with $D_\Gamma$ replacing $D$. The third equation in (4.5.8) follows from the second interface condition in the third equation of (4.5.4) with $D_\Gamma$ and $\phi_\Gamma$ replacing $D$ and $\phi$, respectively. With $D = D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma$ and (4.5.9), the fourth equation in (4.5.8) becomes $\partial_\tau \phi_\Gamma|_{\Omega_-} = \partial_\tau \phi_\Gamma|_{\Omega_+}$ on $\Gamma$ for any unit vector tangential to $\Gamma$. This is true, since $\phi_\Gamma|_{\Omega_-} = \phi_\Gamma|_{\Omega_+}$ on $\Gamma$ by the continuity of $\phi_\Gamma$; cf. the first interface condition in (4.5.4). Finally, by (4.5.9) and the fact that $\partial\Omega$ is a subset of $\partial\Omega_+$, the last equation of (4.5.8) with $D = D_\Gamma$ is the same as the last equation in (4.5.4).

Assume now $D \in [L^2(\Omega)]^3$ satisfies $D|_{\Omega_-} \in [H^2(\Omega_-)]^3$ and $D|_{\Omega_+} \in [H^2(\Omega_+)]^3$, and $D = -\varepsilon_- \nabla \phi_-$ in $\Omega_-$ for some $\phi_- \in H^1(\Omega_-)$. Assume also that $D$ satisfies (4.5.8). Then by the third equation in (4.5.8), we have $D \in H(\mathrm{div}, \Omega)$; cf. the last part of the proof of Theorem 4.2.3. Moreover, $D \in V_\Gamma$ by the first equation in (4.5.8).

It now suffices to show that $D$ is a critical point of the strictly convex functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$, i.e.,

$$\delta J_\Gamma[D][G] = \frac{d}{dt}\bigg|_{t=0} J_\Gamma[D + tG] = 0 \qquad \forall G \in H(\mathrm{div}, \Omega) \text{ such that } \nabla \cdot G = 0 \text{ in } \Omega_-.$$

Fix $G \in H(\mathrm{div}, \Omega)$ with $\nabla \cdot G = 0$ in $\Omega_-$. Suppose $\Omega_- = \cup_i \Omega_-^{(i)}$, where $\Omega_-^{(i)}$ are countably many, disjoint, connected components of $\Omega_-$. Denote $\Gamma^{(i)} = \partial\Omega_-^{(i)}$. Hence, we have the disjoint union $\Gamma = \cup_i \Gamma^{(i)}$. For each $i$, $\Gamma^{(i)}$ is a connected smooth surface. Therefore, by the fourth equation in (4.5.8) and the relation $D \cdot \tau = -\varepsilon_- \partial_\tau \phi_-$, we have $B^{*\prime}(f - \nabla \cdot D|_{\Omega_+}) - \phi_-|_{\Omega_-} = c_i$ on $\Gamma^{(i)}$ for some constant $c_i \in \mathbb{R}$. It now follows from the second and fifth equations in (4.5.8), the divergence theorem, and the fact that the unit normal $n$ points from $\Omega_-$ to $\Omega_+$ that

$$\begin{aligned}
\delta J_\Gamma[D][G] &= \int_{\Omega_-} \frac{D \cdot G}{\varepsilon_-}\, dx + \int_{\Omega_+} \left[ \frac{D \cdot G}{\varepsilon_+} + B^{*\prime}(f - \nabla \cdot D)(-\nabla \cdot G) \right] dx \\
&\quad + \int_{\partial\Omega} g G \cdot n \, dS \\
&= -\int_{\Omega_-} \nabla \phi_- \cdot G \, dx + \int_{\Omega_+} \left[ \frac{D}{\varepsilon_+} + \nabla \left( B^{*\prime}(f - \nabla \cdot D) \right) \right] \cdot G \, dx \\
&\quad + \int_\Gamma B^{*\prime}(f - \nabla \cdot D|_{\Omega_+})(G \cdot n)\, dS \\
&\quad + \int_{\partial\Omega} \left[ g - B^{*\prime}(f - \nabla \cdot D) \right] G \cdot n \, dS \\
&= -\sum_i \int_{\Omega_-^{(i)}} \nabla(\phi_- + c_i) \cdot G \, dx + \int_\Gamma B^{*\prime}(f - \nabla \cdot D|_{\Omega_+})(G \cdot n)\, dS \\
&= \sum_i \int_{\Gamma^{(i)}} \left[ B^{*\prime}(f - \nabla \cdot D|_{\Omega_+}) - (\phi_-|_{\Omega_-} + c_i) \right] (G \cdot n)\, dS \\
&= 0.
\end{aligned}$$

This completes the proof. $\square$

This chapter appeared in "*Legendre Transforms of Electrostatic Free–Energy Functionals*," by Benjamin Ciotti and Bo Li, published in the SIAM Journal on Applied Mathematics in 2018. The dissertation author was the primary researcher and author on this paper.

# Chapter 5

# Conclusions and Future Work

In this dissertation we have demonstrated rigorously the validity of contrasting discrete, continuum and hybrid models of electrostatics that are employed in physical and biological sciences, particularly biophysical models of solvation.

In Section 2.1, we showed that any continuous charge density on a bounded domain can be approximated by a discrete one for which the corresponding energy forms also a good approximation, and key in the proof was the harmonicity of the Coulomb potential. To the author's knowledge this has never been done before, and presents a novel approach to the problem.

In Section 2.2, we approached a reversal of the problem, in that we started with a sequence of discrete charge densities, and by way of a multiscale construction showed that there necessarily exists a continuum density limit, and that the corresponding sequence of energies also converges.

In [59], Serfaty proves a discrete to continuum result (Theorem 2.2), which we briefly summarize: if $H_n$ is a discrete energy functional defined on probability measures of the form

$$\mu = \frac{1}{n}\sum_{i=1}^{n}\delta_{x_i},$$

with

$$H_n[\mu] = \iint\limits_{(x,y)\in\mathbb{R}^3\times\mathbb{R}^3 : x\neq y} \frac{d\mu(x)d\mu(y)}{|x-y|} + \int V d\mu, \tag{5.0.1}$$

and $\mathcal{E}$ is the continuum energy functional defined on probability measures $\mu$ by

$$\mathcal{E}[\mu] = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \frac{d\mu(x)d\mu(y)}{|x-y|} + \int V d\mu, \tag{5.0.2}$$

then with some further details such as conditions on $V$, one has the convergence of minimizers/minima of $H_n$ to $\mathcal{E}$. To rephrase, one has

$$\min_{x_1,\ldots,x_n\in\mathbb{R}^3}\left[\sum_{i\neq j}\frac{1}{|x_i-x_j|} + n\sum_i V(x_i)\right] = n^2 \min \mathcal{E} + o(n^2). \tag{5.0.3}$$

Next order asymptotics of these functionals are analyzed in [52] and [57], so a natural question is to generalize the results of this dissertation on discrete signed measures to next order asymptotics as well.

Moreover, one can define a Gibbs probability measure $\mathbb{P}$ on the set of discrete probability measures whereby

$$\mathbb{P}_{n,\beta}[\mu] = \frac{1}{Z_{n,\beta}}\exp(-\beta H_n[\mu]) \tag{5.0.4}$$

assigns lower energy states a higher likelihood. It can be shown (see [29, 38]) that under (5.0.4), almost surely every sequence of discrete probability measures will converge vaguely to the minimizing (or equilibrium) measure. Contrast this with the counterexample of Section 2.3, in which we demonstrated that without the assumption of Boltzmann statistics, limiting continuum densities need not be unique, even in the simple case of a sequence of discrete probability measures concentrated on an increasing nested sequence of sets of points.

In Chapter 3 we further generalized results of Chapter 2, with the goal of application to a common minimization problem. There remains further work via the concept of capacity to characterize more thoroughly those sets of zero capacity upon which concentrations of charge lead to singularities, and this author believes that there is room for generalization in the assumptions employed in this dissertation. In particular with regard to the roughness of the domain of consideration, which was limited in this dissertation to those with twice continuously differentiable boundary but can likely be generalized to domains with merely Lipshitz or even Hölder continuous boundary. The smoothness of the boundary was crucial in employing the concept of balayage, which is intimately related to the solvability of the Dirichlet problem and the barrier problem (see e.g. [37, 59]). In Theorem 3.3.1 it was shown that discrete measure approximating an induced surface charge density can be assumed to be supported in an arbitrarily small neighborhood of the boundary surface, but the question remains open as to whether it is possible to confine them *to* the surface. The problem can be further generalized in the allowance of unbounded domains, although this introduces many difficulties. The loss of compactness can be moderated by way of a sufficiently coercive confining external potential, as utilized in [61, 60, 59, 62]. With a suitable construction, the problems in Chapter 2 and Chapter 3 of this dissertation could be framed as a minimization problem, and the benefits afforded by this approach may be the subject of future work. While the problem in this dissertation considers measures supported in a bounded domain $\Omega$, one technique to generalize would be to allow for measures supported in $\mathbb{R}^3$ in the presence of an external potential that is $+\infty$ outside $\overline{\Omega}$.

The work in this dissertation has all been static, but a natural follow–up question would be to allow the system to evolve in time, and show that the models remain equivalent. See [28, 62, 61, 16] for solutions to this dynamical problem in which discrete systems of identical particles are considered. To this author's knowledge, no work has been to to generalize these results to systems of signed charge distributions, and this seems to be a natural extension of the problem.

In Chapter 4 we considered the Poison–Boltzmann equation and its associated functionals. Maggs [48] proposed a Legendre transformed functional of electrostatic displacements. This new functional is convex, and is therefore minimized at the critical point. Here, we presented a rigorous proof of the equivalence of these two functionals and apply this approach to the dielectric boundary model of molecular solvation. and proved that they could be modified in such a way as to be convex by way of the Legendre transformation, but there remain unanswered questions. The derivation of the Poisson–Boltzmann statistics relies upon a lattice gas model [34, 69] which has been remarkably effective in producing useful results but the validity of which has yet to be rigorously demonstrated, particularly in a size–modified approach considering non-uniform ionic sizes (see e.g., [40]).

Potentially, a Legendre transformed functional can be coupled with other energy functional to minimize consistently the total energy. For example, in a continuum model of molecular solvation the electrostatic free energy with a dielectric boundary is often coupled with the surface energy of such a boundary. In such a situation, using the Legendre transformed electrostatic free-energy functional of dielectric displacements can be advantageous, as each part of the total energy is to be minimized. A practical issue in using a Legendre transformed electrostatic free-energy functional is to find the Legendre transform $B^*$ of $B$. Only for a special case (1:1 salt), the explicit form of $B^*$ seems to be available [48]. In general, the function $B^*$ can be numerically determined and tabulated. A disadvantage of using a Legendre transformed functional is that the corresponding Euler–Lagrange equation is more complicated, particularly for the case of the functional with a higher-order gradient term. Further work is therefore needed to demonstrate how the new forms of electrostatic free-energy functionals are both theoretically and practically useful.

Our main contributions in this respect are two-fold. One is to provide some mathematical insight into the Legendre transformed electrostatic free-energy functional in various situations. The other is to apply this framework to the solvation of charged molecules. This includes the construction of a new Legendre transformed electrostatic free-energy functional for the molecular electrostatics with a dielectric boundary, and the derivation of a set of interface conditions for the equilibrium electrostatic displacement. Follow–up work includes development of numerical methods for molecular solvation with our newly constructed Legendre transformed electrostatic free-energy functional.

The passage from discrete to continuum models is a rich and vibrant problem, touching upon such varied disciplines as statistical mechanics, fluid mechanics, partial/ordinary differential equations, differential geometry, convex analysis, optimization, complex analysis, quantum field theory, probability, number theory, combinatorics, topology, algebraic geometry, solid state physics, potential theory, and harmonic analysis, with direct application to physics, chemistry, and biology. Despite considerable progress over the last century, many questions remain and are increasingly relevant as technology and interest in the physical sciences evolves.

# Appendix A

# Newton's Theorem

Newton's Theorem (occasionally referred to as the Shell Theorem) is a famous result we utilize repeatedly in this dissertation, and which we here provide a proof for. It states that the potential outside the support of a radially symmetric charge distribution is the same as that were all the charge concentrated at the center.

**Theorem A.1.1** (Newton's Theorem)**.** *Let $\varphi \in L^1(\mathbb{R}^3)$ depend only on $|x|$ and have compact support $supp(\varphi)$. Then*

$$\int \frac{\varphi(y)}{|x-y|}dy = \frac{1}{|x|}\int \varphi(y)dy$$

*for all $x \in \mathbb{R}^3 \backslash supp(\varphi)$.*

*Proof.* Suppose for convenience that $supp(\varphi) \subset \{y \in \mathbb{R}^3 : |y| < 1\} =: B$. Then the potential due to $\varphi$ at a point $x$ outside $B$ is

$$\Phi(x) = \int \frac{\varphi(y)}{|x-y|}dy = \int_0^1 \int_{\partial B} \frac{\varphi(r\omega)}{|x-r\omega|} r^2 dS_\omega dr.$$

Here $dS_\omega$ denotes surface measure on the unit sphere. With abuse of notation,

$\varphi(y) = \varphi(r)$ pulls through the surface integral:

$$\Phi(x) = \int_0^1 \varphi(r) \int_{\partial B} \frac{1}{|x - r\omega|} dS_\omega r^2 dr.$$

By the mean value property,

$$\int_{\partial B} \frac{1}{|x - r\omega|} dS_\omega = \frac{4\pi}{|x|},$$

so

$$\Phi(x) = \frac{4\pi}{|x|} \int_0^1 \varphi(r) r^2 dr = \frac{Q}{|x|},$$

where net charge

$$Q = 4\pi \int_0^1 \varphi(r) r^2 dr = \int_0^1 \int_{\partial B} \varphi(r\omega) r^2 dr dS_\omega = \int_B \varphi(y) dy = \int \varphi(y) dy.$$

$\square$

**Theorem A.1.2.** *For radially symmetric $\varphi \in L^1(\mathbb{R}^3)$ we have*

$$\int \frac{\varphi(x)}{|x - y|} dx = \int \min(\frac{1}{|x|}, \frac{1}{|y|}) \varphi(x) dx.$$

*Proof.*

$$\int \frac{\varphi(x)}{|x - y|} dx = \int_{|x|<|y|} \frac{\varphi(x) dx}{|x - y|} + \int_{|x|>|y|} \frac{\varphi(x) dx}{|x - y|}.$$

Here we disregard the Lebesgue measure zero set $\{x : |x| = |y|\}$. By Newton's theorem, the first integral is

$$\int_{|x|<|y|} \frac{\varphi(x) dx}{|y|}.$$

The second integral is the potential at $y$ due to a thick spherical shell enclosing (but not centered at) $y$. By symmetry, this potential is the same for all points $z$ such that $|z| = |y|$ i.e.,

$$h(z) := \int_{|x|>|y|} \frac{\varphi(x)dx}{|x-z|}$$

is constant for constant $|z|$. It is also harmonic in the region $|z| \leqslant |y|$ (see e.g., Theorem 1.4 in [37]), hence obeys the mean value property, which implies that its value at $z = 0$ should be the same as the average of its value on the sphere $|z| = |y|$, which by the preceding remark is equal to $h(y)$:

$$h(0) = h(y)$$

i.e.,

$$\int_{|x|>|y|} \frac{\varphi(x)dx}{|x-y|} = \int_{|x|>|y|} \frac{\varphi(x)dx}{|x|}.$$

Thus we have

$$\begin{aligned}
\int \frac{\varphi(x)}{|x-y|}dx &= \int_{|x|<|y|} \frac{\varphi(x)dx}{|x-y|} + \int_{|x|>|y|} \frac{\varphi(x)dx}{|x-y|} \\
&= \int_{|x|<|y|} \frac{\varphi(x)dx}{|y|} + \int_{|x|>|y|} \frac{\varphi(x)dx}{|x|} \\
&= \int \min(\frac{1}{|x|}, \frac{1}{|y|})\varphi(x)dx.
\end{aligned}$$

□

**Corollary A.1.1.** *If in addition we have* $\int \varphi = 1$, *then*

$$\int \frac{\varphi(x)}{|x-y|}dx \leqslant \frac{1}{|y|}.$$

**Theorem A.1.3.** *For* $\varphi \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$ *that is nonnegative, radially symmetric, and unit mass, the mutual energy of compactly supported Radon measures* $\mu, \nu$

*satisfies*

(1) $E[\varphi_\epsilon * \mu, \varphi_\epsilon * \nu] \leqslant E[\mu, \nu]$ *for* $\epsilon > 0$*; and*

(2) $E[\varphi_\epsilon * \mu, \varphi_\epsilon * \nu] \to E[\mu, \nu]$ *as* $\epsilon \to 0^+$.

*Proof.*

$$\begin{aligned} E[\varphi_\epsilon * \mu, \varphi_\epsilon * \nu] &= \iint \frac{d(\varphi_\epsilon * \mu) d(\varphi_\epsilon * \nu)}{|x-y|} \\ &= \iint |x-y|^{-1} \left[ \int \varphi_\epsilon(x-x') d\mu(x') \int \varphi_\epsilon(y-y') d\nu(y') \right] dx dy \end{aligned}$$

All terms here are non-negative, so Tonelli allows us to write this as

$$\iint \left[ \iint \frac{\varphi_\epsilon(x-x')\varphi_\epsilon(y-y') dx dy}{|x-y|} \right] d\mu(x') d\nu(y')$$

Twice applying Corollary A.1.1 gives

$$\begin{aligned} \iint \frac{\varphi_\epsilon(x-x')\varphi_\epsilon(y-y') dx dy}{|x-y|} &= \int \varphi_\epsilon(y-y') \left[ \int \frac{\varphi_\epsilon(x-x') dx}{|x-y|} \right] dy \\ &\leqslant \int \varphi_\epsilon(y-y') \frac{1}{|x'-y|} dy \\ &\leqslant \frac{1}{|x'-y'|}. \end{aligned} \tag{A.1.1}$$

Denote Coulomb potential $v(x) := \frac{1}{|x|}$, and for $\alpha > 0$, define the cutoff Coulomb potential

$$v_\alpha(x) := \begin{cases} \frac{1}{|x|} & |x| \geqslant \alpha \\ \frac{1}{\alpha} & |x| < \alpha. \end{cases}$$

Then the improper integral

$$\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v(x-y)dxdy = \lim_{\alpha\to 0^+} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v_\alpha(x-y)dxdy.$$

Since $v_\alpha$ is bounded and continuous, it is straightforward to show that

$$\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v_\alpha(x-y)dxdy \to v_\alpha(x'-y')$$

as $\epsilon \to 0^+$, by well known properties of approximate identities. Using (A.1.1) and the definition of $v_\alpha$ we get

$$\begin{aligned}
&\iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v_\alpha(x-y)dxdy \\
&\leqslant \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v(x-y)dxdy \\
&\leqslant v(x'-y').
\end{aligned}$$

Letting $\epsilon$ tend to 0, we find that

$$\begin{aligned}
v_\alpha(x'-y') &= \lim_{\epsilon\to 0^+} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v_\alpha(x-y)dxdy \\
&\leqslant \liminf_{\epsilon\to 0^+} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v(x-y)dxdy \\
&\leqslant \limsup_{\epsilon\to 0^+} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v(x-y)dxdy \\
&\leqslant v(x'-y').
\end{aligned}$$

If $x' \neq y'$, then for $\alpha < |x'-y'|$, $v_\alpha(x'-y') = v(x'-y')$, so

$$\frac{1}{|x'-y'|} = \lim_{\epsilon\to 0^+} \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \varphi_\epsilon(x-x')\varphi_\epsilon(y-y')v(x-y)dxdy.$$

If $x' = y'$, then

$$\iint \frac{\varphi_\epsilon(x-x')\varphi_\epsilon(y-y')dxdy}{|x-y|} = \iint \frac{\varphi_\epsilon(x-x')\varphi_\epsilon(y-x')dxdy}{|x-y|} = \frac{c}{\epsilon},$$

where

$$c = \int \frac{(\varphi * \varphi)(x)dx}{|x|}$$

is a positive constant depending only on $\varphi$. In either case, we have

$$\iint \frac{\varphi_\epsilon(x-x')\varphi_\epsilon(y-y')dxdy}{|x-y|}$$

converging to $1/|x'-y'|$ from below. Combining this with Fatou's Lemma we have (even if the integrals are infinite) that

$$E[\mu,\nu] \leqslant \liminf_{\epsilon\to 0^+} \iint \left[\iint \frac{\varphi_\epsilon(x-x')\varphi_\epsilon(y-y')dxdy}{|x-y|}\right] d\mu(x')d\nu(y') \leqslant E[\mu,\nu],$$

so equality holds. $\square$

**Corollary A.1.2.** *With $\mu$ and $\varphi$ as above, we have $E[\varphi_\epsilon * \mu]$ increases to $E[\mu]$ as $\epsilon \to 0^+$.*

# Appendix B

# Fourier Transforms of Radon Measures

In this section of the appendix we derive various properties of Fourier transforms of Radon measures that were used in Chapter 2 and Chapter 3. These notes follow [51], beginning with the definition on $L^1$.

**Definition B.1.1.** *The Fourier transform of a function $u$ in $L^1(\mathbb{R}^3)$ is*

$$\widehat{u}(k) := \int_{\mathbb{R}^3} e^{-ik\cdot x} u(x) dx,$$

*and similarly define*

$$\check{u}(k) := \int_{\mathbb{R}^3} e^{ik\cdot x} u(x) dx.$$

Properties of the Fourier transform on $L^1$:

- For $u, v \in L^1$, $\int \widehat{u} v = \int u \widehat{v}$
- For $u, v \in L^1$, $\widehat{u * v} = \widehat{u}\widehat{v}$
- For $u \in L^1$, $\widehat{\widehat{u}} = \bar{\check{u}}$

- For $u \in L^1$, $\check{\bar{u}} = \bar{\hat{u}}$
- For $u \in L^1$, $(\widehat{e^{iy\cdot x}u})(k) = \hat{u}(k-y)$ (translation)
- For $u \in L^1$, $(\widehat{u(\cdot - y)}) = e^{ik\cdot y}\hat{u}(k)$ (translation)
- For $u \in L^1$, $\widehat{u(r\cdot)}(k) = r^{-3}\hat{u}(\frac{r}{k})$ (dilation)

Less trivially is the Fourier inversion formula on $L^1$:

**Theorem B.1.1.** *For $u, \hat{u} \in L^1$, $\check{\hat{u}} = (2\pi)^3 u$, after possibly redefining $u$ on a set of measure 0.*

The proof of Theorem B.1.1 relies on the computation of the transform of a Guassian. One finds that if

$$g(x) := (2\pi)^{-3/2} e^{-|x|^2/2},$$

then

$$\hat{g}(k) = e^{-|k|^2/2}.$$

It follows from the dilation property of Fourier transforms that for

$$g_\epsilon(x) := \epsilon^{-3} g(\epsilon^{-1}x),$$

one has

$$\hat{g}_\epsilon(k) = e^{-\epsilon^2|k|^2/2}. \tag{B.1.1}$$

Equation (B.1.1) will be exploited repeatedly, and exemplifies the behavior of the Fourier transform on a specific well–behaved subspace, the *Schwartz space* $\mathcal{S}(\mathbb{R}^3)$ of infinitely differentiable functions vanishing at infinity faster than any negative integer power of $|x|$. A *tempered distribution* is a continuous linear functional on $\mathcal{S}$. Writing $\mathcal{D} := C_c^\infty(\mathbb{R}^3)$ for the space of *test functions*, we have $\mathcal{D} \subset \mathcal{S}$, hence $\mathcal{S}^* \subset \mathcal{D}^*$, i.e., every tempered distribution is a distribution. If $\alpha$ is a multi-index and $u \in \mathcal{S}$, we get the following properties of the Fourier transform on the Schwarz space:

- $\widehat{(\partial^\alpha u)} = (ik)^\alpha \widehat{u}$
- $\partial^\alpha(\widehat{u}) = (\widehat{(-ix)^\alpha u})$
- $\int uv = \frac{1}{(2\pi)^3}\int \widehat{u}\check{v}$ (Parseval)
- $\|u\|_{L^2} = (2\pi)^{-3/2}\|\widehat{u}\|_{L^2}$ (Plancherel)

Next we address Fourier transforms of measures and distributions:

**Definition B.1.2.** *The Fourier transform of a finite Radon measure $\mu$ on $\mathbb{R}^3$ is*

$$\widehat{\mu}(k) := \int_{\mathbb{R}^3} e^{-ikx} d\mu(x),$$

*and similarly we define*

$$\check{\mu}(k) := \int_{\mathbb{R}^3} e^{ik\cdot x} d\mu(x).$$

Note that $\widehat{\mu}$ is bounded and continuous. This definition easily extends to the difference of two such measures, signed measures in particular.

For a measure $\mu$ that is absolutely continuous with respect to Lebesgue measure, $d\mu = f dx$, we identify $f$ and $\mu$.

For finite Radon measures $\mu, \nu$, and $f, g \in L^1$ we have the following properties of Fourier transforms of Radon measures:

- $\int \widehat{f} d\mu = \int \widehat{\mu} f$

- $\int \widehat{\nu} d\mu = \int \widehat{\mu} d\nu$

- $\widehat{f * \mu} = \widehat{f}\widehat{\mu}$

- $\widehat{f\widecheck{\mu}} = (2\pi)^{-3}\widehat{f} * \mu$

- $\widehat{\mu * \nu} = \widehat{\mu}\widehat{\nu}$

while if $f \in \mathcal{S}$, we have

- $\int \bar{f} d\mu = \frac{1}{(2\pi)^3}\int \bar{\widehat{f}}\widehat{\mu}$

Again, these results extend to signed Radon measures.

Via the $L^2$-isometry between the Schwartz class which is dense in $L^2$, we can extend the Fourier transform to an isometry on $L^2$, and the translation, dilation, Parseval and Plancherel formulas still hold.

In order to apply the theory of Fourier transforms to energy integrals involving Coulomb potentials, we must extend the Fourier transform to distributions:

**Definition B.1.3.** *For $T \in \mathcal{S}^*$, we define*

$$\widehat{T}(\varphi) = T(\widehat{\varphi})$$

*for $\varphi \in \mathcal{S}$.*

Observe that if $f \in L^1_{loc}(\mathbb{R}^3)$, then

$$T_f(\varphi) = \int_{\mathbb{R}^3} f(x)\varphi(x)dx$$

defines a (tempered) distribution. Then the Fourier transform of $T_f$ is given by

$$\widehat{T}_f(\varphi) = \int_{\mathbb{R}^3} f(x)\widehat{\varphi}(x)dx$$

for $\varphi \in \mathcal{S}$.

We now apply the theory of Fourier transforms to energy integrals, starting with the transform of the Coulomb potential $v(x) = 1/|x|$. $v$ is in $L^1_{loc}(\mathbb{R}^3)$, so can be regarded as a (tempered) distribution.

**Theorem B.2.2.** *For Coulomb potential $v(x) = 1/|x|$, we have $\widehat{v}(k) = 4\pi/|k|^2$ in the sense of (tempered) distributions.*

*Proof.* We need to show that

$$\int_{\mathbb{R}^3} \frac{1}{|x|}\widehat{\varphi}(x)dx = \int_{\mathbb{R}^3} \frac{4\pi}{|x|^2}\varphi(x)dx$$

for all $\varphi \in \mathcal{S}$. Observe both of these integrals are then well-defined. By the dominated convergence theorem,

$$\int_{\mathbb{R}^3} \frac{1}{|x|}\widehat{\varphi}(x)dx = \lim_{a\to 0^+} \int_{\mathbb{R}^3} e^{-a|x|}\frac{1}{|x|}\widehat{\varphi}(x)dx.$$

But

$$\int_{\mathbb{R}^3} e^{-a|x|}\frac{1}{|x|}\widehat{\varphi}(x)dx = \int_{\mathbb{R}^3} \widehat{w_a}(x)\varphi(x)dx,$$

where screened Coulomb potential

$$w_a(x) := \frac{e^{-a|x|}}{|x|} \qquad \text{for } a > 0.$$

Then

$$\begin{aligned}
\widehat{w_a}(k) &= \int_{\mathbb{R}^3} e^{-ik\cdot x}\frac{e^{-a|x|}}{|x|}dx \\
&= \int_0^\infty \int_0^{2\pi} \int_0^\pi \left(e^{-i|k|r\cos\theta} e^{-ar}\frac{1}{r}\right) r^2 \sin\theta d\theta d\phi dr
\end{aligned}$$

$$
\begin{aligned}
=&2\pi\int_0^\infty\int_0^\pi e^{-i|k|r\cos\theta}e^{-ar}r\sin\theta d\theta dr \qquad \text{(substituting } t=-\cos\theta)\\
=&2\pi\int_0^\infty\int_{-1}^1 e^{i|k|rt}e^{-ar}rdtdr\\
=&2\pi\int_0^\infty \frac{1}{i|k|}\left(e^{i|k|r}-e^{-i|k|r}\right)e^{-ar}dr\\
=&\frac{2\pi}{i|k|}\int_0^\infty\left(e^{(i|k|-a)r}-e^{(-i|k|-a)r}\right)dr\\
=&\frac{2\pi}{i|k|}\left[\frac{1}{a-i|k|}-\frac{1}{a+i|k|}\right]\\
=&\frac{4\pi}{a^2+|k|^2}.
\end{aligned}
$$

Observe that $\widehat{w_a}(x)$ increases to $4\pi/|x|^2$ as $a\to 0^+$. Then

$$
\int_{\mathbb{R}^3}\frac{1}{|x|}\widehat{\varphi}(x)dx=\lim_{a\to 0^+}\int_{\mathbb{R}^3}e^{-a|x|}\frac{1}{|x|}\widehat{\varphi}(x)dx=\lim_{a\to 0}\int_{\mathbb{R}^3}\widehat{w_a}(x)\varphi(x)dx.
$$

Applying again the dominated convergence theorem, this equals

$$
\int\frac{4\pi}{|x|^2}\varphi(x)dx.
$$

$\square$

Before proceeding, we introduce the notation $\tilde{f}(x):=f(-x)$ for functions $f$, and similarly for measures and distributions we set $\tilde{\mu}(A)=\mu(-A)=\mu(\{x:-x\in A\})$, $\tilde{T}(\varphi)=T(\tilde{\varphi})$.

**Corollary B.2.1.** *If* $w(x)=4\pi/|x|^2$, *then*

$$
\widehat{w}(x)=\frac{(2\pi)^3}{|x|}
$$

*as (tempered) distributions.*

*Proof.* By the previous result, we have

$$\int \frac{1}{|x|}\widehat{\varphi}(x)dx = \int \frac{4\pi}{|x|^2}\varphi(x)dx$$

for all $\varphi \in \mathcal{S}$. Since the Fourier transform is a bijection on $\mathcal{S}$, we can replace $\varphi$ by $\widehat{\varphi}$ to get

$$\int \frac{4\pi}{|x|^2}\widehat{\varphi}(x)dx = \int \frac{1}{|x|}\widehat{\widehat{\varphi}}(x)dx = \int \frac{1}{|x|}\widehat{\widetilde{\varphi}}(x)dx = (2\pi)^3 \int \frac{1}{|x|}\tilde{\varphi}(x)dx$$

$$= (2\pi)^3 \int \frac{1}{|x|}\varphi(x)dx$$

□

**Theorem B.2.3.** *If $\mu$ is a compactly supported Radon measure, then*

$$E[\mu] = (2\pi)^{-3} \int_{\mathbb{R}^3} \frac{4\pi}{|k|^2}|\widehat{\mu}|^2 dk. \tag{B.2.2}$$

*Proof.* First note that for measures $\mu$ of finite total variation, $\widehat{\mu}$ is bounded and continuous. If $g(x) = (2\pi)^{-3/2}e^{-|x|^2/2}$ is the standard normalized Gaussian on $\mathbb{R}^3$ and $g_\epsilon(x) = \epsilon^{-3}g(x/\epsilon)$, then

$$\mu^\epsilon := g_\epsilon * \mu$$

is in $L^1 \cap L^\infty$ since

$$\int g_\epsilon * \mu = \int g_\epsilon \cdot \int d\mu$$

and

$$\|g_\epsilon * \mu\|_\infty \leqslant \|g_\epsilon\|_\infty \int d\mu.$$

Thus $\mu^\epsilon$ is in $L^2$, and thus $\mu^\epsilon$ has a well defined Fourier transform $\widehat{\mu^\epsilon} \in L^2$. It is not hard to show that $\mu^\epsilon$ regarded as a function is in $\mathcal{S}$, since $\mu$ has compact support.

Introducing the notation $\langle u, w\rangle$ for the linear pairing $\int uw$, we have

$$E[\mu^\epsilon] = \langle v * \mu^\epsilon, \mu^\epsilon\rangle = \langle v, \tilde{\mu}^\epsilon * \mu^\epsilon\rangle$$

(with $v$ the Coulomb potential). The product of Schwartz functions is again a Schwartz function, hence by inverting we get that so is the convolution (see e.g., Proposition 8.11 in [25]). Then by Corollary B.2.1

$$\langle v, \tilde{\mu}^\epsilon * \mu^\epsilon\rangle = (2\pi)^{-3}\langle \widehat{v}, (\tilde{\mu}^\epsilon * \mu^\epsilon)\check{}\,\rangle = (2\pi)^{-3}\langle \widehat{v}, \check{\tilde{\mu}}^\epsilon \check{\mu}^\epsilon\rangle$$

$$= (2\pi)^{-3}\langle \widehat{v}, \widehat{\mu^\epsilon}\check{\mu^\epsilon}\rangle = (2\pi)^{-3}\langle \widehat{v}, \widehat{\mu^\epsilon}\overline{\widehat{\mu^\epsilon}}\rangle = (2\pi)^{-3}\langle \widehat{v}, |\widehat{\mu^\epsilon}|^2\rangle.$$

Since $g_\epsilon \in \mathcal{S}$, $\widehat{\mu * g_\epsilon} = \widehat{\mu}\widehat{g}_\epsilon$. Hence

$$E[g_\epsilon * \mu] = (2\pi)^{-3}\int \frac{4\pi}{|k|^2}|\widehat{g}_\epsilon|^2|\widehat{\mu}|^2 dk. \tag{B.2.3}$$

But $\widehat{g}_\epsilon(k) = e^{-\epsilon^2|k|^2/2}$ increases monotonically to 1 as $\epsilon \searrow 0$, hence by monotone convergence the right side of (B.2.3) tends to the right side of (B.2.2). Note that this even holds if the limit is infinite. On the other hand, the left side of (B.2.3) converges to $E[\mu]$ as $\epsilon \to 0^+$ by Corollaary A.1.2.

□

**Corollary B.2.2.** *If $\mu$ and $\nu$ are compactly supported Radon measures with finite energy, then*

$$E[\mu, \nu] = (2\pi)^{-3}\int \frac{4\pi}{|k|^2}\check{\mu}\widehat{\nu} dk.$$

*Proof.* By Theorem A.1.3, $E[\mu,\nu] = \lim_{\epsilon\to 0^+} E[g_\epsilon * \mu, g_\epsilon * \nu]$. But

$$E[g_\epsilon * \mu, g_\epsilon * \nu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{g}_\epsilon|^2 \,\check{\mu}\,\widehat{\nu}\, dk.$$

The integrand here is bounded in absolute value by

$$\frac{4\pi}{|k|^2}|\widehat{\mu}||\widehat{\nu}| \leqslant \frac{4\pi}{|k|^2}(\frac{1}{2}|\widehat{\mu}|^2 + \frac{1}{2}|\widehat{\nu}|^2),$$

both terms of which are integrable by (B.2.2) and the assumption that $E[\mu]$ and $E[\nu]$ are finite. Then the dominated convergence theorem gives

$$E[\mu,\nu] = \lim_{\epsilon\to 0^+} E[g_\epsilon * \mu, g_\epsilon * \nu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} \,\check{\mu}\,\widehat{\nu}\, dk.$$

□

**Corollary B.2.3.** *If $\mu$ and $\nu$ are compactly supported Radon measures with finite energy, then*

$$E[\mu,\nu] \leqslant \sqrt{E[\mu]E[\nu]}.$$

*Proof.* By Corollary B.2.2 and the Cauchy–Schwartz inequality,

$$\begin{aligned} E[\mu,\nu] =& (2\pi)^{-3}\int \frac{4\pi}{|k|^2}\check{\mu}\widehat{\nu} dk \\ \leqslant& \sqrt{(2\pi)^{-3}\int \frac{4\pi}{|k|^2}|\widehat{\mu}|^2 dk \cdot (2\pi)^{-3}\int \frac{4\pi}{|k|^2}|\widehat{\nu}|^2 dk} \\ =& \sqrt{E[\mu]E[\nu]}. \end{aligned}$$

□

**Corollary B.2.4.** *If $\mu$ and $\nu$ are compactly supported Radon measures with finite* *energy, then*

$$E[\mu - \nu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{\mu} - \widehat{\nu}|^2 dk.$$

*Proof.*

$$E[\mu - \nu] = E[\mu] - 2E[\mu, \nu] + E[\mu],$$

with all three terms being finite by assumption and Corollary B.2.3. But from Theorem B.2.2 and Corollary A.1.3,

$$E[\mu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{\mu}|^2 dk,$$

$$E[\mu, \nu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} \check{\mu}\widehat{\nu} \, dk,$$

and

$$E[\nu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{\nu}|^2 dk,$$

so

$$E[\mu - \nu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} \left[ |\widehat{\mu}|^2 - 2\check{\mu}\widehat{\nu} + |\widehat{\nu}|^2 \right] dk = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{\mu} - \widehat{\nu}|^2 dk.$$

□

**Corollary B.2.5.** *If $\mu$ is a signed Radon measure of compact support with $E[|\mu|] < \infty$, then*

$$E[\mu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{\mu}|^2 dk. \tag{B.2.4}$$

*Proof.* Writing $\mu = \mu^+ - \mu^-$ for the Jordan decomposition of $\mu$, substitute $\mu^+$ and $\mu^-$ in place of $\mu$ and $\nu$ in Corollary B.2.4. □

Finally, we present as a theorem that equation (B.2.4) holds *even when the* *energy of signed measure $\mu$ is infinite*, as long as it is defined. Per the discussion at the beginning of Section 3.2, the energy of a signed measure $\mu$ is defined (and possibly infinite) exactly when $E[\mu^+, \mu^-] < \infty$, with $\mu = \mu^+ - \mu^-$ being the Jordan decomposition of $\mu$.

**Theorem B.2.4.** *If $\mu$ is a signed measure of compact support such that $E[\mu]$ is defined, then*

$$E[\mu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{\mu}|^2 dk. \tag{B.2.5}$$

*Proof.* As discussed, $E[\mu]$ is defined exactly when $E[\mu^+, \mu^-]$ is finite, with $\mu = \mu^+ - \mu^-$ being the Jordan decomposition of $\mu$. In this case,

$$E[\mu] = E[\mu^+] - 2E[\mu^+, \mu^-] + E[\mu^-]$$

can be regarded as true and possibly infinite, for the expression on the right has no infinities of opposite sign. Utilizing again the Gaussian $g_\epsilon$ (see (B.1.1)), we have by Theorem A.1.3 that

$$\lim_{\epsilon \to 0^+} E[g_\epsilon * \mu^+] = E[\mu^+]$$

and

$$\lim_{\epsilon \to 0^+} E[g_\epsilon * \mu^-] = E[\mu^-],$$

even if the limits are infinite, and furthermore that

$$\lim_{\epsilon \to 0^+} E[g_\epsilon * \mu^+, g_\epsilon * \mu^-] = E[\mu^+, \mu^-].$$

It follows that

$$E[\mu] = \lim_{\epsilon \to 0^+} E[g_\epsilon * \mu],$$

even if infinite. But

$$E[g_\epsilon * \mu] = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{g_\epsilon}|^2 |\widehat{\mu}|^2 dk$$

by Theorem B.2.2. Since $\widehat{g_\epsilon}$ increases to 1 as $\epsilon \searrow 0$, (see (B.1.1)), the monotone convergence theorem gives that

$$\lim_{\epsilon \to 0^+} (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{g_\epsilon}|^2 |\widehat{\mu}|^2 dk = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{\mu}|^2 dk,$$

even if infinite. But then

$$E[\mu] = \lim_{\epsilon \to 0^+} E[g_\epsilon * \mu] = \lim_{\epsilon \to 0^+} (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{g_\epsilon}|^2 |\widehat{\mu}|^2 dk = (2\pi)^{-3} \int \frac{4\pi}{|k|^2} |\widehat{\mu}|^2 dk.$$

□

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