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Effects of Particle Size and Shape on Vapor Pressure

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Abstract: Thermodynamic theory treats equilibrium in fluid phases separated by an interface as requiring a balance of pressures in each phase with an isotropic tension in the interface. This mechanical model for surface thermodynamics follows from two assumptions in Gibbs' development of surface thermodynamic theory: the assumptions that the influence of interfaces on adjacent phases is limited to regions close to the physical interface and that surfaces are under isotropic tension. The first assumption is shown to be inconsistent with accepted concepts for adsorbed film-vapor equilibrium, and the second assumption is shown to be unnecessary. The predictions of each of two alternate assumptions, 1) that $(\partial G_p / \partial n)_{T,P} = \mu_v$ where G_p is the particle free energy, n the number of molecules in the particle, and μ_v is the chemical potential of the vapor; or 2) that $G_p/n = \mu_v$ are used to derive equations for particle-vapor equilibrium. Either model is shown to yield predictions that agree within reasonable error limits with experimental observations. Reasons are given for preferring the assumption $G_p/n = \mu_v$.

Introduction

The accepted theory of surface thermodynamics for fluids concludes that phases which are separated by a curved surface are under pressures which differ from each other because an isotropic tension in the surface enters the pressure balance.¹⁻⁵ This mechanical model describes the dependence of the vapor pressure of a liquid on its particle size in terms of the Kelvin (or Gibbs-Thomson) equation,^{3,4}

$$RT \ln P_c/P_n = \pm 2 \sigma V_m/r, \quad (1)$$

where R is the gas constant, T is the temperature, P_c is the vapor pressure above the curved surface, P_n the vapor pressure above a surface of negligible curvature, σ is the surface tension, V_m is the molar volume, and r is the radius of curvature. The sign is positive for drops and negative for vapor-filled bubbles.

The purposes of this paper are to point out that this surface thermodynamic theory depends upon two modeling assumptions in Gibbs' classic development which may not be necessary, and to explore the consequences of replacing them by each of two alternate assumptions. The first of these alternate assumptions is that a single component particle is in equilibrium with its vapor when

$$(\partial G_p / \partial \sigma)_{T,p} = \mu_v, \quad (2)$$

where G_p is total free energy of the particle, n is the number of molecules it contains, and μ_v is the chemical potential of its molecules in the vapor. Equation (2) has been considered to be completely

consistent with the mechanical model for surfaces and interfaces,^{5,6,7} but as shown below, Eq. (2), when applied to cavities in isotropic condensed phases, does not yield the predictions for vapor pressure made by the Kelvin equation.

The quantity $(\partial G/\partial T)_{T,p}$ has been called the chemical potential of the particle and given the symbol μ_p , but μ_p as so defined does not have an important characteristic of chemical potentials as defined for the components of phases of negligible surface or interfacial free energies. The quantity which does have is the average molecular free energy of the particle, G_p/n , which will be called \bar{G}_p here. Because \bar{G}_p has properties of a chemical potential, the alternate assumption for particle-vapor equilibrium to be examined is

$$\bar{G}_p = \mu_v \quad (3)$$

It will be shown in the Discussion section that predictions of either Eq. (2) or (3) probably agree with experimental observations to within the uncertainties in the data.

Defay used the assumption represented by Eq. (2) with a relation deduced by Wulff⁸ from a theorem of Gibbs⁴ and of Curie⁹ to derive what may be called a generalized Kelvin equation for solids and liquids. Wulff's relation predicts that the equilibrium shapes of faceted crystals and of cavities in crystals are those for which

$$\sigma_i/h_i = \sigma_j/h_j \dots \quad (4)$$

where σ_i , for example, is the surface tension of facet i and h_i is the distance of the facet from a common center. From Eqs. (2) and (4), Defay finds

$$RT \ln P_p/P_n = 2 \sigma_i V_m/h_i, \quad (5)$$

where P_p is the particle vapor pressure. If the surface tension of a crystal is independent of crystallographic direction, Eq. (5) reduces to Eq. (1) with a positive sign.

The derivation of Eq. (5) from Eq. (2) has been assumed to justify the use of Eq. (5) for cavities when a negative sign is assigned to one side of the equation.⁵ But for the simpler case of a fluid of total bulk free energy nG_b , where G_b is the standard free energy per mole, and m is number of the identical vapor-filled cavities of radius r , $G = nG_b + m \sigma(4 \pi r^2)$; thus $(\partial G/\partial n)_{T,P}$ depends on n and m . For a defined system, m is an integer and r can be replaced by a function of n . Then $(\partial G/\partial n)_{T,P}$ can be calculated; it is not in general $-2 \sigma V_m/r$. To describe the vapor pressures in faceted cavities by Eq. (5) with a minus sign requires the assumption that an envelope of plane surfaces creates pressure effects in the adjacent solid phases that are like those derived for fluids by means of the mechanical model.

Such an assumption is disputed,^{10,11,12} but even when it is accepted, the mechanical model of surfaces has not so far yielded an expression for equilibrium between particles or cavities of metastable shapes and their vapors. Persistent metastable crystal and cavity shapes are common,^{13,14} and it should be possible to describe corresponding metastable vapor pressures.

Theory

As noted in the Introduction, both Eqs. (2) and (3) lead to predictions that are at variance with some predictions of the mechanical model for surfaces. The differences in predictions can be traced to the differences in assumptions underlying the models. It is important, therefore, to identify the alternate assumptions and examine their plausibilities.

Gibbs' proof of Eq. (1) proceeded in two parts, each of which depended on a different assumption. The first part is a proof that the chemical potential of two phases which are in equilibrium are not changed by introducing a plane interface between them. This proof rests on the assumption that the masses of two phases separated by a surface S can "be divided into three parts by two surfaces, one on each side of S and very near to that surface, although at such a distance as to lie entirely beyond the influence of the discontinuity in its vicinity."

(Italics added)

Gibbs' assumption is persuasive if it is believed, as was reasonable at the time of his studies, that the influence of a surface on the thermodynamic properties of adjacent phases is limited by the range of chemical bonding forces. But, as Langmuir suggested later, equilibrium between a condensed phase¹⁵ or an adsorbed film¹⁶ and its vapor is maintained by a balance of independent fluxes of molecules from the condensed phase surface or film to the vapor, and from the vapor to the surface or the film. Gibbs' assumption is not applied to adsorbed film-vapor equilibrium. Instead, it is assumed that the strength or weakness of bonds that hold molecules in the film influences the

equilibrium pressure of those molecules throughout the entire vapor by governing the flux of molecules that leave the film.

The surface layers of a condensed phase can be viewed as an adsorbed film which happens to be on a substrate of the same chemical composition. In light of what is believed to be true for film-vapor equilibria, it may be doubted that the influence of a surface on adjacent phases is limited to a narrow band, as Gibbs envisioned. (One might instead expect that unless equilibration between surface and bulk regions of the condensed phase is rapid compared to condensed phase-vapor molecular exchange, vapor pressures would reflect equilibration with the surface molecules and not the bulk. But at least under free surface sublimation in vacuum, the molecular flux exchanged between a condensed phase and its vapor is usually small compared to exchange between the bulk condensed phase and its self-adsorption layer.¹⁷ Consequently, it is reasonable to assume that the molecules in surfaces of particles that have reached constant shapes are at equilibrium with molecules in the particle interior.)

Gibbs' second assumption was that because his Eq. (499)

$$\sigma \delta s - p' \delta v' - p'' \delta v'' = 0, \quad (6)$$

where δs is the change in surface area and p' and p'' are the pressures in the adjacent phases which are subject to the differential volume changes $\delta v'$ and $\delta v''$, "has evidently the same form as if a membrane without rigidity and with a tension σ , uniform in all directions, existed at the dividing surface," the surface should be treated as in tension. This is not a necessary assumption in that Gibbs' previous

development permits the interpretation of σ to be adopted here, as the free energy per unit area of surface; and Gibbs' assumption is not required by current atomistic models of surface chemical bonding.

This last point is illustrated by recent pseudopotential calculations¹⁸ that lead to the prediction that surface atoms of elemental solid silicon assume positions in the surface layer which are different from those of atoms in the bulk. The predicted positions are those that yield a minimum surface free energy. In the rearranged surface, each atom vibrates in an anisotropic force field about an equilibrium position; nothing in the model requires that an infinite surface plane should be viewed as in a state of tension.

If σ is not assumed to be a tension, then p' and p'' of Eq. (6) need not take unequal values when a surface is curved. It will be shown in the Discussion section that when Gibbs' first assumption is not adopted the known influence of surfaces on equilibrium and kinetic properties can be explained without invoking his second assumption, that surfaces are under tension. Some of the formal distinctions in predictions that arise when the assumption of Eq. (2) or of Eq. (3) replaces Gibbs' assumptions will first be delineated.

The vapor pressure of a single component bulk phase of negligible surface is given by $RT \ln P_b/P^0 = G_b$ where $-G_b$ is the molar free energy of vaporization to molecules at the standard vapor pressure P^0 . According to Eq. (2), $\mu_p = RT \ln P_p/P^0$. Therefore,

$$RT \ln P_p/P_b = \mu_p - G_b \quad (7)$$

The value of μ_p can be calculated from the total surface free energy, from n , and from the particle shape. (To do so requires the assumption that the differential should be taken at constant particle shape. The stable shapes of particles may vary with n ,¹³ so that this differential may not correspond exactly to the path of minimum particle free energy, but the difference between the differential at constant shape and that along the path of minimum free energy is probably small except for very small particles.)

For liquid drops, Eq. (7) reduces to the Kelvin equation. For crystals of the Wulff shapes, it reduces to Defay's Eq. (5). For a planar sheet in which the surface linear dimensions are $\gg \ell$, the film thickness, the total free energy, $G = nG_b + 2\sigma s/\ell$, if both sides of the sheet are exposed. Because s is independent of ℓ , $\mu_p = 0$; just as for the mechanical model, no effect of plane surfaces on vapor pressure is predicted. But as remarked above, for vapor filled cavities μ_p is a function not only of the dimensions of the cavities but of the quantity of the condensed phase in which the cavity is formed.

This paper has conformed to the nomenclature of Defay and Prigogine⁵⁻⁷ in defining $(\partial G/\partial n)_{T,P}$ as μ_p and in calling μ_p a chemical potential; but, as noted in the introduction, μ_p , as so defined, lacks an important characteristic of chemical potentials as defined for components of phases of negligible surface or interfacial free energies. For a single component bulk phase, $\mu_b = \bar{G}_b = G_b$. Consequently, the total free energy of the phase is $n\mu_b$. For a particle, $\mu_p \neq \bar{G}_p$, and in consequence the total free energy is not equal to $n\mu_p$. The inequality results because total surface free energies are proportional to $n^{2/3}$, and the total bulk free energy is proportional to n .

The average molecular free energy of a particle retains the characteristic of chemical potentials as they are defined for phases of negligible surface. To explore the consequence of assuming that particle-vapor equilibrium is defined by $\bar{G}_p = \mu_v$, a particle of fixed n is assumed to be at internal equilibrium if its total surface free energy is a minimum.¹³ This condition is equivalent to specifying either that the total particle free energy or alternately \bar{G}_p be a minimum at fixed n , but (because $\mu_p \neq \bar{G}_p$) is not equivalent to specifying that μ_p be a minimum.

If a system consists of a fixed total number of molecules, n_t , distributed between particles at internal equilibrium characterized by an average molar free energy \bar{G}_p and vapor molecules of average molar free energy \bar{G}_v , the total free energy of the system is a minimum independent of the distribution of molecules between vapor and particles provided $\bar{G}_p = \mu_v$. When $\mu_p = \mu_v$, the total free energy of n_t molecules depends on the molecular distribution between particles and vapor. The writer, therefore, favors the assumption of Eq. (3), $\bar{G}_p = \mu_v$, which by a procedure like that which leads from Eq. (2) to Eq. (7) leads from Eq. (3) to

$$RT \ln P_p/P_b = \bar{G}_p - G_b \quad (8)$$

For faceted crystals of negligible edge and corner excess free energies, Eq. (8) can be expressed in terms of σ_i , the excess surface free energy per unit area of a single facet i . First, it can be shown that the average molar free energy of the pyramid formed by the section

of the particle of base surface area A_i and height h_i is \bar{G}_p , the same average as for the particle as a whole. This follows because

$$\bar{G}_p - G_b = (\sigma_i A_i + \sigma_j A_j + \dots) / (n_i + n_j + \dots) \quad (9)$$

But n_i , for example, is $h_i A_i / 3 V_m$, so that

$$\bar{G}_p - G_b = \frac{3V_m}{h_i} \left[\frac{\sigma_i A_i + \sigma_j h_j A_j + \dots}{A_i + (h_j A_j / h_i) + \dots} \right] \quad (10)$$

Substituting from the Wulff relation, Eq. (4) gives

$$\bar{G}_p - G_b = 3V_m \sigma_i / h_i = 3V_m \sigma_j / h_j = \dots \quad (11)$$

so that

$$RT \ln P_p / P_b = 3 \sigma V_m / h_i \quad (12)$$

or, for spheres

$$RT \ln P_p / P_b = 3 \sigma V_m / r \quad (13)$$

For sheets and hollow thin-walled spheres of thickness $\ell \gg$ the inner radius r

$$RT \ln P_p / P_b = 2 \sigma V_m / \ell \quad (14)$$

The mechanical model predicts that the vapor pressure inside closed spheres of internal radius r will be $RT \ln P_p = -2 \sigma V_m / r$ and outside will be $RT \ln P_p / P_b = 2 \sigma V_m / (r + \ell)$.

Discussion

In principle, the question of which model better describes the behavior of physical and chemical systems should be settled by experimental observation. As a practical matter, however, the logic of the Kelvin equation has been so persuasive that authors^{19,20} whose "extensive and carefully conducted reproducible experiments"²¹ yielded results in conflict with its predictions have assumed that something other than the equation must be at fault. In contrast, the error limits on measurements that yield apparent agreement with the Kelvin equation have sometimes been somewhat optimistically estimated. It will be shown below that experiments which have been accepted as confirming the Kelvin equation for particles [and which are in equally good agreement with the assumption $\mu_p = \mu_v$ and Eq. (7)] are probably consistent, to within realistic assessments of experimental uncertainties, with the assumption $\bar{G}_p = \mu_v$ and Eq. (8).

The writer thinks that the assumptions underlying Eq. (8) are in better accord with known principles of molecular behavior than are assumptions of the mechanical model or of Eq. (2), and that Eq. (8) provides a more widely useful basis for understanding particle-vapor equilibria. Equation (8) will be compared to the generalized Kelvin equation of Defay, Eq. (5), in these terms before the experimental data are reviewed.

The derivation of Eq. (8) requires only the assumption that particles (like phases of negligible surface area) are at equilibrium with their vapor when the average molar free energy content is the same in the particle and the vapor. The derivation of the Kelvin equation assumes that the range over which molecules in a surface can affect

properties of the adjacent phases is limited by the range of molecular forces--an assumption which is inconsistent with the observation that adsorbed films establish an equilibrium pressure throughout the entire adjacent vapor phase. (Equilibration of films with the solid substrate is commonly prevented by purely kinetic factors. For example, given sufficient time, water adsorbed on silica reacts with the silica substrate; because film-condensed phase equilibration is slow, the metastable film-vapor equilibrium can be independently studied.) The assumption that σ of Eq. (6) is a tension is not a necessary assumption, and it is not invoked in the accepted models of adsorbed film-vapor equilibria or in modeling the energetics of atoms in surface layers.

Equation (8) asserts that the influence of surface on vapor pressure of a particle is defined by a single thermodynamic parameter, the change in average molar free energy of the particle that results from creation of the surface. The number of molecules in the surface and the average particle free energy depend on particle size and shape. In consequence, shape is a useful parameter for predicting \bar{G}_p , but the shape per se need not be known to define the particle-vapor equilibrium. Equation (5) requires that n , the surface free energy, and the nonthermodynamic parameter, particle shape, be known. If Eq. (8) is valid, it should be applicable to both stable and metastable particles of any shape.

Equation (8) provides a basis for a single consistent treatment of the nucleation of one phase in another. The assumption commonly used in nucleation theory is that nuclei can grow only after statistical fluctuations produce particles for which a favorable decrease in bulk

free energy exceeds the unfavorable free energy of interface formation.²² But some investigators have evaluated critical nuclei in terms of the mechanical pressure balance of Eq. (5).^{5,23} It has already been shown that Eq. (3) can be used in analyzing the kinetics of nucleation of super-heated vapor bubbles in liquids without recourse to the concept that vapor pressures in bubbles are lower than standard vapor pressures.²⁴

A variety of experimental tests of the Kelvin equation have been attempted. It seems now to be widely agreed²⁵⁻²⁷ that the unmodified Kelvin equation is inadequate to relate the curvature of liquid surfaces in small ($<0.1 \mu\text{m}$) capillaries or crevices. The influence of adsorbed films on effective capillary or crevice dimensions and on the vapor pressure must be taken into account. Adsorption and capillary equilibria will be the subject of a separate paper.

Thomä's measurement of the difference in vapor pressure between the surface of a reservoir and the meniscus of a liquid in a capillary in contact with the reservoir²⁸ is sometimes cited as a successful test of the Kelvin equation. Thomä, in fact, measured the small effect of height in a gravitational field on vapor pressure. The same height of capillary rise can be deduced either from the mechanical model for pressure balance or from minimization of the free energy as a function of surface free energy and gravity.²⁹

Two sets of measurements of vapor pressures as a function of particle size have been credited with confirming the Kelvin equation to within a few percent. La Mer and Gruen³⁰ equilibrated a solution of a volatile and nonvolatile component with droplets which had radii of 0.18 to 0.55 μm . Sambles, Skinner, and Lisgarten³¹ observed with a

transmission electron microscope the change in radii with time as droplets of molten lead and solid silver decreased in radii from 50 nm to ~ 3 nm.

For the range of particles studied by La Mer and Gruen, the expected ratio of vapor pressure of particles to the standard vapor pressure is ~ 1.01 . Equation (8) can be generalized to multicomponent systems by assuming that a component of a condensed phase particle will be in equilibrium with its vapor when the average molar free energy of the component in the particle is equal to that in the vapor. This assumption is consistent with, for example, Pauling's assumption that the thermodynamic properties of complex molecules are additive functions of characteristic bonding energies.³² Equation (13) then can be used for the volatile component to predict that $P_p/P_b \cong 1.015$.

The particles studied by La Mer and Gruen are reported to contain of the order of 95% of the volatile component. The compositions are obtained by an indirect method; it appears that $< 1\%$ error in the calculated compositions could reconcile the data to Eq. (13).

Sambles et al. evaluate their experimental errors as low enough to confirm the Kelvin equation to within $\pm 5\%$. Agreement with Eq. (13) would require that errors in measured rates be a factor of ~ 2 times greater than the true particle vaporization rate or that the true radii be 1.5 times those measured. Their work was carefully executed and their analysis is persuasive, but errors large enough to reconcile the data to Eq. (13) could be expected.

The droplets that Sambles et al. observed were attached to sides of crevices scored into a graphite film on molybdenum (for silver experiments) or palladium (for lead experiments). They believed that by

using a very low density of particles and studying only particles close to the top of a crevice they eliminated significant error from recondensation of vapor on the particles. But their analysis neglects the high probability that the deposition process would deposit more lead or silver at the bottom of a crevice than on its side walls. Evaporation of this additional metal, if its surface-to-volume ratio is high, could generate a vapor flux at the particles under observation high enough to reduce their net flux to \sim one-half that which they would show in vacuum.

Sambles et al. assumed that by measuring only those samples that left no observable residue behind they reduced the influence of impurities to a negligible level. This is a reasonable but unverified hypothesis; a monolayer of impurities over particle surfaces might retard vaporization significantly.

Experience with high-resolution electron microscopes at the National Center for Electron Microscopy³³ indicates that defocusing by 10 nm can cause systematic variations in apparent cross sections of \sim 6% for 25 nm radius particles. Instabilities in the objective lens power supply cause \pm 10 nm variations in focus. Observations of "definite small shape oscillations" by Sambles et al. with some samples caused them to reject those runs, but these oscillations may reflect variations in focus in the runs rejected, and an undiagnosed focusing error in other runs.

A 1 mm change in specimen height is found to produce a 44% change in apparent cross sections at 50,000x.³³ Undoubtedly, Sambles et al. positioned their calibrating screens and samples as close to the same

height as possible in their system, but this possible source of error is not discussed.

It is a nearly impossible experimental task to obtain quantitative proof, convincing to a skeptic, that small spherical particles definitely obey one of the equations: $RT \ln P_p/P_b = 2 \sigma V_m/r$ or $RT \ln P_p/P_b = 3 \sigma V_m/r$. Comparisons of the vapor pressures of unsupported solid films to vapor pressures of bulk solids might provide data with lower error limits. The mechanical model or the assumption $\mu_p = \mu_v$ predicts no difference in vapor pressures; the assumption $\bar{G}_p = \mu_v$ predicts films to have greater vapor pressures than bulk solids. Any possible weight change of the film suspended from a sensitive balance in an isothermal chamber with the bulk solid could be measured, but the difficulty of adequate temperature control would be formidable. The writer hopes that readers will be stimulated to devise and carry out other possibly definitive tests.

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