Resolution of the Problems of Replacement Free Energy, $1/S$, and Internal Consistency in Nucleation Theory by Consideration of the Length Scale for Mixing Entropy

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The problems of (i) replacement free energy, (ii) $1/S$, and (iii) internal consistency in the classical theory of nucleation, based on the capillarity approximation, are resolved by the proper evaluation of mixing entropy. [S0031-9007(97)03303-6]

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In the semiclassical limit, the physical entropy of a system is defined in *phase space.* The definition involves a continuum of microstates represented by a continuous hypervolume consistent with the macrostate. The continuum is resolved into a discrete set of physical states through division by Planck's constant (essentially a length scale of *action*) raised to an appropriate power, and the logarithm of this set of distinct states, multiplied by Planck's constant, then represents the entropy. Frequently, because of the use of a coarse grained model, it becomes necessary to evaluate, in *coordinate space* alone, *only a part* of the total entropy.

For example, in nucleation theory, the translational entropy of clusters (mixing entropy), associated with the continuum of positions available to mesoscopic drops (clusters), is such a partial entropy. In its evaluation, the number of distinct physical states corresponding to the continuum of configurations is a continuous hypervolume, a *pseudoconfiguration* integral that, like the total entropy, must be converted into a number Γ of discrete microstates through division by a length scale raised to an appropriate power. The mixing entropy is then obtained as $k \ln \Gamma$, where k is the Boltzmann constant. The length scale will depend upon the model, and its rigorous choice requires the problem to be referred back to phase space, where Planck's constant serves as an unambiguous scale (of action) [1].

In this Letter we show that, at least for vapor phase nucleation, the first two of the three issues [2–9] referred to in the title are simultaneously resolved by the correct choice of scale, while the third issue is *almost* resolved. A less rigorous partial analysis has appeared elsewhere [10].

The problems arise only because of the use of a model (in this case, the *capillarity approximation* [3]), and they would not arise in a truly molecular theory. Therefore our results are valid and consistent only within the confines of this important and much used model.

Consider a vapor containing stationary drops (clusters) of various sizes. Within the framework of the capillarity approximation, the Gibbs free energy of this system can be expressed as

$$G = N_{\text{vap}}\mu_{\text{vap}} + N_{\text{liq}}\mu_{\text{liq}} + \sigma A \,, \tag{1}$$

where N_{vap}, N_{liq}, μ_{vap}, and μ_{liq} are the total number of vapor molecules, the total number of molecules in drops, and the chemical potentials in the vapor and the bulk liquid, while σ is the surface tension and A is the aggregate surface area of the drops. If the drops are nonstationary their centers can adopt a continuum of positions, and there must be an additional entropy, the *mixing entropy,* that we denote by S_{mix}. Equation (1) is then replaced by

$$G = N_{\text{vap}}\mu_{\text{vap}} + N_{\text{liq}}\mu_{\text{liq}} + \sigma A - TS_{\text{mix}} \,. \tag{2}$$

If the system is dilute in drops, of which there are N_n containing n molecules and a total number $N_D = \sum_{n=2} N_n$, the pseudoconfiguration integral Z_D is V^{N_D}, where V is the volume of the system and $\Gamma = \prod_{n=2} (V/v_n)^{N_n}/N_n!$, where v_n is the volume scale (cube of length scale) for drops of size n.

With Z_D we encounter the first subtle feature generated by the model. Ordinarily, in the evaluation of the configuration integral of a system of molecules, V appears as the volume over which the center of mass of a molecule is integrated. But the drops of the capillarity approximation are located by their spherical boundaries and not by the positions of their centers of mass, which can fluctuate with respect to those boundaries. Thus V in Z_D is the volume of integration of the center of a sphere which, because of fluctuation, does not coincide with the center of mass. Thus, we use the term *pseudoconfiguration* integral.

In Γ, allowance is made for the volume scale to depend on drop size. $S_{\text{mix}} = k \ln \Gamma(\{v_n\})$ can be inserted into Eq. (2) which can be solved for $\{v_n\}$ in terms of G. If G were known exactly this would establish the value of $\{v_n\}$. This step would then represent the (implicit) process of referring the problem back to phase space. There are very few examples in which G can be known exactly, but there are many instances in which it can be estimated with some accuracy. We follow this procedure.

For discussing the issues in the title, the following expression for N_n, the equilibrium number of drops or clusters, is helpful (the classical theory of nucleation relies on the principle of detailed balance, so that the equilibrium distribution is of central importance),

$$N_n = (R/S)\,(N_{\rm vap}\exp\{-[n(\mu_{\rm liq} - \mu_{\rm vap}) + \sigma a_n]/kT\})\,. \tag{3}$$

The quantity in the bold parentheses, in which a_n is the surface area of a drop of n molecules, is the expression obtained within the classical theory [11]. R is a factor arising from the consideration of the so-called replacement free energy [2–6] whose origin lies in the consideration of the translational degrees of freedom of the drop, while $1/S$ [where $S = p_{\rm vap}/p_{\rm vap}^{(e)}$ is the supersaturation, not to be confused with the entropy, and $p_{\rm vap}$ and $p_{\rm vap}^{(e)}$ are, respectively, the actual pressure in the vapor and the saturation (equilibrium) vapor pressure at the temperature in question] is the $1/S$ factor, the necessity of which has been argued from a number of standpoints [7–9], e.g., so that Eq. (3) satisfies the law of mass action with respect to the concentration of single (unclustered) molecules. Both factors have been the subject of controversy.

The third issue is "internal consistency." This is the requirement that, upon setting n equal to unity in Eq. (3), $N_1 = N_{\rm vap}$. Artificial devices for ensuring this result have been introduced [12,13].

We show below that, within the precision of our *estimate* of the scale for the mixing entropy, the first two problems are solved by the use of that scale while the third is almost solved. Again, *both the volume scale and the solution are indigenous to the model based on the capillarity approximation.* The problems would not arise in a fully molecular theory.

Since G in Eq. (2) cannot be known exactly, we concentrate on arriving at a good estimate. Such an estimate has already been made using a strong plausibility argument [10].

Consider the partition function q_n of a *stationary* drop of n molecules. In terms of the capillarity approximation we write $q_n = \exp\{-f_n/kT\} = \exp\{-[(n\mu_{\rm liq} + \sigma a_n - p v_d(n))/kT]\}$, where $\mu_{\rm liq}$ is the chemical potential of the bulk liquid at the pressure p outside the drop and $v_d(n)$ is the drop volume, while f_n is its Helmholtz free energy. Note that the form of f_n appearing in the last equation is only valid for a *fully incompressible,* macroscopic drop [14]. This form appears in the unmodified classical theory, although that theory does not insist that the drop be incompressible. Since a typical liquid is only slightly compressible, the form is a reasonable approximation. However, the classical theory assumes a spherical drop to which (based on the capillarity approximation) it assigns a radius r determined by its volume $v_d(n)$ given by $n v_{\rm liq}$, where $v_{\rm liq}$ is the volume per molecule in the bulk liquid. Thus the drop consists of n molecules located, in effect, within a rigid spherical container of volume v_d, within which the actual volume, shape, and center of mass of the liquid can fluctuate. The theory does not concern itself with these details. Again, the quantity V appearing in Z_D results from an integration of the center of the *container* over V.

In the evaluation of the partition function of a system of molecules, the integration in coordinate space involves the coordinates of the *molecules,* the physical objects that determine the relevant degrees of freedom. In contrast, the containers only represent constraints applied to the integration.

Consider Fig. 1. Suppose the drop (or the center of the container) is moved through a vector distance $\mathbf{d}\lambda$ such that its new profile overlaps its original profile as in Fig. 1 and such that its nonoverlapped volume in the new position in du. All of the molecular configurations in the new position are not new. Those in which all of the molecules lie in the region of overlap belong to the drop in *both* its original and new positions. Thus, in augmenting the partition function, they should not be counted twice. The only contribution from the new position comes from configurations in which at least one molecule is outside the overlap region. This contribution is $q_n - q_n'$, where q_n' is the partition function for the case in which all of the molecules are in the region of overlap. But

$$q_n' = \exp\{-f_n'/kT\}$$
$$\text{and}\quad q_n' = q_n \exp\{-(f_n' - f_n)/kT\}, \tag{4}$$

and $f_n' - f_n$ is the reversible work that must be expended in compressing the fluid from its original spherical shape into the lens shaped region of overlap. In this compression the changes in volume and surface area are $dv_d(n) = -du$ and da_n, respectively. The calculation of the reversible work in this process via a standard thermodynamic formalism would involve the full application of Gibbsian surface thermodynamics [15], including the specification of an appropriate dividing surface and an unambiguous definition of the radius of the drop. But this would involve the quantities σ, ρ^σ, and r (where ρ^σ is the surface density) appropriate to the dividing surface, quantities that cannot be obtained without molecular theory. Thus we turn to another

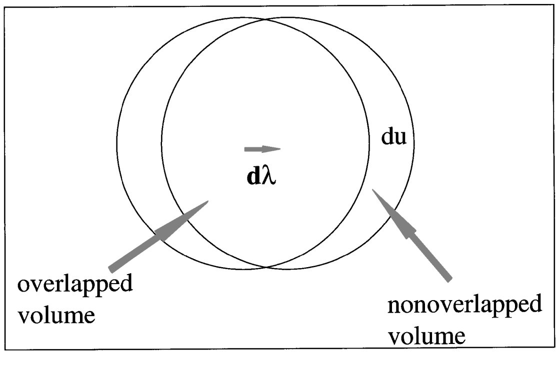

FIG. 1. Displacement of drop center through $\mathbf{d}\lambda$ to generate a nonoverlapped volume du.

method for the estimation of the volume scale. We express $f_n' - f_n$ as $P_n du$, where P_n is a positive quantity having the dimensions of pressure. Using Eq. (4), we find that $q_n' = q_n \exp\{-P_n du/kT\}$, so that the partially augmented partition function $q_n + (q_n - q_n')$ can be written as $Q_n(du) \equiv q_n + (q_n - q_n') = q_n + (q_n - q_n \exp\{-P_n du/kT\}) \approx q_n[1 + (P_n du/kT)]$. In the evaluation of Z_D, the center of the sphere must be moved over the entire volume V. After the first move, it has covered the volume $v_d(n)$ of the drop plus du. The shift of the drop can be repeated, and the further augmented partition function will contain an additional term of the type $q_n(P_n du/kT)$. As the drop is moved over V, the differential terms can be summed to yield the augmented partition function

$$Q_n = q_n[1 + (P_n V/kT)] = q_n(P_n V/kT) \qquad (5)$$

since, in the thermodynamic limit, the unity is ignored in comparison to $P_n V/kT$.

The partition function for a dilute system of drops, N_n of them of size n, immersed in an ideal vapor of N_{vap} molecules is then $Q = Q_{\text{vap}} \prod_{n=2} (Q_n^{N_n}/N_n!)$, where Q_{vap} is the partition function of the vapor. The Gibbs free energy is then $G = -kT \ln Q + pV$ and, after substituting the capillarity version of q_n into Eq. (5) and evaluating G in the prescribed manner, one finds $G = N_{\text{vap}} \mu_{\text{vap}} + N_{\text{liq}} \mu_{\text{liq}} + \sigma A - kT \ln \prod_{n=2} [V/(kT/P_n)]^{N_n}/N_n!$ Comparison of this equation with Eq. (2) shows that the last term represents $-TS_{\text{mix}}$, and that the argument of the logarithm must be identical with the Γ. Thus v_n must be given by kT/P_n, where P_n must still be identified.

The drop in Fig. 1 contains n molecules and is in contact with a uniform vapor of constant pressure p_{vap}. It is thus an example of the constant pressure ensemble [16], and, in the thermodynamic limit, its volume fluctuates with the variance [17] $\sigma_{v_d} = [kT v_d(n) \kappa]^{1/2}$, where κ is the isothermal compressibility of the liquid. This ensemble has enjoyed a less than fundamental physical foundation, but is known to yield correct results in the thermodynamic limit [16], where its pressure is equal to the pressure of the barostat, in this case p_{vap}. Recently, it has been the subject of further analysis [18,19]. In Eqs. (6.2) and (6.3) of Ref. [19], it is shown (in the notation of the present paper) that

$$kT(\partial \ln q_n/\partial v_d)_T = p_{\text{vap}} + [v(n)_d \kappa (\partial \ln q_n/\partial v_d)_{T,n}]^{-1}. \qquad (6)$$

In this equation, q_n may depend on variables additional to n, v_d, and T, e.g., it may also depend on a_n. However, the derivative in Eq. (6) is based on the assumption that a_n is a function of v_d, as would be the case if the system were spherical. Thus a_n enters Eq. (6) implicitly. If the small system was a gas, κ would be a strong function of v_d. However, the drop of the capillarity approximation is forced, by a hidden implicit constraint, to remain liquid, even under the relatively small pressure p_{vap}, so that κ is small and almost constant.

When the drop and v_d are large the second term on the right of Eq. (6) may be neglected, leaving the result $kT(\partial \ln q_n/\partial v_d)_T = p_{\text{vap}}$. Since, for a large system, surface effects are negligible, the left side of this equation is simply the pressure of the system. Thus we recover the result that the pressure *in* the system equals that of the barostat.

For a mesoscopic drop, v_d is small and p_{vap} in Eq. (6) can be ignored, with the result

$$(\partial \ln q_n/\partial v_d)_T = [kT v_d(n) \kappa]^{-1/2} = \sigma_{v_d}^{-1}. \qquad (7)$$

For the problem at hand, Eq. (7) may written as $q_n' = q_n \exp\{dv_d/\sigma_{v_d}\} = q_n \exp\{-du/\sigma_{v_d}\}$. Comparison of this value for q_n' with its use in defining P_n shows that

$$P_n/kT = 1/\sigma_{v_d} \quad \text{or} \quad v_n = kT/P_n = \sigma_{v_d}. \qquad (8)$$

Thus we arrive at the result that the volume scale for S_{mix} is identical with the variance of the fluctuating volume. The physical significance of Eq. (8) is evident; the location of the drop cannot be specified more closely than the range of fluctuation. Thus σ_{v_d} plays a role in resolving states in coordinate space similar to that of Planck's constant in phase space.

From Eq. (6), as the drop becomes large, P_n converges on p_{vap} so that $v_n = kT/P_n = kTp_{\text{vap}}$, and the length scale becomes the volume per molecule in the surrounding vapor. We show below that, under this circumstance, the classical theory is recovered, a physically reasonable result since the capillarity approximation really refers to a macroscopic drop. The volume scale given by Eq. (8) may be expressed as $v_n = kT/P_n = \sigma_{v_d} = n^{1/2}\sqrt{kT\kappa v_{\text{liq}}}$, where $v_d = n v_{\text{liq}}$ and v_{liq} are the volume per molecule in the liquid.

The required referral to the phase space definition of entropy occurred in the comparison of the last expression for G with Eq. (2) and the subsequent use of Eq. (6), since G in that expression was derived directly from the partition function (or phase volume) of the system. The expression for σ_{v_d}, with kT/P_n replaced by σ_{v_d} and V set equal to $N_{\text{vap}} kT/p_{\text{vap}}$, can now be used in the derivation of the equilibrium distribution of drop (cluster) sizes. The chemical potential μ_n of a drop of n molecules is obtained from $\mu_n = (\partial G/\partial N_n)_{N_{\text{vap}}, N_{n' \neq n}, T, p}$ with the result

$$\mu_n = (n\mu_{\text{liq}} + \sigma a_n + kT \ln \rho_{\text{vap}} \sigma_{v_d}) + kT \ln X_n, \qquad (9)$$

where $X_n = N_n/N_{\text{vap}}$, and ρ_{vap} is the vapor density. The quantitity in parentheses is the chemical potential in the standard state. The reader can verify that if P_n were set equal to p_{vap} [as would be the case, according to Eq. (6), if the drop were large] then v_n would be $kT/p_{\text{vap}} = 1/\rho_{\text{vap}}$, i.e., the volume per molecule in the vapor, and

σ_{v_d} in Eq. (9) would be replaced by this quantity. The logarithmic term would then disappear, and the quantity in parentheses would be identical to the result of the classical theory. This shows that the classical theory has (implicitly and incorrectly) chosen the volume scale to be the volume per molecule in the vapor.

The equilibrium size distribution is now obtained by substituting Eq. (9) into the law of mass action, $\mu_n = n\mu_{\rm vap}$. The result is Eq. (3) with

$$R = 1/\sigma_{v_d}\rho^{(e)}_{\rm vap}\,, \qquad S = \rho_{\rm vap}/\rho^{(e)}_{\rm vap}\,. \tag{10}$$

Thus $1/S$ appears naturally, and R, *independent* of S, is of the experimentally reasonable order of 10^4. Both factors have their origin in the inclusion of the mixing entropy.

If one were to assume that the liquid could be accurately modeled by a simple cell model of the liquid [20], the choice of the correct volume scale leads to *full* consistency, and, *in general*, the correct choice *almost* produces consistency. In the cell model, each of the $N_{\rm liq}$ molecules in the total volume $V_{\rm liq}$ behaves like an ideal gas within a cell of volume $v_{\rm liq}$, communal entropy [20] is accounted for, the reference level for energy is that of the ideal vapor, and the internal energy of vaporization is denoted by ΔU. The equilibrium vapor pressure proves to be $p^{(e)}_{\rm vap} = kT\rho_{\rm liq}\exp\{-(\Delta H - kT)/kT\}$, where $\rho_{\rm liq} = N_{\rm liq}/V_{\rm liq}$ is the liquid density and $\Delta H = \Delta U + kT$ is the heat of vaporization per molecule. Furthermore, $\kappa = -(1/V_{\rm liq})(\partial V_{\rm liq}/\partial p_{\rm liq})_{N_{\rm liq},T} = v_{\rm liq}/kT$. Within the capillarity approximation, the Gibbs free energy of vaporization of a single molecule is $\Delta G = \sigma a_1 - kT\ln(V_{\rm vap}/v_1)$, where a_1 is the surface area of a drop (volume $= v_{\rm liq}$) consisting of a single molecule and the last term in is due to the mixing entropy. Neglecting the slight temperature dependences of all other quantities except T itself, substitution of this expression for ΔG into the Gibbs-Helmholtz relation [21] yields $\Delta H = \sigma a_1 + kT$. Substitution of this ΔH into the equation for the saturation pressure yields $p^{(e)}_{\rm vap} = kT\rho_{\rm liq}\exp\{-\sigma a_1/kT\}$. Substitution of the equation for κ into the equation for σ_{v_d} gives $\sigma_{v_d} = v_n = v_{\rm liq}\sqrt{n}$. The theory is internally consistent, i.e., $N_1 = N_{\rm vap}$, since Eq. (3), with this equation for σ_{v_d} substituted into Eq. (10), with the result substituted back into Eq. (4) with n set to unity, and with the use of $\mu_{\rm liq} - \mu_{\rm vap} = -kT\ln S$, yields

$$\begin{aligned} N_1 &= (\rho_{\rm liq}\exp\{-\sigma a_1/kT\}/\rho^{(e)}_{\rm vap})N_{\rm vap} \\ &= (\rho^{(e)}_{\rm vap}/kT)/\rho^{(e)}_{\rm vap} = N_{\rm vap}\,, \end{aligned} \tag{11}$$

where the second step used the expression for the saturation pressure. Equation (11) is exact for the simplest cell model. However, if we had used the compressibility of a typical real liquid, the result for the volume scale would not be much different. Thus, within the caveat of having arrived only at an estimate, internal consistency is preserved and the three issues mentioned in the title are resolved.

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