

# Role of the Model Dependent Translational Volume Scale in the Classical Theory of Nucleation

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The replacement free energy correction, for vapor phase nucleation, in the classical theory of nucleation (CNT), is investigated within the confines of the renormalized representation of the molecular system implicit in the model, based on the capillarity approximation adopted by CNT. The replacement free energy is associated with the translational degrees of freedom of the clusters that serve as embryos for the formation of drops, and it is shown that, unless extreme care is exercised, the evaluation of this contribution to the free energy can involve a redundant counting of molecular configurations that can lead to a predicted nucleation rate in error by many orders of magnitude. It is demonstrated that the problem arises because of the use of a coarse grained renormalized version of the actual system and that the correction can be extremely sensitive to the type of renormalization (model) employed. In the case of CNT, in particular, error can arise from the fact that the drop used to model the cluster cannot be located more accurately than within the fluctuation of its volume. This fluctuation, in effect, generates a lattice whose sites the drop is restricted to occupy and whose lattice parameter is the cube root of the volume of fluctuation. This denial of accessibility of the continuum volume to the drop eliminates redundant counting. The form for the replacement free energy factor is derived, discussions of various subtle issues are presented, and similar problems are mentioned in connection with renormalized versions of molecular systems in other contexts (e.g., in the cases of microemulsions and polymers, and even in cases such as that of the constant pressure ensemble) where renormalization does not play a role.

## 1. Background

Recently, the authors published a letter in *Physical Review Letters*,<sup>1</sup> which dealt with the role in the classical theory of nucleation (CNT), of the so-called “length scale for configurational entropy” in the specification of (1) the replacement free energy,<sup>2–6</sup> (2) the  $1/S$  factor,<sup>7–9</sup> and (3) so-called internal consistency.<sup>10,11</sup> Now we have obtained additional results and also a new and more transparent derivation of the theory of that letter. In the present paper we report both of these developments.

In ref 1 the analysis was tied to the length scale (or volume scale) that resolved distinct physical states in coordinate space *alone* rather than in phase space (where the appropriate length scale is Planck’s constant). The problem only arises when one is forced to use a model that constitutes a renormalized version of a system, and when that model requires the evaluation of only the part of the *total* system entropy that refers to coordinate space alone. The problem is also widespread, appearing, in various forms, in such diverse systems as polymers, microemulsions, and nucleating systems. It also emerges in the constant pressure ensemble (at least the length scale problem emerges), even though entropy is not explicitly involved and a renormalized version may not be at issue.<sup>12–14</sup> Previous work

has shown that the relevant volume scale depends sensitively on the model.<sup>15</sup>

In CNT the model in question is based on the “capillarity approximation,”<sup>3</sup> (i.e., a cluster or *embryo* of the nucleating phase is regarded as a spherical liquid drop of uniform density equal to that of the bulk liquid and having a sharply defined interface with the surrounding metastable mother phase, which, in the case of a vapor, is regarded as an ideal gas). The surface tension associated with this interface is also chosen to be that of the bulk liquid. In ref 1, attention was focused on the nucleation of drops in a supersaturated vapor, and this focus will be continued in the present paper.

## 2. Partition Function of a Single Model Drop in a Vapor and Origin of the Volume Scale

Our ultimate goal is to derive an equilibrium distribution of clusters (drops) to be used in an application of the principle of detailed balance. In CNT this distribution proves to be<sup>16</sup>

$$N_n = \left[ N_{\text{vap}} \exp \left\{ - \frac{1}{kT} [n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \gamma a_n] \right\} \right] \quad (1)$$

where  $N_n$  is the equilibrium number of clusters consisting of  $n$  molecules,  $N_{\text{vap}}$  is the number of single molecules in the vapor,

$\mu_{\text{vap}}$  is the chemical potential of single molecules in that vapor,  $\mu_{\text{liq}}$  is the chemical potential of a molecule as if it were part of a bulk liquid at the pressure  $P$  outside of the drop,  $\gamma$  is the surface tension of the bulk liquid,  $a_n$  is the surface area of the drop assumed to have the uniform density of the bulk liquid,  $k$  is the Boltzmann constant, and  $T$  is the temperature. Both experimental and theoretical considerations have suggested that this expression should be modified to the form

$$N_n = \frac{R}{S} \left[ N_{\text{vap}} \exp \left\{ -\frac{1}{kT} [n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \gamma a_n] \right\} \right] \quad (2)$$

where  $S$  is the degree of supersaturation of the vapor given by

$$S = P/P_{\text{sat}} \quad (3)$$

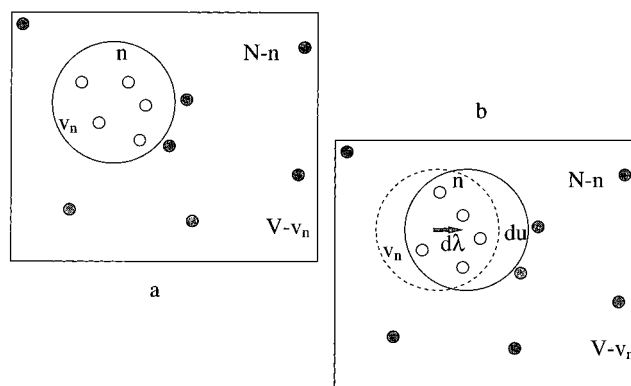
where again  $P$  is the pressure of the vapor and  $P_{\text{sat}}$  is the saturation pressure of the vapor at the temperature in question. The appearance of  $S$  in eq 2 is the so-called  $1/S$  correction<sup>7-9</sup> (whose origin is rooted in several considerations,<sup>9,17</sup> but without which the equilibrium distribution would not satisfy the law of mass action<sup>9</sup>). The factor  $R$  in eq 2 is due to the so-called replacement free energy<sup>2-6</sup> (closely connected to the translational degrees of freedom of the cluster) and is independent of  $S$ . A major goal of the present paper is the evaluation of  $R$  by the determination of a correct translational volume scale.

If we consider a spherical drop of  $n$  molecules at rest, its partition function within the canonical ensemble and within the confines of the capillarity approximation, may be expressed as

$$q_n = \exp \left\{ -\frac{1}{kT} (n\mu_{\text{liq}} + \gamma a_n - P v_n) \right\} \quad (4)$$

where  $v_n$  is the volume of the drop of uniform density equal to that of the bulk liquid. The expression in the numerator of the exponent is the Helmholtz free energy of the drop and is strictly correct only for a fully incompressible drop.<sup>18,19</sup> However, it is a reasonable approximation for drops having the small compressibility of a normal liquid. Because such a drop is to be used as a model of a cluster or embryo of the nucleating liquid phase, we will be interested in the full canonical ensemble partition function of a system of volume  $V$  consisting of an ideal gas of vapor molecules, at pressure  $P$  and temperature  $T$ , containing the drop (cluster).  $q_n$ , defined by eq 1, is then regarded as the partition function of a stationary cluster, and it is necessary to evaluate a kind of *configurational partition function* (configuration integral) for the cluster before the full partition function of the system can be specified. The configuration integral of a molecule is usually obtained by integrating the *center of mass* of the molecule over  $V$ , but in the case of the model drop the location of the center of mass is unknown since both that center and the volume of the drop are fluctuating. To proceed, therefore, we can integrate the geometric center of the drop over  $V$  (even though the fluctuating center of mass may not lie at that center) and then adjust for the consequences. The configuration integral derived in this manner may thus be referred to as a *pseudoconfiguration integral*. As indicated, it is convenient to use it in the evaluation of the full partition function, and to make the necessary corrections as we go along.

However, before proceeding further, it may be instructive to view the fundamental problem in another (more general) way. The CNT (capillarity approximation) model of the cluster represents a coarse grained, highly renormalized version of the actual system. Ideally (as in the case of almost all such models), the goal is to integrate over certain molecular degrees of freedom (usually, those that are most difficult to address by rigorous



**Figure 1.** (a) Drop of volume  $v_n$ , containing  $n$  molecules (open circles), embedded in an ideal gas of volume  $V - v_n$ , and consisting of  $N - n$  molecules (filled circles). (b) Drop profile (continuous circle) with center displaced by  $d\lambda$ . Dashed circle represents drop in original location. Drop molecules are in the lens shaped region created by the overlap of the original and displaced profiles. Nonoverlapped volume is denoted by  $du$ .

mathematical means) so as to arrive at a partly averaged system whose remaining degrees of freedom are more amenable to rigorous analysis. Unfortunately, the initial integration, aimed at the elimination, from explicit consideration, of difficult degrees of freedom, cannot usually be accomplished in a rigorous manner. Consequently, one is forced into an educated guess of the result of that integration, were it in fact to be carried out. The model that one is then presented with, *after the fact*, may then contain inaccuracies whose quantitative effects may be difficult to assess. Nevertheless, it may be possible to take steps, based on physical reasoning, to minimize this inaccuracy, subject to whatever subsidiary information is available. The present paper forms an example of this procedure.

Returning to the evaluation of the model partition function, we consider Figure 1. Figure 1a is a schematic of the drop, in a fixed position, embedded in a surrounding ideal vapor. The total volume and total number of molecules in the system are  $N$  and  $V$ , respectively. The open circles within the spherical drop of volume  $v_n$  represent the  $n$  molecules in the drop, while the filled circles in  $V - v_n$ , the remaining volume of the system, represent the  $N - n$  ideal vapor molecules in that volume. Because the molecules in the surrounding ideal vapor are decoupled from those in the drop, the partition function of the configuration shown in Figure 1a can be written in the following form

$$Q_n(0) = q_n(v_n) Q_{N-n}^{\text{id}}(V - v_n) \equiv q_n Q_{N-n}^{\text{id}} \quad (5)$$

The 0 in  $Q_n(0)$  indicates that the partition function corresponds to a configuration in which the center of the drop is fixed at an origin and  $q_n(v_n)$  is simply the drop partition function presented in eq 4. The second factor on the right is the partition function of the ideal vapor containing  $N - n$  molecules in the volume  $V - v_n$ , and the id in the superscript indicates "ideal". The product form in the middle of eq 5 results from the decoupling of the molecules of the vapor from those of the drop, and the product at the extreme right is simply a notational contraction.

In the next step we begin to allow the system to assume more than one configuration, by allowing additional positions for the center of the drop (i.e., we begin the implicit evaluation of the configuration integral). In this context, Figure 1b illustrates a configuration in which the center of the drop has been displaced through a vector distance  $d\lambda$ . The original location in Figure 1a is shown by the dashed outline. The important conclusion

to be gleaned from Figure 1b is that the movement of the model drop (by moving its center) does not necessarily lead to *molecular* configurations that were not possible in Figure 1a. For example, the configuration of the molecules in the drop, shown in Figure 1b, such that all drop molecules lie in the lens shaped region of overlap between the original and the displaced outline of the drop, is a possible configuration of the same molecules in Figure 1a. Thus, at least as far as the drop is concerned, the configuration of drop molecules in Figure 1b does not represent a new physical state. To have a new physical state there would have to be *at least one* drop molecule in the nonoverlapped volume designated as  $du$  in Figure 1b. Such a configuration is not possible in Figure 1a. A similar consideration (not addressed in ref 1) applies to the molecules of the surrounding ideal vapor, and we will address it below. For the moment we concentrate on the drop.

To represent the augmented partition function that includes the new configuration, both factors in eq 5 must be modified, but the modifications must avoid counting the redundant configurations. This means that in considering the augmented partition function of the drop, for example, the addition to  $q_n$  is not merely another  $q_n$  centered at the new location of the drop. Instead, the addition to  $q_n$  should include only new configurations in which there is at least one drop molecule in the nonoverlapped volume  $du$ . Denote by  $q'_n$  the partition function for the drop "compressed" into the lens shaped form appearing in Figure 1b. Since the compression is really differential ( $du$  is a differential volume),  $q'_n$  clearly is given by

$$q'_n = q_n - \frac{\partial q_n}{\partial v_n} du \quad (6)$$

where the minus sign appears because  $du$  is positive.  $q'_n$  is the partition function of the redundant configurations so that the required addition to the partition function, less this redundancy, is  $q_n - q'_n$ . Substituting eq 6 into this expression gives, for the addition,

$$q_n - q'_n = \frac{\partial q_n}{\partial v_n} du \quad (7)$$

so that the augmented partition function becomes

$$q_n + \frac{\partial q_n}{\partial v_n} du \quad (8)$$

This is the factor that must replace  $q_n$  in eq 5 if the partition function is to include the displaced position of the drop.

We still have to deal with  $Q_{N-n}^{\text{id}}$  the second factor on the right of eq 5 that was not addressed in ref 1. When the drop is displaced, and even if its molecules are in a configuration within the lens shaped overlap region, the configuration of the *total* system, vapor plus drop, will not be redundant as long as there is at least one vapor molecule within the nonoverlapped region to the *left* of the lens, since such a position for a vapor molecule was impossible in the original configuration in Figure 1a. Thus, in order for the configuration to be fully redundant, the configurations of the vapor molecules must lie outside of the composite figure generated by the two spheres in Figure 1b. Thus, like the drop, the volume of the vapor must be compressed in order to generate a redundant configuration...but this time, from the original  $V - v_n$  to  $V - v_n - du$ . Then the argument for the augmented second factor proceeds in exactly the manner of the argument for the first factor and leads to the result

$$Q_{N-n}^{\text{id}} + \frac{\partial Q_{N-n}^{\text{id}}}{\partial (V - v_n)} du \quad (9)$$

The substitution of eqs 8 and 9 for  $q_n$  and  $Q_{N-n}^{\text{id}}$  on the right of eq 5 then yields for the augmented partition function the result

$$Q_n(du) = \left[ q_n + \frac{\partial q_n}{\partial v_n} du \right] \left[ Q_{N-n}^{\text{id}} + \frac{\partial Q_{N-n}^{\text{id}}}{\partial (V - v_n)} du \right] \quad (10)$$

corresponding to translational motion restricted to the volume  $du$ .

We can write

$$\frac{\partial q_n}{\partial v_n} = q_n \frac{\partial \ln q_n}{\partial v_n} = q_n \frac{P_n}{kT} \quad (11)$$

$$\frac{\partial Q_{N-n}^{\text{id}}}{\partial (V - v_n)} = Q_{N-n}^{\text{id}} \frac{\partial \ln Q_{N-n}^{\text{id}}}{\partial (V - v_n)} = Q_{N-n}^{\text{id}} \frac{P}{kT} \quad (12)$$

where  $P_n$  and  $P$  have the dimensions of pressure and where indeed, from the usual relations in the canonical ensemble for a system in the thermodynamic limit,  $P$  must be the pressure of the surrounding vapor.

$P_n$ , however, demands further discussion. When the drop is small enough, surface as well as volume work must be considered. Indeed, there may be other kinds of work that depend on "shape" or deformation. To simplify the discussion, consider a case in which the only additional work is surface work. Then, a simple analysis of the canonical ensemble for a system (small enough so that surface terms are important) shows that pressure is specified by

$$p_n = kT \left( \frac{\partial \ln q_n}{\partial v_n} \right)_{T,n,a_n} \quad (13)$$

and that surface tension is given by

$$\gamma = -kT \left( \frac{\partial \ln q_n}{\partial a_n} \right)_{T,n,v_n} \quad (14)$$

On the other hand, if we impose a geometrical condition on the drop such that the surface area  $a_n$  is a known function of  $v_n$ , (e.g., if the drop is forced to remain spherical, as in CNT) then we can write

$$kT \left( \frac{\partial \ln q_n}{\partial v_n} \right)_{T,n} = kT \left( \frac{\partial \ln q_n}{\partial v_n} \right)_{T,n,a_n} + kT \left( \frac{\partial \ln q_n}{\partial a_n} \right)_{T,n,v_n} \left( \frac{\partial a_n}{\partial v_n} \right)_{T,n} = P_n \quad (15)$$

where  $P_n$  is the quantity appearing in eq 11. The substitution of eqs 13 and 14 into eq 15 yields

$$P_n = p_n - \gamma \left( \frac{\partial a_n}{\partial v_n} \right)_{T,n} \quad (16)$$

If the drop is constrained to remain spherical, then

$$\left( \frac{\partial a_n}{\partial v_n} \right)_{T,n} = \frac{2}{r} \quad (17)$$

where  $r$  is its radius, so that substitution of eq 17 into eq 16 yields

$$P_n = p_n - \frac{2\gamma}{r} \quad (18)$$

which is identical to the Laplace equation.<sup>20</sup> This identity shows that  $p_n$  is the pressure *inside* of the drop, while  $P_n$  is the pressure *P outside* of the drop. There are several caveats. One refers to the fact that the canonical ensemble relations, eqs 13 and 14, are *equilibrium relations*. Thus, in the absence of a carrier gas,  $P_n$  and  $P$  should be the vapor pressure of the drop, or in the presence of a carrier gas of partial pressure  $P^\circ$ ,  $P_n$  and  $P$  should equal the vapor pressure of the drop plus  $P^\circ$ . But if the surrounding vapor is supersaturated, only the drop that serves as a condensation nucleus (i.e., the drop that satisfies the Kelvin relation,<sup>21,22</sup> can be in (unstable) equilibrium with the vapor and have  $P_n$  given by its vapor pressure augmented by  $P^\circ$ . In a saturated vapor the relation applies trivially to a drop of infinite radius. Another *important* caveat relates to the fact that there can be circumstances under which eq 18 may *not* be valid! We discuss this issue in the following section.

It is useful to continue this line of reasoning concerning  $P_n$  by returning to Figure 1 which involves a compression of the drop from a spherical form to the lens shaped region of overlap corresponding to the initial and displaced positions of the drop. As long as the displacement is infinitesimal (i.e.,  $d\lambda$ ) it is a simple matter of geometry to show that the changes in volume and surface area of the drop during such a compression are given by

$$dv_n = -\pi r^2 |d\lambda|, \quad da_n = -2\pi r |d\lambda| \quad (19)$$

so that the ratio of the first to the second differential is once again  $2/r$ , as in eq 17. In this case the constraint that relates the change in surface area to volume is the required transformation of the drop from a sphere to a lens shape. In any event, the result is again eq 18 and  $P_n$  is again seen to be the external pressure. This simple result, although intuitively satisfying, is somewhat misleading for reasons that are elaborated in the following section. Thus for the time being we do not set  $P_n = P$ , even for the nucleus, but continue to refer to it as  $P_n$  without attempting to establish its precise physical meaning.

The substitution of eqs 11 and 12 into eq 10, and expansion of the result to terms linear in  $du$ , yields

$$Q_n(du) = q_n Q_{N-n}^{\text{id}} + q_n Q_{N-n}^{\text{id}} \left[ \frac{P_n}{kT} + \frac{P}{kT} \right] du \quad (20)$$

We can now repeat the process of drop displacement, and some thought will show that in each displacement there will be an augmentation of the partition function exactly equal to the second term on the right of eq 20. If the process of displacement is continued until the entire volume  $V$  is covered, the resulting partition function will then contain a sum of such terms that represents an integral over  $V$  such that, in place of eq 20, we obtain

$$Q_n(V) = q_n Q_{N-n}^{\text{id}} + q_n Q_{N-n}^{\text{id}} \left[ \frac{P_n}{kT} + \frac{P}{kT} \right] V \approx q_n Q_{N-n}^{\text{id}} \left[ \frac{V}{kT(P_n + P)} \right] \quad (21)$$

where in the last step we have retained only the term in  $V$  because of its overwhelming macroscopic size. Equation 21 is

the partition function of a single drop of size  $n$ , surrounded by an ideal vapor of pressure  $P$ , in the volume  $V$ . The *pseudoconfiguration* integral has been evaluated implicitly and is represented by the factor  $V$ . However, because of the redundancy, illustrated by the discussion concerning Figure 1, its magnitude must be reduced (i.e., the redundancy in the enumeration of configurations must be removed). In eq 21, we see that in fact this reduction is accomplished through division by the volume  $\vartheta_n = kT/(P_n + P)$ . It is as if the center of the drop was restricted to a simple cubic lattice of sites (with lattice parameter  $(\vartheta_n)^{1/3}$ ), instead of being allowed to move continuously throughout  $V$ .

Since  $Q_{N-n}^{\text{id}}$  refers to an ideal gas, we can write it explicitly as

$$Q_{N-n}^{\text{id}}(V - v_n) = \frac{(V - v_n)^{N-n}}{\Lambda^{3(N-n)} (N-n)!} \approx \frac{V^{N-n}}{\Lambda^{3(N-n)} (N-n)!} e^{-(N-n)v_n/V} = Q_{N-n}^{\text{id}}(V) e^{-Pv_n/kT} \quad (22)$$

where, in the second step, we have taken advantage of the fact that  $v_n \ll V$ , and in the last step we have used the equation of state of an ideal gas.  $\Lambda$  is the thermal deBroglie wavelength of a single molecule. The substitution of this result into eq 21 yields, finally, for the single drop partition function, the expression

$$Q_n(V) = Q_{N-n}^{\text{id}}(V) \left[ \frac{V}{kT(P_n + P)} \right] q_n(v_n) e^{-Pv_n/kT} \quad (23)$$

In closing this section it is appropriate to reiterate that we have now identified the volume scale as  $\vartheta_N = kT/(P_n + P)$ , but that the problem remains the explicit evaluation of  $P_N$ .

### 3. Determination of $P_n$ : Effect of the Model

The identification of  $P_n$  (or  $\vartheta_n$ ) brings to the fore the central role played by the *model*. In the CNT a physical cluster is represented by a liquid drop (capillarity approximation), but still the model is not clear about many specifics. For example, in eq 1, the exponent contains the free energy of an *incompressible* drop, but it is never specifically stated that the model drop is incompressible. In fact, if it were, it would not represent a real drop since a real drop *is* compressible! However, since its compressibility is very small, the free energy in the exponent can be regarded as an excellent approximation, so that the issue of "compressible versus incompressible" never arises. Nevertheless, we can inquire into how the translational free energy of the drop is affected if we do insist that it is *completely* incompressible. In such a case, as long as the drop is required to remain spherical as is assumed in the CNT, the center of mass would have to coincide with the geometric center of the drop. It can be demonstrated that the immediate effect is to set  $\vartheta_n$  equal to the cube of the thermal deBroglie wavelength of a particle having the mass of the drop. Then it can be shown that, in essence, this leads to the exceedingly large value of  $R$  determined by Lothe and Pound.<sup>2</sup> Since both experiment and the popular consensus deny this large value, a model in which the drop is completely incompressible does not seem satisfactory.

If we then allow the drop to be compressible and to have the compressibility of the bulk liquid, the drop volume must be allowed to fluctuate. The fluctuation is at fixed  $n$  (not fixed *average*  $n$ ) so that the drop is not necessarily in *material* equilibrium with the surrounding vapor. The easiest way to



visualize this situation is to imagine that the drop is contained within a closed volume delineated by an abstract membrane having no elastic tension. The membrane does not allow the mixing of molecules of the surrounding vapor with those of the drop (i.e., it is impermeable to both drop and vapor molecules). Considering, in the interest of simplicity, the case in which carrier gas is absent, if  $P$  the pressure of the vapor is less than the vapor pressure of the drop within the membrane, *inside* the membrane molecules will “evaporate” from that drop so that, in a crude sense (since the system is not in the thermodynamic limit), inside the membrane vapor and a *smaller* drop will coexist and  $v_n$  will have increased. Because of surface tension, the vapor pressure of the smaller drop will exceed that of the original drop, and evaporation will continue until only vapor remains inside the membrane, and this vapor will expand until its pressure equals the external pressure  $P$ .  $v_n$  will then be that of a vapor rather than a liquid (contrary to the requirements of the CNT model).

The preferred method for dealing with detailed balance in vapor phase nucleation theory (the so-called *kinetic method*<sup>17</sup>) involves reference to the equilibrium distribution of clusters in the *saturated* vapor. In deference to the importance of this procedure we will continue the immediate discussion by considering drops in such a saturated vapor, but the conclusion can easily be demonstrated for a vapor that is either unsaturated or supersaturated. If  $P$  is the pressure in the saturated vapor (i.e., the vapor pressure of the bulk liquid, then any drop of less than infinite radius will exhibit a vapor pressure that exceeds  $P$ ). Thus the argument of the preceding paragraph will apply to drops of any size and each will evolve toward a vapor as a final state, thereby violating a requirement of the CNT model.

The only way to ensure this requirement would involve the application of additional constraints to the drop so that the fluctuation of its volume remained within the limits typical of the bulk liquid. Such constraints would provide another means for the drop to exchange work with its environment (i.e., work could be done against the constraints). This would generate additional terms in eq 15 because forces in addition to  $p_n$  and  $\gamma$  would be involved and would also involve these forces. The simple Laplace relation would be compromised. This constitutes the elaboration of the second caveat mentioned below eq 19. The argument of the above few paragraphs is of course closely connected to the Kelvin relation<sup>21,22</sup> that specifies the vapor pressure of a drop. However that relation is usually applied to a drop that can exchange molecules with *all* of the surrounding vapor. Since our drop is a *closed* system in which  $n$  must remain constant, some qualifying explanation beyond simple mention of the Kelvin relation seems necessary.

The single exception to the above scenario occurs in the case of very large, essentially infinite, drops. In that case the vapor pressure of the drop would be that of the bulk liquid (i.e., the pressure of the saturated vapor) so that the drop would have no tendency to expand, and additional constraints would be unnecessary. Then the Laplace relation would still hold and  $P_n$  would equal  $P$ .

In the analysis surrounding Figure 1, the choice of  $v_n$  was dictated by the density of the bulk liquid; the CNT model **specifically** chooses a cluster of fixed volume given by  $v_n = n\rho_{\text{liq}}$  where  $\rho_{\text{liq}}$  is the density of that bulk liquid. In a real drop  $v_n$  would fluctuate, and the choice of  $v_n$  in CNT is therefore an *average* volume that we are forced to use within the framework of the model. The relative magnitude of the fluctuation should be small as it is in the bulk liquid, and it should be controlled by the isothermal compressibility of that liquid at its normal

density. In view of the previous discussion, this situation may have to be conditioned by the application of constraints that force the drop to have this value of compressibility. Of course, these constraints enter into  $q_n$ . It is actually possible to determine  $P_n(v_n)$ , where  $v_n$  is the volume required by CNT, through an analysis of the fluctuation of a compressible drop.

This determination is facilitated by the introduction of an equation similar to eq 5 and differing from it in that  $q_n$  is replaced by  $dq_n$  given by

$$dq_n = q_n(v_n + dv_n) - q_n(v_n) = \frac{\partial q_n}{\partial v_n} dv_n = q_n \frac{\partial \ln q_n}{\partial v_n} dv_n \quad (24)$$

The meaning of  $dq_n$  is obvious. It is the difference between  $q_n$  for a drop of volume  $v_n$  and one of volume  $v_n + dv_n$ . As such, it is a partition function that includes only those molecular configurations found in  $v_n + dv_n$  that *are not* found in  $v_n$ . Clearly, in the larger volume, all of the configurations in the smaller volume could be realized as well as additional configurations that are characterized by having *at least* one molecule in  $dv_n$ . This molecule has been termed the “shell molecule” and has now been discussed in a variety of contexts.<sup>13,14,23,24</sup> It allows one to avoid redundant counting of configurations. It is the way in which the volume of the drop must be defined in terms of the degrees of freedom of its *molecules* rather than by the volume of some container in which it resides.<sup>25,26</sup>

Since the drop is fluctuating, its full partition function, with its center fixed, must involve a sum over all volumes  $v_n$ , and the partition function of the full system, vapor plus drop, must also involve this sum. At *one* particular volume, the full partition function is given by eq 5 with  $q_n$  replaced by  $dq_n$  and, so for the sum over all volumes, the partition function is given by

$$\mathcal{Q}_n(0) = \int_{v_n} dq_n \mathcal{Q}_{N-n}^{\text{id}}(V - v_n) = \int_{v_n} \frac{\partial \ln q_n}{\partial v_n} q_n \mathcal{Q}_{N-n}^{\text{id}}(V - v_n) dv_n = \int_{v_n} \frac{P_n}{kT} q_n \mathcal{Q}_{N-n}^{\text{id}}(V - v_n) dv_n \quad (25)$$

where we have used eq 11. Substituting eq 22 gives

$$\mathcal{Q}_n(0) = \mathcal{Q}_{N-n}^{\text{id}}(V) \int_{v_n} \frac{P_n(v_n)}{kT} q_n(v_n) e^{-Pv_n/kT} dv_n \quad (26)$$

The integral in this equation is the partition function for a *constant pressure ensemble* in which the volume scale is  $kT/P_n$ . This ensemble and its volume scale, especially for the case of a small system, has recently been the subject of considerable attention.<sup>13–15</sup> For the purposes of CNT, we need to determine  $P_n(v_n)$  where  $v_n$  is the volume dictated by the density of the bulk liquid, so that  $v_n$  is the average volume of the fluctuating drop. For a macroscopic drop, where the mode and the mean can be considered equal, this average could be obtained by determining the value of  $v_n$  that maximizes the integrand in eq 26. For a small drop, this procedure begins to lose accuracy, but usually it remains an excellent approximation down to extremely small systems. For this reason, and because of the simple physically satisfying result that it yields, we adopt it here.

Then, differentiating the integrand with respect to  $v_n$ , and setting the result equal to zero to determine the maximum, yields the relation

$$-kT \frac{\partial \ln P_n}{\partial v_n} = kT \frac{\partial \ln q_n}{\partial v_n} - P = P_n - P \quad (27)$$

where in the last step we have used eq 11. The left side of eq 27 can be expressed as

$$-kT \frac{\partial \ln P_n}{\partial v_n} = -\frac{kT}{P_n} \frac{\partial P_n}{\partial v_n} = \frac{kT}{P_n v_n} \left( -v_n \frac{\partial P_n}{\partial v_n} \right) = \frac{kT}{P_n v_n \kappa} \quad (28)$$

where  $\kappa = -(\partial v_n / \partial P_n)_T / v_n$  is the isothermal compressibility of the drop. The substitution of eq 28 into eq 27 yields

$$P_n^2 - P P_n - \frac{kT}{\kappa v_n} = 0 \quad (29)$$

The physically meaningful root of this quadratic equation is

$$P_n = \frac{P}{2} + \sqrt{\frac{P^2}{4} + \frac{kT}{\kappa v_n}} \quad (30)$$

This simple result is remarkable in many respects. It is general in the sense that it is valid, independent of whether constraints of the sort discussed above (required in order to maintain the drop at the uniform average density characteristic of the bulk liquid) are present. Furthermore, for a very large drop,  $\kappa v_n$  would be large enough so that the second term under the square root sign could be neglected to yield the result,

$$P_n = P \quad (31)$$

This confirms the conclusion arrived at in the qualitative discussion at the beginning of this section, namely that  $P_n$  would equal the external pressure, and the simple Laplace relation would hold for a large drop.

In the opposite extreme, with  $\kappa$  and density still typical of a liquid, the second term under the square root sign dominates so that, to a high degree of approximation,

$$P_n = \sqrt{\frac{kT}{\kappa v_n}} \gg P \quad (32)$$

This is also in accord with the qualitative discussion at the beginning of this section (of the caveat of the preceding section), and that discussion therefore explains the physical basis of eqs 31 and 32. Finally, if the "drop" consisted of vapor so that  $\kappa$  was large, the second term would again be negligible and  $P_n$  would again be equal to  $P$ .

The remarkable (and useful) aspect of the fluctuation analysis is that it has allowed us to treat the effects of the constraining forces (when such forces are present), to the degree necessary for the determination of  $P_n$ , without having to specify the precise nature of those forces! The minimum information required is the value of an assumed (uniform) average density and that of the corresponding  $\kappa$ .

Equation 32 requires

$$\vartheta_n = \frac{kT}{P_n + P} \approx \frac{kT}{P_n} = \sqrt{kT \kappa v_n} = \sigma_n \quad (33)$$

where, in the second step, we have used the fact that  $P_n$  specified by eq 32 is much larger than  $P$ . The quantity  $\sigma_n$  is the variance of the volume fluctuation in the standard formulation of the constant pressure ensemble.<sup>27</sup> Thus in the case of the liquid drop, eq 33 shows that the volume scale is the variance of the volume fluctuation of the drop or, more simply, the volume of

fluctuation. It is as if there is an *uncertainty principle*, in coordinate space alone, such that the drop cannot be located more precisely than within its volume of fluctuation.

#### 4. An Assembly of Drops

We now turn our attention to an assembly of drops of varying size, and attempt to derive the equilibrium size distribution  $N_n$  such that there are  $N_n$  drops containing  $n$  molecules. In the interest of generality, we do not restrict the argument to the cases in which the vapor is either undersaturated or at most saturated, but allow supersaturation as well. However, in the latter case the vapor must be subject to an implicit formal constraint (whose nature we need not specify) that preserves supersaturation. If, in the development of the full theory of nucleation, the preferred *kinetic method* is used, the necessary equilibrium distribution, at saturation, can be extracted as a special case of the distribution derived here.

For the purpose of deriving the equilibrium distribution, eq 23 must be replaced by the partition function for the assembly. The first step in this process is the replacement of the partition function for the ideal vapor in eq 22 with the corresponding function appropriate to the multidrop system. Thus denoting the number of single molecules by  $N_1$  we write

$$Q_{N_1, N_n}^{\text{id}} (V - \sum_{n=2} N_n v_n) = \frac{(V - \sum_{n=2} N_n v_n)^{N_1}}{\Lambda^{3N_1} N_1!} \approx Q_{N_1, N_n}^{\text{id}} (V) \prod_{n=2} (e^{-P v_n / kT})^{N_n} \quad (34)$$

where in the last step, the same expansion was used as in the last two steps of eq 22. Assuming that the drops (clusters) do not interact with one another, we can then write for the complete partition function of the drops-vapor system in a particular distribution  $N_n$ , the expression

$$Q_{N_n} (V) = Q_{N_1, N_n}^{\text{id}} (V) \prod_{n=2} (e^{-P v_n / kT})^{N_n} \prod_{n=2} \left[ \frac{(P_n + P) q_n V}{kT} \right]^{N_n} / N_n! = Q_{N_1, N_n}^{\text{id}} (V) \prod_{n=2} \left[ \frac{(P_n + P) q_n V e^{-P v_n / kT}}{kT} \right]^{N_n} / N_n! = \frac{V^{N_1}}{\Lambda^{3N_1} N_1!} \prod_{n=2} \left[ \frac{(P_n + P) q_n V e^{-P v_n / kT}}{kT} \right]^{N_n} / N_n! \quad (35)$$

where we have made use of both eqs 21 and 34. The full partition function, including all distributions, is then

$$Q_n (V) = \sum_{\{N_n\}} Q_{N_n} (V) = \sum_{\{N_n\}} \frac{V^{N_1}}{\Lambda^{3N_1} N_1!} \prod_{n=2} \left[ \frac{(P_n + P) q_n V e^{-P v_n / kT}}{kT} \right]^{N_n} / N_n! \quad (36)$$

where the sums are over all distributions  $N_n$  such that

$$N_1 + \sum_{n=2} n N_n = N \quad (37)$$

The equilibrium distribution is found in the usual manner by

finding the maximum term in the sum of eq 36 subject to the conservation condition, eq 37. The result is

$$N_n = \frac{(P_n + P)V}{kT} q_n \exp \left\{ -\frac{1}{kT}(Pv_n - nkT\lambda) \right\} \quad (38)$$

$$N_1 = \frac{V}{\Lambda^3} e^\lambda \quad \text{or} \quad \lambda = \ln \left( \frac{\Lambda^3 N_1}{V} \right) = \frac{\mu_{\text{vap}}}{kT} \quad (39)$$

In these equations,  $\lambda$  is a Lagrange multiplier and  $\mu_{\text{vap}}$  is the chemical potential of the vapor. The last equality in the second equation of eq 39 follows upon recognition of the standard form for the chemical potential of an ideal gas. The substitution of the expression for  $\lambda$  in eq 39 into eq 38, together with the expression for  $q_n$  from eq 4, yields

$$N_n = \frac{(P_n + P)V}{kT} \exp \left\{ -\frac{1}{kT}[n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \gamma a_n] \right\} \quad (40)$$

Neglecting  $P$ , in view of eq 32, while making use of eq 33 and multiplying and dividing the right side of eq 41 by  $N_{\text{vap}}$ , gives rise to

$$N_n = \frac{V}{\sigma_n N_{\text{vap}}} \left[ N_{\text{vap}} \exp \left\{ -\frac{1}{kT}[n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \gamma a_n] \right\} \right] = \frac{1}{S \left( \frac{1}{\rho_{\text{vap}}^{\text{sat}}} \right)} \left[ N_{\text{vap}} \exp \left\{ -\frac{1}{kT}[n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \gamma a_n] \right\} \right] \quad (41)$$

where  $\rho_{\text{vap}}^{\text{sat}}$  is the density of the saturated vapor and we have used the relations,

$N_{\text{vap}} = S N_{\text{vap}}^{\text{sat}}$  and  $\rho_{\text{vap}}^{\text{sat}} = N_{\text{vap}}^{\text{sat}}/V$ , where  $N_{\text{vap}}^{\text{sat}}$  is the number of single molecules in the saturated vapor. Comparison of eq 41 with eq 2 shows that

$$R = \frac{1}{\rho_{\text{vap}}^{\text{sat}} \sigma_n} \quad (42)$$

and that  $1/S$  appears naturally. For typical liquids, the value of  $R$  specified by eq 42 is of the order of  $10^4$ , as experiment suggests, rather than the  $10^{17} - 10^{18}$  suggested in the original work of Lothe and Pound.<sup>2</sup> Bell and Strey<sup>28</sup> have recently noted that the use of  $R$  as specified by eq 42 improves the agreement between CNT and experiment, insofar as the temperature dependence of the rate of nucleation is concerned.

If, for the implementation of the *kinetic method*, the vapor was just *saturated*, eq 41 would still apply, but  $S$  would be set to unity. Then  $S$  would reappear, in the rate theory, through the consideration of the ratio of the condensation coefficients in the supersaturated and saturated vapors, respectively.

There is one other question that deserves comment. This is the so-called “internal consistency” requirement<sup>10,11</sup> in which  $N_n$  should reduce to  $N_{\text{vap}}$  when  $n = 1$ . It will be noticed that, from the beginning, the theory treats single molecules and clusters differently. In fact eqs 31 and 32 provide separate expressions for  $N_n$  and  $N_1$ . Thus, in fact, there *is* no requirement for internal consistency! Nevertheless, it can be shown<sup>1</sup> that eq 42 is *exactly* internally consistent for some simple free volume models of the liquid, and *almost* internally consistent for most typical liquids. This proof is presented in ref 1 and will not be repeated here.

## 5. Concluding Remarks

Although the explicit goal of the present paper is the resolution of the “replacement free energy” controversy, there

is an implicit underlying theme that deserves comment. This concerns the volume scale  $v_n$  (or the length scale  $v_n^{1/3}$ ). This scale is required for the proper treatment of the translational free energy of a model cluster. In a fully molecular theory, the problem would *never* arise, since a clean separation of translational and internal degrees of freedom would be effected. As indicated in the opening section, it is the representation of the cluster by a coarse-grained renormalized model that leads to the problem. By its nature, the model requires one to evaluate a *part* of the entropy (or free energy) of the system in *coordinate* space alone and not in the full *phase* space of the system. In the full phase space where the full physical entropy of the system is defined, the length scale is constant and well-known (i.e., it is Planck’s constant). In coordinate space, the length scale for the relevant *part* of the entropy proves to be extremely sensitive to the model. We have already mentioned this in connection with a completely incompressible drop. In another case<sup>28</sup> treated almost 30 years ago, the drop was modeled as encapsulated in a rigid, impermeable spherical container centered on its center of mass, thereby isolating it entirely from the surrounding vapor. In this case, the length scale proved to be the distance of fluctuation of the center of mass of a similar droplet confined to a *rigid* spherical container in which the center of mass and the center of the container were *not* required to coincide. For drops in the size range of typical condensation embryos, this length proved to be of magnitude similar to that of the length derived in the present paper. However, for large drops it approached zero, leading to an infinite translational free energy. This was a direct consequence of the isolation of the drop from the surrounding vapor. The length scale of the present paper does not collapse to zero as the drop becomes large, but assumes a finite value determined by the other limiting value of the root, eq 30, namely eq 31. This is a direct consequence of the fact that the model drop is coupled to the vapor.

However, it should be emphasized that one is at liberty to choose from a variety of models. The fundamental question is “*how accurately does the averaging, implicit in the model, conform to the desired integration over the difficult degrees of freedom that one wishes to avoid?*” For example, in the capillarity approximation, the drop is assumed to be incompressible for the purpose of representing its free energy, and this approximation is acceptable since the compressibilities of real liquids are quite small. At the same time, the volume of a real drop (cluster) is known to fluctuate. Although, this fluctuation is also small, it cannot be ignored *in the evaluation of the redundancy that is compensated by the volume scale connected to the fluctuation*. To ignore it would be equivalent to including the redundancy in the theory and would lead to an unacceptably large replacement free energy factor!

Another point should be made. This is the fact that it is not strictly correct to define the nucleus as the **stationary** drop in unstable equilibrium with the supersaturated vapor, as is conventional in nucleation theory. After all, the translational free energy is part of the work of formation of the drop. This free energy is in essence given by the negative of the logarithm of the preexponential factor in the expression for  $N_n$  and itself depends on  $n$ . Thus, the top of the free energy barrier, and the size of the nucleus, is determined in part by these free energy contributions. In most cases the effect is small vis a vis the determination of the critical supersaturation, but it is rigorously present. Despite this, it can be shown, by a fully molecular analysis<sup>24</sup> of the nucleation process, that the main effect of translation is to scale the nucleation rate by the volume of the system.

We have shown that the length scale itself may depend on  $n$  and also on the thermodynamic state of the complete system. It is important to recognize this because of its ramifications in fields outside of nucleation. In microemulsions, for example, the importance of translational or mixing entropy,<sup>15,29</sup> in connection with models involving renormalization, is beginning to receive attention, although it was not always so, the argument having been that the length scale was independent of the macrostate so that the associated *constant* mixing entropy canceled out of the problem. In the field of polymer statistics where models based on renormalization are frequently used<sup>30</sup> the problem, for the most part, has been swept under the carpet for the same reason.

In closing, it should also be noted that there are situations in which little damage results from the neglect of length scale considerations. These situations are those in which the problem (loosely speaking) depends linearly on the mixing entropy as is the case in the determination of phase diagrams for microemulsions. But there are cases in which the problem depends exponentially on the mixing or translational entropy (or free energy). Such is the case in the formula for  $N_n$  in nucleation theory. Here, an enormous variation can be generated by the use of different length scales; witness the difference between the replacement free energy factors of  $10^4$  and  $10^{18}$  that can be generated.

Finally, we call attention to the close relation that these problems have with the length scale problem of the constant pressure ensemble, even though translational entropy is not the explicit center of focus in that case.

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