

Treatment of Droplike Clusters by Means of the Classical Phase Integral in Nucleation Theory

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The "translation" inconsistency in the theory of nucleation is discussed in historical perspective. A theory is then developed, beginning with the classical phase integral, which not only allows all approximations to be well defined, but also leads to the most "natural" droplike model for the cluster. The theory makes it possible to apply, in a consistent manner, the thermodynamics of curved surfaces or, alternatively, molecular-dynamic numerical computation schemes to the evaluation of the partition function of the cluster. If the cluster is treated as a macroscopic drop (having the free energy of a macroscopic drop), the result for the distribution of clusters differs in only a minor way from that prescribed by the conventional theory of nucleation. It is concluded that for liquid nuclei the conventional theory is consistent, but that a replacement factor may be necessary for solid nuclei. In general, however, the major problems confronting the theory involve the precise evaluation of the work of cluster formation.

KEY WORDS: Nucleation; condensation; rate; partition function; clusters; surface layer; unstable equilibrium; fluid.

1. INTRODUCTION

The theory of the condensation of supersaturated vapor into liquid has received much attention recently.⁽¹⁻⁷⁾ Considerable disagreement exists over some of its details, especially in connection with the so-called "translation-rotation paradox." As of now, there seems to be general consensus, however, that the conventional theory contains not only errors in approximation but logical inconsistencies. What controversy remains surrounds the proper method of eliminating these incon-

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sistencies and the magnitude of the correction it entails. In order to be able to refer to these various questions in a more concrete manner, it will be convenient to have a brief description of the conventional theory.⁽⁸⁻¹³⁾

The rate process leading to condensation, and occurring in an initially homogeneous mother phase of supersaturated vapor, is assumed to consist in the formation of large clusters of molecules (embryos of the new phase) by the sequential accretion of single molecules. Thus, if A_i is the symbol for a cluster of i molecules, the reactions leading to A_i may be diagrammed as



It is recognized at the outset that a truly *nonequilibrium* theory of rate is impractical (although desirable). Consequently, detailed balancing is invoked in order to estimate the rate constants for the *reverse* reactions exhibited in Eq. (1). For this reason, it is necessary to consider the so-called *equilibrium* distribution of clusters imagined to occur when a *formal* constraint is imposed upon the vapor, forbidding condensation. Knowledge of this distribution is equivalent to knowing the equilibrium constant for each of the reactions in Eq. (1), and permits the use of detailed balancing.

The theory which then emerges provides an expression for the rate at which nuclei are produced in the mother phase. A nucleus is considered to be a cluster which can *gain* or *lose* molecules with a *decrease* of system free energy. When, as in the conventional theory, it is approximated as a liquid drop, it is that drop which (in the absence of the constraint forbidding condensation) can nevertheless remain in *unstable* equilibrium with the supersaturated vapor. Thus, the formation of a nucleus requires an *increase* in free energy. This free-energy barrier is associated with the formation of the interface between the liquid (nucleus) and the vapor.

The rate of nucleus formation is assumed to correspond to the rate at which liquid drops appear in the system. The theory is constructed in such a way that it loses meaning as soon as the supersaturated state begins to collapse catastrophically, and is therefore a precatastrophe theory aimed at predicting the *onset* of collapse rather than the actual *rate*. The rate J appears as a function of the so-called supersaturation ratio

$$S = p/p_0 \quad (2)$$

where p is the actual pressure in the vapor and p_0 the saturation pressure at the temperature in question. The rate J also depends on temperature, liquid density, molecular weight, and surface tension. The rate proves to be spectacularly sensitive to S , passing from an immeasurably small to an enormous value within ranges of S typically of the order of $\Delta S \approx 0.1$. Thus, the point of collapse is well defined experimentally.

In the conventional theory, a cluster (drop) containing i molecules is itself regarded as a distinct molecular species in an ideal-gas mixture.

Its chemical potential should therefore have the form

$$\mu_i = B_i(T, V) + kT \ln(n_i/N) \quad (3)$$

where n_i is the number of clusters of size i and

$$N = \sum_{i=1}^{\infty} n_i \quad (4)$$

is the total number of “molecules” in the system,² while T is the temperature, V the volume, and k the Boltzmann constant. The condition of equilibrium among clusters is of standard form,

$$i\mu_1 = \mu_i \quad (5)$$

and substitution of (3) into (5) gives

$$n_i = N \exp[-(B_i - i\mu_1)/kT] \quad (6)$$

for the equilibrium distribution.

According to Eq. (3), B_i is the chemical potential of species i when $n_i = N$, i.e., when only the species i is present! But the chemical potential of a *one-component* system (component i) is the free energy per i -molecule, and since an i -molecule is a drop of i *single* molecules, B_i must be the free energy of a drop composed of i single molecules! Thus, early writers set

$$B_i = i\mu_1 + 4\pi\sigma(3v/4\pi)^{2/3} i^{2/3} \quad (7)$$

where μ_1 is the chemical potential per molecule in bulk liquid at the temperature in question and at the pressure *outside* the drop, while σ is the surface tension and v the volume per molecule in bulk liquid. The first term on the right of Eq. (7) is the usual bulk contribution to the free energy of the drop, while the second term can be expressed as $\alpha i^{2/3}$, where

$$\alpha = 4\pi\sigma(3v/4\pi)^{2/3} \quad (8)$$

is the surface contribution. Substitution of Eqs. (7) and (8) into (6) yields

$$n_i = N \exp(-W_i/kT) \quad (9)$$

where

$$W_i = (\mu_i - \mu_1) i + \alpha i^{2/3} \quad (10)$$

is usually called the reversible work of formation of a drop of size i . Actually, it would only be this if the process of formation were a constant-pressure one. The error in identification is, however, negligible.

² The number of clusters is usually so small that N can be accurately approximated by the number of *single* molecules in the system, except when the vapor contains dimers initially.

There are several serious approximations in Eq. (7), not the least of which is the fact that clusters containing very small numbers of molecules cannot be identified with drops having macroscopic characteristics. However, Lothe and Pound⁽¹⁾ pointed to a more fundamental difficulty having to do with logical consistency. To understand this, consider the partition function Q in the canonical ensemble of an ideal gaseous mixture,

$$Q = \prod_i \frac{q_i^{n_i}}{n_i!} \quad (11)$$

where q_i is the molecular partition function of the i th species. Since the Helmholtz free energy is

$$A = -kT \ln Q \quad (12)$$

and

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T,V} \quad (13)$$

we find, exactly,

$$\mu_i = \{-kT \ln(q_i/N)\} + kT \ln(n_i/N) \quad (14)$$

Comparison with Eq. (3) yields

$$B_i = -kT \ln(q_i/N) \quad (15)$$

Substituting Eq. (14) into (5) gives

$$n_i = q_i \exp(i\mu_i/kT) \quad (16)$$

Now, q_i , being a molecular partition function, contains contributions from translational, rotational, and several internal degrees of freedom. Lothe and Pound call attention to the fact that in using Eq. (7) one is in effect using in q_i , the translational and rotational degrees of freedom of a drop which is in some sense at rest in the laboratory frame of reference, whereas the translation ordinarily dealt with in q_i extends throughout the whole volume V of the vapor. Therefore, if Eq. (7) is to be used, some correction is necessary.

It is really at this juncture that the various disagreements among authors arise. Assuming only that the vapor consists of an assembly of noninteracting clusters, Eq. (16) is perfectly rigorous! However, we have no exact method for evaluating q_i . In the conventional theory, it is evaluated, in effect, by making the approximation Eq. (7). Lothe and Pound recognize that Eq. (7) accounts for the surface contribution to W_i in a consistent manner (at least if clusters are identified with drops having macroscopic properties), so in making what they feel is a needed correction, they concentrate on a situation in which there is no drop surface, namely a fixed spherical region (of the size of the drop) within bulk liquid.

Suppose λ_i represents the partition function of this region. They assume that the degrees of freedom that are translational and rotational when the region is

“released” into the vapor as a drop may nevertheless, in λ_i , be considered vibrational. Thus, we may write

$$q_i = q_i^{(t)} q_i^{(r)} q_i^{(\text{int})} q_i^{(\text{surf})} \quad (17)$$

$$\lambda_i = \lambda_i^{(t)} \lambda_i^{(r)} \lambda_i^{(\text{int})} \quad (18)$$

where the symbols (t), (r), (int), and (surf) stand for translational, rotational, internal, and surface degrees of freedom. Let $\lambda_i^{(d)}$ represent the partition function of an isolated stationary drop which differs from the spherical region only in the possession of surface. It follows that

$$\lambda_i^{(d)} = \lambda_i q_i^{(\text{surf})} \quad (19)$$

Furthermore, if $a_i^{(d)}$ is the Helmholtz free energy of a drop, it follows [see Eq. (12)] that

$$\lambda_i^{(d)} = \exp(-a_i^{(d)}/kT) \quad (20)$$

But, except for the negligible (for a liquid) difference between Helmholtz and Gibbs free energy, $a_i^{(d)}$ is the same as the right side of Eq. (7), so we may write

$$\lambda_i^{(d)} = \exp(-B_i/kT) \quad (21)$$

If it is now assumed that

$$q_i^{(\text{int})} = \lambda_i^{(\text{int})} \quad (22)$$

we can write

$$q_i = \left\{ \frac{q_i^{(t)} q_i^{(r)}}{\lambda_i^{(t)} \lambda_i^{(r)}} \right\} \lambda_i q_i^{(\text{surf})} = \left\{ \frac{q_i^{(t)} q_i^{(r)}}{\lambda_i^{(t)} \lambda_i^{(r)}} \right\} \lambda_i^{(d)} = \left\{ \frac{q_i^{(t)} q_i^{(r)}}{\lambda_i^{(t)} \lambda_i^{(r)}} \right\} \exp \frac{-B_i}{kT} = \Gamma_i \exp \frac{-B_i}{kT} \quad (23)$$

where

$$\Gamma_i = \left\{ \frac{q_i^{(t)} q_i^{(r)}}{\lambda_i^{(t)} \lambda_i^{(r)}} \right\} \quad (24)$$

has been called by Lothe and Pound the “replacement factor.”

Substitution of Eq. (23) into (16) yields

$$n_i = \Gamma_i \exp[-(B_i - i\mu_1)/kT] = N(\Gamma_i/N) \exp(-W_i/kT) \quad (25)$$

Comparison of Eq. (25) with (9) shows that we now have a correction factor Γ_i/N which will eventually appear as a multiplicative factor in the rate J . Using reasonable values of vibration frequencies in the liquid and of moments of inertia for the cluster, Lothe and Pound estimate this factor to be of the order of 10^{17} , truly enormous.

Now, it must be understood that the correction represents a new heuristic guess grafted on to an earlier one. As we show later, a replacement factor may be indicated for crystalline clusters, but not for fluid ones.

What is needed is a less heuristic approach in which all the approximations are well defined and from which it is possible to see in which direction it is necessary to go to obtain improvement. These requirements suggest that a theory be developed starting with the classical phase integral so that it is possible to see what approximations are being made on the *molecular* level. The proper treatment of all degrees of freedom should then occur automatically, and it will not be necessary to invoke adjustment and counteradjustment. A treatment of this sort will be pursued in the remainder of this paper. In closing this section, it should be remarked that we have discussed only those aspects of the theory in connection with which detailed balancing is to be used. Detailed balancing may not be a good approximation in the rate theory. If so, additional errors of another kind are involved. Our treatment only applies to those situations in which an equilibrium theory of rate is satisfactory.

2. DECOMPOSITION OF THE PHASE INTEGRAL

Consider a vapor consisting of N molecules (which for simplicity we take to be monatomic and in their lowest electronic and nuclear states) contained within a volume V . Denote by $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ the potential energy of interaction of these N molecules, depending upon the coordinates of position $\mathbf{r}_1, \dots, \mathbf{r}_N$ of molecules 1 through N . Then, if we denote by \mathbf{p}_i the momentum of the i th molecule, the partition function of the vapor, written as a classical phase integral, assumes the form

$$Q = \frac{1}{N! h^{3N}} \int_{-\infty}^{\infty} \cdots \int_V \exp \left\{ -\beta \left(\sum_i \frac{p_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) \right) \right\} d\mathbf{r}_1 \cdots d\mathbf{r}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N \quad (26)$$

where h is Planck's constant, m is the mass of the molecule, and β is $1/kT$. The integrations over the momenta go from $-\infty$ to ∞ , while those over the coordinates of position span the volume V of the vapor. The Hamiltonian in the exponent in this equation is separable in the momenta but not in the coordinates. Immediate integration over the momenta is possible, but the remaining integration over coordinates presents an exceedingly difficult problem which usually can only be resolved by introducing approximations.

For example, in highly attenuated vapors (including those which are super-saturated), the following approximation, which we shall call the "physical-cluster" approximation, might be used. Suppose a molecular snapshot of the gas is taken. Then, it is assumed that in the photograph the N molecules will appear to be partitioned among clusters, n_i of which contain i molecules, the clusters being sufficiently separated in space so that they do not interact with each other (a molecule in one cluster does not interact with a molecule in another). If we take another snapshot, the configuration may be different, but the molecules will still be partitioned into clusters.

Actually, at this point, no approximation has been made because the set of numbers n_1, n_2, \dots, n_i , etc., which will be denoted by \mathbf{n} , can assume any values consistent with the conservation requirement

$$\sum_i i n_i = N \quad (27)$$

For example, we could have

$$\mathbf{n} = \{n_i = 0, \quad i < N; \quad n_N = 1\} \quad (28)$$

in which case the entire gas would be one large cluster. Obviously, all intermediate situations are possible, and so any realizable configuration of the gas can be described as a distribution of clusters. The approximation occurs only when we define the detailed natures of the clusters!

In the integral of Eq. (26), the N molecules are to be regarded as distinguishable, the indistinguishability being accounted for by the $1/N!$ preceding the integral. Corresponding to any given snapshot, we may write the integrand as

$$\prod_j \left\{ \exp \left\{ -\beta \left[\frac{p_{1j}^2 + \dots + p_{ij}^2}{2m} + u(\mathbf{r}_{1j}, \dots, \mathbf{r}_{ij}) \right] \right\} d\mathbf{r}_{1j} \dots d\mathbf{r}_{ij} d\mathbf{p}_{1j} \dots d\mathbf{p}_{ij} \right\} \quad (29)$$

where j refers to the j th cluster which contains ij molecules, and \mathbf{r}_{kj} and \mathbf{p}_{kj} are the coordinates and momenta of the k th particle in the j th cluster. In arriving at Eq. (29), we have used the fact that

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_j u(\mathbf{r}_{1j} \dots \mathbf{r}_{ij}) \quad (30)$$

where $u(\mathbf{r}_{1j} \dots \mathbf{r}_{ij})$ is the potential energy of interaction among all the molecules within the j th cluster. Thus, U , as represented in Eq. (30), contains no contributions from interaction *between* clusters. If we sum the terms like Eq. (29) corresponding to *all possible distinguishable* snapshots, we shall have the integral of Eq. (26).

At this point, we can proceed with some generality without yet fixing the fine details of the cluster. The only requirement is that the molecules of a cluster be close enough so that any one interacts with *at least* one other, and that no interaction with the molecules of another cluster occurs in any configuration of the first cluster which satisfies the first criterion.

Take a particular snapshot in which definite sets of distinguishable molecules are in definite clusters. In each cluster, choose a particular molecule, say molecule ij in the j th cluster, and agree to hold its position fixed. Now, consider all other snapshots in which the same distinguishable molecules are grouped into the same clusters and in each of which the first molecule is held to the fixed position, and sum the terms like Eq. (29) for this set of snapshots now integrating over the momenta as well. We will get

$$\prod_j \left\{ \frac{d\mathbf{r}_{1j}}{(A/h)^{3ij}} \int_{C_j} \exp\{-\beta u(\mathbf{r}_{1j} \dots \mathbf{r}_{ij})\} d\mathbf{r}_{2j} \dots d\mathbf{r}_{ij} \right\} \quad (31)$$

in which

$$A = h(2\pi mkT)^{1/2} \quad (32)$$

where m is the molecular mass. The symbol C_j in Eq. (31) indicates that the integral only goes over that range of cluster coordinate space in which the molecules are so arranged relatively that they constitute a cluster, \mathbf{r}_{1j} remaining fixed.

The part of the phase integral which Eq. (31) represents may be called a "specific pin-down" to indicate that the integration is constrained to the domains C_j which in turn are "pinned" to the various fixed molecules, and that "specific" molecules are in "specific" clusters. We note from considerations of symmetry that

$$\frac{d\mathbf{r}_{1j}}{(\Lambda/h)^{3ij}} \int_{C_j} \exp\{-\beta u(\mathbf{r}_{1j} \cdots \mathbf{r}_{1j})\} d\mathbf{r}_{2j} \cdots d\mathbf{r}_{1j} = d\mathbf{r}_{1j}(h)^{3ij} q'_{ij} \quad (33)$$

where q'_{ij} depends only on ij , the number of molecules in the j th cluster, and in particular not upon \mathbf{r}_{1j} . Continuing with the "specific pin-down" of Eq. (31), we "release" all the molecules $1j$ and begin to integrate over the various \mathbf{r}_{1j} so as to obtain an even larger portion of the phase integral. Here, however, we have to begin making approximations!

As the various \mathbf{r}_{1j} are moved (carrying their clusters with them), situations will arise in which the domains C_j of separate clusters will be so close that the clusters will interact. Thus, two or more clusters will have to be merged, and we will be dealing with a different "specific pin-down." Clearly, these regions of integration will have to be avoided. However, if the vapor is sufficiently attenuated, as it usually is in the case of most nucleation phenomena, we can assume that such regions represent a negligible portion of the integral and simply ignore them. This is the first approximation, and with it Eq. (31) can be integrated to yield [using Eq. (33)]

$$\prod_j \{V(h)^{3ij} q'_{ij}\} = \prod_j \{h^{3ij} q''_j(ij)\} \quad (34)$$

where

$$q''_j(ij) = Vq'_{ij} \quad (35)$$

and depends only on ij , the number of molecules in the j th cluster. If in the original "specific pin-down" there were n_i clusters containing i molecules, it is clear that Eq. (34) would be expressible as

$$h^{3N} \prod_j \{q''_j(i)\}^{n_i} \quad (36)$$

where $q''_1(i)$ is simply the symbol for all the identical $q''_j(ij)$ in which $ij = i$,

$$q''_i(i) = \frac{V}{\Lambda^{3i}} \int_{C_i} \exp\{-\beta u_i\} d\mathbf{r}_2 \cdots d\mathbf{r}_i \quad (37)$$

In fact, $q''_1(i)$ is simply the partition function of a cluster of size i except for a correction for the indistinguishability of the i molecules. The integrations in Eq. (37), including the one over \mathbf{r}_1 , need not have been performed in exactly the manner indicated. Transformations of coordinates as well as integration in some other order are possible as long as the domain of integration is consistent with the definition of the cluster. The particular route we have followed is merely convenient for the purposes of counting and combinatorial analysis.

Next, we note that there is a large number of “specific pin-downs” consistent with a given distribution \mathbf{n} . These can be obtained by permuting the distinguishable molecules among the clusters. The number of permutations will be

$$N! / \prod_j (i!)^{n_i} \quad (38)$$

Not all of these will represent new “specific pin-downs” because some permutations will differ from others by merely having all the molecules in one cluster exchanged for all the molecules in another, or by having several such exchanges. Such permutations will only move the positions of the various clusters in the “pin-down,” an act which is eventually accomplished by the integration over the various \mathbf{r}_{1j} leading to Eq. (36), and so it would be redundant to count these permutations. Their number is

$$\prod_i n_i ! \quad (39)$$

The proper number of permutations N_p is thus obtained by dividing the quantity specified by Eq. (38) by that in Eq. (39),

$$N_p = N! / \prod_i (i!)^{n_i} n_i ! \quad (40)$$

When we refer to a “pin-down” only by giving the distribution \mathbf{n} and the location of the fixed molecule in each cluster, we will call it a “generic pin-down.”

The portion of the phase integral corresponding to \mathbf{n} is obtained by multiplying the quantity in Eq. (36) by N_p and the factors before the integral sign in Eq. (26). We get,

$$\prod_i \frac{(q_i''/i!)^{n_i}}{n_i !} \quad (41)$$

The complete phase integral is obtained by summing Eq. (41) over all distributions \mathbf{n} consistent with Eq. (27). Thus,

$$Q = \sum_{\mathbf{n}} \prod_i \frac{q_i^{n_i}}{n_i !} \quad (42)$$

where we have written

$$q_i = q_i''/i! \quad (43)$$

and where q_i is the correct partition function for a cluster of size i adjusted for the indistinguishability of the i molecules.

Now the average value of n_i , $\langle n_i \rangle$ is obtained by identifying the maximum term in Eq. (42). This is easily shown^(2a) to be

$$\langle n_i \rangle = q_i \exp i\mu_1 \quad (44)$$

where μ_1 is the chemical potential of a single molecule in the gas. This equation is identical with Eq. (16) if $\langle n_i \rangle$ is identified with n_i , as of course it may be. This result

is limited only by the requirement that the vapor be sufficiently attenuated that clusters may be defined by the domains C_j in such a way that, at the boundary of C_j , one of the cluster molecules does indeed (for all intents and purposes) cease to interact with any of its partners, and furthermore so that the volume of configuration space in which clusters interact is negligible. Otherwise, it is perfectly exact and general.

As in the case of Eq. (16), the real problem involves the evaluation of

$$q_i = \frac{1}{i! \Lambda^{3i}} \int \exp -\beta u_i \, d\mathbf{r}_1 \cdots d\mathbf{r}_i \quad (45)$$

and it is *here* where the various authors have parted company. The usual procedure has been to use, somehow, the information available about the free energy of a "liquid drop" of i molecules in order to evaluate q_i . Notice that this need not mean that the cluster is a drop; only that its properties can somehow be related to those of a drop. Lothe and Pound actually use this approach. In Eq. (23), q_i is *not* the partition function of a drop—in fact, according to Eq. (21), $\exp\{B_i/kT\}$ is the drop partition function. The replacement factor is the *means* of relating q_i to the properties of a drop. In a more recent paper by Reiss *et al.*,^(2b) another model was used. It was characterized by having C_j be a spherical region, centered on the center of mass of the molecules in the cluster, and having a radius equal to that of a drop of the same number of molecules. Neither could this cluster be identified with a drop. Among other things, in a drop, the center of mass fluctuates with respect to the Gibbs dividing surface^(14,15) which constitutes its boundary, while in the described cluster, the center of mass is stationary with respect to the bounding surface. Nevertheless, using this model and relating *it* to the properties of a drop, Reiss *et al.* were able to evaluate what was essentially a new replacement factor, many orders of magnitude smaller than the one estimated by Lothe and Pound.

Because of the arbitrariness in the models for the clusters in both treatments, it is difficult to argue for one model over the other. The only way out of the difficulty would involve using a model demanded by the *natural requirements* of the phenomenon itself. Since macroscopic drops are the first visible products of the nucleation process, this suggests that clusters be defined so that *they are as much like drops as possible*. A treatment of this kind is presented in the next section.

3. DROPLIKE CLUSTERS

Consider how we ordinarily think of a drop in thermodynamic terms. It is a body of liquid bounded roughly by a spherical surface, and usually in contact with its vapor. If the drop is truly macroscopic, there is no practical difficulty in locating the spherical bounding surface, but when it is very small, account must be taken of the fact that the fluid in the drop is not separated from the vapor by a physical boundary at which the density changes abruptly from that in the drop to that of the vapor. Instead, a transition zone^(14,15) exists within which the density changes continuously from that of the liquid to that of the vapor. The thermodynamic treatment of equilibrium between drop and vapor now requires the introduction of an arbitrary

mathematical surface (a Gibbs dividing surface) such that all the material inside the surface is said to belong to the drop, the remainder belonging to the vapor. It is convenient to locate the dividing surface in the vicinity of the transition zone.

The dividing surface is commonly thought of as at rest in the laboratory frame of reference. If the drop is moving—for example, if it is floating in its vapor—the movement is defined by the dividing surface. Notice that if the dividing surface is at rest, the center of mass can still fluctuate—a stationary drop does not mean a stationary center of mass. It is also true that the material in the drop is fluctuating through and about the dividing surface—the distribution of these local fluctuations in density lead, on the average, to the distribution of matter in the transition zone.

Figure 1 is a plot of density ρ versus radial distance r from the center of drop in equilibrium with its vapor. The dashed line at r_D represents a typical dividing surface within the transition zone. The other dashed line at r_C is another possible choice of dividing surface, lying just outside the transition zone where the density, for all practical purposes, has attained its value in the vapor. If we were to replace the dividing surface at r_C with a perfectly repelling, nonattracting physical surface (i.e., one upon which the potential of a molecule became infinite), the average distri-

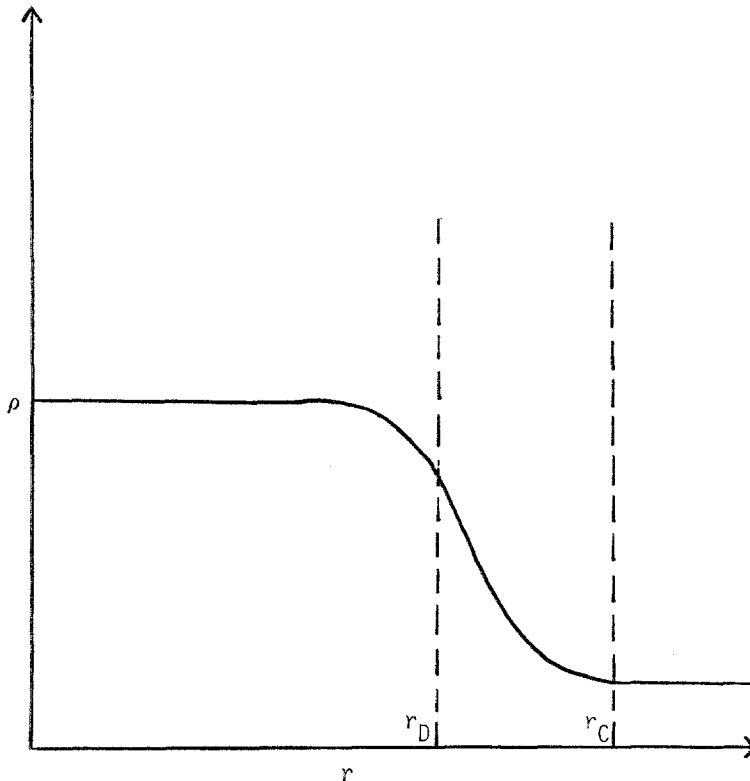


Fig. 1. Radial distribution of matter in a cluster.

bution of matter (the curve in Fig. 1) would be unchanged as long as the introduction of the surface did not change the density $\rho(r_C)$ at r_C . If the vapor density $\rho(r_C)$ is low enough so that the vapor approximates an ideal gas, this will be the case. In most real nucleation processes, the vapor possesses this requisite low density.

Thus, it is possible to think of a spherical container for a drop whose walls do not alter the distribution of matter within the drop. Notice that the number of molecules within the container (within the drop) is determined not only by r_C , but by the temperature T and the pressure p of the vapor with which the drop is in equilibrium. Even though this number

$$i = \int_0^{r_C} 4\pi r^2 \rho(r) dr \quad (46)$$

is difficult to know, it is nevertheless uniquely determined by r_C , T , and p . Conversely, if i is given along with T and p , r_C is uniquely determined. This unique value of $r_C(i)$ for given T and p is typically as plotted in Fig. 2. The sharp rise of r_C with i beyond i^* occurs because of passage into the vapor phase where a very large change in r_C includes only a small additional number of molecules in the container.

If the curve of Fig. 1 were known, a reasonably well defined (although not

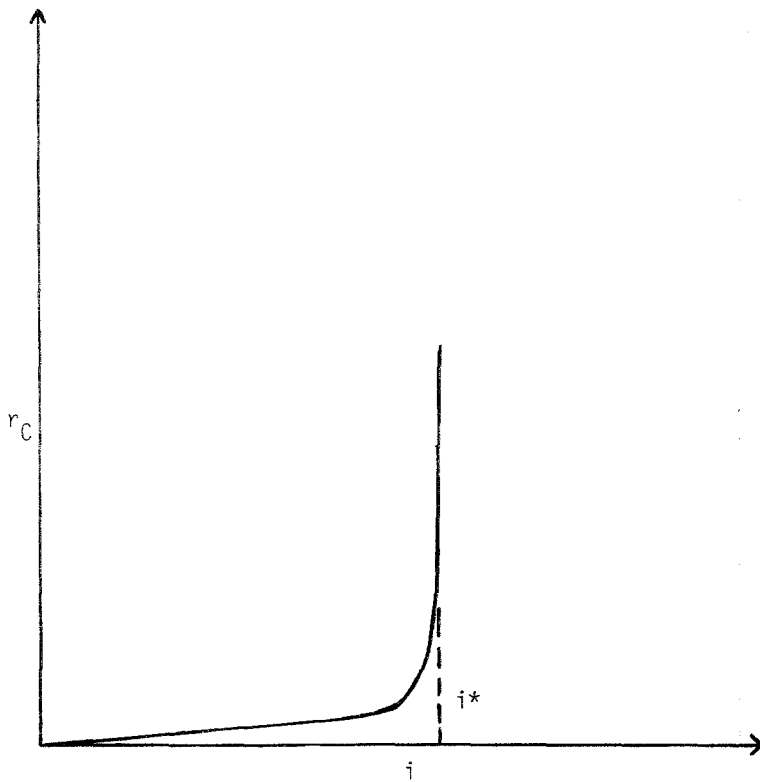


Fig. 2. Container radius versus number of molecules in cluster.

absolutely unique) choice for i^* and therefore $r_c = r_c^*$ could be made. The definition would become more precise the larger the drop, becoming essentially unique in the macroscopic limit. In general, r_c^* could then be called "the radius of the drop."

Let us assume that by some separate calculation we are in possession of the curves in Figs. 1 and 2. To every value of r_c^* at a given temperature there then corresponds a vapor pressure p such that a drop of size r_c^* (or i^*) can be in equilibrium with the vapor. We will use the unique (or approximately unique) relation between r_c^* and i^* in the development of our cluster model.

In Section 2, a cluster was defined, quite generally, by the condition that each of its molecules interacts with at least one of its partners and with none of the molecules in any other cluster. This criterion is easy to state but almost impossible to apply directly. For one thing, there is a degree of arbitrariness about the radius of interaction for a given molecule because its forces do not go abruptly to zero at some definite distance. Even if they did, the definition depends on the collective behavior of the group of molecules, and there exists no simple *collective* property which can be used for its application. Therefore, some approximate *collective* criterion is necessary. It has already been mentioned that *Reiss et al.* ^(2a,2b) made use of the collective property "center of mass" in order to define a cluster by requiring that all molecules within the cluster lie within some prescribed distance of its center of mass. Unfortunately, such a cluster could never be identified with a drop, since its center of mass could not fluctuate with respect to its bounding surface. We therefore consider another collective criterion.

Consider a cluster of i molecules. It can of course adopt many distinct configurations. Each of these configurations can be fitted into some sphere of minimum radius. Several examples of this are illustrated in Fig. 3 for a hypothetical cluster of eight molecules.

It is obvious that configurations requiring very large spheres will occur only infrequently. Not only is there a limited probable number of such configurations, but they possess small binding energy. Thus, both entropy and energy considerations militate against configurations requiring large spheres. Very small spheres are similarly discriminated against by entropy, and the binding energy will not only be small, but probably negative. Thus, a plot, versus r , of the probable number of configurations requiring a sphere of radius r will look something like Fig. 4. There will be a fairly well defined radius which can be associated with each cluster such that the chance of

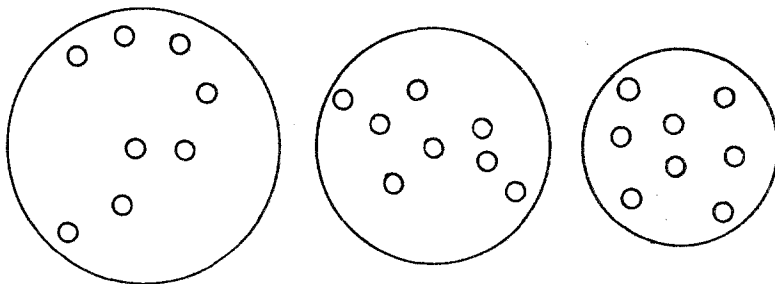


Fig. 3. Possible extensions of cluster of eight molecules.

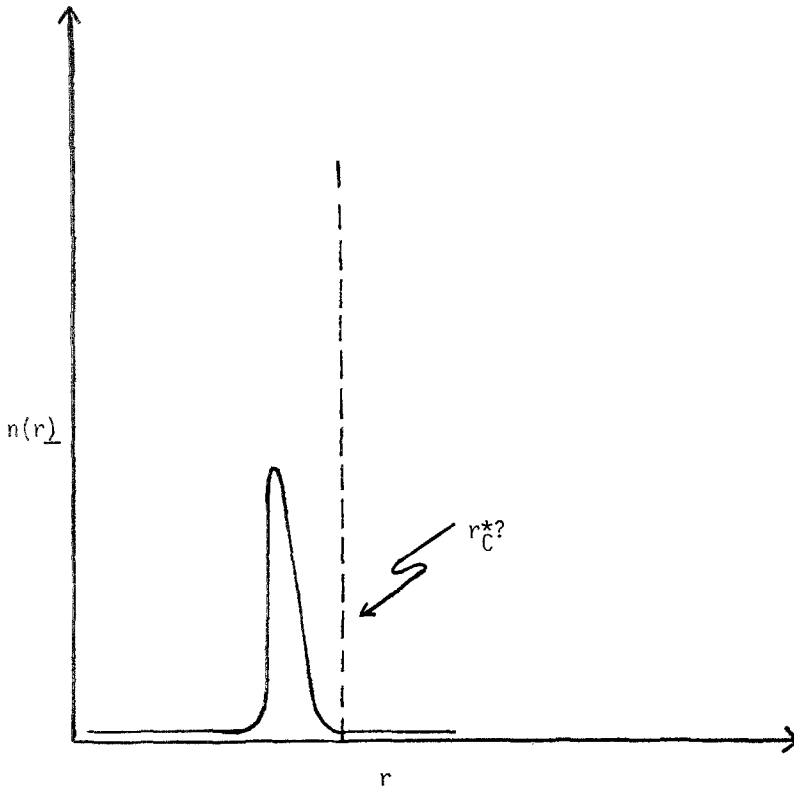


Fig. 4. Probable number of cluster configurations requiring radius r versus r .

observing configurations requiring a larger radius is negligible. We show this radius by the dashed line in Fig. 4 and ask whether it is reasonable to identify it with r_C^* discussed previously.

If the pressure of the supersaturated vapor is p , then, according to our earlier discussion, there will be an r_C^* determined by p and going with the drop which can remain in (unstable) equilibrium with the vapor. For this particular cluster of size i^* , it is reasonable that the radius of the limiting sphere in Fig. 4 and r_C^* are the same. For clusters of nonequilibrium size, however, the situation is by no means so clear. On the other hand, since a cluster, once formed, is supposed to be a relatively isolated group of molecules, its internal configuration should be governed largely by the interactions among those molecules and not by the vapor pressure (which is determined by molecules outside the group; the vapor pressure does, however, affect the frequency of occurrence of the cluster). We can therefore assume that the "radius" of the cluster will be the same, independent of whether it *is* or *is not* in equilibrium with the surrounding vapor. When *it is* at equilibrium, however, we can estimate the radius by the r_C^* which goes with i^* . Both r_C^* and i^* will belong to a different pressure than that prevailing in the vapor, but this presents no difficulty since it is only the relation between r_C^* and i^* which we need to know. For the purpose of

determining it, we can set a "drop" of i^* molecules in equilibrium with vapor at the requisite pressure and, in principle, generate curves such as Figs. 1 or 2, from either of which r_C^* can be determined.

By the preceding description, we therefore have a means of associating a sphere of given radius with a cluster of a given number of molecules. We can now drop the asterisk without confusion and speak of r_C and i in place of r_C^* and i^* .

Notice that the collective criterion which has now been introduced allows the cluster to be interpreted as a drop. The sphere acts like a dividing surface, and as the cluster assumes different configurations *within the sphere*, its center of mass fluctuates with respect to the sphere.

It now remains to evaluate q_i for the cluster defined in this way, and to insert it into Eq. (16). We do this in the next section.

4. EVALUATION OF q_i FOR THE DROPLIKE CLUSTER

In order to determine q_i for the clusters defined in the preceding section, we evaluate the phase integral Q in a manner different from that invoked in Section 2. We consider the volume V in which the vapor is contained, and dispose throughout V a set of spherical dividing surfaces at rest in the laboratory frame of reference. The radii of these surfaces will be the various allowable $r_C(i)$ discussed in the preceding section. In general, there will be n_i surfaces of "size" i , where \mathbf{n} satisfies Eq. (27). These may be distributed with centers in arbitrary positions.

Now, with the given set of surfaces fixed, we take snapshot after snapshot of the gaseous molecular configuration until we arrive at one in which, by chance, each of the spherical dividing surfaces encloses *exactly* the right number of molecules (i.e., those with radius $r_C(i)$ enclose i molecules), and none of the N molecules lies outside a surface. To this configuration we assign the weight

$$\prod_{ij} \exp\{-\beta u_{ij}\} d\mathbf{R}_{ij} \quad (47)$$

where u_{ij} is the potential energy of interaction of i molecules in a j th configuration and $d\mathbf{R}_{ij}$ is the combined volume element for a cluster of i molecules in a j th configuration, i.e.,

$$\prod_{ij} d\mathbf{R}_{ij} = d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \quad (48)$$

the product \prod_{ij} being taken over all clusters.

We do not count a configuration (giving it zero weight) in which, for example, more than i molecules are within a dividing surface of radius $r_C(i)$ even if, for this configuration, none of the N molecules lies outside of dividing surfaces, since, by the definition of $r_C(i)$ and our assumptions, this will be an infrequent occurrence, and can be ignored at the outset. This means that we also give zero weight to configurations in which surfaces with radii $r_C(i)$ contain *less* than i molecules, since, by Eq. (27), if none of the N molecules are outside of dividing surfaces, such a configuration will demand that some dividing surfaces have *more* molecules than their "sizes" warrant.

If we keep taking snapshots in this manner, assigning a weight factor such as Eq. (47) each time the same dividing surfaces are filled with the *same* molecules (the analog of a “specific pin-down”³ of Section 2), and never accepting the same total configuration of molecules twice, we will, by summing these factors, eventually arrive at a total weight,

$$\prod_i (z_i^{(d)})^{n_i} \quad (49)$$

where

$$z_i^{(d)} = \int_{v_i} \cdots \int \exp(-\beta u_i) d\mathbf{r}_1 \cdots d\mathbf{r}_i \quad (50)$$

in which

$$v_i = \frac{4}{3}\pi r_C^3(i) \quad (51)$$

and is the volume inside a dividing surface of size i . In Eq. (49), all the ij factors in (47) corresponding to size i have, by symmetry, become the same upon integration. The integrations correspond to the sum over all possible configurations of the total gas consistent with the given fixed set of dividing surfaces.

Actually, z_i is the configuration integral for i molecules confined to a volume v_i . The complete partition function for this system is obviously

$$q_i^{(d)} = z_i^{(d)} / (i! \Lambda^{3i}) \quad (52)$$

and represents the partition function for a *stationary* drop with dividing surface at r_C . If we knew the free energy $a_i^{(d)}$ for this drop (all of the material inside r_C in Fig. 1), we could calculate $q_i^{(d)}$ as

$$q_i^{(d)} = \exp(-\beta a_i^{(d)}) \quad (53)$$

As i becomes very large, $a_i^{(d)}$ can of course be estimated accurately by B_i of Eq. (7).

Returning to the evaluation of Q , we must now consider configurations in which one, several, or all of the dividing surfaces have their centers shifted. In this process, we ignore the possible overlap of two surfaces—the gas of clusters being so highly attenuated. On the other hand, there is one problem of overlap which we cannot ignore. Consider Fig. 5. This shows two possible positions of a given dividing surface such that the center has been shifted by the relative distance λ . The i molecules within the surface, at its first position at the left, will, on the average, be distributed throughout the volume v_i according to a density profile such as that shown in Fig. 1. When the volume is shifted to right, they will be similarly distributed throughout the shifted volume. As long as there is at least *one* molecule in the shaded region at the right, the unshifted and shifted configurations will correspond to different *total* configurations for the N molecules of the gas since the molecules in the shaded region will be in previously unoccupied regions of space after the shift.

³ It is worth re-emphasizing that we deal here only with an *analog* of a “specific pin-down.” The integrand in Eq. (33) cannot be equated with the integrand in Eq. (50). In this section we are re-evaluating the phase integral, from the start, by a different method.

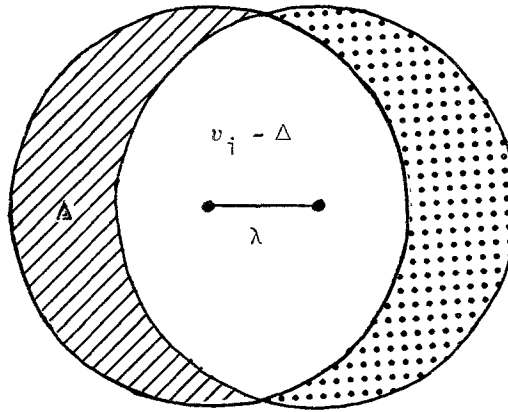


Fig. 5. Overlap between two positions of a given dividing surface.

On the other hand, consider the volume $v_i - \Delta$ corresponding to the overlap of the two spheres. In *either* the shifted or unshifted case, it is possible for the i molecules to “fluctuate” into this common region of overlap. Thus, a mere shifting of the dividing surface does not guarantee a new *total* configuration.

We treat this difficulty as follows. Since the clusters are so few that we can ignore those portions of configuration space in which they encounter one another, we can deal with the shift of each cluster independently. Before the sphere is shifted, we have only the contribution z_i . Assume, however, that the sphere’s center is shifted by the distance $d\lambda$ (replacing λ in Fig. 5 by an infinitesimal). The nonoverlapped volume (Δ in Fig. 5) may now be represented by dv . Corresponding to the shifted configuration, we are not permitted to add another $z_i^{(d)}$, since most of the configurations will overlap those in the original z_i and would then have been counted twice. Integration only over configurations confined to the region of overlap would yield a configuration integral which we may denote by $z_i^{(d)'}$. Using the canonical ensemble relation between Helmholtz free energy a_i and configuration integral, it follows that

$$z_i^{(d)'} / z_i^{(d)} = \exp[-(a_i' - a_i)/kT] = \exp(-p_i dv/kT) \quad (54)$$

where a_i and a_i' are the Helmholtz free energies of the i molecules in the respective volumes, and p_i is the pressure required to compress the “drop” from the volume v_i to $v_i - dv$, i.e., compression from v_i to the volume of overlap. Since by the arguments of Section 3 the relation $r_C = r_C(i)$ is obtained by assuming that a “drop” of size i is subjected to its equilibrium pressure (even though this is true in the vapor only for the nucleus), p_i must be the equilibrium pressure. Put in another way, p_i is the pressure exerted by the hard wall of the container at r_C in Fig. 1.

The last relation in Eq. (54) follows from the fact that, at constant temperature,

$$da_i = -p_i(-dv) = p_i dv \quad (55)$$

Clearly, the part of z_i which is nonredundant is

$$z_i^{(d)} - z_i^{(d)'} = z_i^{(d)} [1 - \exp(-p_i dv/kT)] = (z_i^{(d)}/kT) p_i dv \quad (56)$$

and it is this (rather than $z_i^{(d)}$) which must be added to the original unshifted configuration. Thus, we get

$$z_i^{(d)} + (z_i^{(d)}/kT) p_i dv \quad (57)$$

If we shift the center a second time, there will again be redundant configurations, and after a third and fourth time, etc. Consider some shift $d\lambda$ (after many shifts) in the process of covering the entire volume V . Let V_c be the volume already covered. The sphere, in its position before this particular shift, must have formed part of V_c . Therefore, if dv , the new volume—not part of V_c —is exposed by the shift, the new contribution can once again be represented by Eq. (56) where, of course, dv may differ from shift to shift. Thus, if dv in the k th shift is denoted by

$$(z_i^{(d)}/kT) p_i dv^{(k)} \quad (58)$$

the total contribution over all shifts may be denoted by

$$z_i = z_i^{(d)} + \frac{z_i^{(d)}}{kT} \sum_k p_i dv^{(k)} = z_i^{(d)} + \frac{z_i^{(d)}}{kT} \int_V p_i dv = z_i^{(d)} \left(1 + \frac{p_i V}{kT}\right) \quad (59)$$

where V is the volume of the gas. The unity in the last form of Eq. (59) may be ignored in comparison with $p_i V/kT$ (which is of the order of Avogadro's number), and so we obtain

$$z_i = (p_i V/kT) z_i^{(d)} \quad (60)$$

Now, each factor in Eq. (49) can be treated in this manner independently (ignoring, as we do, rare encounters between clusters) so that we arrive at a still larger portion of the gas configuration integral including, thereby, the sum of contributions available when all possible dispositions of the given set of dividing surfaces are taken into account,

$$\prod_i \left\{ \frac{p_i V}{kT} z_i^{(d)} \right\}^{n_i} \quad (61)$$

We obtain a still larger portion by permuting the N molecules among the various clusters discounting, as in Section 2, permutations which merely exchange whole clusters. Thus, we multiply Eq. (61) by N_p , given by Eq. (40), and get

$$N! \prod_i \frac{\{(p_i V/kT) z_i^{(d)}/i!\}^{n_i}}{n_i!} \quad (62)$$

The corresponding portion of the phase integral is obtained by multiplying Eq. (62) by the momentum contribution $1/\Lambda^{3N}$ and by $1/N!$ to reassert the indistinguishability of the molecules. We thus get

$$\prod_i \frac{(q_i)^{n_i}}{n_i!} \quad (63)$$

where now

$$q_i = \frac{p_i V}{kT} \frac{z_i^{(d)}}{i! \Lambda^{3i}} = \frac{p_i V}{kT} q_i^{(d)} \quad (64)$$

where we have used Eq. (52), and $q_i^{(d)}$ is the partition function of a *stationary* drop.

To complete the evaluation of the phase integral, we have only to sum Eq. (63) over all distributions \mathbf{n} ,

$$Q = \sum_{\mathbf{n}} \prod_i \frac{(q_i)^{n_i}}{n_i!} = \sum_{\mathbf{n}} \prod_i \frac{\{(p_i V/kT) q_i^{(d)}\}^{n_i}}{n_i!} \quad (65)$$

an equation which is the analog of Eq. (42). Clearly, the *analog* of Eq. (44) follows immediately:

$$\langle n_i \rangle = q_i \exp i\mu_1 = (p_i V/kT) q_i^{(d)} \exp i\mu_1 \quad (66)$$

in which, instead of the replacement factor, there now appears the quantity

$$\Gamma'_i = p_i V/kT \quad (67)$$

5. CONCLUDING REMARKS

The $q_i^{(d)}$ in Eq. (66) is the quantity denoted by $\lambda_i^{(d)}$ in Eq. (23), namely the partition function of a stationary drop. Except for the assumptions (now well defined and mild) which have been made in describing the cluster, the "translation-rotation" problem and the question of internal consistency have been resolved. All other difficulties must now be relegated to the evaluation of $q_i^{(d)}$. If the drop is very large, $a_i^{(d)}$ in Eq. (53) is given by B_i of Eq. (7), and Eq. (66) becomes

$$\langle n_i \rangle = (p_i V/NkT) N \exp(-W_i/kT) \quad (68)$$

where W_i is given by Eq. (10) and we have the conventional result except for the factor

$$p_i V/NkT \quad (69)$$

Normally, the cluster of nuclear size corresponds to the drop which can be in unstable equilibrium with the vapor. Because of the new factor which depends on i in Eq. (69), the cluster size corresponding to the minimum in $\langle n_i \rangle$ no longer corresponds to this drop, and so the nucleus and the equilibrium drop are different. For the equilibrium drop, however, p_i is the actual pressure in the supersaturated vapor, and since the vapor is ideal, the factor, Eq. (69), for this drop is unity. Thus, for the equilibrium drop, there is no correction at all, i.e., assuming that $a_i^{(d)}$ is B_i , there is no replacement factor. If the nuclear size lies close to the equilibrium drop, there can only be a very small correction and the conventional theory would apply. That this is so has been determined by specific numerical computations.⁽¹⁶⁾

The $(p_i V/NkT)$ in Eq. (68) does in fact have a very simple origin, as we shall now demonstrate by considering clusters large enough to be represented by macro-

scopic drops. In this case, we appeal to the conventional “thermodynamic” theory and calculate the work of formation of the drop—but now with certain corrections. These corrections originate from the precise way in which the clusters are defined in Section 3, where it was agreed to assume that the internal condition of a cluster of i molecules was sensibly the same as that of cluster in equilibrium with *its own vapor pressure* p_i .

Suppose we calculate the reversible work of formation of such a cluster, large enough to be a drop. We do this in three steps:

(1) Compress the supersaturated vapor from its pressure p to p_i . The work in this step is

$$W_i^{(1)} = NkT \ln(p_i/p) \quad (70)$$

(2) Form a drop of i molecules. The work here is

$$W_i^{(2)} = i\{\mu_l - \mu_v(p_i)\} + \alpha i^{2/3} = ikT \ln(p_0/p_i) + \alpha i^{2/3} \quad (71)$$

This resembles Eq. (10) except that μ_l is now that which goes with p_i rather than p . Actually, μ_l should also correspond to p_i rather than p , but here the error is so small (dependence of the free energy of a condensed system on pressure) that we ignore it. As before, p_0 is the saturation pressure of the vapor.

(3) Expansion of the system back to the pressure p . In the expansion, there are only $N - i$ original gas molecules and one cluster, thus, $N - i + 1$ molecules. The work here is

$$W_i^{(3)} = (N - i + 1) kT \ln(p/p_i) \quad (72)$$

During the expansion, it is assumed that the drop remains in metastable (superheated) equilibrium. Thus, we arrive at the vapor-cluster state required by our original assumption.

The total reversible work is

$$\begin{aligned} W_i' &= W_i^{(1)} + W_i^{(2)} + W_i^{(3)} = \{ikT \ln(p_0/p) + \alpha i^{2/3}\} \\ &\quad - kT \ln(p_i/p) = W_i - kT \ln(p_i/p) \end{aligned} \quad (73)$$

where W_i is identical with the quantity of Eq. (10). Use of W_i' in place of W_i in Eq. (9) yields

$$n_i = Np_i/p = (p_i V/NkT) N \exp(-W_i'/kT) \quad (74)$$

which is the same as Eq. (68).

Thus, we see that the new factor is *not* a replacement factor but rather a correction arising from the assumption that a cluster has the same internal properties as it would under its own vapor pressure. For the large cluster, the conventional thermodynamic approach therefore agrees with that based on the classical phase integral.

What about the replacement factor? It seems clear that for the case of fluid nuclei it simply doesn't exist! To demand its existence requires rejection of conven-

tional statistical mechanics, and in particular of the customary application of the Gibbs phase integral. On the other hand, it could exist for crystalline nuclei. The reasoning is as follows.

In the evaluation of the phase integral, all accessible configurations of the system are to be included. On the other hand, approximate methods usually ignore those configurations with small probability. For example, in the preceding treatment, we neglected configurations which could not be analyzed into clusters.

Ordinarily, in the treatment of solids, we include only those configurations in which the system looks like a crystal. In these configurations, there are long-range correlations so that a constraint applied at the surface of the crystal is propagated throughout the body. Surface constraints forbidding translation and rotation of the crystal as a whole therefore fix the positions of all lattice sites. The only configurations considered (those with nonnegligible probability) locate molecules on lattice sites, and hence a crystal which is not rotating or translating at its surface *does* have these degrees of freedom suppressed.

Because of the absence of long-range correlation, this is not the case in the fluid—surface constraints are attenuated within a surface layer of at most a few molecular diameters thickness. Thus, the free energy of liquid at rest in its container does include *all* degrees of freedom.

Since, as in Fig. 1, a drop may be thought of as a fluid in a container, it already possesses the requisite translational and rotational motions, and this is confirmed by the more precise analysis. For crystalline nuclei, however, it may be necessary to include additional factors to account for such motions.

In any event, the most serious questions are associated with the identification of $a_i^{(d)}$ with B_i , except when the nuclei prove to be very large. Strictly speaking, in most cases, any discrepancy between the conventional theory and experiment cannot be ascribed to the replacement factor (taking this to mean a correction for an inconsistent treatment of translational degrees of freedom), but rather to an erroneous evaluation of $a_i^{(d)}$. In fact, it is probably best to rewrite Eq. (68) as

$$\langle n_i \rangle = (p_i V / NkT) N \exp \{ -(a_i^{(d)} - i\mu_1) / kT \} \quad (75)$$

to emphasize this fact.

The present treatment opens the way, however, to the correct evaluation of $a_i^{(d)}$. For example, the treatment places one on relatively firm ground in the use of techniques now available for the statistical thermodynamics^(14,15) of curved surfaces and of small drops in evaluating $a_i^{(d)}$. Alternatively, using the arrangement described in Fig. 1, enclosing i molecules in a spherical container with hard, repelling walls at r_0 , $q_i^{(d)}$ (and hence $a_i^{(d)}$) could be evaluated numerically using large-scale computers, since i will usually be only of the order of 100. In any event, the way should now be open to further progress in the theory of nucleation.

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