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Distribution of density fluctuations in a molecular theory of vapor-phase nucleation

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A statistical-mechanical theory of the distribution of density fluctuations involved in homogeneous vapor-phase nucleation is presented which improves on previous work. Specifically, a refined characterization of a physical cluster is developed. This cluster is known as an i/v cluster, since it is defined by both a molecular number i and a volume v (i/v is the average density of molecules in the cluster). The i/v cluster represents the density fluctuations that have the potential to serve as condensation centers for the formation of liquid drops. The refinement involves a so-called *shell* molecule which defines the volume v . The equilibrium distribution of the refined i/v clusters is derived, using an approach involving fluctuation theory. This method is as rigorous as prior approaches and, moreover, sheds light on the nature of the cluster distribution and the cluster itself. Through an analysis of a cluster defined *without* a shell molecule, it is shown that the shell molecule is necessary if the cluster characterization is to be consistent with the fundamental statistical-mechanical description of the supersaturated vapor. Finally, as a by-product of this work, it is shown that the awkwardness of the constant-pressure ensemble associated with its expression as a *sum* over volume is automatically removed once the necessary presence of a shell molecule is recognized.

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I. INTRODUCTION

Density fluctuations are always occurring in any vapor and are an integral part of its equilibrium character. Indeed, they occur even in a noncondensable ideal gas. The process of homogeneous vapor-phase nucleation in a supersaturated vapor depends on the occurrence of certain fluctuations, called *embryos*, that serve as condensation centers for the formation of macroscopic liquid drops. However, in most vapor-phase nucleation measurements the temperature is well below critical. Under this condition, the supersaturated vapor is usually so attenuated that it is, at the most, an imperfect gas that can be regarded as *ideal* [1,2]. The vast majority of vapor molecules are separated by distances so great that they do not interact with each other. As a result, virtually all density fluctuations that form within the vapor are so rarefied that they never develop into liquid drops. Nevertheless, if enough time passes, the random collisions between molecules will eventually lead to a group in which the molecules are close enough to interact through their intermolecular potentials. For this fluctuation to have the potential to be involved in the dynamic process lead-

ing to nucleation and condensation, its molecules must remain mutually close for a time appreciably longer than say the duration of a bimolecular collision. This leads to the intuitive notion of a density fluctuation as a *physical cluster*, which persists in the vapor with a finite lifetime, adopting a variety of configurations within a rapidly fluctuating local domain of volume, before gaining or losing a molecule.

Such clusters are dynamic in nature, developing into liquid drops at different rates in a complex time-dependent manner. These individual rates, one for every possible fluctuation, should somehow be "incorporated" into the true nucleation rate. Exactly how to do this remains, at present, an unsolved and seemingly intractable problem. This is unfortunate, since a complete understanding of the molecular mechanism of nucleation hinges on its solution. As an alternative, every viable theory of nucleation has effected an "inversion of the order of averaging" such that an average cluster is first characterized and then the average rate of development of this average cluster is evaluated in order to specify the nucleation rate.

The first attempt at characterizing such an average

physical cluster for use in a theory of vapor-phase nucleation goes back to the 1920s and 1930s when Farkas [3], Volmer and Weber [4], Becker and Doring [5], Frenkel [6], and Zeldovich [7] developed what is now called the "classical theory" of nucleation. In this approach, embryos for the formation of liquid drops are modeled in accordance with the so-called "capillarity approximation" in which the embryos, although of molecular dimensions, are viewed as macroscopic drops, possessing both the uniform density and surface tension of the bulk liquid. Furthermore, the embryos are viewed as stationary objects lacking translational motion in the laboratory coordinate system.

For single-component vapors, the agreement between measured supersaturations for the onset of condensation (critical supersaturations) and those predicted by the classical theory has been remarkably good. Recently, however, reliable methods for measuring the *rate* of nucleation have become available [8–15] and the predictions of the classical theory concerning rate appear to differ from the measured rates by *orders of magnitude*.

One of the problems with the classical theory is that it represents an average *microscopic* embryo as a *stationary, macroscopic* liquid drop. In a departure from the classical theory, Ellerby, Weakliem, and Reiss [1] and Ellerby and Reiss [2] defined an average physical cluster in *molecular* terms to be used in a molecular theory of vapor-phase nucleation. This cluster is known as an *i/v cluster*, since it is defined by both a molecular number *i* and a volume *v* (*i/v* is the average density of molecules in the cluster). In Sec. II of this paper, we briefly review this definition and discuss some important requirements that any average cluster should fulfill. Then, in Sec. III, we present a refined characterization of the *i/v cluster*, also discussed by Weakliem and Reiss [17].

In developing a rate theory based on *any* average cluster, the transition probability for loss of monomers from the cluster, the "reverse" rate constant, must be determined. However, the physics behind this probability is so poorly defined that the *principle of detailed balance* is used so that reverse rate constants can be derived from forward ones [1–6,16,17]. Application of detailed balance requires the determination of the so-called *equilibrium distribution* of clusters. This distribution has therefore become a centerpiece in all viable nucleation theories.

Thus, beginning in Sec. IV and continuing through Sec. VI, the equilibrium distribution of *i/v clusters* is derived from a new method based on fluctuation theory [18,19]. While remaining as rigorous as earlier approaches, the method also avoids a physically ambiguous approximation made previously [1]. Moreover, the refined *i/v cluster* is considered in the derivation.

The characterization of the *i/v cluster* involves a so-called *shell molecule*. This molecule defines the cluster volume *v* (which contains *i* cluster molecules) by occupying the volume shell *dv*, between *v* and *v + dv*. This (*i + 1*)st shell molecule can, at first glance, appear somewhat restrictive, and even artificial, as part of a cluster definition. In this regard, in Secs. VII and VIII, we define an average cluster *without* a shell molecule and derive the

corresponding equilibrium distribution. The result is only slightly different from that derived for the original *i/v cluster*.

Since an average physical cluster can be defined without a shell molecule, it is tempting to do away with it altogether. However, in Sec. IX, we demonstrate that it is required in the definition of an average cluster if that cluster is to be consistent with the fundamental statistical-mechanical description of the total supersaturated vapor. Moreover, it is shown that the shell molecule must be *implicitly* included as part of any cluster characterization that includes volume as an *independent* variable. Thus the shell molecule's role in the theory is clarified and solidified.

As a by-product of the work in Sec. VIII, the awkwardness of the constant pressure ensemble [20] associated with its expression as a *sum* over volume is shown to be automatically removed once the necessary presence of the shell molecule is recognized.

Finally, in Sec. X, we discuss, among other topics, the inherent difficulties in characterizing a physical cluster with the *i* property alone and show how the theory provides a framework for a modern molecular theory of vapor-phase nucleation, independent of what method is used to calculate the free energy of cluster formation, so long as that method is in basic accordance with the *i/v cluster* characterization.

II. CHARACTERIZATION OF THE *i/v CLUSTER*

The development of the *i/v cluster* was guided by the following physical picture of the supersaturated vapor. Since, as discussed in Sec. I, the vapor is essentially ideal, its major component is an effectively infinite reservoir of monomers, separated from each other by distances so great that they *do not* interact. Within this reservoir, the molecules that *are* close enough to interact with each other form physical clusters of various "sizes." Since the density fluctuations that do serve as embryos are extremely rare [1,2], the physical clusters are, in essence, separated from each other by large distances, such that they *do not* interact. Viewed in this way, the clusters are "decoupled" from each other and from the surrounding vapor.

As discussed in Sec. I, the molecules in a cluster pass through a variety of configurations between the time it gains or loses a molecule. We just do not know how many configurations or which ones are involved. Therefore, even though we cannot follow the complicated trajectories traced out by such configurations, the fact that some will express themselves, between the time of cluster growth or decay, leads to the idea of an average cluster whose molecules are allowed to assume some well-defined set of configurations within some locally defined volume.

The usual assumption is that when an average physical cluster is characterized properly, one can still use it without generating much error, relative to the result that would be obtained if the true dynamical process could be treated by theory. Thus, instead of being drawn into the overwhelmingly detailed kinetics of individual configurations, we concentrate on the kinetics involved in

the evolution of this average cluster. A significant advantage of this approach is that once such an average cluster has been characterized, conventional rate expressions [21–23], or variants thereof [16,17], can be used to find the nucleation rate.

Density fluctuations, some of which constitute embryos, are an integral part of the equilibrium aspects of the supersaturated vapor. A physically consistent definition of an average cluster must be in accordance with this fact. In spite of this, most current theories have paid little attention to this requirement in fashioning a cluster definition, opting instead (as far as the requirement is concerned) for an *ad hoc* definition [24]. The easiest way to satisfy the requirement is to define physical clusters that can be used *rigorously* as tools for the evaluation of the partition function of the supersaturated vapor within which they reside or such that any approximations that are necessary represent well-defined minimal departures from this goal. Thus the physical clusters should be usable in the same way that *mathematical* clusters [25] have been used in the evaluation of the partition function of a vapor.

The importance of this requirement cannot be overstated. For when a cluster can be used in the rigorous evaluation of the partition function, then we are assured that the corresponding equilibrium distribution (required for the development of the rate theory) is correct.

The above requirement is satisfied by choosing a physical cluster with characteristics summarized as follows (Fig. 1).

- (1) The cluster is composed of i molecules.
- (2) These molecules *alone* determine the center of mass (c.m.) \mathbf{R} of the cluster.
- (3) The cluster molecules occupy a volume v , centered on \mathbf{R} .
- (4) For a given \mathbf{R} , cluster molecules assume *only* those configurations that keep \mathbf{R} fixed.
- (5) One ideal gas molecule, the *shell* molecule, must occupy a volume shell dv , about \mathbf{R} .
- (6) Only molecules within the same cluster interact with one another.

A physical cluster with these characteristics is called an i/v cluster. Since this cluster represents a density fluctuation, it makes sense to attribute the property of volume to it such that an i/v cluster has an average density i/v .

In addition to the rigorous requirement enunciated above, it is convenient to be able to compute the physical properties of the cluster by means of computer simulation. The i/v cluster lends itself well to this purpose in that it is closely related to the so-called Lee-Barker-Abraham (LBA) cluster elaborated by Lee, Barker, and Abraham, in a now classic paper [26]. Weakliem and Reiss [16], used the LBA method to calculate the reversible work of formation of an i/v cluster, $W_i(v)$, for argon, thus demonstrating the convenience of the i/v cluster with regard to computer simulation.

Because model potentials are not generally available for more complex molecules, it is also useful to have a *heuristic* model of the cluster that can be employed at the

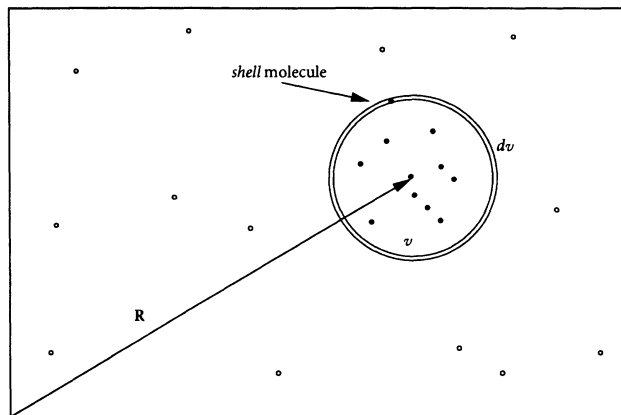


FIG. 1. An illustration of the i/v cluster characterization. The solid dots are the i interacting cluster molecules each shown relative to the position \mathbf{R} of the center of mass (c.m.). The solid dot on the surface of v is the *shell* molecule, which lies somewhere in dv and defines v . The ideal gas molecules outside of v are represented by open dots. The c.m. (the vector \mathbf{R}) of the cluster must *always* correspond to the center of v . For a cluster defined *without* a shell molecule the picture remains the same except that there is no shell molecule and no dv .

stage where simulation is required. Weakliem and Reiss [16] developed such a model, called the “modified liquid-drop model” (MLDM), guided by properties of the more rigorous molecular i/v cluster. They found that, at least for argon, the values of $W_i(v)$ derived both from the molecular theory via Monte Carlo simulation and the MLDM agree quite well. Then, they used the MLDM together with the cluster distribution derived previously [1,2] and variants of the conventional rate equations [1,17] to calculate rates of nucleation for argon [17].

Unfortunately, experimental data on nucleation rates in argon vapor that would allow a comparison between theory and experiment do not exist, although there are some sparse data on critical supersaturation. Applications of the MLDM to vapors other than argon (for which experimental data do exist), as well as work on the development of a truly molecular theory of rates using the i/v cluster, are presently underway.

Currently, as far as agreement between theory and experiment for the nucleation *rate* is concerned, the most successful theory seems to be that due to Dillmann and Meier [24]. This theory does *not* define the relevant physical clusters in molecular terms but rather models the average cluster as a Fisher droplet [27]. The theory is *phenomenological* but contains *no adjustable* parameters. Only ones that are fixed by the equation of state of the vapor and its critical constants are involved.

However, it must be emphasized that, in addition to developing a theory that is quantitatively accurate, it is equally important to produce one that provides important new insights into the *mechanism* of nucleation. Phenomenological theories, however successful, cannot provide insight at the molecular level. For example, the theory of Dillmann and Meier cannot distinguish between fluctuations that do and do not serve as embryos.

III. REFINED CHARACTERIZATION OF THE i/v CLUSTER

The original characterization of the i/v cluster contained an approximation, in that it was assumed that the shell molecule formed part of the ideal gas surrounding the cluster, and as such did not interact with the i molecules in the interior [1,2]. However, the shell molecule *can* interact with the interior molecules, the more so for small clusters with small v . Thus the following refined characterization allows for this interaction by including the shell molecule in the cluster.

In a "snapshot" (a frozen configuration) of the supersaturated vapor we notice a group of $i+1$ molecules in a configuration recognizable as a density fluctuation in that none of the peripheral molecules in the group are close enough, according to some reasonable distance criterion, to molecules in the surrounding "ideal" vapor to interact with them. Next, we find the group's c.m. \mathbf{R} and locate the molecule in this group that is the farthest away from \mathbf{R} . We then construct a sphere of volume $v = (4/3)\pi R^3$, centered on \mathbf{R} , such that this farthest molecule, which we now denote as the *shell* molecule, lies somewhere in the shell of volume between v and $v+dv$ (Fig. 1). The cluster then consists of i molecules within the spherical volume v plus the shell molecule in dv (all in all $i+1$ molecules), but is still referred to as an i/v cluster. An i/v cluster at a given position \mathbf{R} in the total volume V is then represented by all possible configurations of the i molecules in v that keep \mathbf{R} fixed and all possible locations of the shell molecule in dv . Furthermore, the position of the i/v cluster, as represented by \mathbf{R} , can be found anywhere in V .

IV. PARTITION FUNCTION OF THE i/v CLUSTER

Since the i/v clusters are decoupled from each other and from the surrounding vapor, we can write the canonical ensemble partition function $q_{i/v}(\mathbf{R}, T)$ for an i/v cluster at a *fixed position* \mathbf{R} of the c.m. in the volume V as though the cluster were in isolation, as

$$q_{i/v}(\mathbf{R}, T) = \frac{\gamma^{(i+1)}}{i!} (i+1)^3 \times \int_{dv} d\mathbf{r}_i \int_v \cdots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \cdots \mathbf{r}_i)]} \times d\mathbf{r}_1 \cdots d\mathbf{r}_{i-1}, \quad (1)$$

where $\gamma = (2\pi mkT)^{3/2}/h^3$, m is the mass of a molecule, h is Planck's constant, $\beta \equiv (kT)^{-1}$, k is Boltzmann's constant, and T is the temperature. The configuration integral $Z_{i/v}(\mathbf{R}, T)$ for an i/v cluster at a fixed position \mathbf{R} is given by

$$Z_{i/v}(\mathbf{R}, T) = (i+1)^3 \int_{dv} d\mathbf{r}_i \int_v \cdots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \cdots \mathbf{r}_i)]} \times d\mathbf{r}_1 \cdots d\mathbf{r}_{i-1}, \quad (2)$$

so that Eq. (1) can be written as

$$q_{i/v}(\mathbf{R}, T) = \frac{\gamma^{(i+1)}}{i!} Z_{i/v}(\mathbf{R}, T). \quad (3)$$

We have expressed $Z_{i/v}(\mathbf{R}, T)$, and therefore $q_{i/v}(\mathbf{R}, T)$, in the coordinate system natural to describing the position of a cluster in V , i.e., in the center-of-mass system. The transformation of the volume elements from laboratory coordinates (primed) to c.m. coordinates is given by

$$(i+1)^3 d\mathbf{R} \prod_{j=1}^i d\mathbf{r}_j = \prod_{j=1}^{i+1} d\mathbf{r}'_j, \quad (4)$$

where the c.m. (given by \mathbf{R}) and the relative coordinates (given by \mathbf{r}_j) are related by

$$\mathbf{R} = \frac{\left[\sum_{j=1}^{i+1} \mathbf{r}'_j \right]}{(i+1)} \quad (5)$$

and

$$\mathbf{r}_j = \mathbf{r}'_j - \mathbf{R}. \quad (6)$$

The intermolecular potential energy of the cluster is specified by $u_{i+1}(\mathbf{r}_1, \dots, \mathbf{r}_i)$, where now the interaction of the shell molecule is included. This energy is calculated in the c.m. reference frame at a given \mathbf{R} , with the positions of the $i+1$ molecules relative to \mathbf{R} specified by the set $\{\mathbf{r}_j\}$. The integral over \mathbf{r}_i corresponds to the permissible locations of the shell molecule, anywhere in dv . The term $\gamma^{(i+1)}$ in Eq. (1) is the momentum partition function for the $i+1$ molecules, and $i!$ in the denominator of Eq. (1) removes redundant configurations generated by $Z_{i/v}(\mathbf{R}, T)$ that simply interchange the positions of the i indistinguishable molecules in the interior of the cluster.

We limit the integrals over $\mathbf{r}_1, \dots, \mathbf{r}_{i-1}$ in Eq. (1) to $v \leq \hat{v}$, where \hat{v} is a cutoff volume that prevents the volume from becoming so large that the clusters begin to interact with each other and invalidate the theory. Moreover, it is implied that $i \leq \hat{i}$, where \hat{i} is a cutoff number that prevents the clusters from becoming so large that they condense and again invalidate the theory.

We must emphasize that, in addition to providing a precise definition of a cluster's position in V , use of the c.m. coordinate system provides an unambiguous separation of the *internal* free energy of the cluster from its *translational* free energy [2] (thus avoiding the so-called *replacement free-energy problem* [28,29]) and permits the required nonredundant enumeration of configurations involved in the evaluation of the total system partition function [1]. Furthermore, it is important to emphasize that the translational free energy of the cluster is explicitly, and unambiguously, included in the theory, unlike classical theory that treats the cluster as a stationary body.

The partition function $q_{i/v}(V, T)$ for an i/v cluster *somewhere* in V is related to $q_{i/v}(\mathbf{R}, T)$ by relation

$$q_{i/v}(V, T) = \int_V q_{i/v}(\mathbf{R}, T) d\mathbf{R}, \quad (7)$$

where it should be noted that, in the limit $V \rightarrow \infty$, the volume occupied by the clusters themselves is negligible compared to that of the system. Thus each cluster has the entire volume V available to its c.m. Substituting Eq. (1) into Eq. (7), we find

$$\begin{aligned}
q_{i/v}(V, T) &= \frac{\gamma^{(i+1)}}{i!} (i+1)^3 \\
&\times \int_V d\mathbf{R} \int_{dv} d\mathbf{r}_i \int_v \dots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \dots \mathbf{r}_i)]} \\
&\quad \times d\mathbf{r}_1 \dots d\mathbf{r}_{i-1}. \quad (8)
\end{aligned}$$

Furthermore, the value of $q_{i/v}(V, T)$ is, by symmetry, *independent* of the position of the shell molecule in dv and *independent* of the position of the c.m. in V , so that Eq. (8) becomes

$$\begin{aligned}
q_{i/v}(V, T) &= \frac{\gamma^{(i+1)}}{i!} (i+1)^3 V dv \\
&\times \int_v \dots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \dots \mathbf{r}_i)]} \\
&\quad \times d\mathbf{r}_1 \dots d\mathbf{r}_{i-1}. \quad (9)
\end{aligned}$$

The configuration integral $Z_{i/v}(V, T)$ for an i/v cluster *somewhere* in the volume V is given by

$$\begin{aligned}
Z_{i/v}(V, T) &= (i+1)^3 V dv \int_v \dots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \dots \mathbf{r}_i)]} \\
&\quad \times d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} \quad (10)
\end{aligned}$$

so that Eq. (9) becomes

$$q_{i/v}(V, T) = \frac{\gamma^{(i+1)}}{i!} Z_{i/v}(V, T). \quad (11)$$

V. PROBABILITY OF EXACTLY ONE i/v CLUSTER

The probability $P_i(v)dv$ of having *exactly one* i/v cluster *somewhere* in V can be expressed in the language of fluctuation theory [18,19] as the ratio of the partition function $Q_R(N, V, T)$ of the supersaturated vapor *restricted* to always have *exactly one* i/v cluster *somewhere* in V , to the *unrestricted* partition function $Q(N, V, T)$ of the vapor,

$$P_i(v)dv = \frac{Q_R(N, V, T)}{Q(N, V, T)}, \quad (12)$$

where for notational convenience we have "embedded" a dv in $Q_R(N, V, T)$.

The restricted partition function $Q_R(N, V, T)$ can be expressed as

$$Q_R(N, V, T) = q_{i/v}(V, T) Q_R(N-i-1, V-v, T), \quad (13)$$

where dv is now embedded in $q_{i/v}(V, T)$, the partition function for an i/v cluster somewhere in V , as given by Eq. (9). The partition function $Q_R(N-i-1, V-v, T)$ is for the remaining $N-(i+1)$ molecules and refers to a system restricted to have *no* i/v clusters. The factoring of $Q_R(N, V, T)$ follows immediately from the decoupling of the cluster from the surrounding vapor. Substituting Eq. (13) into Eq. (12) then gives

$$P_i(v)dv = \frac{q_{i/v}(V, T) Q_R(N-i-1, V-v, T)}{Q(N, V, T)}. \quad (14)$$

Virtually all of the N total molecules of the supersaturated vapor lie outside the clusters, forming an effectively *infinite* reservoir of ideal gas monomers such that the number of monomers $N_1 \cong N$. Furthermore, clusters whose molecules are close enough to interact are extremely rare. This means that the ratio of partition functions $Q_R(N-i-1, V-v, T)/Q(N, V, T)$ in Eq. (14) can be written, with negligible error, as the ratio of partition functions corresponding to ideal gas vapors,

$$\begin{aligned}
\frac{Q_R(N-i-1, V-v, T)}{Q(N, V, T)} &= \frac{[\gamma(V-v)]^{[N-(i+1)]}}{[N-(i+1)]!} \\
&= \frac{[\gamma V]^N}{N!} \\
&= \frac{N!}{[N-(i+1)]!} \left[1 - \frac{v}{V}\right]^N \left[\frac{1}{\gamma(V-v)}\right]^{(i+1)}. \quad (15)
\end{aligned}$$

The first factor on the right-hand side of Eq. (15) can be written as

$$\begin{aligned}
\frac{N!}{[N-(i+1)]!} &= \frac{N(N-1) \dots (N-i)(N-i-1) \dots}{(N-i-1)(N-i-2) \dots} \\
&= N(N-1) \dots (N-i) = N^{(i+1)}, \quad (16)
\end{aligned}$$

where the last form follows in the limit $N \gg i$. Expanding the logarithm of the second factor in Eq. (15) in a Taylor series and taking the limit $N \rightarrow \infty$, $V \rightarrow \infty$, gives

$$\left[1 - \frac{v}{V}\right]^N \rightarrow e^{-\rho v}, \quad (17)$$

where $\rho = N/V$, so that ρ is the density of the supersaturated vapor. And, finally, in the limit $V \rightarrow \infty$, the term $(V-v)$ in the denominator of the third factor in Eq. (15) becomes V .

Substituting Eqs. (16) and (17) into Eq. (15) then gives

$$\frac{Q_R(N-i-1, V-v, T)}{Q(N, V, T)} = \left[\frac{\rho}{\gamma}\right]^{(i+1)} e^{-\rho v}, \quad (18)$$

and substituting this result into Eq. (14) yields

$$P_i(v)dv = q_{i/v}(V, T) \left[\frac{\rho}{\gamma}\right]^{(i+1)} e^{-\rho v}. \quad (19)$$

The chemical potential μ of the *ideal* supersaturated vapor can be expressed as [1,2]

$$\mu = -\frac{1}{\beta} \ln \left[\frac{\gamma}{\rho}\right]. \quad (20)$$

Substituting Eq. (20) and the ideal gas law $\beta p = \rho$, where p is the pressure of the vapor, into Eq. (19) then gives

$$P_i(v)dv = q_{i/v}(V, T) e^{-\beta[pv - (i+1)\mu]}. \quad (21)$$

Finally, substituting Eq. (9) into Eq. (21) results in

$$P_i(v)dv = \left[\frac{\gamma}{e^{\beta\mu}} \right] dv e^{-\beta(pv - i\mu)} \frac{\gamma^i}{i!} (i+1)^3 V \\ \times \int_v \cdots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \cdots \mathbf{r}_i)]} \\ \times d\mathbf{r}_1 \cdots d\mathbf{r}_{i-1}, \quad (22)$$

which can be immediately rearranged using Eq. (20) to give

$$P_i(v)dv = \rho dv e^{-\beta(pv - i\mu)} \frac{\gamma^i}{i!} (i+1)^3 V \\ \times \int_v \cdots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \cdots \mathbf{r}_i)]} d\mathbf{r}_1 \cdots d\mathbf{r}_{i-1}. \quad (23)$$

The *internal* Helmholtz free energy \tilde{A}_{iv}^* of the molecules in the cluster (under the restriction that the shell molecule remains in dv and that the c.m. is fixed) is given by

$$\tilde{A}_{iv}^* = -\frac{1}{\beta} \ln \left\{ \frac{\gamma^{i-1} (i+1)^{3/2}}{i!} \right. \\ \left. \times \int_v \cdots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \cdots \mathbf{r}_i)]} \right. \\ \left. \times d\mathbf{r}_1 \cdots d\mathbf{r}_{i-1} \right\}. \quad (24)$$

Combining this result and Eq. (23) then gives the final expression for the probability $P_i(v)dv$ of having exactly one i/v cluster somewhere in V as

$$P_i(v)dv = \rho dv \exp \left\{ -\beta \left[\tilde{A}_{iv}^* - \frac{1}{\beta} \ln[\gamma(i+1)^{3/2} V] \right. \right. \\ \left. \left. + pv - i\mu \right] \right\}. \quad (25)$$

We also note that the second term in the exponent of Eq. (25) is the *translational* Helmholtz free energy of the cluster. While this new approach gives a result, Eq. (25), that is identical to that obtained previously using fundamental probability theory [2], it benefits from an immediate connection to statistical mechanics.

VI. EQUILIBRIUM DISTRIBUTION OF i/v CLUSTERS

The ensemble average number of i/v clusters $n_i(v)dv$, which is also the equilibrium distribution of clusters, can be expressed as [2]

$$n_i(v)dv = \sum_{j=1}^{\infty} j P_j^i(v)dv, \quad (26)$$

where $P_j^i(v)dv$ is the probability of *exactly* j such clusters. Since the clusters do not interact with one another, $P_j^i(v)dv$ can be expressed as the product of j identical uncorrelated probabilities, each being the probability of exactly one i/v cluster, Eq. (25),

$$P_j^i(v)dv = [P_i(v)dv]^j. \quad (27)$$

However, because the terms in $P_j^i(v)dv$ for $j \geq 2$ are

higher order in the infinitesimal volume dv they can be ignored, so that substitution of Eq. (27) into Eq. (26) yields

$$n_i(v)dv = P_i(v)dv, \quad (28)$$

and upon substitution of Eq. (25) gives finally

$$n_i(v)dv = \rho dv \exp \left\{ -\beta \left[\tilde{A}_{iv}^* - \frac{1}{\beta} \ln[\gamma(i+1)^{3/2} V] \right. \right. \\ \left. \left. + pv - i\mu \right] \right\} \quad (29)$$

for the equilibrium distribution, where \tilde{A}_{iv}^* is given by Eq. (24). We note, in passing, that Eq. (28) holds for *any* average cluster characterization that involves a continuous volume v .

If we "turn off" or "ignore" the interaction between the shell molecule and the remaining molecules of the cluster, $u_{i+1}(\mathbf{r}_1 \cdots \mathbf{r}_i)$ may be replaced by the residual potential $u_i(\mathbf{r}_1 \cdots \mathbf{r}_{i-1})$ and the corresponding Helmholtz free energy \tilde{A}_{iv}^* will then be denoted by A_{iv}^* . At the same time, Eq. (29) becomes

$$n_i(v)dv = \rho dv \exp \left\{ -\beta \left[A_{iv}^* - \frac{1}{\beta} \ln[\gamma(i+1)^{3/2} V] \right. \right. \\ \left. \left. + pv - i\mu \right] \right\}, \quad (30)$$

where

$$A_{iv}^* = -\frac{1}{\beta} \ln \left\{ \frac{\gamma^{i-1} (i+1)^{3/2}}{i!} \right. \\ \left. \times \int_v \cdots \int_v e^{-\beta[u_{i+1}(\mathbf{r}_1 \cdots \mathbf{r}_i)]} \right. \\ \left. \times d\mathbf{r}_1 \cdots d\mathbf{r}_{i-1} \right\}. \quad (31)$$

The theory published thus far uses Eqs. (30) and (31) with $(i+1)$ replaced by i [1,2,16,17]. Clearly, for the larger clusters the error is smaller. The terms in parentheses in the exponent of Eq. (30) represent $W_i(v)$, the reversible work of formation of an i/v cluster, i.e.,

$$W_i(v) = A_{iv}^* - \frac{1}{\beta} \ln[\gamma i^{3/2} V] + pv - i\mu, \quad (32)$$

where $i+1$ has been replaced by i in both the translational term and in A_{iv}^* .

This approach to calculating $n_i(v)dv$ is more direct than, and as rigorous as, that of previous work [1], where the total partition function of the supersaturated vapor was derived, and then the formula for $n_i(v)dv$ was obtained through the use of the "maximum-term method" [25]. The use of that method required, in turn, the use of Stirling's approximation for $[n_i(v)dv]!$. This approximation, and the factorial itself, is somewhat in conflict with the fact that $n_i(v)dv$ is a probability [= $P_i(v)dv$], and hence a fraction. The above method avoids the use of this physically ambiguous approximation. For completeness, it should be mentioned that, in spite of this fact, the maximum term method does yield the correct result for

the equilibrium distribution of clusters [30]. The approach presented here does contain its own mild approximation, embodied in Eq. (18). However, this approximation is well defined and physically consistent with the properties of the supersaturated vapor.

VII. AVERAGE CLUSTER DEFINED WITHOUT A SHELL MOLECULE

The molecular number i and volume v are intuitively attractive features of the i/v cluster characterization. However, the shell molecule can appear to be a rather restrictive, even artificial, feature. This motivates us to derive an equilibrium distribution for an average cluster having the following characterization.

- (1) The cluster is composed of i molecules.
- (2) These molecules *alone* determine the c.m. \mathbf{R} of the cluster.
- (3) The cluster molecules occupy a volume v , centered on \mathbf{R} .
- (4) For a given \mathbf{R} , cluster molecules assume *only* those configurations that keep \mathbf{R} fixed.
- (5) Only molecules within the same cluster interact with one another.

This cluster will be called an iv cluster and differs from the i/v cluster in that there is *no* shell molecule. However, the cluster is still characterized by a *discrete* volume v . The canonical ensemble partition function $q_{iv}(V, T)$ for an iv cluster, somewhere in the volume V , is then given by

$$q_{iv}(V, T) = \frac{\gamma^i}{i!} i^3 V \int_v \dots \int_v e^{-\beta[u_i(r_1 \dots r_{i-1})]} \times d\mathbf{r}_1 \dots d\mathbf{r}_{i-1}, \quad (33)$$

where we emphasize that there is *no* dv (for that matter no Δv) in Eq. (33). The volume v is a fixed boundary, appearing only as the limit on the integrals over $\mathbf{r}_1 \dots \mathbf{r}_{i-1}$.

In analogy to the treatment of the i/v cluster, the probability P_{iv} of having exactly one iv cluster somewhere in V can also be expressed in the language of fluctuation theory [18,19] as

$$P_{iv} = \frac{q_{iv}(V, T) Q_R(N-i, V-v, T)}{Q(N, V, T)}, \quad (34)$$

where $q_{iv}(V, T)$ is the partition function, Eq. (33), for an iv cluster and $Q_R(N-i, V-v, T)$ is the partition function for the remaining $N-i$ molecules and to a system restricted to have no iv clusters.

The ratio of partition functions $Q_R(N-i, V-v, T)/Q(N, V, T)$ in Eq. (34) can be written, with negligible error, and in direct analogy to the development of Eq. (18) from Eq. (15) as

$$\frac{Q_R(N-i, V-v, T)}{Q(N, V, T)} = \left[\frac{\rho}{\gamma} \right]^i e^{-\rho v}, \quad (35)$$

which upon substitution into Eq. (34) yields

$$P_{iv} = q_{iv}(V, T) \left[\frac{\rho}{\gamma} \right]^i e^{-\rho v}. \quad (36)$$

Substitution of Eqs. (20) and (33) and the ideal gas law into Eq. (36) then gives the probability P_{iv} of having exactly one iv cluster somewhere in the volume V as

$$P_{iv} = e^{-\beta(pv - i\mu)} \frac{\gamma^i}{i!} i^3 V \int_v \dots \int_v e^{-\beta[u_i(r_1 \dots r_{i-1})]} \times d\mathbf{r}_1 \dots d\mathbf{r}_{i-1}, \quad (37)$$

which is a pure number. Finally, using the definition

$$A_{iv}^* \equiv -\frac{1}{\beta} \ln \left\{ \frac{\gamma^{i-1} i^{3/2}}{i!} \int_v \dots \int_v e^{-\beta[u_i(r_1 \dots r_{i-1})]} \times d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} \right\}, \quad (38)$$

we can write Eq. (37) as

$$P_{iv} = \exp \left\{ -\beta \left[A_{iv}^* - \frac{1}{\beta} \ln(\gamma i^{3/2} V) + pv - i\mu \right] \right\}. \quad (39)$$

This result for the equilibrium distribution of clusters (where we set $n_{iv} = P_{iv}$) was originally obtained by Reiss, Tabazadeh, and Talbot [31] by a more complicated analysis.

The probability P_i of having exactly one iv cluster, *regardless* of the volume v , can be expressed as the sum of P_{iv} over all allowable v 's in Eq. (39),

$$P_i = \sum_v P_{iv}. \quad (40)$$

On substitution of Eq. (39) into Eq. (40) we obtain

$$P_i = \sum_v \exp \left\{ -\beta \left[A_{iv}^* - \frac{1}{\beta} \ln(\gamma i^{3/2} V) + pv - i\mu \right] \right\}. \quad (41)$$

The sum over *discrete* volume "states" in Eq. (41) is *formally* exact. Yet Eq. (41) does not explicitly express the fact that the cluster volume v is, in reality, a *continuous* variable in our problem. However, the sum in Eq. (41) can be converted to an integral over volume. Let Δv be the interval in the summation over v in Eq. (41). Physically this means that Δv is formally the proper "quantum of volume," the proper *volume scale*, which is as yet undetermined.

Multiplying and dividing Eq. (41) by Δv , we find

$$P_i = \sum_v \left[\frac{\Delta v}{\Delta v} \right] \exp \left\{ -\beta \left[A_{iv}^* - \frac{1}{\beta} \ln(\gamma i^{3/2} V) + pv - i\mu \right] \right\}. \quad (42)$$

We can then immediately write the sum over volume v in Eq. (42) as an integral [20,32] to give

$$P_i = \int_v \frac{dv}{\Delta v} \exp \left\{ -\beta \left[A_{iv}^* - \frac{1}{\beta} \ln(\gamma i^{3/2} V) + pv - i\mu \right] \right\} \quad (43)$$

or

$$P_i = \int_v \hat{\rho} dv \exp \left\{ -\beta \left[A_{iv}^* - \frac{1}{\beta} \ln(\gamma i^{3/2} V) + pv - i\mu \right] \right\}, \quad (44)$$

where we define the scale $\hat{\rho}$, i.e., the "density of volume states," by the relation

$$\hat{\rho} \equiv \Delta v^{-1}. \quad (45)$$

Now, Eq. (44) can be expressed as

$$P_i = \int_v P_i(v) dv, \quad (46)$$

where

$$P_i(v) dv = \hat{\rho} dv \exp \left\{ -\beta \left[A_{iv}^* - \frac{1}{\beta} \ln(\gamma i^{3/2} V) + pv - i\mu \right] \right\}, \quad (47)$$

where $P_i(v)dv$ is the probability of having exactly one iv cluster when volume is treated naturally as a continuous variable. We note that $\hat{\rho}$ times the exponential in Eq. (47) is a density so that $P_i(v)dv$ is a pure number.

If the scale $\hat{\rho}$ is set equal to the number density ρ , then Eq. (47) is identical to the result for $P_i(v)dv$, and therefore for $n_i(v)dv$, obtained earlier by approaches that explicitly employ a shell molecule [1,2]. However, at this point, we have not shown that, in fact, the scale $\hat{\rho}$ is identical to ρ .

VIII. CALCULATION OF THE SCALE $\hat{\rho}$

The scale $\hat{\rho}$ involved in the integration over the volume v in Eq. (47) can be estimated using the constant pressure ensemble partition function $\Delta(i,p,T)$ [20]. Consider a stationary cluster whose internal behavior is that of an ideal gas. In accordance with the formulation of the constant pressure ensemble, p must be the pressure of the "barostat," namely, that of the surrounding supersaturated vapor, and

$$\Delta(i,p,T) = \sum_v Q(i,v,T) e^{-\beta pv}, \quad (48)$$

where $Q(i,v,T)$ is the canonical ensemble partition function for the i ideal gas molecules in the volume v at temperature T , given by

$$Q(i,v,T) = \frac{(\gamma v)^i}{i!}. \quad (49)$$

Referring to the preceding section, $\Delta(i,p,T)$ can be written in the continuous volume picture as

$$\Delta(i,p,T) = \int_v \hat{\rho} dv Q(i,v,T) e^{-\beta pv}, \quad (50)$$

where, again, $\hat{\rho} \equiv \Delta v^{-1}$. Substituting Eq. (49) into Eq. (50) then yields

$$\Delta(i,p,T) = \hat{\rho} \int_v dv \frac{(\gamma v)^i}{i!} e^{-\beta pv}, \quad (51)$$

where we take the scale $\hat{\rho}$ to be independent of the volume v . Although strictly for convenience, we will permit the volume v to range from 0 to ∞ . Then, on performing the integration, we find

$$\Delta(i,p,T) = \frac{\hat{\rho} \gamma^i}{(\beta p)^{i+1}}, \quad (52)$$

and, upon using the ideal gas law $\beta p = \rho$, we can write

$$\Delta(i,p,T) = \frac{\hat{\rho}}{\rho} \left[\frac{\gamma}{\rho} \right]^i, \quad (53)$$

where since the surrounding vapor is the barostat, ρ is the density of that vapor.

The relation between the partition function $\Delta(i,p,T)$ and the corresponding thermodynamic characteristic function, the Gibbs free energy $G(i,v,T)$, is given by [20]

$$G(i,v,T) = -\frac{1}{\beta} \ln \Delta(i,p,T). \quad (54)$$

Substituting Eq. (53) into Eq. (54) then gives

$$G(i,v,T) = -\frac{1}{\beta} \ln \left[\frac{\hat{\rho}}{\rho} \left[\frac{\gamma}{\rho} \right]^i \right]. \quad (55)$$

The chemical potential μ of a molecule in the cluster, i.e., of the ideal gas in the cluster, is given by [20]

$$\mu = -\frac{1}{\beta} \ln \left[\frac{\gamma}{\rho'} \right], \quad (56)$$

where ρ' is the density of the gas in the cluster. However, since the gas inside and outside the cluster is ideal, it is clear that the equilibrium value of v in the constant pressure case will be such that $\rho' = i/v = \rho$. This argument depends on i being large enough so that the constant pressure and canonical ensembles lead to the same thermodynamic results. Therefore, for small clusters the argument involves an approximation.

The relation between the Gibbs free energy of an ideal gas of i molecules in a volume v at temperature T and its chemical potential μ is given by [33]

$$G(i,v,T) = i\mu. \quad (57)$$

Substituting Eq. (56) into Eq. (57) then yields

$$G(i,v,T) = -\frac{1}{\beta} \ln \left[\frac{\gamma}{\rho} \right]^i, \quad (58)$$

where we set $\rho' = \rho$. Finally, comparison of Eqs. (58) and (55) requires that

$$\hat{\rho} = \rho, \quad (59)$$

thus yielding as an *estimate* of the scale $\hat{\rho}$ the number density ρ of the molecules in the system.

Assuming that the scale $\hat{\rho}$ is roughly independent of the size of the cluster, independent of whether it is treated as real or ideal, or of where it is located in the volume V , we can write Eq. (47) as

$$n_i(v) dv = \rho dv \exp \left\{ -\beta \left[A_{iv}^* - \frac{1}{\beta} \ln(\gamma i^{3/2} V) + pv - i\mu \right] \right\}, \quad (60)$$

where we note from Eq. (28) that $P_i(v)dv = n_i(v)dv$. This result is identical to the result obtained for the original i/v cluster characterization [1,2] that include a *noninteracting* shell molecule. Thus it *might* appear as though it is not absolutely necessary to include the shell molecule as part of the characterization.

However, a moment's reflection will show that a shell molecule is *implicitly* included in the above derivation. In the quantum-statistical development leading to the formulas connecting the various partition functions to thermodynamic properties, molecules are described by wave functions that "occupy" the entire volume v simultaneously. The molecules must know about the presence of the wall prescribed by v , since that wall enters the boundary conditions which determine the wave functions and their corresponding eigenvalues. It is exactly in this way that the volume, in addition to molecular number i , defines the quantum state of the cluster.

In the classical limit, and in a macroscopic system, the requirement that the system sense the volume is likely transformed into the requirement that some cluster molecule (a "shell" molecule) is *always* near the wall. But in a macroscopic system it is overwhelmingly probable that *some* molecule will always be near enough to the wall to interact with it, so that the requirement does not have to be stated explicitly. However, for a small system such as the i/v cluster, *explicit* specification is necessary, in the form of the shell molecule.

We note further that the awkwardness of the pressure ensemble associated with its expression as a *sum* over volume is automatically removed once the necessary presence of the wall molecule is recognized. Then the sum can be converted naturally to an integral in terms of the coordinates of the wall molecule.

The scale $\hat{\rho}$ can be related to a corresponding length scale ξ given by

$$\xi \equiv \hat{\rho}^{-1/3} = \rho^{-1/3}. \quad (61)$$

This length scale is the amount by which the radius of a spherical volume v must change in order that a new "volume state" can be defined for the cluster, and hence for the entire vapor system. This is closely analogous to the length scale λ involved in the evaluation of the configurational entropy of microemulsions [34]. There the scale defines how far an element of interface must be displaced before a new configuration (new "shape state") of a globule (the analog of the cluster) can be considered to have been generated, and hence a new configuration of the entire microemulsion. For a real microemulsion, the length scale λ has been estimated to be equal to $\rho^{-1/3}$ [34].

Although speculative at this point, there might be a fundamental reason that *both* of these scales are, within an order of magnitude, equal to $\rho^{-1/3}$. The idea is that a distinguishable state, in the sense of the semiclassical phase integral, in either system is generated by the occupation of an element of volume $d\tau$ by a molecule. The probability that such an element is occupied by a specific molecule is always proportional to $d\tau/V$. Since there are N total molecules in the system, the total probability that the element is occupied by some molecule is always pro-

portional to $N d\tau/V = \rho d\tau$. Thus the probability of generating a new classical state is related to the probability that a new volume element $d\tau$ is occupied, and any such element has a probability proportional to $\rho d\tau$ of being occupied.

IX. FUNCTION OF THE SHELL MOLECULE

At the beginning of this paper, the scale $\hat{\rho}$ was determined as a natural consequence of the introduction of the shell molecule. Furthermore, in the preceding section, the shell molecule was implicitly present in the derivation of the scale. However, it remains *possible* that a theory of nucleation could be based on an average cluster defined with a volume, but without a shell molecule, which from the *quantitative* point of view might differ little from one developed with a shell molecule.

Since the shell molecule adds another level of complexity to the cluster characterization, it would be tempting to do away with it, unless, of course, there is a compelling reason to keep it. There is such a reason. A cluster must be defined with a shell molecule if, in addition to nucleation theory, it is to be used in the rigorous evaluation of the total system partition function [1]. In order to see why this is true, consider Fig. 2.

In the figure, the N molecules of the supersaturated va-

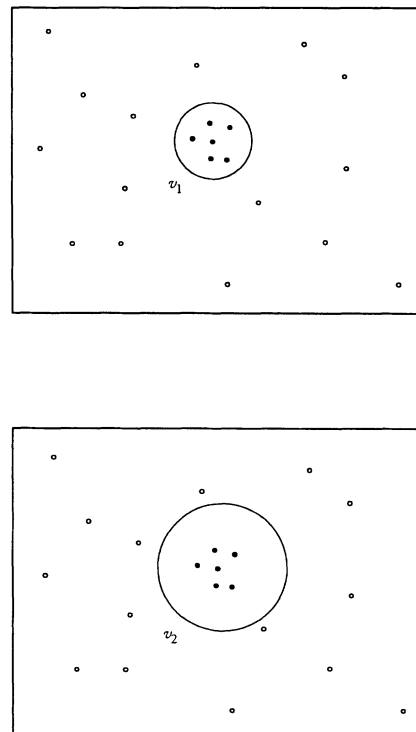


FIG. 2. A demonstration of the redundant counting of configurations that follows from the use of a cluster defined without a shell molecule. We show *two* "volume states" of the cluster, labeled v_1 in the top panel and v_2 in the bottom panel, but only *one* actual physical state (configuration) for the molecules in the system. The configuration of the molecules is identical in both panels. The classical phase integral "counts" this configuration *twice* (once for v_1 and once for v_2), thus leading to redundant counting.

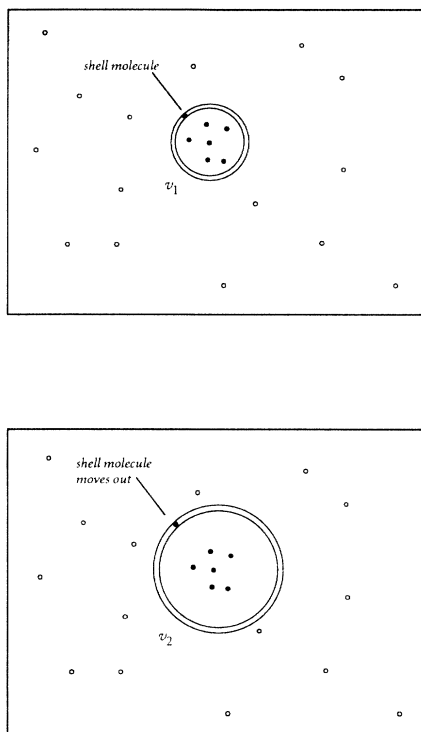


FIG. 3. A demonstration of the nonredundant counting of configurations that follows from the use of an i/v cluster. We show two "volume states" of the cluster, labeled v_1 in the top panel and v_2 in the bottom panel, each defined by the *shell* molecule in dv . Since the only way to change the volume v is to change the position of an actual molecule in the system, the shell molecule, there is no redundant counting of configurations in the classical phase integral, for here there are two physical states (configurations) for the molecules in the system.

por are "frozen" in one of the configurations available to them. In the classical phase integral for the N molecules this configuration should be counted *only once*. However, without a shell molecule, it will be counted more than once. In the figure we show how it would be counted twice—once when the cluster volume v is equal to v_1 and again when that volume is equal to v_2 .

The problem lies in the fact that the "volume state" of the cluster defined without a shell molecule is not connected to the actual physical state of the molecules in the vapor. Introduction of the shell molecule solves this problem, since then the volume v is defined by the position of a molecule. Thus the actual physical configuration of the cluster molecules and therefore of the overall physical configuration of the N molecules in the vapor changes when the volume changes (see Fig. 3). In this way, the shell molecule aids in the exhaustive and nonredundant counting of the configurations that enter into the classical phase integral of the total system.

It should also be emphasized that in addition to the shell molecule, the centering of the volume v on the c.m. is also required for nonredundant counting. Both the shell molecule and the c.m. endow the cluster with natural "markers" that enable the unambiguous and proper evaluation of the partition function of the system.

X. DISCUSSION

Most theories of nucleation, including modern ones such as the phenomenological theory of Dillman and Meier theory [24], characterize the average physical cluster by a single parameter i , namely, the number of molecules in the cluster. In reality, the clusters represent density fluctuations and *no* prescription is given for distinguishing those fluctuations that contribute to the formation of the stable phase from those that do not. As discussed previously [1,2,16,17], the distinction must really be made on a *kinetic* basis (i.e., on the basis of the rate theory) rather than on a *thermodynamic* basis.

It turns out that the possibility of making the distinction in this way depends on the ability to distinguish between clusters with the *same* molecular number i , but *different* volumes v , or different other parameters. Since the overwhelming number of density fluctuations are *not* involved in the dynamics of the phase transition, the failure to provide the theory with a fundamental means of distinction represents a serious problem in the attempt to devise a fundamental theory.

In the existing theories the distinction is made on an *ad hoc* basis, usually requiring those clusters that serve as embryos to exhibit a density identical to that of the bulk liquid or a density that is some simple function of that density. By suppressing the mutual independence of i and v in this manner, one is limited to a much narrower view of molecular events and loses considerable insight into the molecular mechanism of nucleation. All theories of nucleation that identify embryos by i alone are liable to this criticism. Thus the properties of the volume v , the number i , and the shell molecule are all vital elements in the cluster characterization.

In closing, we should emphasize that the cluster distribution based on the i/v cluster can be used in modest variants of the conventional rate equations (involving the new property of cluster volume) to form the foundation on which a theory of nucleation can be built, once the free energy of formation of the i/v cluster is calculated. Many approaches exist for the evaluation of this free energy. It can be determined by computer simulation (requiring model potentials) [16]. Also, the modified liquid drop model [16], discussed in the Introduction, provides a simple way to calculate it. Another approach involves the use of *density-functional theory* [35–37] to calculate the work of formation of the i/v cluster [38].

Future work may address the development of an optimum method for calculating the free energy of an i/v cluster, using a cluster model whose complexity lies somewhere in between the strict *microscopic* i/v cluster and the more *macroscopic* MLDM. A rate theory based on such a model will hopefully provide both an accurate prediction of rates *and* insight into the mechanism of nucleation.

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