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Nucleation Near a Critical Temperature

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In this paper we extend the conventional theory of nucleation to take in the effects of excluded-volume interference between the precritical droplets present prior to phase transformation. It is shown that, close to the critical point, the effect of excluded volume is to cause a sizable increase in the surface free energy of the critical nucleus. A corresponding increase in the barrier to nucleation explains the large undercoolings achieveable experimentally in this region. Our results are compared with recent experimental measurements of Heady and Cahn and favorable agreement is found.

KEY WORDS: Nucleation near critical point; excluded volume in nucleation; hard sphere boundary tension; scaled particle theory; supercooling limit.

1. INTRODUCTION

Investigations of nucleation processes near a critical temperature have yielded what seems to be the unequivocal experimental result that far greater degrees of metastability are possible than would be predicted by conventional nucleation theory. In particular this situation occurs both in the nucleation of a new phase in binary solutions of methylcyclohexane and perfluoromethylcyclohexane$^{(1,2)}$ cooled into the miscibility gap below the critical temperature, and in the formation of CO_2 bubbles$^{(3)}$ in liquid CO_2. In the respective cases degrees of supercooling and superheating far in excess of those required by conventional theory must be attained before nucleation is observed.

Sundquist and Oriani$^{(1)}$ attempted to explain this discrepancy by pointing out that the usual expression for the equilibrium distribution of embryos

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of the new phase is

$$N_n = F\exp(-W_n/kT) \tag{1}$$

where N_n is the number of embryos containing n molecules, F is the total number of species in the parent phase, and W_n is the reversible work required to form an embryo of n molecules, while k and T are the Boltzmann constant and temperature, respectively. However, according to these authors, the proper expression is

$$N_n = Fx^n \exp(-W_n{}^0/kT) \tag{2}$$

where x is the mole fraction of *monomers* in the parent phase. If x departs appreciably from unity, as it must near the critical point, then Eq. (2) no longer approximates Eq. (1) and the former [Eq. (2)] rather than the latter [Eq. (1)] must be used. However, in assessing the experiments only Eq. (1) was used.

Later, Hillig and McCarroll$^{(4)}$ showed that Eq. (1) must still be correct and that the problem lies in the incorrect choice of reference state. For example, W_n has the form

$$W_n{}^0 = n(\mu_l - \mu_v{}^0) + \alpha n^{2/3} \tag{3}$$

where μ_l and $\mu_v{}^0$ are the chemical potentials of "bulk" embryo and parent phases, respectively, and $\alpha n^{2/3}$ represents the free energy required to form the interface between the embryo and parent. However, the parent phase is considered one composed of monomers alone, whereas this is clearly not the case. Assuming that the mixture of monomers and clusters forms an ideal solution [an assumption made in arriving at Eqs. (1) and (2)], we obtain for the actual chemical potential

$$\mu_v = \mu_v{}^0 + kT\ln x \tag{4}$$

Solving for $\mu_v{}^0$ and substituting the result into Eq. (3) and *that* result into Eq. (2), we recover Eq. (1) with W_n now defined (properly) not as $W_n{}^0$ but as

$$W_n = n(\mu_l - \mu_v) + \alpha n^{2/3} \tag{5}$$

Thus the suggestion of Sundquist and Oriani is not applicable.

Recently Mou and Lovett$^{(5)}$ as well as Peak$^{(6)}$ have attempted to explain the discrepancy between theory and experiment, at least for the miscibility gap, in terms of the formation of a "depletion layer" surrounding an embryo of the new phase. However, these explanations have been criticized$^{(7)}$ on the basis that they do not conform with the requirements of time reversal. Furthermore, Reiss and Shugard$^{(8)}$ have shown that the "classical" theory of nucleation omits a term in the chemical potential for a component of a binary embryo which, upon reinsertion, merely enlarges the discrepancy. The reality of the anomalous behavior seems well established.

In the present paper we outline and establish an effect of sufficient magnitude to resolve the difficulty.

2. EXCLUDED-VOLUME EFFECTS

Most applications of nucleation theory require a calculation of the reversible work needed to produce a critical size embryo, or fluctuation, of an inherently more stable nucleating phase. The traditional approach to this problem utilizes the capillarity approximation, thereby treating the precritical embryo as a droplet of the nucleating phase endowed with a surface tension and uniform density characteristic of the bulk at equilibrium. More recently a diffuse droplet model has been introduced by Cahn and Hilliard.(9) Each of these approaches, which are known to become identical near the critical point,(2) treats the droplets as being statistically independent from one another. The most important result of this paper will be to show that an additional *positive* contribution to the reversible work of droplet formation arises when material volume exclusion between droplets is properly taken into account.

The conventional expression for the reversible work W_n which must be expended in forming a droplet of the nucleating phase is given by (5), which can be rewritten in terms of the experimentally measured interfacial tension σ_0 as

$$W_n = n(\mu_l - \mu_v) + \sigma_0 a_n \tag{6}$$

where a_n is the surface area of the droplet. For a system cooled into the region within the coexistence curve, $\mu_l - \mu_v$ is negative and W_n will have a maximum at a critical size n^* beyond which the droplet will continue to grow to observable size, indicating the onset of nucleation. Sunquist and Oriani have shown that the threshold for perceptible nucleation is expected to occur when the height of the barrier W_{n^*} is in the range $(60\text{–}70)kT$.(1) If the barrier height is greater than this, the system will remain in the supercooled state for time scales exceeding those of typical observations. Since the reversible work given by the relation (5) or (6) pertains to the growth of a single fixed drop without other droplets present (or with interactions with other droplets ignored), it is necessary to go beyond these equations in a study of volume exclusion.

Consider again a fixed drop of size n, now with a specified distribution of other droplets also present in the system. If the integrity of the distribution is to be preserved, droplets cannot overlap. For example, if two droplets overlapped, the overlapping pair would be counted as a single larger droplet and the distribution would be altered. The exclusion is therefore in fact a "counting" restriction in the phase space of the system and has been previously described by Stillinger$^{(10)}$ and others.$^{(11)}$ Following Reiss,$^{(12)}$ we will treat the problem by assigning a hard-sphere radius to each droplet. Thus, in order for a drop to grow to critical size, it must occupy a volume not available to any of the other droplets present. This results in a decrease in the total configurational entropy of the system over the value it would have if the droplets were independent of one another.

As a result, the entropy of activation for nucleation is reduced, with a consequent reduction in the rate at which nucleation occurs. This is the central feature of our explanation of the occurrence of anomalously high degrees of metastability near the critical temperature. The remainder of this paper represents an attempt to place this qualitative explanation on a quantitative basis.

3. OUTLINE OF THE DEVELOPMENT

There are quite a few distinct parts to the argument we shall advance. It is therefore of value to have a perspective overview of the entire development so that one does not lose sight of the connecting thread when focusing on the sometimes absorbing details of a particular step. We provide such an overview in this section.

Throughout this paper we rely on the well-known "capillarity approximation" so that none of the development is more rigorous than the liberties taken by this approximation allow. However, the derivation is *internally consistent* with this approximation. A primary task is to show how the chemical potential of a drop (cluster) in the supercooled phase differs from the conventional form, adopted in nucleation theory, when excluded-volume effects are taken into account. This task is undertaken in Section 6, where, surprisingly, it emerges that the new formula is the same as the old one except for the fact that, where the interfacial tension σ_0 between a liquid and its *saturated* vapor appears in the old formula, one must now use the difficultly measurable (perhaps unmeasurable) interfacial tension σ between the liquid and the supersaturated phase. All volume exclusion effects are accounted for by this simple change within the limits of the capillarity approximation. Along the way, in Section 6, it is necessary to make use of a formula derived in Section 4 for the difference between the chemical potential of an ordinary molecule and one held stationary.

Another important step in the development is the evaluation of σ and its relation to σ_0. This is accomplished in Section 5. It is shown that the configuration integral for the vapor can be evaluated by a procedure which arbitrarily partitions the molecules in the vapor between "physical clusters" and "monomers." The set of physical clusters may contain monomers, but they are *formally* defined as clusters. In any event the program for evaluating the configurational integral involves separate procedures for those molecules defined as "monomers" and those in "clusters." The largest term in the evaluation of the "cluster" part of the integral always involves a distribution of cluster sizes which depends upon the particular partitioning employed. Under many conditions typical of nucleation the integration over the coordinates of the "monomers" is independent of the location of the clusters. When this is true it may be shown that σ can be decomposed into two parts σ_0' and σ_{HS}, i.e., $\sigma = \sigma_0' + \sigma_{\mathrm{HS}}$. Furthermore, if the partitioning is carried out by applying the well-known "lever rule" to the coexistence curve of the phase diagram, σ_0' may be identified with σ_0, the interfacial tension between the liquid and its saturated vapor. The quantity σ_{HS} has the following meaning when the capillarity approximation is used.

The clusters (drops) in the vapor phase are regarded as hard spheres with a size distribution identical to that of the clusters. One then considers the interaction of this fluid mixture of hard spheres with a perfectly hard, flat wall. The boundary tension in the fluid against this wall is σ_{HS}. Note that since the size distribution depends on the partitioning, so does σ_{HS}, but the sum $\sigma_0' + \sigma_{\mathrm{HS}} = \sigma$ is *independent* of the partitioning. Partitioning according to the lever rule is particularly convenient because σ_0' becomes the measurable quantity σ_0. Furthermore, it turns out that in many situations most of the "clusters" are monomers. In this case only the total number of clusters is necessary for the evaluation of σ_{HS}, and this number is available from the lever rule. σ_{HS} can be easily evaluated using scaled particle theory.

The same development applies to the case of the nucleation of phase separation within the miscibility gap of a binary liquid system. Here σ_0 is the interfacial tension between the two phases which coexist at equilibrium and σ is still given by $\sigma_0 + \sigma_{\mathrm{HS}}$, when σ_{HS} is evaluated when most clusters are monomers, with the aid of the lever rule.

With the chemical potential of the cluster available it is then possible to calculate the equilibrium distribution of clusters and to use this distribution in the usual manner in deriving an expression for the rate of nucleation. Calculated limits of metastability can then be compared with those determined experimentally.

4. TWO USEFUL FORMULAS

In this section we derive some relatively simple formulas which will prove useful in the development we have in mind. The first of these is the formula for the difference in chemical potentials between an ordinary molecule in a phase (which may or may not be multicomponent) and the same molecule whose center of mass is constrained to be stationary. In this proof we assume the potential energy of the system to be separable in the center-of-mass and "internal" coordinates of the molecules. We shall be interested in the chemical potentials of a molecule of the jth species in a phase of volume V.

The classical phase integral for this system may be written as

$$Q(\{N_n\}, T, V) = \left(\prod_n{}' \frac{(\gamma_n\lambda_n)^{N_n}}{N_n!}\right) \frac{(\gamma_j\lambda_j)^{N_j}}{N_j!} Z(\{N_n\}, T, V) \tag{7}$$

where $\{N_n\}$ represents the set of numbers in which N_n is the number of molecules of species n in the system, while γ_n is the momentum partition function of a molecule of species n, and λ_n is the "internal" partition function of a molecule of species n, separable from Z, the configurational integral, because of the above-mentioned separability of the potential energy. Z depends only on the coordinates of the centers of mass of the various molecules. The prime on the continued product indicates that the index j is to be omitted. The Helmholtz free energy of the system is given by

$$F(\{N_n\}, T, V) = -kT \ln Q(\{N_n\}, T, V) \tag{8}$$

For a system having $N_j + 1$ molecules of species j, Q is given by Eq. (7) with $N_j + 1$ substituted for N_j and may be denoted by $Q(\{N_n\}, 1, T, V)$ with a corresponding free energy

$$F(\{N_n\}, 1, T, V) = -kT \ln Q(\{N_n\}, 1, T, V) \tag{9}$$

The chemical potential of the jth species is then

$$\begin{aligned} \mu_j &= F(\{N_n\}, 1, T, V) - F(\{N_n\}, T, V) \\ &= -kT \ln \frac{\gamma_j\lambda_j}{N_j + 1} - kT \ln \frac{Z(\{N_n\}, 1, T, V)}{Z(\{N_n\}, T, V)} \end{aligned} \tag{10}$$

Next, we write the phase integral for the case where the additional molecule of species j has its center of mass held stationary. We have, using an obvious notation since the added j-type molecule is now distinguishable from the other j-type molecules,

$$Q(\{N_n\}, 1_{\text{st}}, T, V) = \left(\prod_n{}' \frac{(\gamma_n\lambda_n)^{N_n}}{N_n!}\right) \frac{(\gamma_j\lambda_j)^{N_j}}{N_j!} \lambda_j Z(\{N_n\}, 1_{\text{st}}, T, V) \tag{11}$$

and

$$F(\{N_n\}, 1_{\text{st}}, T, V) = -kT \ln Q(\{N_n\}, 1_{\text{st}}, T, V) \tag{12}$$

Then the chemical potential of the stationary molecule is

$$\mu_j^{st} = F(\{N_n\}, 1_{\text{st}}, T, V) - F(\{N_n\}, T, V) = -kT \ln \lambda_j - kT \ln \frac{Z(\{N_n\}, 1_{\text{st}}, T, V)}{Z(\{N_n\}, T, V)} \tag{13}$$

and, combining Eqs. (10) and (13), we find

$$\mu_j - \mu_j^{st} = -kT \ln \frac{\gamma_j}{N_j + 1} - kT \ln \frac{Z(\{N_n\}, 1, T, V)}{Z(\{N_n\}, 1_{\mathrm{st}}, T, V)} \tag{14}$$

The ratio of Z's on the right of Eq. (14) may be simplified. Thus it is well known$^{(13)}$ that

$$Z(\{N_n\}, 1, T, V) = VZ(\{N_n\}, 1_{\mathrm{st}}, T, V) \tag{15}$$

so that substitution of this relation into Eq. (14) gives

$$\mu_j - \mu_j^{st} = kT \ln \frac{(N_j + 1)\gamma_j}{V} = kT \ln \frac{N_j \gamma_j}{V} \tag{16}$$

where on the right we have ignored the difference between $N_j + 1$ and N_j. This is the result we wished to establish.

Another useful formula can be derived. Suppose the molecules in a possibly multicomponent system are divided into two classes, I and II. Now, assume that the situation is such that in the configurational partition function Z for this system an integration over the coordinates of the molecules in class I only is independent of the locations of the molecules of class II. Denote this integration by $Z_{\mathrm{I}}^*(\{N_n\}_{\mathrm{I}}, \{N_n\}_{\mathrm{II}}, T, V)$, where $\{N_n\}_{\mathrm{I}}$ and $\{N_n\}_{\mathrm{II}}$ denote the molecular numbers of species in classes I and II, respectively. (Note that the same species may form part of each class; the subdivision is arbitrary.) Then the total configuration integral is

$$Z = \iint_V \cdots \int Z_{\mathrm{I}}^* e^{-U_{\mathrm{II}}/kT} \{d\mathbf{r}\}_{\mathrm{II}} = Z_{\mathrm{I}}^* \iint_V \cdots \int e^{-U_{\mathrm{II}}/kT} \{d\mathbf{r}_{\mathrm{II}}\} \tag{17}$$

where $\{d\mathbf{r}_{\mathrm{II}}\}$ is the total volume element of molecules in class II and U_{II} is the potential energy of interaction among molecules of class II only. The last step in Eq. (17) follows from the fact that Z_{I}^* is independent (by assumption) of the coordinates of the molecules of class II.

Defining

$$Z_{\mathrm{II}} = \iint_V \cdots \int e^{-U_{\mathrm{II}}/kT} \{d\mathbf{r}\}_{\mathrm{II}} \tag{18}$$

Eq. (17) may be written as

$$Z = Z_{\mathrm{I}}^* Z_{\mathrm{II}} \tag{19}$$

This is the formula we have in mind.

It is important to note that in Eq. (19) we have not *ignored* the interactions between molecules of class I with class II. This is not the basis for the factorization, and Z_{I}^* is not a conventional configuration integral. The only assumption is that the *integral*,

$$Z_{\mathrm{I}}^* = \iint_V \cdots \int e^{-(U_{\mathrm{I}} + U_{\mathrm{I,II}})/kT} \{d\mathbf{r}\}_{\mathrm{I}} \tag{20}$$

in which U_{I} represents the interaction among molecules of class I alone, and $U_{\text{I,II}}$, the interclass interaction. Examples of physical situations in which Eq. (19) is approximately the case are easy to find. A simple case is furnished by a system consisting of a mixture of two kinds of hard spheres, one type of sphere being much larger than the other. Then the large hard spheres constitute, in essence, part of the bounding surface for the effective volume containing the small hard spheres. The extent of this surface is approximately independent of the locations of the large spheres, and therefore the integral over the coordinates of the small spheres is independent of these locations. Of course, when two large spheres are close together, some volume between them, available to the small spheres when they were further apart, will become unavailable. Thus there will be some dependence on the location of the large spheres. However, the volume whose availability changes constitutes only a small fraction of the whole and so Z_{I}^* will be almost independent of the locations of the large spheres. When the spheres in both classes are comparable in both number and size the volume of changing availability will represent an appreciable fraction of the whole and the approximation will lose its strict validity. On the other hand, when the number of molecules in class II is small compared to the number in class I the approximation will still retain its value.

5. REVISED CAPILLARITY APPROXIMATION

The expression for W_n in Eq. (5) is an example of the "capillarity approximation" basic to conventional nucleation theory.(14) The quantity α is specified by

$$\alpha = 4\pi\sigma_0(3v_l/4\pi)^{2/3} \tag{21}$$

in which v_l is the volume per molecule in the bulk of the phase, nucleating out of the parent phase, and σ_0 is the interfacial tension between the two phases which coexist in equilibrium when the transformation has been

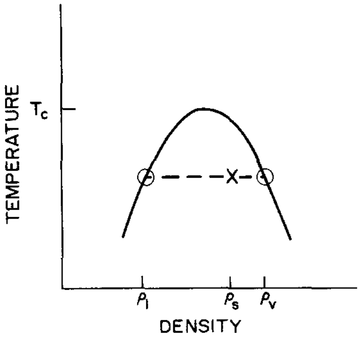

Fig. 1. Liquid–vapor coexistence curve for a one-component system. The tie line connecting the conjugate phases into which the metastable state (×) separates is indicated as the dashed horizontal line.

completed. The result we shall arrive at in this section can be shown to apply generally to any nucleating system where the capillarity approximation is used, but, in the interest of clarity, we shall derive it for the case of nucleation of a liquid from supersaturated vapor. It will, for example, be equally applicable to phase separation in a binary liquid(1,2) system supercooled into a miscibility gap.

If we consider the condensation of a one-component vapor, then σ_0 is the interfacial tension between the liquid and its *saturated* vapor, while v_l is the volume per molecule in the bulk liquid. Figure 1 will be helpful in considering this system. It illustrates a liquid–vapor coexistence curve for a one-component system, temperature on the coexistence curve being plotted against molecular number density ρ. The two-phase region occurs within the coexistence curve and is clearly marked in the figure. The critical temperature T_c is also indicated. The liquid of density ρ_l is in equilibrium with vapor of density ρ_v, at a temperature T below T_c. The tie line connecting ρ_v with ρ_l is indicated as the dashed horizontal line. The state of a supersaturated vapor phase of density ρ_s is marked by the × lying within the coexistence curve. The conventional theory of nucleation models this supersaturated phase as consisting of monomers and clusters of the nucleating (liquid) phase. Actually, even the saturated vapor at density ρ_v would contain some clusters, but as the work of Hillig and McCarroll,(4) cited in Section 1, indicates, these are accounted for in the chemical potential μ_v of the vapor. The main assumptions of the "capillarity approximation" embodied in this liquid drop model are:

1. The cluster is an incompressible spherical "drop" having macroscopic properties, e.g., a macroscopic interfacial tension σ_0 and a physically *abrupt* interface with the surrounding phase.
2. The effects of curvature on interfacial tension are ignored.
3. There is a replacement free energy correction to the cluster's free energy associated with the fluctuation of its center of mass (within the drop).(15) The net effect of this replacement free energy is to change the cluster free energy from that of a simple drop by the addition of the term(15)

$$kT \ln \gamma_n v_f \tag{22}$$

where γ_n is the momentum partition function of a particle having the same mass as a drop with n molecules and v_f is the "volume of fluctuation"(15) of the center of mass within the drop.

4. An implicit requirement of the model is that material within different clusters does not interact or else clusters will not be distinctly and unambiguously defined. For example, two clusters in substantial contact or overlap could be counted as a single larger cluster; a "counting" procedure

employed by a statistical mechanical analysis utilizing sums over well-defined distributions will lose its meaning. Thus, within the confines of the conventional theory, for the purposes of counting, the clusters must be regarded as hard spheres which cannot overlap. This requirement is "academic" in the usual situation where the concentration of clusters is low, but, as indicated in Section 2, becomes important near a critical temperature.

In the present section we show that σ_0 is *not* the proper quantity to be used in Eq. (5), i.e., in α specified by Eq. (21). Instead, another term σ_{HS} must be added to σ_0 to give σ, essentially the interfacial tension between the cluster modeled as a liquid drop and the surrounding *supersaturated* phase. The form of σ_{HS} and consequently of

$$\sigma = \sigma_0 + \sigma_{\mathrm{HS}} \tag{23}$$

will be derived. This derivation will be rigorous only within the confines of the capillarity approximation, since we still wish to use that approximation, which has proved to be a remarkably good predictive tool. The intent is to demonstrate the major factors which cause the standard capillarity approximation to fail near the critical temperature. A treatment that is more rigorous from the beginning is likely to exhibit the same trends near the critical point. We shall derive σ_{HS} for the case of condensation, but the same result is applicable, as indicated, to other cases, e.g., phase separation in a binary liquid, and we shall apply it to that case.

As a beginning we make some remarks about the interfacial tension σ_0. We consider the situation illustrated in Fig. 2, which shows a mass of liquid of volume V_l immersed in its saturated vapor of volume V_v. The interfacial area is denoted by A_0, and N_l and N_v are the numbers of molecules in the liquid and vapor phases, respectively. In line with the capillarity approximation the liquid is regarded as incompressible, σ_0 is considered independent of curvature, and the interface is abrupt.

We consider the mass of the liquid to be sufficiently large so that its shape can be varied to increase A_0 while V_l remains constant, and at the same time not induce a change of pressure within the liquid. Because of the

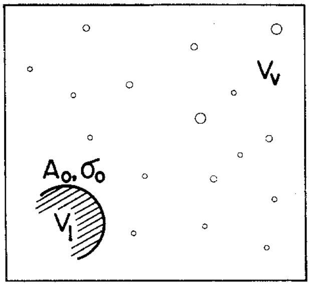

Fig. 2. Liquid mass of volume V_l immersed in its *saturated* vapor of volume V_v. The interfacial area is denoted by A_0 and σ_0 is the interfacial tension.

abruptness (in our model) of the interface, the total Helmholtz free energy of the system may be presented as

$$F = F_l + F_v \tag{24}$$

where F_l is simply the bulk free energy which N_l molecules of liquid would have as part of a homogeneous bulk phase without boundaries and where F_v is the free energy of the N_v vapor molecules *including their interactions with the liquid molecules on the other side of the abrupt interface.* In other words, all interfacial effects are included in F_v. (In fact there will have to be a gradient of density in the vapor near the interface, but as long as we do not have to deal with it explicitly we ignore it, remaining faithful to the model.)

Now, as in the most rudimentary treatment of surface thermodynamics, the interfacial tension is defined as

$$\sigma_0 = \left(\frac{\partial F}{\partial A_0}\right)_{T,V_l+V_v,N_l+N_v} = \left(\frac{\partial(F_l + F_v)}{\partial A_0}\right)_{T,V_l+V_v,N_l+N_v} = \left(\frac{\partial F_v}{\partial A_0}\right)_{T,V_v,N_v} \tag{25}$$

where the last step follows from the fact that F_l is independent of A_0 and the assumption that the liquid is of uniform density up to the abrupt interface, so that A_0 can be changed without changing V_l. Since

$$N_l = \rho_l V_l \tag{26}$$

this implies that with $N_l + N_v$ constant, N_v will be constant. Furthermore, with V_l and $V_l + V_v$ constant, V_v will be constant. We do here have an imposition of the material properties, implicit in the capillarity approximation, on the thermodynamics, so that Eq. (25) is inapplicable to substances in general. Nevertheless it is consistent with the capillarity approximation.

Now

$$F_v = -kT \ln Q_v \tag{27}$$

where

$$Q_v = Q_v(T, V_v, N_v, A_0) \tag{28}$$

is the partition function of the vapor phase *including* interactions of the vapor molecules with the liquid molecules on the other side of the interface. Substitution of Eq. (28) into Eq. (25) gives

$$\sigma_0 = -kT\left(\frac{\partial \ln Q_V}{\partial A_0}\right)_{T,V_v,N_v} \tag{29}$$

Now, in analogy with Eq. (7), Q_v may be expressed as

$$Q_v = [(\gamma_1\lambda_1)^{N_v}/N_v!]Z_v(T, V_v, N_v, A_0) \tag{30}$$

where γ_1 is the momentum partition function of a single molecule and λ_1 its internal partition function, while Z_v is the configurational partition function, dependent on A_0 through the interaction of the vapor molecules with the liquid. Since neither γ_1 nor λ_1 depends upon A_0, substitution of Eq. (30) into Eq. (29) yields

$$\sigma_0 = -kT\left(\frac{\partial \ln Z_v}{\partial A_0}\right)_{T,V,N_v} \tag{31}$$

Now we examine a situation similar to that in Fig. 2 except for the fact that the vapor phase is supersaturated. Of course we will have to introduce a "formal" constraint to prevent the systems from collapsing to equilibrium. Our goal is to determine how the interfacial tension σ for this case differs from σ_0. The relevance of the question comes from the fact that the "liquid drop" clusters of conventional nucleation theory to which the capillarity approximation is applied are in fact modeled as liquid masses immersed in a *supersaturated* vapor.

We now refer to Fig. 3, which resembles Fig. 2 except for the fact that σ_0 has been replaced by σ, and the vapor contains clusters drawn as shaded spheres. As we indicated earlier, even the saturated vapor contains clusters, and the clusters considered in the figure are those *excess* to those found in the saturated vapor. Some of them may be indistinguishable from those in the saturated vapor. In keeping with the capillarity approximation, we model these clusters as incompressible liquid drops. Furthermore, to satisfy the statistical "counting" requirement, the "drops" cannot overlap one another, nor any monomers which are present. Neither can they overlap the liquid phase; otherwise the clear distinction between the phases would be lost. Hence the clusters must be treated formally as hard spheres, and the liquid–vapor interface, as a hard wall.

Besides the excess clusters, in Fig. 3, which may themselves include monomers, we show N_v' additional molecules. The volume of the supersaturated vapor phase is now denoted by V_v' and the total volume of the "hard-sphere" clusters will be denoted by V_c. The number N_v' of the additional molecules will eventually be chosen so that

$$N_v' = \rho_v(V_v' - V_c) \tag{32}$$

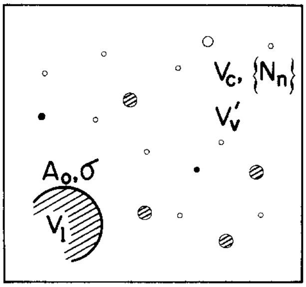

Fig. 3. Liquid mass immersed in a *supersaturated* vapor prior to nucleation. Shaded circles denote the *excess* clusters, while the clear circles denote the constituents of the saturated vapor. The interfacial tension is σ. The number of clusters containing n molecules is denoted by N_n and the set of cluster numbers by $\{N_n\}$. Here V_c is the total volume of the clusters and V_l and V_v are as defined in Fig. 2.

where ρ_v is the density of the saturated vapor (on the coexistence curve) at temperature T. The reasons for this will become clear, but for the moment we have N_v' arbitrary. The number of clusters containing n molecules will now be denoted by N_n and the set of cluster numbers by $\{N_n\}$.

The partition function of the supersaturated vapor, including interactions with the liquid phase on the other side of the interface, may now be denoted by

$$Q_v^{(s)} = Q_v^{(s)}(T, V_v', N_v', \{N_n\}, A_0) \tag{33}$$

where the superscript (s) indicates supersaturation. The total number of molecules in the vapor is clearly

$$N_v' + \sum_n nN_n = \rho_s V_v' = N \tag{34}$$

The rigorous evaluation of $Q_v^{(s)}$ can be *organized* so that physical clusters play a natural role as "bookkeeping" entities.[16,17] When this is done it becomes clear (see Ref. 16) that the subdivision of N that determines N_v' is arbitrary and that the total partition function is a *sum* of terms corresponding to all the distributions $\{N_n\}$ that satisfy Eq. (34). Among these distributions there is one whose term in the sum is largest and, as usual, this term will dominate $\ln Q_v^{(s)}$ and is the only one which need be retained. The $\{N_n\}$ appearing in Eq. (33) corresponds to this term. Clearly this $\{N_n\}$ depends on the arbitrary choice of N_v'. The N_v' molecules themselves may engage in clustering, but in performing integrations over their coordinates in $Q_v^{(s)}$ the calculation is not explicitly organized along the lines of the cluster formalism. Reference 16 does not explicitly treat the case in which some of the molecules are not mapped into clusters, but it is easy to see, upon reading it, that this hybrid approach is allowable with no loss of generality. Again it is to be emphasized that the clusters implicit in the treatment of the N_v' additional molecules can be identical in constitution with some of those which are treated explicitly.

Adopting this approach, it is possible to write $Q_v^{(s)}$ as

$$Q_v^{(s)} = \frac{(\gamma_1\lambda_1)^{N_v'}}{N_v'!} \prod_n \frac{(\gamma_n\lambda_n)^{N_n}}{N_n!} Z_v^{(s)}(T, V_v', N_v', \{N_n\}, A_0) \tag{35}$$

where γ_n and λ_n have the same meanings as in Eq. (7), the clusters of n molecules themselves being treated as molecules, and the continued product going over all cluster sizes. $Z_v^{(s)}$ is the configurational partition function for the system.

Now suppose that the clusters making a dominant contribution to $Z_v^{(s)}$ are either large compared to the size of a single molecule or else that the total number of clusters is small. Then the factorization of the configurational partition function discussed in Section 3 becomes possible (see discussion at the end of Section 3). We have

$$
\begin{aligned}
&Z_v^{(s)}(T, V_v', N_v', \{N_n\}, A_0) \\
&\qquad = Z_{v\mathrm{I}}^{(s)*}(T, V_v' - V_c, N_v', A_0 + \sum_n N_n a_n) Z_{v\mathrm{II}}^{(s)*}(T, V_v', \{N_n\}) \qquad (36)
\end{aligned}
$$

in which a_n is the surface area of a cluster containing n molecules. The functional dependences appearing in Eq. (36) are explained as follows. First, the clusters are modeled according to the capillarity approximation. This means that the N_v' molecules, *not* treated by use of a cluster formalism, behave in $Z_{v\mathrm{I}}^{(s)*}$ as a vapor phase of volume $V_v' - V_c$, bounded in part by its interface with a fragmented (into drops) but nontheless *stationary* liquid phase of interfacial area $A_0 + \sum_n N_n a_n$, where $\sum_n N_n a_n$ is the total interfacial area due to the (clusters) drops. So $Z_{v\mathrm{I}}^{(s)*}$ is just the configurational partition function for this vapor *including* its interactions with the liquid on the other side of the interface. The functional dependence of $Z_{v\mathrm{I}}^{(s)*}$ in Eq. (36) should then be obvious.

As far as $Z_{v\mathrm{II}}^{(s)}$ is concerned, since to satisfy the "counting" requirement the drops are to be treated as hard spheres, $Z_{v\mathrm{II}}^{(s)}$ is the configurational partition function for a fluid consisting of a mixture of hard spheres having the distribution $\{N_n\}$. The integration over the coordinates of these hard spheres goes over the entire volume V_v'. Hence we explain the arguments of $Z_{v\mathrm{II}}^{(s)}$.

As we have indicated, for a completely rigorous theory in which the clusters are not modeled as liquid drops, the subdivision of molecules into vapor and clusters, i.e., the choice of N_v' is arbitrary as long as it satisfies Eq. (34). A satisfactory theory could be developed with any allowable N_v'. Presumably a quasiindependence of N_v' will be retained even when the rigor of the theory is compromised by use of the capillarity approximation.

Our ultimate goal is the evaluation of σ defined in Fig. 3. As is shown below, this evaluation evolves as the sum of two terms corresponding, respectively, to the two factors on the right of Eq. (36). However, it is *convenient* to have σ decomposed so that Eq. (23) holds, i.e., so that one of the terms, namely σ_0, is the interfacial tension between the liquid and its *saturated* vapor. This will only be true for a *particular* selection of N_v'. Of course σ_{HS} will also depend on N_v', whose selection simultaneously determines $\{N_n\}$. It will turn out, however, that there are situations in which only the total number of molecules $\sum_n nN_n$ in clusters is important in establishing the value of σ_{HS} and not the details of the distribution $\{N_n\}$. Since σ_0 will be a *measured* quantity, depending on the right selection of N_n', and σ_{HS} will be determinable from the known total number $N - N_v'$ of molecules in clusters, the value of the desired quantity σ will then be available.

The convenient selection of N_v' treats the clusters as "excess" to the vapor phase in a manner which, incidentally, is quite consistent with the spirit of the capillarity approximation (although this last is *satisfying* but not *necessary*). For this purpose (the convenient selection of N_v' which allows σ_0 to be the ordinary measured quantity) the supersaturated phase is described as containing clusters not found in a saturated phase. These clusters, modeled as liquid drops, are therefore thought of as drops (even if monomers) bathed in a saturated vapor. Thus N_v' and $V_v' - V_c$ should be chosen so that

$$N_v'/(V_v' - V_c) = \rho_v \tag{37}$$

where ρ_v is the density of the saturated vapor on the coexistence curve. Now the density of the supersaturated vapor is

$$\rho_s = N/V_v' \tag{38}$$

Now under the capillarity approximation V_c is given by

$$V_c = (N - N_v')/\rho_l \tag{39}$$

where N is the total number of molecules specified by Eq. (34), and ρ_l is the density of the liquid on the coexistence curve. Equations (37)–(39) can be solved to yield

$$N - N_v' = \sum_n nN_n = \frac{\rho_s - \rho_v}{\rho_l - \rho_v} \rho_l V_v' \tag{40}$$

$$N_v' = \frac{\rho_l - \rho_s}{\rho_l - \rho_v} \rho_v V_v' \tag{41}$$

$$V_c = \frac{\rho_s - \rho_v}{\rho_l - \rho_v} V_v' \tag{42}$$

$$V_v' - V_c = \frac{\rho_l - \rho_s}{\rho_l - \rho_v} V_v' \tag{43}$$

The two last equations can be combined to give

$$V_c(\rho_l - \rho_s) = (V_v' - V_c)(\rho_s - \rho_v) \tag{44}$$

This is simply an example of the well-known "lever rule" for the liquid and vapor volumes into which a supersaturated phase separates as the phase equilibrium is established. Thus N_v', $N - N_v'$, V_c, and $V_v' - V_c$ are the quantities related by the lever rule and the supersaturated phase may be thought of as having been constructed in the following manner.

We begin with liquid and vapor phases, containing N total molecules and occupying a total volume V_v', in equilibrium along the coexistence curve. Maintaining N and V_v', the liquid phase is fragmented into clusters (drops) of the proper distribution and mixed with vapor phase. The resulting system represents the supersaturated phase. The total pressure of the system then includes effects due to the cluster "molecules" and exceeds the saturation pressure along the coexistence curve.

It is to be noted that the entire discussion thus far could have been carried forth for a binary liquid system. The fact that clusters will now have a distribution of composition as well, and that the densities of the two phases along the coexistence curve are similar, introduces no difficulty. Just as in the liquid–vapor case, the fact that in the supercooled phase of the binary system some clusters belonging to each of the separating phases may have identical constitutions is of no consequence. However, there will be one difference. Since the coexistence curve for a binary liquid system will generally be specified in terms of the mole fraction X of one of its components, the appropriate "lever rule" will involve mole fractions. Thus we will have

$$N_A(X_s - X_A) = N_B(X_B - X_s) \tag{45}$$

where N_A and N_B are the numbers of moles in phases A and B, of mole fractions X_A and X_B in equilibrium along the coexistence curve, into which the supercooled phase of mole fraction X_s separates.

Denoting the molar volumes of phases A and B by $\overline{V}_A$ and $\overline{V}_B$, respectively, we then have

$$N_A = V_A/\overline{V}_A \qquad \text{and} \qquad N_B = V_B/\overline{V}_B \tag{46}$$

where V_A and V_B are the actual volumes of these phases after the separation has occurred. The phase we have designated as B is that which describes the composition of the nuclei or clusters in the supercooled state. In the terminology adopted to describe the binary system V_B is equivalent to V_c of Eq. (44) and, similarly, V_A takes the place of $V_v' - V_c$. Substitution of Eq. (46) into Eq. (45) and rearranging yields

$$\frac{V_B}{V_A} = \frac{X_s - X_A}{X_B - X_s}\frac{\overline{V}_B}{\overline{V}_A} \tag{47}$$

The quantities on the right side of Eq. (47) are readily determined from experiment; in fact, if the volume change upon mixing of the phase components is ignored, we have

$$\overline{V}_B = X_B\overline{V}_1 + (1 - X_B)\overline{V}_2 \qquad \text{and} \qquad \overline{V}_A = X_A\overline{V}_1 + (1 - X_A)\overline{V}_2 \tag{48}$$

where $\overline{V}_1$ and $\overline{V}_2$ represent the molar volumes of the components in their pure form. Equations (47) and (48) will be used in Section 8 to estimate the fraction of available volume occupied by clusters (droplets) of the nucleating phase in order to determine σ_{HS} for the binary liquid.

Now we return to Fig. 3 and consider the interfacial tension σ defined in connection with this figure. Clearly σ will be given by the analog of Eq. (31) for σ_0. Thus

$$\sigma = -kT\left(\frac{\partial \ln Z_v^{(s)}}{\partial A_0}\right)_{T,V_{v'},N} \tag{49}$$

Introducing Eq. (36), we get

$$\sigma = -kT\left(\frac{\partial \ln Z_{v\mathrm{I}}^{(s)*}}{\partial A_0}\right)_{T,V_{v'}-V_c,N_{v'}} - kT\left(\frac{\partial \ln Z_{v\mathrm{II}}^{s}}{\partial A_0}\right)_{T,V_{v'},\{N_n\}} \tag{50}$$

where the variables held constant in the partial derivatives are consistent with those held constant in Eq. (49), and with the fact that V_c is constant and that Eq. (34) applies. Now, as has been shown, $Z_{v\mathrm{I}}^{(s)*}$ is the configuration integral for a vapor phase in contact with a liquid consisting of the central mass, in Fig. 3, and the stationary drops. Interactions, across the interface, with the liquid are included in $Z_{v\mathrm{I}}^{(s)*}$. If, as we have discussed, the density of this vapor is chosen to be ρ_v, it is the same vapor dealt with in Fig. 2. The total interfacial area is

$$A = A_0 + \sum_n N_n a_n \tag{51}$$

and for this vapor we can write

$$\sigma_0 = -kT\left(\frac{\partial \ln Z_{v\mathrm{I}}^{(s)*}}{\partial A}\right)_{T,V_{v'}-V_c,N_{v'}} \tag{52}$$

where σ_0 has the same value as in Eq. (31) since σ_0 is independent of the extent of interface and has the same value whether the interface has the extent A or A_0. However, with $\{N_n\}$ held constant,

$$dA = d\left(A_0 + \sum_n N_n a_n\right) = dA_0 \tag{53}$$

so that substitution in Eq. (52) gives

$$\sigma_0 = -kT\left(\frac{\partial \ln Z_{v\mathrm{I}}^{(s)*}}{\partial A_0}\right)_{T,V_{v'}-V_c,N_{v'}} \tag{54}$$

When Eq. (54) is substituted into Eq. (50) we get

$$\sigma = \sigma_0 - kT\left(\frac{\partial \ln Z_{v\mathrm{II}}^{(s)}}{\partial A_0}\right)_{T,V_{v'},\{N_n\}} \tag{55}$$

The analysis of the second term on the right of Eq. (55) is quite simple. Suppose that in Fig. 2 the vapor consisted of a fluid of hard spheres and that the central mass was a hard body, so that the interface was hard and could not be violated by the hard-sphere molecules. Then σ_0 in that figure would be σ_{HS}, the boundary tension of the hard-sphere fluid, and clearly Eq. (31) would be replaced by

$$\sigma_{\mathrm{HS}} = -kT\left(\frac{\partial \ln Z_{\mathrm{HS}}}{\partial A_0}\right)_{T,V,\{N_n\}} \tag{56}$$

where $\{N_n\}$ stands for the molecular numbers of hard spheres in the fluid. If we set $V = V_v'$ and let $\{N_n\}$ be the same distribution as appears in $Z_{v\mathrm{II}}^{(s)}$, then Z_{HS} can be identified with $Z_{v\mathrm{II}}^{(s)}$ and comparison of the second term on the right of Eq. (55) with the right-hand side of Eq. (56) shows it to be σ_{HS}, for the equivalent hard-sphere fluid represented by the drops (clusters). Then Eq. (55) becomes

$$\sigma = \sigma_0 + \sigma_{\mathrm{HS}} \tag{57}$$

This is the result we have been seeking [see Eq. (23)]. It shows that, within the limits of the capillarity approximation, the interfacial tension between a liquid and a supersaturated vapor is not σ_0, the measurable interfacial tension between liquid and saturated vapor, but must be augmented by σ_{HS}, the boundary tension (against the interface regarded as a hard boundary) of a fluid consisting of mixture of hard spheres having the same size distribution as the excess drops (clusters) in the supersaturated vapor. The σ_0 in Eq. (56) is the interfacial tension between the liquid and its saturated vapor only if the evaluation of the vapor configurational partition function is undertaken with a partitioning between vapor and clusters according to the requirements of the "lever rule". However, σ itself is independent of the particular partitioning, i.e., of the choice of N_v'. The choice involving the application of the lever rule has the advantage of representing σ_0 by a measurable quantity.

6. EQUILIBRIUM DISTRIBUTION OF CLUSTERS

In the conventional theory of nucleation(14) a central step in the derivation of an expression for the rate of nucleation is the calculation of the so-called equilibrium distribution of clusters *in the supersaturated vapor.* This distribution is required for the application of the principle of detailed balance. We now calculate this distribution in a manner which makes it clear that the revised interfacial tension, σ of Eq. (57), rather than σ_0 is the proper quantity to be used in the formula for the distribution. Again our derivation will be rigorous only within the limits of the capillarity approximation. We make use of a "thought" experiment illustrated in Fig. 4.

This figure shows a spherical cluster being extruded from a hypodermic syringe into a supercooled or supersaturated vapor at pressure p and temperature T. The internal pressure of the cluster (spherical drop) is given by

$$P = p + (2\sigma/r) \tag{58}$$

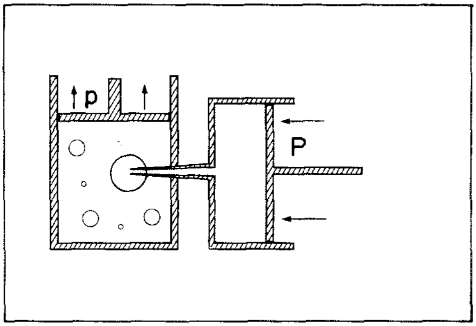

Fig. 4. Spherical droplet being extruded from a hypodermic syringe into a supercooled vapor at pressure p. Here P is the pressure inside the drop.

where r is the radius of the drop. The extrusion is accomplished by a press which exerts a pressure P as shown. The liquid is also at the temperature T. The interfacial tension of the drop is σ rather than σ_0 since the surrounding vapor is supersaturated. When the drop contains n molecules its surface area is a_n. Now the net reversible work involved in the addition of the drop to the system is

$$w = \int_0^r [P(r) - p] 4\pi r^2 \, dr \tag{59}$$

It is necessary to subtract p from P in the integrand because the element of work $p(4\pi r^2 \, dr)$ is returned to the surroundings by the piston (so labeled in Fig. 4) because the liquid drop is assumed incompressible, and because we are interested in adding the drop to the vapor system, isothermally and at constant pressure p. Substitution of Eq. (58) into Eq. (59) and performing the integration yields for the work performed at constant T and p,

$$w_{T,p} = 4\pi r^2 \sigma = \sigma a_n \tag{60}$$

if the final drop is such as to contain n molecules. The subscripts T, p appended to w indicate that the process is isothermal and isobaric.

Now for any *isothermal* process undertaken by a *closed* system, the change in Helmholtz free energy of the system is given by

$$dF = Dw \tag{61}$$

where Dw is the *total* reversible work performed *on* the system. For an *open* system

$$dF = Dw + (dF)_{\text{trans}} \tag{62}$$

where $(dF)_{\text{trans}}$ is the Helmholtz free energy transported into the open system by the matter which enters it. For the process to which Eq. (60) applies

$$(dF)_{\text{trans}} = \bar{f}_l dn \tag{63}$$

where $\bar{f}_l$ is the partial molar Helmholtz free energy in the liquid and dn is the differential number of extruded molecules. Then

$$dF = (Dw)_{T,p} + \bar{f}_l\, dn \tag{64}$$

and

$$(\Delta F)_{T,p} = w_{T,p} + \bar{f}_l n = \sigma a_n + \bar{f}_l n \tag{65}$$

The change in Gibbs free energy for this same process is

$$\begin{aligned}(\Delta G)_{T,p} &= (\Delta F)_{T,p} + p\,\Delta V = (\Delta F)_{T,p} + pv_n = \sigma a_n + \bar{f}_l n + pv_n \\ &= \sigma a_n + \bar{f}_l n + pv_l n = \sigma a_n + n(\bar{f}_l + pv_l) = \sigma a_n + n\mu_l\end{aligned} \tag{66}$$

In this equation μ_l is the bulk chemical potential of the added liquid, equal to $\bar{f}_l + pv_l$. There is no difference between $\bar{f}_l$ at pressure p and that at P, since the liquid is regarded as incompressible.

The $(\Delta G)_{T,p}$ in Eq. (45) is the isothermal, isobaric change in Gibbs free energy for the supercooled vapor system upon the addition of a stationary drop of size n. If this drop (cluster) is regarded as a chemical species, then $(\Delta G)_{T,p}$ must be its chemical potential μ_n^{st},

$$\mu_n^{st} = (\Delta G)_{T,p} = n\mu_l + \sigma a_n \tag{67}$$

We need the chemical potential μ_n for the *nonstationary* drop. For this purpose we can make immediate use of Eq. (16) and get

$$\mu_n = \mu_n^{st} + kT \ln(N_n/\gamma_n V) = n\mu_l + \sigma a_n + kT \ln(N_n/\gamma_n V) \tag{68}$$

Now we still must add the replacement free energy from Eq. (22) to μ_n given by Eq. (68) if we wish to make contact with the most modern form of conventional nucleation theory. Thus μ_n in Eq. (68) is changed to

$$\begin{aligned}\mu_n &= n\mu_l + \sigma a_n + kT \ln \frac{N_n}{\gamma_n V} + kT \ln \gamma_n v_f \\ &= n\mu_l + \sigma a_n + kT \ln \frac{v_f}{V} N_n\end{aligned} \tag{69}$$

In order to derive the equilibrium distribution of clusters we note that the condition of equilibrium is

$$n\mu = \mu_n \tag{70}$$

where μ is the chemical potential of a molecule in the supersaturated phase. Substituting Eq. (70) into Eq. (69) and rearranging gives

$$N_n = (V/v_f) \exp\{-[(\mu_l - \mu)n + \sigma a_n]/kT\} \tag{71}$$

which is the desired result, showing that the capillarity approximation should be revised so that σ rather than σ_0 appears in the expression for the equilibrium distribution of clusters. Substituting Eq. (57) into Eq. (71) then gives

$$N_n = \frac{V}{v_f}\exp\left(-\frac{(\mu_l - \mu)n + \sigma_0 a_n}{kT} - \frac{\sigma_{\mathrm{HS}} a_n}{kT}\right) \tag{72}$$

It may be shown that in systems far from the critical temperature the last term in the parentheses in Eq. (72) is practically zero. The expression which then remains is the formula from conventional nucleation theory. However, near the critical temperature the last term exercises considerable influence.

7. EVALUATION OF σ_{HS}

The quantity σ_{HS} required for use in Eq. (72) may be evaluated in the following manner. Consider a fluid consisting of a mixture of hard spheres in which the combined volumes of the hard spheres constitute a fraction y of the total volume V of the system. Consider the reversible work required to introduce an additional hard sphere of radius r into this fluid. This work given by the sum

$$W_{\mathrm{HS}}(r) = \tfrac{4}{3}\pi r^3 p_{\mathrm{HS}} + 4\pi r^2 \sigma_{\mathrm{HS}}(r) \tag{73}$$

where p_{HS} is the pressure in the fluid, and $\sigma_{\mathrm{HS}}(r)$, the boundary tension at the surface of the additional sphere, has been derived by Lebowitz, *et al.*(18) using scaled particle theory.(19) For $\sigma_{\mathrm{HS}}(r)$ they find

$$\sigma_{\mathrm{HS}}(r) = \frac{kT}{4\pi}\left\{\frac{3\langle b^2\rangle}{\langle b^3\rangle}\frac{y}{1-y}\frac{1}{r} + \frac{3\langle b\rangle}{\langle b^3\rangle}\frac{y}{1-y} + \frac{9}{2}\left(\frac{\langle b^2\rangle}{\langle b^3\rangle}\right)^2\left(\frac{y}{1-y}\right)^2\right\} \tag{74}$$

where $\langle b\rangle$, $\langle b^2\rangle$, and $\langle b^3\rangle$ are the first three moments of the radius distribution of the hard-sphere molecules in the mixture. This boundary tension depends on curvature $1/r$, whereas the σ_{HS} in Eq. (57), consistent with the capillarity approximation, refers to the case of zero curvature. We therefore let r in Eq. (74) go to infinity and obtain

$$\sigma_{\mathrm{HS}} = \frac{3kT}{4\pi}\left\{\frac{\langle b\rangle}{\langle b^3\rangle}\frac{y}{1-y} + \frac{3}{2}\left(\frac{\langle b^2\rangle}{\langle b^3\rangle}\right)^2\left(\frac{y}{1-y}\right)^2\right\} \tag{75}$$

which is the result we have been seeking.

In order to obtain the moments of b required for Eq. (75), the distribution of hard-sphere radii in the mixture must be known. For application to nucleation theory this means that the distribution of drop (cluster) sizes must be known. In Eq. (57), for example, the required distribution is that corresponding to the partitioning (according to the lever rule) which fixes N_v' at a value such that σ_0 will be the interfacial tension between the two phases conjugate to each other along the coexistence curve. Since we do not know that distribution, we cannot, in general, use Eq. (75). However, there will be situations, which we discuss later, in which most of the "drops" are *monomers*. In this case $\langle b^2 \rangle = b^2$ and $\langle b^3 \rangle = b^3$, where b is the radius of a monomer. Since y is determinable from the lever rule, σ_{HS} is then fully determined. These are the situations in which it will be used.

We must also note, recalling the discussion of Section 1, that the term $\sigma_{\mathrm{HS}} a_n$ appearing in Eq. (72) represents part of the work (the surface part) of introducing the cluster into the fluid consisting of the other "excess" clusters. Thus, as anticipated, the revision of the theory involves a term due to the interaction with these other clusters (actually an excluded-volume effect); however, it is only the "surface" work involved in overcoming the exclusion of the other spheres that has to be added. The volume work is already accounted for in μ_l, which also appears in Eq. (72).

8. COMPARISON WITH EXPERIMENT

In this section we apply the foregoing theory to an interpretation of the more recent measurements of Heady and Cahn[(2)] (HC) on the methylcyclohexane–perfluoromethylcyclohexane system cooled into the immiscibility gap. The revised capillarity approximation developed in Section 5 is applied to precritical droplets of the perfluoromethylcyclohexane-rich phase which nucleates out of the supercooled mixture upon reaching a critical degree of undercooling.

Sufficiently far below the critical point the interfacial tension becomes large enough that the overwhelming majority of precritical droplets are dispersed as "monomers" throughout the supercooled phase. We assume the Heady–Cahn data to correspond to a temperature range where this is the case, although their higher temperature measurements may not satisfy this requirement. After the calculations are complete the validity of this assumption may be checked.

We use the subscripts B and A to denote, respectively, the perfluoromethylcyclohexane-rich phase and its conjugate along the coexistence curve. If $\bar{V}_B$ is the volume of phase B per mole of molecules, then we have from Eq. (48)

$$\bar{V}_B = X_B \bar{V}_{\mathrm{C_7F_{14}}} + (1 - X_B)\bar{V}_{\mathrm{C_7H_{14}}} \tag{76}$$

with X_B denoting the mole fraction of $\mathrm{C_7F_{14}}$ in the nucleating phase (phase B) and $\bar{V}_{\mathrm{C_7F_{14}}}$ and $\bar{V}_{\mathrm{C_7H_{14}}}$ the molar volumes of the pure components.

For the monomeric radius $\bar{r}$ we use the average molecular radius in the droplet phase; it is defined as

$$\bar{r} = \left(\frac{3\bar{V}_B}{4\pi L}\right)^{1/3} = \left(\frac{3}{4\pi L}\right)^{1/3} [X_B \bar{V}_{\mathrm{C_7F_{14}}} + (1 - X_B)\bar{V}_{\mathrm{C_7H_{14}}}]^{1/3} \tag{77}$$

where L is Avogadro's number.

Use of Eq. (77) implies that the "monomer" is being treated as representative of the bulk phase possessing not only the average composition of this phase, but a representative fraction of intermolecular volume as well. Although such a treatment is consistent with the capillarity approximation, it goes beyond it in assuming a specific composition for the precritical embryo. The error introduced by this assumption is not expected to be large, as any reasonable assignment of the monomeric radius will not lead to results substantially different from those obtained here. Additional remarks concerning the composition of the critical embryo and its relation to that of the bulk phase are given in Section 9.

In computing the hard-sphere boundary tension using Eq. (75) we set $\langle b\rangle = \bar{r}$, $\langle b^2\rangle = (\bar{r})^2$, and $\langle b^3\rangle = (\bar{r})^3$. Our estimate of Y, the fraction of space occupied by the totality of precritical droplets, follows directly from Eqs. (47) and (48) thus:

$$\frac{V_B}{V_A} = \frac{X_s - X_A}{X_B - X_s} \frac{X_B\bar{V}_{\mathrm{C_7F_{14}}} + (1 - X_B)\bar{V}_{\mathrm{C_7H_{14}}}}{X_A\bar{V}_{\mathrm{C_7F_{14}}} + (1 - X_A)\bar{V}_{\mathrm{C_7}H_{14}}} \tag{78}$$

with

$$Y = V_B/(V_A + V_B) \tag{79}$$

A properly subscripted X denotes the mole fraction of perfluoromethylcyclohexane present in phase A, B, or the supercooled state s, respectively.

The quantities needed to calculate $\bar{r} = \langle b\rangle$ and Y using Eqs. (77)–(79) are directly measurable and consequently no adjustable parameters appear in the theory.

For convenience we list in Table I the values of these quantities as measured by HC$^{(2)}$ as a function of distance from the critical point. Table I also gives the experimentally measure interfacial tension σ_0. Table II lists the values of $\bar{r}$ and Y obtained from Eqs. (77)–(79). Also shown in Table II are

Table I. Summary of the Experimental Data (from Ref. 2) Used in the Calculation of the Quantities Shown in Tables II and III According to the Theory Described

$T_c - T$,	$\bar{V}_{\mathrm{C_7F_{14}}}$, cm^3	$\bar{V}_{\mathrm{C_7H_{14}}}$, cm^3	X_A	X_B	X_s	σ_0, dyne/cm
21.13	195.6	128.4	0.0809	0.8399	0.0927	0.734
16.13	196.8	129.1	0.0961	0.7792	0.1049	0.524
11.13	197.9	129.9	0.1131	0.7116	0.1240	0.329
6.13	199.1	130.6	0.1430	0.6309	0.1563	0.156
4.13	199.6	130.9	0.1641	0.5909	0.1777	0.954
2.13	200.1	131.2	0.1983	0.5396	0.2100	0.0417
1.13	200.4	131.4	0.2273	0.5032	0.2340	0.0189

Table II. Experimental and Calculated Values of ΔF Needed to Produce Nucleation as a Function of Distance from the Critical Point[a]

$T_c - T$,	$\bar{r}$, Å	Y	$-\Delta F(\mathrm{exp})$	$-\Delta F(\sigma = \sigma_0)$	$-\Delta F(\sigma = \sigma_0 + \sigma_{\mathrm{HS}})$
21.13	4.18	0.021	2.10×10^6	1.57×10^6	1.99×10^6
16.13	4.16	0.018	1.13×10^6	9.41×10^5	1.25×10^6
11.13	4.13	0.023	9.56×10^5	4.64×10^5	8.03×10^5
6.13	4.10	0.034	6.85×10^5	1.50×10^5	5.81×10^5
4.13	4.08	0.038	3.48×10^5	7.17×10^4	5.19×10^5
2.13	4.06	0.040	1.31×10^5	2.07×10^4	4.45×10^5
1.13	4.04	0.027	2.41×10^4	6.29×10^3	2.23×10^5

[a] Units of F are dynes/cm^2.

our calculated results, which are compared with experiment. Undercoolings required for nucleation are given in terms of ΔF, the driving free energy per unit volume, for the separation of the nucleating phase. In terms of previously defined quantities, ΔF is given as

$$\Delta F = 3(\mu_B - \mu)/4\pi(\bar{r})^3 \tag{80}$$

Where a minor notational change has been made; μ_l and μ_v of Sections 1 and 2 are now replaced respectively by μ_B, the chemical potential of the "bulk" phase (B phase), and μ, the chemical potential of the system supercooled into the miscibility gap.

Experimental values of ΔF are shown in column four (in units of dynes/cm^2). Column five gives the values predicted using the conventional theory, Eq. (6). The revised capillarity approximation presented in Section 5 implies an equation of the same form as Eq. (6) but with σ_0 replaced by σ of Eq. (57). Substitution of Eq. (57) into Eq. (6) yields

$$W(n) = n(\mu_l - \mu_v) + (\sigma_0 + \sigma_{\mathrm{HS}})a_n \tag{81}$$

Using Eqs. (80) and (81), we readily obtain the expression for the barrier height in our revised theory

$$W(r^*) = 16\pi(\sigma_0 + \sigma_{\mathrm{HS}})^3/3(\Delta F)^2 \tag{82}$$

This relationship differs from the conventional expression[1,2] in that σ_0 has been replaced by σ of Eq. (57). Column six gives the values of ΔF obtained from Eq. (82), the values predicted from our theory. In both columns, five and six, each of the values of ΔF shown leads to a fixed barrier height of $65kT$ corresponding to the threshold for perceptible nucleation. Since the height of the nucleation barrier is inversely proportional to the square of ΔF and in view of the fact that $W(r^*)$ appears in the exponent of the rate expression for nucleation, there is seen to be considerable discrepancy between experiment and predictions of the conventional theory. For example, at $T_c - T = 6.13$ deg, using the conventional theory, we find that the barrier height implied by the observed undercooling limit is a factor of 20 smaller than predicted, whereas in the new theory the barrier height implied by experiment differs from its predicted value by less than 40% and is, in fact, within the range of uncertainty set by HC for their measurements. The values of ΔF calculated from Eq. (82) with the assumption of a monomerically dispersed nucleating phase are seen to be in much better agreement with experiment at all temperatures to within 2 deg of the critical point. Closer to T_c our calculation predicts undercooling *larger* than observed, a situation just opposite to that encountered in the conventional theory. Here the difficulty is more readily resolved. As T_c is approached higher order aggregates having the composition of the nucleating phase will begin to dominate the droplet distribution (as, for example, when the range of density correlation increases). These contribute less per unit volume to the hard-sphere boundary tension. As may be seen from an inspection of Eq. (75), the assumption of a monomeric dispersion leads to values of ΔF that are too high near the critical point.

Table III separates the barrier to nucleation, given by our theory, into its three components. Each of these is evaluated at the drop radius r^* for which the barrier height assumes its maximum value $W(r^*)$. The fourth column in Table III corresponds to the first term on the right side of Eq. (81), which derives from undercooling. The second column gives the contribution to the barrier resulting from the interfacial tension σ_0. Finally, the third column gives the contribution resulting from the hard-sphere boundary tension. This last term, as discussed previously, accounts for the excluded-volume interactions between droplets. Far below T_c the contribution to the

Table III. Evaluation of the Components of the Nucleation Barrier According to Our Theory[a]

$T_c - T$, deg	$\frac{4\pi(r^*)^2\sigma_0}{kT}$	$\frac{4\pi(r^*)^2\sigma_{HS}}{kT}$	$\frac{4\pi(r^*)^3\Delta F}{3kT}$	$\frac{W(r^*)}{kT}$	$r^*(\sigma=\sigma_0+\sigma_{HS})$, cm	$r^*(\sigma=\sigma_0)$ cm
21.13	166.6	28.4	−130.0	65	8.63×10^{-7}	9.33×10^{-7}
16.12	161.4	33.5	−129.9	65	1.01×10^{-6}	1.11×10^{-6}
11.13	135.3	59.6	−129.9	65	1.18×10^{-6}	1.42×10^{-6}
6.13	79.2	115.6	−129.8	65	1.32×10^{-6}	2.07×10^{-6}
4.13	52.1	142.7	−129.8	65	1.38×10^{-6}	2.66×10^{-6}
2.13	25.2	169.7	−129.9	65	1.45×10^{-6}	4.04×10^{-6}
1.13	18.1	177.2	−130.3	65	1.83×10^{-6}	6.01×10^{-6}

[a] The critical radius used is shown in column six, and column seven gives the critical radius predicted in the absence of excluded volume.

barrier height from the interfacial tension greatly overshadows that due to the excluded-volume interference between droplets and the conventional theory is recovered. Closer to T_c, Table III shows that the excluded-volume term dominates in accordance with the failure of the conventional theory in this region. Columns six and seven give the critical radius of the droplet predicted according to our theory and the conventional theory, respectively.[3] The excluded-volume interaction between droplets is seen to result in critical nuclei that are substantially smaller than those predicted using the conventional theory. For example, at $T_c - T = 6.13$ deg the critical droplet is predicted, by our theory, to contain 3.4×10^4 "monomers", while the conventional theory leads to a corresponding value of 1.3×10^5 for this quantity.

The failure of the conventional theory can be clearly seen when the surface tension needed to bring the conventional theory into agreement with

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[3] In each theory a fixed barrier height of $65kT$ was assumed.

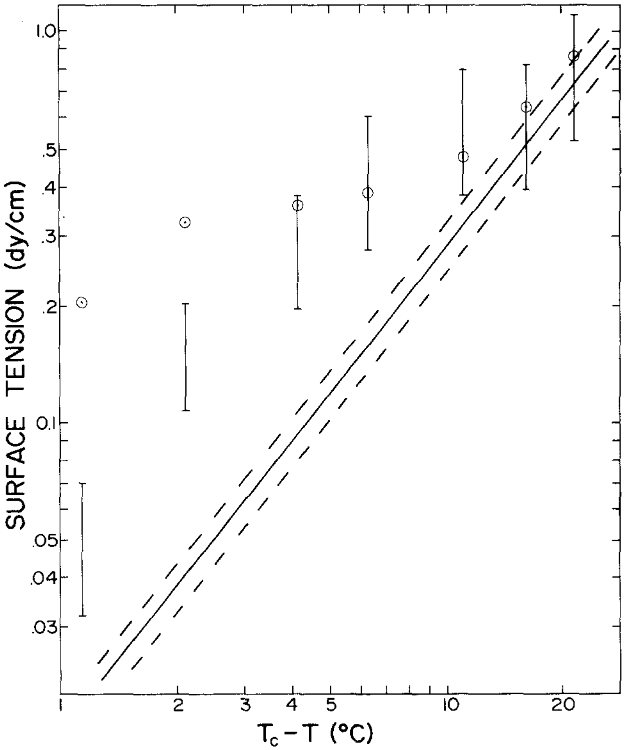

Fig. 5. Experimental and calculated interfacial free energy vs. degrees below the critical temperature. Circles are obtained using Eq. (57).

the experimental undercoolings is compared to the measured value σ_0. Heady and Cahn made such a comparison$^{(2)}$ in their Fig. 7, which we reproduce here, indicating the error bounds assigned by the authors as their best estimate of the overall error in the calculated and measured values of the interfacial free energy. Figure 5 illustrates this comparison. The solid line is the measured interfacial tension σ_0, while the vertical error bars indicate the value range *expected* for σ_0 from the conventional theory (HC assume a 10% uncertainty in their critical undercooling). Also shown in the figure are the values of σ calculated using our theory, i.e., Eq. (57). It is seen that the conventional theory fails precisely where σ_{HS} becomes large enough that σ differs noticeably from σ_0. Again σ is too high close to T_c since our assumption of a dispersion of monomers becomes invalid. Our calculated σ is, nevertheless, an upper bound in this region.

9. SUMMARY AND DISCUSSION

In this paper we have developed a theory within the framework of the capillarity approximation of classical nucleation theory and which contains no adjustable parameters. We did this by (a) choosing conditions where formal "monomeric" clusters dominate the cluster distribution, (b) using the lever rule in a partitioning of the supercooled phase arbitrarily into clusters having the uniform composition of the nucleating phase and a surrounding environment having the composition of the phase conjugate to the nucleating phase along the coexistence curve, and (c) using scaled particle theory to quantititively evaluate the excluded-volume interference between clusters treated formally as drops.

The results are quite good where they should be and deviate in the expected manner where they should not. Furthermore, the theory we have described is unique in that it provides a consistent mechanism for the achievement of greater, rather than lesser, supercoolings than those predicted by the conventional theory. This trend, i.e., toward higher supercooling, might be expected to continue as the critical point is approached, although some of the approximations used in our development of the theory are expected to become less valid in this region.

Finally, it is appropriate to make a few remarks, in the spirit of "notes added in proof," concerning points not treated in our development up to now.

(i) In applying the capillarity approximation to the methylcyclohexane–perfluoromethylcyclohexane binary mixture we have assumed the composition of the critical embryo to lie along the coexistence curve. In essence this is equivalent to the use of the tangent rule by Heady and Cahn in their specification of the nucleus size and composition in binary systems since their method leads to the prediction of a nucleus having a composition close to that of one branch of the coexistence curve. Further support for this choice comes from a recent and more complete thermodynamic study on the composition of nuclei in binary mixtures(8) which indicates that the "correct" nucleus composition is indeed close to that obtained by the tangent rule near the critical point. The differences that are found are too small to have a bearing on the results we present here.

(ii) Following the treatment given in Refs. 1 and 2, we have assumed that the barrier height at the threshold for perceptible nucleation is of the order of (60–70)kT over the range of the study. This is equivalent to assuming that there is no appreciable change in the preexponential factor of the nucleation rate expression over this same range. Now, it has been proposed(20) that there is a "slowing down" in the rate of nucleation near the critical point due to a reduction in size of this preexponential factor. None of these theories are, however, sufficiently well developed to yield quantitative results that can be compared to experiment. Furthermore, in these arguments the reduction occurs due to an increased clustering, to an extent that the clusters which dominate the distribution are of higher order than monomeric. We have shown here that the conventional theory of nucleation fails even in the absence of such clustering and for reasons which are completely different in origin. Since our results are reported in a range where monomers apparently dominate the distribution, no significant change in the preexponential factor is expected to occur. Furthermore, in the realm that clustering does occur (apparently within 2 deg of T_c if our interpretation of the deviation in Fig. 5 is correct) its primary effect on the rate expression will almost certainly be in the reduction of the boundary tension σ_{HS} appearing in the exponent, leading to an *increase* in the nucleation rate since this is known to be a much less sensitive function of the kinetically determined preexponential factor than it is of the surface free energy.

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