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The Effect of Spatial Correlations on Steady-State Nucleation Kinetics in Dense Fluid Systems

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A widely used expression for the steady-state nucleation rate is determined, in part, by the concentration of critical nuclei in a constrained equilibrium state of the system under consideration. We show that when a dense solvent is present, the values of the constrained equilibrium concentrations reflect the spatial correlations that arise from reactant–solvent molecule collisions. We evaluate the effect of such correlations for a simple, model fluid in terms of measurable reaction rate constants; our analysis shows that correlations influence each step in the multistep process of cluster formation and that the overall impact on the nucleation rate is cumulative. We argue that the very low, homogeneous nucleation rates observed in certain miscibility gap experiments are easily understood in the context of our analysis.

KEY WORDS: Nucleation; diffusion-controlled kinetics; phase transitions in condensed media.

1. INTRODUCTION

Nucleation processes that develop in the presence of inert host media are known to occur in many important phenomena found in nature.[4] Thus, raindrops condense in the presence of atmospheric molecules, crystals grow in supersaturated liquid solutions, voids form in crystal lattices, and so on. The same situation is often encountered in the laboratory as well, in such experimental apparatus as supersonic nozzles and diffusion chambers. Despite being nominally termed "inert," nonreactive solvents can nonetheless participate indirectly in the evolution of chemical reactions through the spatial correlations arising from reactant–solvent molecule collisions (see,

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[4] For a rather broad survey, see Zettlemoyer.(1)

e.g., Ref. 2). For example, a reversible bimolecular reaction of the type $A + B \rightleftarrows C$ is affected by the presence of a solvent in two ways: The rate of the "forward" reaction is limited by the diffusion of As and Bs through the solvent; in consequence, close-lying A, B pairs are removed from the system as the forward reaction proceeds; the rate of the "backward" reaction is also effectively limited by the solvent due to the "caging" of dissociating C molecules. As a result, both the time course and the equilibrium state of the reaction can be altered by the properties of the host species. The solvent effect in nucleation can be even more complicated because the emergence of the new phase requires a *hierarchy* of coupled, reversible, bimolecular reactions of the form (cluster of size j) + (monomer) $\rightleftarrows$ (cluster of size $j + 1$). The spatial correlations associated with each step in this hierarchy are thus passed on to all successive steps. While various aspects of the solvent effect in nucleation have been discussed in the literature,(3-7) little analysis of the cumulative nature of the spatial correlations associated with the nucleation process exists.[5] In this paper, we present a semiempirical method for describing these cumulative effects and argue that their inclusion in a theoretical description of nucleation kinetics leads to a natural resolution of some well-known discrepancies between theory and experiment.

For the sake of specificity, we treat the simple case of a binary, fluid mixture in which the minority (reactant) species is supersaturated.[6] The attendant nucleation is assumed to be isothermal and homogeneous and to take place in the absence of convective mixing. Clusters are assumed to be compact and spherical.[7] For such a system there is a well-defined algorithm for determining the rate at which critical nuclei form during the quasi-steady state which precedes the collapse of the supersaturation.[8] We restrict our attention to this regime and follow the steps of the algorithm. The elements of this strategy are: (i) determine the partition function for the system; (ii) minimize the free energy under the condition that the system is constrained to maintain its initial degree of supersaturation; (iii) obtain cluster concentrations appropriate to the *constrained equilibrium state* in the form $n_j = \Phi_j \exp(-W_j/k_B T)$, where n_j is the concentration of clusters of size j, Φ_j is a factor containing information about the center-of-mass energy of the cluster, k_B is Boltzmann's constant, T is the absolute temperature, and W_j is the reversible work necessary to assemble j free monomers into a bound j-mer; (iv) determine the size j^* of a critical cluster by setting $\partial W_j/\partial j$ equal

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[5] But see, e.g., Mou and Lovett.(8)

[6] The same correlations treated here must be accounted for in solid systems as well, of course.

[7] A similar analysis for diffuse clusters—as discussed, e.g., by Cahn and Hilliard(9)—would be more complicated but not essentially different.

[8] For a clear and detailed discussion of this procedure see Abraham.(10)

to zero[9]; and, finally, (v) write the steady-state nucleation current I as $Z_{j^*}n_{j^*}$, where Z_j is a kinetic coefficient containing the monomer–j-mer encounter rate.

In the next section we will expand on the outline given above with details appropriate to our model fluid system. We will show that the usual formal intractabilities associated with a straightforward statistical description of dense fluids can be usefully circumvented by employing semiempirical chemical kinetics arguments. The specific forms of the rate coefficients utilized in Section 2 are derived in a discussion of diffusion-controlled reactions in Section 3. In Section 4 we discuss our results and show how they are relevant to the analysis of certain dense vapor and liquid–liquid experiments.

2. CONSTRAINED EQUILIBRIUM AND STEADY-STATE NUCLEATION

We consider a system of volume V and uniform temperature T, consisting, at any instant, of N_1 monomers of a reactant A, N_2 dimers,..., N_j j-mers, and so on, along with a fixed number N_s of solvent molecules. The total number of reactant molecules is fixed and equal to N_0. The reactant clusters are assumed to change by absorption or ejection of monomers only. That is, we assume that the reactant participates in the reaction scheme

$$A_1 + A_j \rightleftarrows A_{j+1}, \qquad j = 1, 2,... \tag{1}$$

where A_1 designates the monomer and A_j a bound cluster of j monomers. For the moment, the new phase of A is assumed to be artificially excluded from the sample by applying some external constraints. The equilibrium cluster size distribution for this constrained system is the set $\{\tilde{N}_j; j = 1, 2,...\}$ which extremizes the Helmholtz free energy of the system.

We assume that the total partition of our system can be expressed as

$$Z = \left[\prod_{i=1}^{N_0} (\lambda_i r_i q_i V)^{N_i}/N_i!\right][(\lambda_s r_s q_s V)^{N_s}/N_s!]Q(N_1, N_2,..., N_s, T, V) \tag{2}$$

where λ_i is the reciprocal cube of the thermal de Broglie wavelength of a cluster of size i, r_i is the partition function for rotations about the center of mass of an i-mer, q_i is the partition function corresponding to internal modes of vibration of an i-mer (in the presence of the solvent), and Q is the normalized configurational partition function describing the center-of-mass interactions between all clusters and unbound molecules in the system; note that

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[9] Actually, one should set $\partial n_j/\partial j$ equal to zero, but the value of j^* so obtained varies only slightly from that derived by setting $\partial W_j/\partial j$ to zero.

λ_s, r_s, and q_s are defined similarly to λ_i, r_i, and q_i, respectively. We assume, further, that Q can be approximated by the classical phase integral

$$Q = \left(\prod_{i=1}^{S} V^{-N_i}\right) \int \cdots \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2, \ldots)/k_B T]\, d\{\mathbf{r}\} \qquad (3)$$

where U is the total potential energy of interaction and the integrations are over all possible center-of-mass positions.

Extremization of the Helmholtz free energy of the system, $-k_B T \ln Z$, is attained when each reaction in the sequence (1) is in equilibrium, i.e., when $\tilde{\mu}_1 = j\tilde{\mu}_j$, where $\mu_j \equiv \partial F/\partial N_j$, $\tilde{\mu}_j \equiv \mu_j(n_1, n_2, \ldots, n_s, T)$, and $n_j \equiv \tilde{N}_j/V$. Using this criterion, we find that

$$n_j = \lambda_j r_j \exp(\tilde{X}_j) \exp[-j \ln(\lambda_1 r_1 q_1/n_1) + \ln q_j] \qquad (4)$$

The quantity $\tilde{X}_j$ is the equilibrium value of

$$X_j = \frac{\partial \ln Q}{\partial N_j} - j\frac{\partial \ln Q}{\partial N_1} \qquad (5)$$

It is convenient to formally approximate the potential energy function U as

$$U = \sum_{i=1}^{N_0} \left[iN_i\phi_{is} + \sum_{k=1}^{N_i} \sum_{j=1}^{N_s} h_{kj}(|\mathbf{r}_k - \mathbf{r}_j|) \right] + U_{ss} \qquad (6)$$

where ϕ_{is} is the potential energy per molecule of an average cluster of size i in the solvent S due to the long-range interactions between reactant and solvent molecules (ϕ_{is} clearly depends in some nontrivial way on temperature, pressure, solvent density, etc.), h_{kj} is the short-range part of the cluster–solvent molecule potential energy of interaction, and U_{ss} is the contribution to U due only to interactions among solvent molecules. Note that in writing (6) we have neglected the direct interactions between various clusters, because the reactant is assumed to be very dilute. With this expression for U, Eq. (4) can be cast into the form[10]

$$n_j = Y_j \exp(\zeta_j) \exp(-W_j/k_B T) \qquad (7)$$

In writing Eq. (7) we first employ the replacement

$$\ln q_j = -(j\mu_\beta + \sigma j^{2/3} + k_B T \ln q_{\mathrm{rep}})/k_B T \qquad (8)$$

where μ_β is the chemical potential per particle in the *bulk* reactant phase, σ is an effective surface energy, and q_{rep} is a correction introduced to compensate for the multiple counting of certain collective modes in μ_B and again in λ_j and r_j. Next, we write the reversible work necessary to assemble a

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[10] See Ref. 10; compare, especially, Eq. (4.7.9) with (7) of this paper.

j-mer, in the presence of the solvent, from j unbound monomers, also initially in the solvent, as

$$W_j = j[\mu_\beta + \phi_{js} + k_B T \ln(\lambda_1 r_1 q_1/n_1) - \phi_{1s}] + \sigma j^{2/3} \tag{9}$$

Then, the preexponential term Y_j is expressed as

$$Y_j = \lambda_j r_j q_{\mathrm{rep}}^{-1} \tag{10}$$

Finally, we note that ζ_j is determined solely by the short-range interactions h_{kj} and therefore represents the effects of the spatial correlations resulting from reactant, solvent molecule collisions.

The preceding discussion completes steps (i)–(iii) of the algorithm set down in Section 1. We now consider the steady-state nucleation current.

In an actual supersaturated system—not the constrained equilibrium system above—clustering fluctuations will carry the system toward an achievable equilibrium state in which the new phase of the reactant is present in bulk. Prior to the emergence of equilibrium, however, the system will pass through a quasi-steady-state regime in which all of the reactant concentrations are virtually stationary in time, while the initial degree of supersaturation is essentially unaltered.

To facilitate a description of the actual system, we denote by f_j the sample-average j-mer concentration during the steady state. Furthermore, we designate by ρ_j the effective rate at which j-mers form by coalescence in the sample and by δ_j the effective rate at which j-mers dissociate; both ρ_j and δ_j are steady-state values. Then, the number I of critical nuclei that form per unit volume per unit time in the steady state is$^{(11)}$

$$I = \rho_2 - \delta_2 = \rho_3 - \delta_3 = \cdots = \rho_j - \delta_j = \cdots \tag{11}$$

In general, due to the collisional controlling of the reaction rates, both ρ_j and δ_j are complicated functions of the reactant concentrations. The usual assumption, however, is that ρ_j has the simple bimolecular form

$$\rho_j = k_{j-1} f_1 f_{j-1} \tag{12}$$

while δ_j is taken to be of simple unimolecular form,

$$\delta_j = b_j f_j \tag{13}$$

Additionally, it is assumed that (12) and (13) remain unchanged—except for the replacement of f_j by n_j—in the equilibrium state. In fact, none of these assumptions is trivially valid. In the next section we examine the conditions under which they may be applicable. For the moment, though, we accept these assumptions as postulates.

The standard trick in the analysis of steady-state nucleation is to eliminate the dissociation rate coefficient b_j from the sequence (11) by setting the equilibrium value of ρ_j equal to the equilibrium value of δ_j. The sequence (11) is then summed from $j = 2$ to $j = N_0$; if the constrained equilibrium state is used for the elimination of b_j, then one obtains$^{(11)}$

$$I = n_1 \left[\sum_{j=1}^{N_0} (k_j n_j)^{-1} \right]^{-1} \tag{14}$$

Equation (14), with the concentrations n_j from (7), is a complete formal solution to the problem at hand. Unfortunately, one has to insert an appropriate interaction potential into the collision factor $\exp(\zeta_j)$ in (7) and perform the required integrations. For dense systems, such a procedure is not very productive.

A more useful method than the straightforward approach can be constructed from the following arguments. First, we define a fictitious *reference* system in which the short-range collisions between reactant and solvent molecules are completely negligible. Equilibrium in such a system is characterized, therefore, by cluster concentrations n_j^0 given by (7) with ζ_j set equal to zero; that is,

$$n_j = [\exp(\zeta_j)] n_j^0 \tag{15}$$

The reaction $A_1 + A_j \rightleftarrows A_{j+1}$ comes to equilibrium in this system when

$$n_{j+1}^0 / n_j^0 = k_j^0 n_1^0 / b_{j+1}^0 \tag{16}$$

where k_j^0 and b_{j+1}^0 are, respectively, the bimolecular coalescence rate constant and the unimolecular dissociation rate constant appropriate to conditions of *free molecular flow*. In particular, k_j^0 can be written as

$$k_j^0 = \pi R_j^2 \langle v_{1j} \rangle \gamma_j \tag{17}$$

where R_j is the critical separation of monomer and j-mer at which coalescence ensues, $\langle v_{1j} \rangle$ is the mean monomer–j-mer relative (Maxwellian) speed, and γ_j is the fraction of encounters resulting in coalescence. The constants b_j and b_j^0 can be simply related by introducing an *escape fraction* ϵ_j,[11] which is the fraction of monomers escaping immediate recombination with a freshly created cluster of size j just after the dissociation of a $(j + 1)$-mer; clearly, $\epsilon_j = 1$ for free molecular flow conditions, while $\epsilon_j \to 0$ for increasingly dense, real solvents surrounding the dissociating cluster. In other words, the effective dissociation rate constant b_j is

$$b_j = \epsilon_{j-1} b_j^0 \tag{18}$$

Now, if we multiply (16) by similar fractional expressions over ever smaller j, we ultimately find that

$$n_j^0 = \prod_{i=1}^{j-1} (k_i^0 / b_{i+1}^0) n_1^0 \tag{19}$$

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[11] See, e.g., Peak and Corbett.$^{(11)}$

while the same procedure applied to the condition analogous to (16) for equilibrium in the actual system yields the same result for n_j as in (19), but with all superscripts 0 removed. If the reference system is required to have the same monomer concentration as the actual system, we can then use (19) and the analogous form for n_j to write

$$n_j = \alpha_{j-1} n_j^0 \tag{20}$$

where

$$\alpha_{j-1} = \prod_{i=1}^{j-1} (k_i/\epsilon_i k_i^0) \tag{21}$$

Thus, we can delete the collision term, $\exp(\zeta_j)$, in (15) in favor of the product of semiempirically determinable rate constants seen in (21).

The result (21) indicates the cumulative nature of the collisional correlations in our dense fluid system. A beautifully simple expression of how the buildup of these correlations, in the process of the formation of a critical nucleus, affects the steady-state nucleation rate can be achieved as follows: Approximate (14) by a continuous integral (11) and evaluate it by the method of steepest descents to obtain

$$I = Z_{j^*} n_{j^*} \tag{22}$$

where j^* is the cluster size for which W_j is maximal and Z_{j^*} is given by

$$Z_{j^*} = k_{j^*} n_1 \left(-\frac{1}{2\pi k_B T} \frac{\partial^2 W_j}{\partial j^2} \bigg|_{j=j^*} \right)^{1/2} \tag{23}$$

Then, if I_0 is the nucleation current in the (collision-free) reference system, we can write simply

$$I/I_0 = \epsilon_{j^*} \alpha_{j^*} \tag{24}$$

3. DIFFUSION-CONTROLLED KINETICS

To establish the kinetics results of the preceding section, the forms of the sample-average rates ρ_j and δ_j must be elucidated. Since collisions between reactants and solvent molecules limit the reaction rates, neither ρ_j nor δ_j will be as simple as in (12) and (13), in general. In order to determine approximate expressions for ρ_j and δ_j, some simplifying assumptions are necessary. The ones we invoke are not very unusual; they are: The diffusion of the reactants through the solvent is Fickian; the reactant diffusivities are independent of concentration, position, and time; and the reaction potential between cluster and monomer is spherically symmetric. Furthermore, we assume that dissociation follows a sequence of events which includes: activation of the cluster; dissociation of a monomer from the activated complex followed by the free molecular flight of the escaping monomer and the new, deactivated complex; and stopping collisions of the monomer and cluster with solvent molecules. The first two of these events are assumed to be adequately described by the *truly* unimolecular rate constant b_j^0 introduced in (16).

The reaction sequence (1) deals only with monomers and clusters and implies that all of the spatial information in the problem can be contained in the *pair* concentration $c_j(r)$,[12] where

$c_j(r)$ = the average number of monomer-j-mer pairs with monomer and j-mer separated by a distance r per unit squared volume during the steady state (25)

If by D_j is meant the sum of the monomer and j-mer diffusivities (relative to the solvent), then the pairwise diffusion current J_j is

$$J_j = -D_j\, \partial_r c_j \tag{26}$$

and the total coalescence rate K_{j+1} is

$$K_{j+1} = -4\pi R_j^2 J_j(R_j) \tag{27}$$

In the latter expression, R_j is the minimum allowable monomer-j-mer separation; when the reactants come within R_j of each other, either coalescence is initiated or reflection occurs. The total coalescence rate K_{j+1} includes both first time coalescences as well as recombinations. Thus, the third step in the dissociation sequence outlined above is accounted for in K_{j+1}. We can then write I either as (11) or as

$$I = K_j - b_j^0 f_j, \qquad \text{for} \quad j = 2, 3, \ldots \tag{28}$$

The central quantity in our analysis is, clearly, the gradient of c_j. To determine it, we need to know the field equation which c_j satisfies. Formally, at least, we can write

$$-\frac{1}{r^2}\, \partial_r(r^2 J_j) + \text{reaction terms} = 0 \tag{29}$$

in the steady state. The enumeration of the reaction terms in (29) is just a matter of proper bookkeeping and a little patience. For what follows it may be helpful to consult Fig. 1. Monomer-j-mer pairs of separation r are removed from or added to the sample through a variety of processes which compete with the direct mutual diffusion of the pair members. The rate of removal of such pairs due to competitive events includes: ($i-$) the spontaneous dis-

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[12] In this section we extend the formalism of Waite(13) to the study of spatial correlations in diffusion-controlled reaction kinetics.

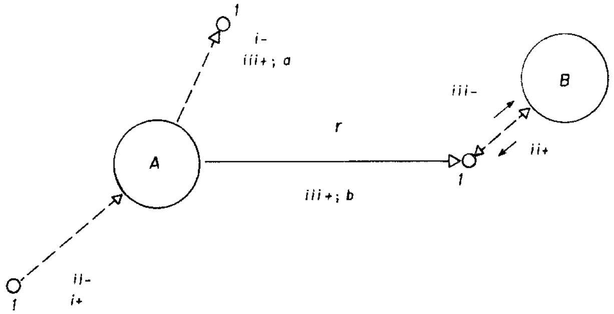

Fig. 1. Competitive contributions to the field equations for $c_j(r)$; the processes (i−) to (iii+ ; *b*) are as described in the text; for processes (i−), (ii−), (iii−), and (ii+), *A* is of size *j*; for process (*i*+), *A* is of size $j - 1$; for processes (iii+ ; *a*) and (iii+ ; *b*), *A* is of size $j + 1$; *B* is of arbitrary size *i*.

sociation of the *j*-mer; (ii−) the coalescence of the *j*-mer with any other monomer except the one a distance *r* away; and (iii−) the coalescence of the monomer with any other cluster in the sample. Each of these events contributes to (29) a term of the form (probable rate of the event) × (probability of having a monomer–*j*-mer pair of separation *r*). Thus, (i−) contributes a term $-b_j{}^0c_j$; (ii−) a term $-(K_{j+1}f_j^{-1})c_j$; and (iii−) a term $-[(\sum_i K_{i+1} + K_2)f_1^{-1}]c_j$. The additional part of this last expression is necessary because *two* monomers are lost in each K_2 event. The index *i* in the sum starts at $i = 1$.

The rate of addition of monomer–*j*-mer pairs of separation *r* arises from somewhat more complicated events. Included in these are: (i+) the coalescence of a $(j - 1)$-mer; (ii+) the dissociation of any cluster and the simultaneous production of at least one monomer, which, in turn, pairs with all *j*-mers existing at that instant; such pairs occur with completely random initial separations throughout the sample; and (iii+) the spontaneous dissociation of a $(j + 1)$-mer leading to a monomer–*j*-mer pair of separation *r* provided, on the one hand, (a) the $(j + 1)$-mer has been previously paired with a monomer at *r*, or, alternately, (b) the dissociation product *j*-mer and monomer come instantaneously "to rest" (relative to each other) a distance *r* apart just subsequent to the dissociation. The respective terms these additive processes contribute to (29) are: (i+) $(K_jf_{j-1}^{-1})c_{j-1}$; (ii+) $(\sum_i b_{i+1}^0 f_{i+1} + b_2{}^0 f_2)f_j$; and (iii+) $b_{j+1}^0[c_{j+1} + f_{j+1}\eta_j(r)]$. In (ii+) the extra terms accounts for the production of *two* monomers in each dimer dissociation. In (iii+) the quantity $\eta_j(r)$ is the probability density that the dissociation product *j*-mer and monomer will achieve a separation *r* before their initial momenta of escape become uncorrelated. We expect that η_j will have some kind of exponential form, though, in practice, it may be sufficient to assume that η_j is a delta function of the form $\delta[r - (R_j + \lambda)]/4\pi r^2$, where λ is a momentum correlation length (determinable, in principle, from viscosity data). In any case, we require η_j to be normalized:

$$4\pi \int_{R_j}^{\infty} r^2 \eta_j(r)\, dr = 1 \tag{30}$$

The enumeration of the reaction terms in (29) for $j = 1$ proceeds similarly to the above discussion, but is simpler. Losses in monomer–monomer pairs occur only by coalescence. Each cluster contributes to these losses, and each monomer in the pair is affected equally. Thus, the rate of loss in (29) due to competitive coalescences is $-2[(\sum_i K_{i+1} + K_2)f_1^{-1}]c_1$. Additions occur by dissociation and lead to two positive terms, $(\sum_i b_{i+1}^0 f_{i+1})f_1$ and $b_2{}^0 f_2 \eta_1(r)$.

A reasonable expectation which can be placed on the spatial variation of c_j is that the pair concentration should take on the corresponding sample-average value for large intrapair separations. That is, we require

$$c_j(r \to \infty) \to f_1 f_j \tag{31}$$

for $j \geqslant 2$, and

$$c_1(r \to \infty) \to \tfrac{1}{2} f_1{}^2 \tag{32}$$

for $j = 1$. Then, as well, (29) should describe just the sample-average kinetics of the various reactions in the same limit. To show that this is indeed the case, set $\partial_r J_j = 0$ for $r = \infty$, and make the replacements (31) and (32) in the remaining parts of (29).

A complete specification of the full diffusion-reaction problem requires a supplementary boundary condition on c_j, in addition to (31) or (32). The other boundary condition on c_j is chosen, for its generality, to be

$$\partial_r c_j(R_j) = \beta_j c_j(R_j) \tag{33}$$

This condition allows for the possible reflection of monomer and j-mer upon collision. The parameter β_j describes the probability that such a collision will result in coalescence: When $\beta_j \to \infty$, coalescence occurs with unit probability; when $\beta_j \to 0$, only reflection occurs.

In accord with the above comments, (29) can be written

$$\begin{aligned} 0 = {} & D_j \nabla^2 c_j - b_j{}^0 c_j - (I + b_{j+1}^0 f_{j+1}) f_j^{-1} c_j \\ & - \left(\sum_{i=1}^{N_0} b_{i+1}^0 f_{i+1} + b_2{}^0 f_2 + N_0 I \right) f_1^{-1} c_j + (I + b_j{}^0 f_j) f_{j-1}^{-1} c_{j-1} \\ & + \left(\sum_{i=1}^{N_0} b_{i+1}^0 f_{i+1} + b_2{}^0 f_2 \right) f_j + b_{j+1}^0 (c_{j+1} + f_{j+1} \eta_j) \end{aligned} \tag{34}$$

for $j \geqslant 2$, and

$$0 = D_1 \nabla^2 c_1 - 2\left(\sum_{i=1}^{N_0} b_{i+1}^0 f_{i+1} + b_2{}^0 f_2 + N_0 I\right) f_1^{-1} c_1$$
$$+ \sum_{i=1}^{N_0} b_{i+1}^0 f_{i+1} f_1 + b_2{}^0 f_2 \eta_1 \tag{35}$$

for $j = 1$. Equations (34) and (35) can also be used to determine the equilibrium concentrations if I is set equal to zero and f_j is replaced by n_j, everywhere.

Equations (34) and (35) represent the general, steady-state, field equations for the pair concentrations. These equations are very complicated, of course; the attainment of detailed solutions would appear to be a remote possibility. Nonetheless, for the kind of system we are studying considerable headway *can* be made by noting that the competition terms in both equations are different from zero only for small r values. If, as we have previously assumed, the reactant concentrations are small compared to that of the solvent, then competition among close-lying reactant pairs can be ignored. Only when there are many pairs of small separation will this approximation be inappropriate. Thus, we can write both (34) and (35) as one equation,

$$0 = D_j \nabla^2 c_j + b_{j+1}^0 f_{j+1} \eta_j \tag{36}$$

which is valid for all j. Note that the last term in (36) cannot be ignored, in general, because the distributions η_j may well (in sufficiently condensed media) be sharply peaked close to the reaction surfaces.

Equation (36) is readily integrated, resulting finally in

$$K_{j+1} = 4\pi R_j D_j \Gamma_j f_1 f_j + b_{j+1}^0 f_{j+1} \Gamma_j R_j \langle r^{-1} \rangle_j \tag{37}$$

where

$$\Gamma_j = \beta_j R_j (1 + \beta_j R_j)^{-1} \tag{38}$$

and

$$\langle r^{-1} \rangle_j = 4\pi \int_{R_j}^{\infty} r \eta_j \, dr \tag{39}$$

The quantity $\langle r^{-1} \rangle_j$ is the expectation value of r^{-1}, where r is the "initial" separation of a typical dissociation product monomer and j-mer, computed with respect to the distribution η_j. Using (37), we can write

$$I = 4\pi R_j D_j \Gamma_j f_1 f_j - \epsilon_j b_{j+1}^0 f_{j+1} \tag{40}$$

where ϵ_j is the probability that a dissociation product monomer and j-mer will escape recombination and is given by

$$\epsilon_j = 1 - \Gamma_j R_j \langle r^{-1} \rangle_j \tag{41}$$

Thus the effective coalescence rate constant k_j is

$$k_j = 4\pi R_j D_j \Gamma_j \tag{42}$$

and the effective dissociation rate constant b_j is as presented in (18), with the explicit form of the escape fraction, (41).

To summarize the findings of this section, then, the assumptions of the previous section are seen to be valid only when competition for reactant monomers among the various clusters already formed leads to small, higher order corrections.

4. DISCUSSION

There is, of course, a so-called "classical" theory of nucleation kinetics—associated with such names as Volmer, Becker, Döring, Zeldovich, and Frenkel[13]—which essentially starts with step (iii) of the algorithm cited in Section 1 and rather arbitrarily assigns to the preexponential Φ_j the value of the monomer concentration n_1. Much discussion has appeared in the literature over the years dealing with the sometime success, sometime failure of this classical nucleation theory. For example, in some experiments involving vapor-to-liquid transitions, homogeneous nucleation rates well *in excess* of the rates predicted by the classical theory have been observed.(15) On the other hand, in certain liquid–liquid systems, in which the components become immiscible at some composition, the observed homogeneous nucleation rates can be many orders of magnitude *smaller* than the relevant classical predictions.(16,17) Such disparities should not be unexpected, though, since the classical assignment $\Phi_j^{cl} = n_1$ is not really based on standard statistical mechanical principles (a point made most notably by Lothe and Pound(18)).

The usual treatment of the kinetics of condensation from a supersaturated vapor approximates the system as an ideal gas mixture. In this approximation, one takes Φ_j^{id} to be equal to the expression Y_j of Eq. (10). For most vapors, Φ_j^{id} is many orders of magnitude greater than Φ_j^{cl}, which implies a similar relation between I^{id} and I^{cl}. As noted previously, many experiments do display nucleation rates close to the appropriate I^{id}; however, many other experiments yield results much closer to I^{cl}. The presence of carrier gases, which are often quite dense, in these experiments can be an important factor in the observed results. The correct theoretical current will, in general, be neither I^{id} nor I^{cl}, but will be, according to (24), more like $\alpha_{j*} I^{\mathrm{id}}$. Since j^* may well be on the order of 100 molecules, then $\alpha_{j*} \sim \Delta^{100}$, where Δ is a typical value of the ratio of k_j to k_j^0 (ϵ_j will be very nearly one in gaseous systems); Δ does not have to be much less than one to get a vast reduction

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[13] See the introductory remarks by Dunning.(14)

in the correct nucleation current from I^{id}. Frisch and Collins$^{(19)}$ have shown that an analysis of this problem using diffusion-controlled kinetics is applicable, even though the monomer mean free path in a vapor may be large compared to R_j. They also show that the parameter Γ_j will be smaller than γ_j, but their expressions for Γ_j are approximate and are not of immediate use. A more complete and quantitative discussion of these matters awaits further investigation.

The situation in liquid–liquid experiments can be discussed more directly. The close packing of solvent about a reactant cluster not only serves to reduce the average center-of-mass kinetic energy of the cluster, but also provides a substantial barrier to the flow of additional monomers to the aggregate. Clearly, the appropriate Φ_j will be much smaller than Φ_j^{id} in this case, but why even then it should be comparable to Φ_j^{cl} is not at all obvious. In Table I we display some results calculated from the data of Heady and Cahn$^{(17)}$ on the system C_7F_{14} in C_7H_{14}. The second column in Table I shows that the observed nucleation rate in this study was about 25 orders of magnitude smaller than predicted by I^{cl} at some temperatures. Now, the nucleation rate given in Eq. (24) can be written as $I = \epsilon_{j*}\alpha_{j*}Y_{j*}I^{cl}/n_1$, which means that in order for $I \approx I^{\mathrm{obs}}$ we must require $\epsilon_{j*}\alpha_{j*} \approx 10^x n_1/Y_{j*}$, where x is the value from column two of the table corresponding to the chosen j^* value. If again we write α_{j*} as Δ^{j*}, then the values of Δ required to make $I \approx I^{\mathrm{obs}}$ are shown in the last column of the table.

As opposed to the situation found in gases, $\gamma_j = \Gamma_j$ in liquids. Thus, we can write $\Delta = 4D(\epsilon R\langle v\rangle)^{-1}$, where D is a typical monomer–j-mer diffusivity, ϵ is a typical escape fraction, R is a typical monomer–j-mer reaction distance, and $\langle v\rangle$ is a typical monomer–j-mer relative (free flow) speed. For the C_7F_{14}–C_7H_{14} system, typical values of these parameters might be $D = 10^{-5}$ cm^2/sec, $R = 5R_1 = 2 \times 10^{-7}$ cm, and $\langle v\rangle = 1.3 \times 10^4$ cm/sec. Furthermore, if we assume that the distribution function in (39) is a delta

Table I

T (°K)	$\log_{10}$ (I^{obs}/I^{cl})	j^* ($\times 10^3$)	n_1 ($\times 10^{20}$ cm^{-3})	n_1/Y_{j*} ($\times 10^{-30}$)	Δ
298	0	12.5	2.46	15.9	0.995
303	0	20.4	3.06	2.62	0.997
308	−19.2	6.98	3.65	217	0.990
313	−25.3	2.11	5.14	34,700	0.946
315	−25.3	4.18	5.43	2,360	0.972
317	−26.1	5.44	6.32	934	0.978
318	−25.0	71.1	7.51	0.0388	0.998

shell distribution at $r = R + \lambda$, then $\epsilon = 1 - \Gamma R(R + \lambda)^{-1}$. By setting $\Gamma = 1$ and $\lambda = R_1$, we obtain $\epsilon = 0.17$, which is about the smallest value one might expect for the escape from a compact spherical cluster. The value of Δ corresponding to these typical values is therefore about 0.09, or about ten times smaller than is needed to account for the low nucleation rates observed by Heady and Cahn. Obtaining Δ's sufficiently small so that the corrected theoretical nucleation rates are much smaller than the classical rates is no problem whatsoever. Indeed, the "typical Δ" calculation given above implies even lower rates than the ones actually observed. This should not be too upsetting, however, since the experiment under discussion deals with behavior near the critical point. The enormous critical nuclei involved are likely to be diffuse and nonspherical: Escape fractions associated with such aggregates may be much smaller than the figure quoted here. Nonetheless, our central theme would seem to be well supported: *Spatial correlations in dense fluid systems affect the nucleation kinetics in a markedly cumulative manner.*

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