Time lag in diffusion-controlled nucleation^{a)}

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Nucleation occurring in the presence of a dense solvent is accompanied by spatial correlations among the reactant clusters and monomers which affect the aggregation rates. The classical theory of nucleation, which does not take such correlations into account, overestimates the observed nucleation rate and underestimates the time lag in condensed systems. An explicit expression for the time lag in diffusion-controlled nucleation is derived. Values associated with miscibility gap experiments differ from the classical predictions by factors of 5 to 10.

I. INTRODUCTION

The steady rate of critical-cluster formation and the time lag in achieving the steady rate are two parameters which are often of use in characterizing the pretransition period of a phase change. Predicted values for these parameters, extracted from the classical theory of homogeneous nucleation,¹ have been calculated for a variety of different systems—even though the classical theory was originally developed to describe only the condensation of a pure, dilute vapor. In at least one class of experiments—investigations on phase separation in liquid binary mixtures—nucleation rates have been reported which are many orders of magnitude smaller than the corresponding classical values.^{2,3} Since it had been assumed prior to these experiments that the classical rates were associated with paths of *least* nucleation, these observations were unexpected. Recently, however, the presence of condensed solvent in these experiments has been suggested as a possible cause for the very low, observed rates.^{4,5} In fact, calculations based on the models of Ref. 4 and 5, which incorporate solvent effects, do indeed yield much lower rates of nucleation than the classical theory. With this in mind one might then ask, What is the effect of the solvent on the time lag? Intuitively, it would seem that the classical time lag—in cases where the solvent impedes nucleation—is too short, but by how much? These questions are examined in this paper.

Before proceeding to the details of the problem at hand the meaning of the term “classical theory of homogeneous nucleation”—as it is used here—and the suggested reason for the theory’s failure in some condensed systems should be clarified.

The classical formalism is essentially an analysis of the kinetics of the hierarchy of coupled reactions⁶ (monomer) + (cluster of size j) $\rightleftharpoons$ (cluster of size $j+1$), where j can be 1, 2, . . . , and so on. The standard algorithm for this analysis can be summarized as follows: (i) Write down expressions for the time rates of change of the sample-average concentrations of clusters of different sizes in terms of simple chemical kinetics forms; (ii) solve the steady state versions of the resulting equations for the nucleation rate and the steady state concentrations; (iii) integrate the time-dependent equations, employing steady state values as required, to find the time lag. To progress from step (i) to step

(ii), however, unknown dissociation rate constants must be eliminated by a procedural trick which involves the exploitation of detailed balance relations associated with some equilibrium reference state of the system of interest. The form of this procedure which distinguishes the “classical” approach from any other takes as the reference state one in which monomers and clusters are completely randomly distributed with respect to each other *and*, at the same time, assumes that the rate constants characteristic of such a configuration are identical to those corresponding to the nonequilibrium nucleation process.

The latter assumption is responsible, according to the arguments posed in Ref. 4 and 5, for the large disparity between the calculated and observed nucleation rates referred to previously. For a system in which there is a nonreactive host medium the nonequilibrium growth of a cluster is driven by concentration gradients as monomers are depleted locally in the vicinity of the cluster. The larger the cluster, the larger the depletion zone; the larger the depletion zone, the more difficult it is for further coalescences to occur. Hence, very large clusters will form at rates very much lower than those predicted on the basis of the spatially uniform, classical picture. In the liquid-liquid systems studied in Ref. 2 and 3 critical nuclei are enormous, each consisting of thousands of monomers; the effects of spatial nonuniformities in such systems can therefore be quite pronounced and it is little wonder that the classical theory greatly overestimates the nucleation rates.

The methods of Ref. 5 represent only a slight perturbation of the classical theory and, as such, are easily used in analyzing the time lag in the presence of a dense solvent. In the next section an explicit expression for the time lag associated with a general, model system is determined. This result is discussed in the context of a specific numerical example in Sec. III. A derivation of the rate constants used in Secs. II and III is given in a concluding Appendix.

II. MODIFICATION OF THE CLASSICAL TIME LAG

The model system to be considered here is one in which there are, at any instant, N_1 reactant monomers, N_2 dimers, . . . , N_j j -mers, . . . , all immersed in N_s nonreactive solvent molecules. The reactants are taken to be widely dispersed, i. e., $N_s \gg N_j$ for all j . The clusters are assumed to be pure and spherical in shape. The system is isothermal with absolute temperature T . Convective effects are ignored.

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The first step of the calculational algorithm set down in the Introduction is initiated by defining a sample-average concentration of clusters of size j, f_j , which satisfies a rate equation of the form

$$df_j/dt = I_j - I_{j-1} \quad (1)$$

for $j = 2, 3, \dots, G-1$. The current I_j , appearing in Eq. (1) is the instantaneous difference between the rate of coalescence of monomers and $j-1$ -mers and the rate of dissociation of j -mers (each rate is per unit volume). The range of validity of Eq. (1) reflects the usual assumptions that during the regime of interest the concentration of monomers is to be held fixed ($f_1 = \text{constant}$) and that G -mers, when formed, are immediately broken up into monomers and redistributed ($f_G = 0$).⁶

The dissociation of a cluster, in this model system, is presumed to be activated by collisions with solvent molecules. The j -mer dissociation rate therefore can be written as $b_j f_j$, where b_j is an intrinsic (independent of solvent and reactant concentrations) unimolecular rate constant. The coalescence rate Φ_{j-1} of monomers and $j-1$ -mers is more complicated, however. The coalescence process is controlled by the diffusion of the reactants through the solvent; in such cases Φ_{j-1} can have a time dependence that defies categorization in terms of a single order of reaction. On the other hand, it is often the case that the time scale associated with diffusion-related transients is much shorter than the time lag of the total reaction scheme. Assuming this to be so for the model system discussed here Φ_{j-1} can be approximated (see the Appendix) by the relatively simple form

$$\Phi_{j-1} = k_{j-1} f_1 f_{j-1} + (1 - \epsilon_{j-1}) b_j f_j. \quad (2)$$

The right-hand side of Eq. (2) is a superposition of a bimolecular rate term and a unimolecular rate term. In the absence of dissociation Φ_{j-1} would be purely bimolecular in nature. The unimolecular contribution arises from the high degree of spatial correlation between a monomer and a $j-1$ -mer which have been freshly produced by the dissociation of a j -mer; the prompt recombination of such monomers and clusters is a *first-not second*-order reaction. In the expression for Φ_{j-1} given above, the rate constant k_{j-1} and the factor $(1 - \epsilon_{j-1})$ (which, incidentally, can be interpreted as the probability that a monomer, $j-1$ -mer dissociation pair will recombine) are steady state values which mirror the presence of spatial correlations in the steady state. In consequence of Eq. (2) I_j , which, according to its definition, is $\Phi_{j-1} - b_j f_j$, can also be written

$$I_j = k_{j-1} f_1 f_{j-1} - \epsilon_{j-1} b_j f_j. \quad (3)$$

Now, as indicated in the Introduction the rate constant b_j can be eliminated from the discussion by appealing to a convenient reference state of the model system. Consider a state of the system in which all reactions are in equilibrium. Assume that in this state the concentration of monomers is constrained to be f_1 . Further, assume that the reactants are distributed completely randomly throughout the sample, i.e., that there are no spatial correlations among the reactants. Denote by $\tilde{n}_j$ the sample-average concentration of j -mers

in this state. Since each reaction is assumed to be in equilibrium, detailed balance yields the relation

$$b_j = \tilde{k}_{j-1} f_1 \tilde{n}_{j-1} / \tilde{n}_j, \quad (4)$$

where b_j is, as before, the intrinsic j -mer dissociation rate constant and $\tilde{k}_{j-1}$ is a bimolecular rate constant which reflects the spatial uniformity of the distribution of monomers about each cluster in the reference state. Clearly, the constants k_{j-1} and $\tilde{k}_{j-1}$ will, in general, be different. For the moment write k_{j-1} as $\tilde{k}_{j-1} / \Delta_{j-1}$; an explicit expression for Δ_{j-1} is derived in the Appendix. This form for k_{j-1} , in conjunction with Eq. (4), allows Eq. (3) to be recast as

$$I_j = \tilde{k}_{j-1} f_1 \tilde{n}_{j-1} \left(\frac{f_{j-1}}{\tilde{n}_{j-1}} - \Delta_{j-1} \epsilon_{j-1} \frac{f_j}{\tilde{n}_j} \right). \quad (5)$$

The classical approximation alluded to in the Introduction makes the tacit assumption that all the Δ 's and ϵ 's introduced above are equal to unity. A particularly simple and useful form for the current is thereby obtained which greatly facilitates the determination of nucleation rates, steady state concentrations, and time lags. Equation (5) can be converted into an analogous form by multiplying the right-hand side by $1 = Q_{j-1}/Q_{j-1}$, where

$$Q_{j-1} = \prod_{i=1}^{j-2} \Delta_i \epsilon_i \quad (6)$$

(note that $Q_1 \equiv 1$). If a new concentration distribution

$$n_j = \tilde{n}_j / Q_j \quad (7)$$

is then defined, Eq. (5) becomes

$$I_j = k_{j-1} f_1 n_{j-1} \left(\frac{f_{j-1}}{n_{j-1}} - \frac{f_j}{n_j} \right), \quad (8)$$

which is formally exactly the same as that given by the classical approach.

The reader may be interested to note, in passing, the physical significance of the distribution n_j . Substitution of Eq. (7) into (4) gives rise to the relation

$$\epsilon_{j-1} b_j = k_{j-1} f_1 n_{j-1} / n_j. \quad (9)$$

Equation (9) is just what one would expect as a condition for equilibrium in a reference state if the same spatial correlations as exist in the steady state were somehow maintained. Moreover, thermodynamics considerations allow $\tilde{n}_j$ to be rendered as⁷

$$\tilde{n}_j = Y_j \exp(-W_j/k_B T), \quad (10)$$

where the pre-exponential Y_j describes the kinetic energy (if any) associated with the cluster's center of mass, W_j is the reversible work necessary to construct a bound j -mer from j unbound monomers (all "in solution"), and k_B is Boltzmann's constant. Using Eq. (10) n_j can be reexpressed as $Y_j \exp(-W'_j/k_B T)$, provided W'_j is defined as $W_j + k_B T \ln Q_j$. Clearly, the term $k_B T \ln Q_j$ plays the role of the reversible work required to maintain the spatial nonuniformities appropriate to the steady state around each j -mer. The concentrations n_j can, therefore, be interpreted as appropriate to a new constrained equilibrium state in which the rate constants are truly the same as those in the steady state.

In any event, once Eq. (8) has been established then all of the standard techniques of the older nucleation theory apply. It is sufficient to list the principal results without repeating details described elsewhere. In the steady state all currents I_j take on a common value I —the steady state nucleation rate. This quantity is given by⁶

$$I = \left[\sum_{i=1}^{G-1} (k_i f_i n_i)^{-1} \right]^{-1}. \quad (11)$$

The steady state cluster concentrations $\hat{f}_j$ are found to be⁶

$$\hat{f}_j = n_j I \sum_{i=j}^{G-1} (k_i f_i n_i)^{-1}. \quad (12)$$

Equations (11) and (12) complete step (ii) in the algorithm outlined in the Introduction of this paper. The final result [step (iii) of the algorithm]—and the central quantity of the problem under investigation—is the time lag L . The Daynes' time lag discussed by Frisch⁸⁻¹¹ is the amount of time required before I_G becomes approximately I . This version of L can be written in terms of previously defined quantities and the initial j -mer distribution $f_j(0)$ as

$$L = \sum_{i=1}^{G-1} (k_i f_i n_i)^{-1} \sum_{j=i+1}^{G-1} [\hat{f}_j - f_j(0)]. \quad (13)$$

III. TIME LAG IN A MISCIBILITY GAP EXPERIMENT

The arguments presented in the previous section are quite general. Detailed specification of the parameters Δ_j , ϵ_j , Y_j , and W_j allows one to utilize the results (11)–(13) for the description of diffusion-controlled nucleation in essentially any system where the basic premises set down at the outset of Sec. II seem reasonable. In this section the example of the phase separation in a liquid binary mixture is treated.

Assume that the fractional composition of one component of the mixture is very much larger than the other. The major component can be treated as solvent, the minor component as reactant. Assume that initially (the moment of undercooling in such experiments) only single molecules of the reactant are present, i.e., $f_1(0) = f_1$, while $f_j(0) = 0$ for $j > 1$. To compare the predictions of this paper with classical predictions it is convenient to approximate the sums in Eqs. (11)–(13) by continuous integrals. To do this first find the classical critical nucleus size j^* by setting $\partial W_j / \partial j$ equal to zero. Choose $G > j^*$ ($G \approx 2j^*$ should do); then by expanding $\exp(-W_j/k_B T)$ about j^* and carrying out a well-known approximation scheme⁶ Eq. (11) can be rewritten as

$$I = k_j f_j n_j Z_{j^*}, \quad (14)$$

where $Z_j = (-\partial^2 W_j / \partial j^2)^{1/2} (2\pi k_B T)^{-1/2}$. Similarly, L can be approximated by

$$L = I^{-1} \int_{j=j^*}^G \hat{f}_j dj, \quad (15)$$

which, to first order at least, is¹⁰⁻¹²

$$L = (G - j^*) \hat{f}_{j^*} / I = (G - j^*)^2 (k_{j^*} f_1)^{-1}. \quad (16)$$

Relations (14) and (16) allow a simple comparison between the theory presented here and the classical theory. Inasmuch as the classical nucleation rate $\bar{I}$ is given by $\bar{k}_j f_j n_j Z_{j^*}$, Eq. (14) shows that

$$I/\bar{I} = (k_j n_j) / (\bar{k}_j n_j) = \epsilon_j / Q_{j^*+1}. \quad (17)$$

A similar argument using Eq. (16) provides

$$L/\bar{L} = \bar{k}_j / k_j = \Delta_{j^*}. \quad (18)$$

The relations (A11) and (A13) for Δ_j and ϵ_j , respectively, allow the nature of the ratios (17) and (18) to be revealed. The classical rate constant $\bar{k}_j$ for a liquid system can be expressed as¹³

$$\bar{k}_j = \pi R_j^2 \nu (n_s R_0^2)^{-1}, \quad (19)$$

where R_j is the monomer, j -mer collision radius, R_0 is the monomer radius, n_s is the solvent concentration, and ν is the effective vibrational frequency of molecules in the liquid (including the activation energy for diffusion). The effective mean free path of Eq. (A7)—which is necessary for the evaluation of Δ_j and ϵ_j —can be determined by setting $\nu_j \lambda_j = \nu (n_s R_0^2)^{-1}$ and by requiring that $\nu_j \lambda_j^2/3$ equal the monomer, cluster mutual diffusivity in the given solvent. In a liquid the diffusivity of a cluster falls off as the reciprocal of the cluster radius so that it is reasonable to write $D_j = D_0(1 + j^{-1/3})$, where D_0 is the monomer diffusivity. As a result λ_j can be written as

$$\lambda_j = 3D_0 n_s R_0^2 (1 + j^{-1/3}) / \nu. \quad (20)$$

The studies of Sundquist and Oriani² and of Heady and Cahn³ on the liquid binary mixture C_7F_{14} in C_7H_{14} yield data useful for the conclusion of the discussion of this section. These experiments were performed at temperatures near the critical point for this system and are characterized by critical nuclei containing thousands of molecules. It is unlikely that the model described in Sec. II is appropriate for an exact analysis of these experiments since the reactant is present in relatively high concentrations ($\sim 20\%$) and the large clusters are probably diffuse. Nonetheless, the numbers cited below are indicative of the behavior of the ratios (17) and (18).

For the sake of specificity take as a typical run the data of Heady and Cahn for $T = 313^\circ \text{K}$. The concentration of solvent at this temperature is $3.67 \times 10^{21} \text{ cm}^{-3}$, while a critical embryo contains about 2110 molecules. Let the monomer diffusivity be $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, the monomer radius be $2 \times 10^{-8} \text{ cm}$, and the frequency ν be 10^9 sec^{-1} . Furthermore, choose $R_j = R_0(1 + j^{1/3})$. Then, values of the quantity X_j in Eq. (A12) range from $X_1 = 0.45$ to $X_{2110} = 5.8$. Corresponding to these are Δ_j values between 1.2 and 5.1, and $\Delta_j \epsilon_j$ values between 1.03 and 1.11. A typical value of the latter product is about 1.06, so that $Q_{j^*+1} \sim (1.06)^{2110}$, which implies that $I/\bar{I} \sim 10^{-60}$ (the data of Heady and Cahn suggest an observed nucleation rate about 25 orders of magnitude less than $\bar{I}$ for this run). On the other hand, $L/\bar{L}$ is just 5.1.

IV. CONCLUSION

Spatial correlations associated with dense solvents can impede nucleation in ways not accounted for in the

classical theory. In such systems the classical theory overestimates the nucleation rate and underestimates the time lag. Where critical nuclei are very large the error in the predicted nucleation rate can be enormous, while the discrepancy in the time lag is probably never much more than a factor of 10.

APPENDIX

To treat the significant spatial correlations in the system described in Sec. II it is sufficient (because of the assumed dilution of the reactant and the pairwise nature of the coalescence reaction) to define a mean pair concentration p_j such that¹⁴ $p_j(r, t)$ = the average number of monomer, j -mer pairs in the sample, at time t , with pair member separation r , per unit squared volume. The concentration p_j satisfies a diffusion-reaction equation of the form⁵

$$\partial_t p_j = \frac{1}{r^2} \partial_r (r^2 D_j \partial_r p_j) + b_{j+1} f_{j+1} \eta_j(r), \quad (\text{A1})$$

where D_j is the sum of the empirically determined monomer and j -mer diffusivities (in the specified solvent) and each cluster is assumed to have isotropic surroundings. The quantity η_j in Eq. (A1) describes the distribution of separations that a j -mer and monomer, produced by the dissociation of a $j+1$ -mer, can achieve at the instant their momenta become completely uncorrelated, i.e., $4\pi r^2 \eta_j dr$ is the probability of finding such a pair with separation between r and $r+dr$ immediately following the $j+1$ -mer dissociation. Because the reactant is assumed to be widely dispersed in the host medium, no other source or sink terms in Eq. (A1) need be considered; for the case of a highly concentrated reactant, however, competition among the clusters for available monomers would have to be taken into account.¹⁵

The coalescence rate Φ_j is determined by the gradient of p_j ; in other words

$$\Phi_j = 4\pi R_j^2 D_j \partial_r p_j(R_j), \quad (\text{A2})$$

where R_j is the monomer, j -mer collision radius. Note that R_j can be written as $R_0(1+j^{1/3})$, where R_0 is the radius of a monomer. To determine Φ_j Eq. (A1) must be solved subject to suitable boundary conditions. One condition is that for large separations p_j should take on the sample-average value

$$p_j(\infty, t) = f_1 f_j. \quad (\text{A3})$$

A second condition should describe the behavior of p_j over the reaction sphere of radius R_j . In many cases of interest the effective mean free path of the reactants will be comparable to or greater than R_j . In this instance a technique due to Frisch and Collins,¹⁶ modified to incorporate the motion of both the monomer and the cluster, can be employed to find a second boundary condition. Start by assuming the cluster is fixed and surrounded by mobile monomers able to jump every ν_j^{-1} seconds some effective distance λ_j before collision (ν_j and λ_j must be selected so that the motion of the cluster is included; see below). Denote by $\psi_j(r)$ the probability that a monomer a distance r from the center of the j -mer will fall, in its next jump, on a sphere or radius

R_j surrounding the cluster; obviously, $\psi_j(r) = 0$ for $r > R_j + \lambda_j$. Then Φ_j can be rewritten as:¹⁷

$$\Phi_j = 4\pi \nu_j \int_{r=R_j}^{R_j+\lambda_j} p_j \psi_j r^2 dr, \quad (\text{A4})$$

which, when equated to Eq. (A2), produces the boundary condition

$$\partial_r p_j(R_j) = (\nu_j/D_j R_j^2) \int_{r=R_j}^{R_j+\lambda_j} p_j \psi_j r^2 dr. \quad (\text{A5})$$

The probability ψ_j can be determined as follows: Imagine a sphere of some as yet unspecified radius about the monomer; provided the radius is chosen properly ψ_j is just the fraction of the surface area of this sphere intersecting the sphere of radius R_j about the j -mer. But what radius should be assigned to the monomer jump sphere? If $r > (R_j^2 + \lambda_j^2)^{1/2}$, then this radius should be a full λ_j . If, however, $r < (R_j^2 + \lambda_j^2)^{1/2}$, then the radius should only be $(r^2 - R_j^2)^{1/2}$, because the longest monomer flight under these circumstances will terminate on the reaction sphere tangentially. Thus, ψ_j has the form

$$\psi_j(r) = [1 - (r^2 + \lambda_j^2 - R_j^2)/2r\lambda_j]/2 \quad (\text{A6a})$$

if $R_j + \lambda_j \geq r \geq (R_j^2 + \lambda_j^2)^{1/2}$, and

$$\psi_j(r) = [1 - (r^2 - R_j^2)^{1/2}/r]/2 \quad (\text{A6b})$$

if $(R_j^2 + \lambda_j^2)^{1/2} \geq r \geq R_j$.

In the classical approach $\tilde{p}_j = f_1 f_j$ for all r , so that the classical coalescence rate $\tilde{\Phi}_j$ is [after the integration in Eq. (A4)]

$$\tilde{\Phi}_j = \pi R_j^2 \nu_j \lambda_j f_1 f_j = \tilde{k}_j f_1 f_j. \quad (\text{A7})$$

The steady state solution of Eq. (A1) subject to the conditions (A3) and (A5) can be effected once η_j is specified. For simplicity η_j can be approximated by the delta shell distribution¹⁸

$$\eta_j = \delta(r - R_j - \lambda_j/2)/4\pi r^2. \quad (\text{A8})$$

The steady state coalescence rate $\hat{\Phi}_j$ is subsequently found to be

$$\hat{\Phi}_j = k_j f_1 \hat{f}_j + (1 - \epsilon_j) b_{j+1} \hat{f}_{j+1}, \quad (\text{A9})$$

where

$$k_j = \tilde{k}_j/\Delta_j, \quad (\text{A10})$$

$$\Delta_j = 1 + (\nu_j \lambda_j^2/3D_j) \left\{ 3X_j^2 \ln \left[\frac{1 + (1 + X_j^2)^{1/2}}{X_j} \right] + 2X_j^3 + (1 - 2X_j^2)(1 + X_j^2)^{1/2} - 1 \right\} / 4, \quad (\text{A11})$$

$$X_j = R_j/\lambda_j, \quad (\text{A12})$$

and

$$\epsilon_j = 1 - (3X_j/4\Delta_j)(\nu_j \lambda_j^2/3D_j)2X_j/(1 + 2X_j). \quad (\text{A13})$$

In order to be able to use the sequence of equations listed above the effective frequency ν_j and effective jump length λ_j must be evaluated. The arguments given in Sec. III should be applicable to any system (of course, $\tilde{k}_j$ will vary according to the phase of the solvent). Note, also, that $\Delta_j \approx \nu_j \lambda_j R_j/4D_j$ for $R_j \gg \lambda_j$ so that k_j approaches $4\pi R_j D_j$, the usual diffusion-controlled

bimolecular rate constant, as X_j becomes large. Condition (A5) is, therefore, very general.

The full time dependence of Φ_j is, generally much more difficult to obtain than is Eq. (A9). Diffusional transients will last for times on the order of R_j^2/D_j . Since these times are often negligible compared with the overall course of the reactions involved (for the system described in Sec. III $R_j^2/D_j \sim 10^{-9}$ sec compared with $L \sim 10^{-3}$ sec), it may be assumed that Φ_j rapidly achieves the form displayed in Eq. (A9), a sum of a bimolecular term and a unimolecular term, and that the rate constants are the steady state values k_j and $(1 - \epsilon_j)b_{j+1}$, respectively.

¹An excellent discussion of the classical theory of vapor condensation can be found in F. F. Abraham, *Homogeneous Nucleation Theory* (Academic, New York, 1974).

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¹¹For other definitions and discussion of time lags see Ref. 1, Chap. 5.

¹²Different approximations give slightly different forms for L ; the important dependence on spatial correlations is contained solely in k_{j*}^1 , however.

¹³This expression is essentially that given by J. Lothe and G. M. Pound, in *Nucleation*, edited by A. C. Zettlemoyer (Dekker, New York, 1969), p. 115; the n_s in the denominator reflects the fact that of all the molecules surrounding the cluster only f_1/n_s of them are reactant monomers. Another slightly different form can be found in E. R. Buckle, *Proc. R. Soc. (London) Ser. A* **261**, 189 (1961).

¹⁴See, for example, T. R. Waite, *Phys. Rev.* **107**, 463 (1957).

¹⁵See Ref. 5 for a discussion of competition terms.

¹⁶H. L. Frisch and F. C. Collins, *J. Chem. Phys.* **20**, 1797 (1952).

¹⁷The "sticking probability" is chosen to be unity, for simplicity.

¹⁸The actual distribution will be smooth, of course; it will be small for $r \approx R_j$ (few solvent molecules immediately adjacent to the cluster) and for $r > R_j + \lambda_j$, and will be peaked somewhere between R_j and $R_j + \lambda_j$.