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Nucleation in disordered systems

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A theory of nucleation is proposed for materials with static disorder, such as glasses and doped crystals. Such disorder makes the barriers to nucleation (W) different in different local regions of the system. We develop an optimum fluctuation method, based on the Cahn-Hilliard approach, to find the probability distribution of barriers $g(W)$. The distribution reaches its maximum at $W=\langle W\rangle$, determined by the average parameters of the system, and decays exponentially for both $W<\langle W\rangle$ and $W>\langle W\rangle$. The particular shape of $g(W)$ depends on the relationship between the distance over which the disorder is correlated and the radius of the critical nucleus. In the steady-state regime the nucleation rate is determined by an optimum barrier $W_{\mathrm{opt}}=W_{\mathrm{opt}}(T)<\langle W\rangle$ resulting from the competition between the exponential increase in the nucleation rate $\exp(-W/kT)$ and the exponential decrease in $g(W)$. Associated with $g(W)$ is also the probability distribution of nucleation rates $I=I_0\exp(-W/kT)$. Because of the latter, the nucleus concentration is nonlinear in time and exhibits an S-shaped transient nucleation. [S0163-1829(96)03438-8]

I. INTRODUCTION

As is well known, nucleation of a second phase occurs via appropriate fluctuations that allow the system to surmount the thermodynamic barrier between the two phases. The fluctuation exhibits a critical nonuniformity that develops spontaneously into a stable particle. The barrier to nucleation (W) is the minimum work needed to create this critical nonuniformity. In the capillarity model[1–4] the nonuniform region is assumed to have a sharp boundary, and the barrier originates from the surface energy. Since the early Cahn-Hilliard density functional approach,[5] modern theories (see the review in Ref. 6) are free of the postulate of a sharp boundary but still consider critical fluctuations that are well localized in space.

It is important that the original phase is assumed to be homogeneous in the framework of the above approaches. However, this assumption fails for some structures, such as glasses, amorphous films, crystals containing imperfections, or amorphous solids, which are inhomogeneous systems. Thus, in doped crystals the local impurity concentration fluctuates in space, while in amorphous solids the microscopic atomic parameters (valence angles, bond lengths, etc.) fluctuate between different local regions. This is schematically illustrated in Fig. 1. Associated with these fluctuations must be local fluctuations in the parameters determining the barrier to nucleation. Supposing that the original phase is inhomogeneous, these parameters will be random quantities characterized by their average values and dispersions. The standard nucleation theory applies only if the dispersions are set to zero. This raises the question: What are the possible deviations from standard nucleation theory results due to fluctuations in material parameters?

It is worth noting that the average parameters of corresponding disordered and ordered systems are different. This difference has nothing to do with the above question and can be taken into account by renormalizing the parameters in the standard nucleation theory without making allowance for local fluctuations in those parameters. In what follows the average parameters governing the nucleation in a disordered system are considered as given and the emphasis is on a description of the fluctuation-induced effects.

That disorder influences the nucleation rate significantly can be concluded on experimental grounds. A large body of data shows that adding a small concentration of impurities can change the second-phase nucleation rate in a crystal dra-

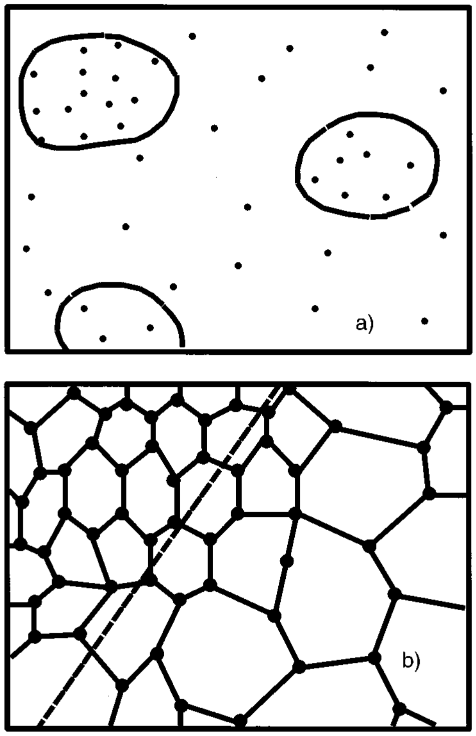

FIG. 1. The nucleation barrier varies between different local regions. (a) In the case of doped crystals the barriers are different in the regions depicted because of space fluctuations in impurity concentration. (b) In the case of amorphous solids local fluctuations in microscopic structural parameters make crystal nucleation barriers different in the two regions separated by the dashed line.

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matically, causing it to increase or to decrease by many orders of magnitude depending on which element is added.[7–10] This effect was qualitatively attributed to the change in the diffusion coefficients of alloying elements and/or in the energy of the boundary between a precipitate and matrix. Although the possibility of changing the nucleation by means of small dopings has already found practical uses, the underlying mechanisms remain unexplored. Another case in which small dopings are known to affect structural transformations drastically is the nucleation of vacancy voids in materials subjected to radiation.[11]

Not less puzzling are the experimental results on crystal nucleation in glasses (both nonmetallic and metallic) and amorphous films. The crystallization can be either polymorphic (without a change in chemical composition, such as crystal nucleation in chalcogenide glasses) or nonpolymorphic [such as crystal nucleation in $(\mathrm{SiO}_2)_x(\mathrm{Li}_2\mathrm{O})_{1-x}$ glass]. The conclusion has been drawn that the steady-state crystal nucleation rates calculated by theory are many orders of magnitude smaller than the experimental values[12–17] in inorganic glasses. Even though the theory is consistent with the observed temperature dependences of nucleation rates, the corresponding absolute values are in some cases 20 orders of magnitude smaller than the measured quantities. Besides, the nucleation rates in glasses are nonmonotonic in time, and the nucleus concentration exhibits an S shape. Note that crystal nucleation in glasses has also found practical applications. In particular, it is used to create I-VII or II-VI semiconductor microcrystals [say, CuBr and Cd(S)Se] in insulating glasses.[18–23] These composites containing ‘‘quantum dots’’ are materials of great promise in modern electronics.

It is the main purpose of this work to discuss the role of disorder in nucleation processes. The idea is that there are some local favorable inhomogeneities in randomly disordered media, which effectively decrease the thermodynamic nucleation barrier and thus increase nucleation rates exponentially. We find the probability distribution for the nucleation barriers in a randomly disordered system and use that distribution to calculate both the effective steady-state nucleation rate and nucleus concentration as a function of time. The results will be shown to depend both on the correlation range of the disorder and on its amplitude.

In its simple form our idea is illustrated in Fig. 2. Despite a rapid (exponential) decrease in the barrier probability distribution in the region of small barriers, this region is still very important since the probability of nucleation increases exponentially as the barrier decreases. The competition of the above exponential factors results in an optimum barrier W_{opt} that combines a relatively high nucleation rate with a not extremelly small probability of its realization and thus provides the maximum partial nucleation rate. Because this barrier is smaller than the average one and because it depends on temperature, the observed nucleation rate will be exponentially larger than the one corresponding to the average barrier and predicted by classical nucleation theory and will have different temperature dependence.

Note that the above examples imply that the nucleation occurs via the diffusion of some mobile component below the melting point of a matrix. In this sense the fluctuations dealt with below are of a static nature: Their lifetimes are much longer than the characteristic time needed for a nucleus to add an additional molecule. That is why the nucleation rates are expected to be different in different local regions of a disordered material. (Note that the above arguments do not apply to nucleation in flexible, liquidlike systems where fluctuations are short-lived.)

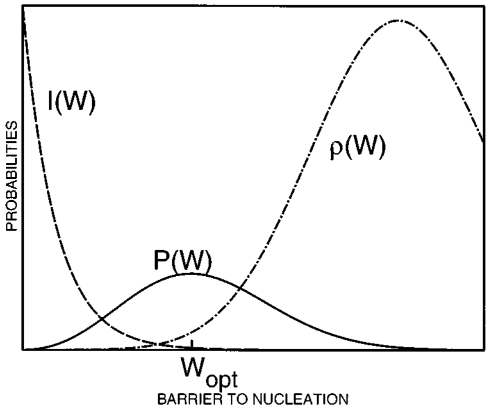

FIG. 2. Probability of nucleation, $I \propto \exp(-W/kT)$, probability distribution for nucleation barriers, $\rho(W)$, and partial nucleation rate $P(W) \propto \rho(W) I(W)$. The optimum barrier $W_{\mathrm{opt}}(T)$ corresponds to a maximum of $P(W)$.

Two theoretical papers have been published regarding nucleation in disordered solids. Harrowell and Oxtoby[24] considered nucleation in glasses and incorporated a phenomenological concept of local nucleation times and their distribution in a glass. Although restricted to the case of the simplest two-mode distribution, the approach in Ref. 24 enables one to qualitatively explain the major deviations of nucleation kinetics in glasses from that in homogeneous systems. Karpov[25] considered the effect of disorder on nucleation in the capillarity approximation, which is ill controllable as applied to the problem. In particular, while the ideas of the probability distribution of nucleation barriers and of an optimum barrier put forward in Ref. 25 are adequate and are retained in what follows, these ideas were implemented in Ref. 25 by considering (rather arbitrarily) a layer-by-layer nucleus growth in a random matrix. Such uncontrolled use of the capillarity approximation led to a distribution function that differs from that found in the present work by means of a consistent density-functional approach.

In this paper the Cahn-Hilliard approach to nucleation is extended to the case of disordered media. To allow for static fluctuations we consider the free energy density to be a random function of coordinate. The barrier to nucleation will then be a functional of the random function. To describe the probability distribution for such a functional we use the approach known as the optimum fluctuation method in the theory of disordered systems, where it enables one to describe the density of states in band tails. We extend that method to the problem of phase transitions in random media and find the nucleation barrier distribution function for the limiting cases of uncorrelated and strongly correlated disorder. We then use that function to determine the optimum barrier corresponding to a given temperature and to calculate the nucleus concentration as a function of time.

II. OPTIMUM FLUCTUATION METHOD

The optimum fluctuation method has been developed by Lifshitz,[26] Halperin and Lax,[27] and Zittarz and Langer[28] to calculate electron band tails in disordered systems (reviews are given in Refs. 29 and 30), a problem that has much in common with that under consideration here. In the problem of band tails it is assumed that the electron is in a random potential caused by randomly distributed impurity atoms or structural disorder in a semiconductor. Some local configurations of the disorder cause fluctuation potential wells strong enough to localize the electron. Because of that, localized state tails appear in the mobility gap of a semiconductor. The deeper the state in the mobility gap, the stronger must be the corresponding fluctuation. Since the probability of a fluctuation decreases exponentially with its strength, the density of states in a band tail decays exponentially with the energy E measured from the mobility edge, $g(E) = g_0\exp[-S(E)]$. The optimum fluctuation method was used to calculate the exponent $S(E)$ and thus to establish the probability distribution for the functional E containing a random function.

It was assumed in the framework of the method that a state of any given energy is dominated by a corresponding particular shape of the potential fluctuation, and that large deviations from this shape are unlikely to occur. The reasoning behind this assumption is that fluctuations much stronger than the optimal one are unlikely because the probability of a fluctuation decreases exponentially with an increase in strength; on the other hand, fluctuations much narrower than the optimal one become unlikely because it is then difficult to overcome the kinetic energy resulting from localization. Optimum fluctuations are believed to give the main contribution to the density of states.

Much as in the band-tail problem, we assume in what follows that the nucleation barrier of any given energy in a disordered system is dominated by a corresponding optimum shape of a disorder fluctuation. Fluctuations much stronger than the optimal one are unlikely because the probability of a fluctuation decreases exponentially with an increase in strength; fluctuations much narrower than the optimal one become unlikely because it is then difficult to overcome the surface free energy resulting from the nucleation.

In fact, the problem of nucleation in disordered systems fits the optimum fluctuation method even better than the original band-tail problem. The electronic states in the near proximity of the gap edge have very large radii and thus overlap. Since the optimum fluctuation method is restricted to an isolated (nonoverlapping) fluctuation, it does not cover the range of energies near the band edges. In contrast, the nucleation process never ends up with enough of the second phase to make nuclei overlap, and thus the optimum fluctuation concept is applicable without restriction.

To illustrate the approach we are going to implement, let us for simplicity consider the capillarity model and assume that its parameters depend linearly on some impurity concentration c that fluctuates in space. In the spirit of the sharp boundary approximation we consider a uniform spherical fluctuation of amplitude δc and radius R within a nucleus (a kind of ‘‘impurity nucleus’’ embedded in the original one). This will change the nucleus energy by

$$\delta W = a_1 \delta c R^3 + a_2 \delta c R^2, \tag{1}$$

where the first and second terms represent the bulk and interface contributions, repectively, and a_1 and a_2 are material parameters. In the absence of spatial correlations the probability of finding a fluctuation δc in the region of the volume R^3 is given by Gaussian statistics,

$$P(\delta c) \sim \exp - \left[\frac{(\delta c)^2 R^3}{2\bar{c}} \right] \equiv \exp(-S), \tag{2}$$

provided that the average number of impurity atoms in the fluctuation is large. The most probable, optimum, fluctuation corresponds to the minimum of the exponent S in Eq. (2). This minimum must be found with respect to δc and R under an additional condition that they satisfy Eq. (1). On expressing δc from Eq. (1) the exponent to optimize becomes

$$S = \frac{(\delta W)^2}{2R(a_1 R + a_2)^2}.$$

From this we see that the barrier statistics is Gausssian and that the optimum fluctuation, if any, is characterized its radius and amplitude

$$R = -\frac{a_2}{3a_1} \quad \text{and} \quad \delta c = \frac{\delta W}{a_1 R^3 + a_2 R^2}.$$

Although the above example illustrates the optimum fluctuation method, the sharp boundary approximation we used remains ill controlled. This approximation is known to apply near the binodal, which is a particular case among those considered below.

To implement the above idea we use the Cahn-Hilliard approach, with the free energy functional

$$F = \int [\phi(c) + \kappa(\nabla c)^2] d\mathbf{r}, \tag{3}$$

where κ is a constant and ϕ is the local change in the free energy density due to the deviation $c(\mathbf{r})$ of the order parameter $n(\mathbf{r})$ from its average value $\langle n \rangle$. Although the parameter n stands for the solute concentration in the original Cahn-Hilliard work,[5] its meaning can be extended. For the case of crystallization n can be understood as a material density.[6] In both cases the conservation of material law implies

$$\int c(\mathbf{r}) d\mathbf{r} = 0. \tag{4}$$

The change ϕ can be expressed as

$$\phi = f(\langle n \rangle + c) - f(\langle n \rangle) - \frac{\partial f(\langle n \rangle)}{\partial \langle n \rangle} c, \tag{5}$$

where $f(n)$ is the free energy density corresponding to the order parameter n and the last term on the right-hand side accounts for the conservation condition in Eq. (4).

In accordance with Cahn-Hilliard, an initially unstable fluctuation $c(\mathbf{r})$ grows into a stable one by overcoming a free energy barrier, the top of which is a saddle point, and the fluctuation becomes a critical nucleus at that point. Since the system is in (unstable) equilibrium at a saddle point, the free energy F in Eq. (3) must be stationary; that is, its variational derivative must be zero:

$$\frac{\delta F}{\delta c}=0. \tag{6}$$

The corresponding barrier to nucleation is

$$W=F[\phi_0]\equiv\int[\phi_0+\kappa(\nabla c_0)^2]d\mathbf{r}, \tag{7}$$

where $c_0(\mathbf{r})$ and $\phi_0\equiv\phi(c_0)$ are determined by Eq. (6).

Because of static fluctuations of material parameters in a disordered system, in Eq. (3) the function $\phi(c)$ and the parameter κ will change between different local regions. To a first approximation one can neglect the fluctuations in κ. The reasoning behind this approximation is that in the vicinity of a phase transition the function $\phi(c)$ has a certain shape and even small deviations from that shape may affect the transition significantly. In contrast, small variations in κ would cause a correspondingly small effect.

To describe the effect of fluctuations on the function $\phi(c)$ we note that the shape of the latter is known to depend on material parameters, say, ξ_i, that are normally considered fixed while the order parameter c is allowed to change. As an example, we mention the Landau-Ginzburg approximation [see also Eq. (23) below] for which ξ_i are represented by the three coefficients at c^2, c^3, and c^4. In their turn, the parameters ξ_i depend on temperature, pressure, deformations, etc. It is then natural to consider these parameters random quantities varying between different local regions that possess different structures in a random system. We thus consider $\xi_i\equiv\xi_i(\mathbf{r})$ to be random functions of coordinates. We recall that a phase transition is described by a qualitative change in the shape of $\phi(c)$ (say, from a single-well to a double-well shape). This change is typically achieved by small variations in only one (critical) parameter of the set ξ_i, while all others are considered constant (such as the coefficient of c^2 in the Landau-Ginzburg theory). With that in mind, we assume that fluctuations of only one of the parameters ξ_i is of importance. In this one-parameter approximation we put

$$\phi(c)=\overline{\phi(c)}+\xi(\mathbf{r})\phi_1(c), \tag{8}$$

where $\overline{\phi}$ stands for the function $\phi(c)$ averaged over all possible realizations and $\xi\equiv\xi(\mathbf{r})$ is a random quantity. The above is the simplest conceivable choice of free energy density that contains only one random parameter.

Substituting Eq. (8) into Eq. (3) gives

$$F=\int[\overline{\phi(c)}+\kappa(\nabla c)^2]d\mathbf{r}+u, \tag{9}$$

with

$$u=\int\xi(\mathbf{r})\phi_1[c(\mathbf{r})]d\mathbf{r}$$

being a random quantity. One limiting case to consider is the situation in which the random quantity u in Eq. (9) is the sum of a large number of random contributions and, in accordance with the central limit theorem, obeys Gaussian statistics,

$$\rho(u)=\exp\left(-\frac{u^2}{2\sigma}\right)\equiv\exp(-S), \tag{10}$$

with dispersion

$$\sigma\equiv\langle u^2\rangle=\int\int d\mathbf{r}d\mathbf{r}'A(\mathbf{r}-\mathbf{r}')\phi_1[c(\mathbf{r})]\phi_1[c(\mathbf{r}')]. \tag{11}$$

Here the kernel A is the pair correlation function of the disorder,

$$A(\mathbf{r}-\mathbf{r}')=\langle\xi(\mathbf{r})\xi(\mathbf{r}')\rangle.$$

As long as Gaussian statistics applies, this function is the only characteristic of the disorder. Note that Eq. (11) implies the averaging to be taken over the disorder configurations at a given (although not specified) function $\phi_1(\mathbf{r})$ whose particular optimum shape must be determined in what follows. A second limiting case (Poisson statistics) is considered in Sec. IV below.

The most probable fluctuation corresponds to the minimum of the exponent in Eq. (10), that is,

$$\frac{\delta S}{\delta c}=\frac{\delta S}{\delta u}=0.$$

The latter equations determine a conditional minimum of the functional S provided that the free energy F in Eq. (9) is an extremum, in accordance with the Cahn-Hilliard approach. Optimizing the probability exponent S under the additional condition $\delta F=0$ is tantamount to finding the absolute extremum of the functional

$$\Phi=\frac{u^2}{2\sigma}+\lambda F, \tag{12}$$

where λ is the undetermined Lagrange multiplier. Optimizing Φ over u and c gives, respectively,

$$u=-\lambda\sigma \tag{13}$$

and

$$-2\kappa\nabla^2c(\mathbf{r})+\frac{\partial\overline{\phi(\mathbf{r})}}{\partial c(\mathbf{r})}-\lambda\left[\int d\mathbf{r}'A(\mathbf{r}-\mathbf{r}')\phi_1(\mathbf{r}')\right]\frac{\partial\phi_1(\mathbf{r})}{\partial c(\mathbf{r})}=0. \tag{14}$$

The solution of Eq. (14) determines the optimum fluctuation $c_0(\mathbf{r})$. Note that Eq. (14) can be equally represented in the form $\delta J=0$ with the functional

$$J=\int d\mathbf{r}\left\{\kappa(\nabla c)^2+\overline{\phi(c)}-\frac{\lambda}{2}\int d\mathbf{r}'A(\mathbf{r}-\mathbf{r}')\phi_1[c(\mathbf{r})]\phi_1[c(\mathbf{r}')]\right\}, \tag{15}$$

which is convenient to use for the direct variational procedure. The Lagrange multiplier λ is determined from the condition for the nucleation barrier height,

$$W=\int d\mathbf{r}\left\{\kappa(\nabla c_0)^2+\overline{\phi(c_0)}-\lambda\int d\mathbf{r}'A(\mathbf{r}-\mathbf{r}')\phi_1[c_0(\mathbf{r})]\phi_1[c_0(\mathbf{r}')]\right\}. \tag{16}$$

Once $c_0(\mathbf{r})$ and λ have been determined, the probability exponent is given by

$$S=\frac{\lambda^2}{2}\int d\mathbf{r}d\mathbf{r}'A(\mathbf{r}-\mathbf{r}')\phi_1[c_0(\mathbf{r})]\phi_1[c_0(\mathbf{r}')]. \tag{17}$$

Given particular shapes of $A(\mathbf{r})$, $\overline{\phi(c)}$, and $\phi_1(c)$, Eqs. (14), (16), and (17) enable one to determine the probability distribution

$$\rho(W)=\rho_0\exp[-S(W)] \tag{18}$$

and thus obtain the solution to the problem under consideration.

Some conclusions can be drawn for the range of small deviations $|W-\langle W\rangle|\ll\langle W\rangle$ without specifying the above shapes. Since the first-order correction to a functional corresponds to the zeroth-order approximation for the functions in its integrand, we get from Eq. (16)

$$W-\langle W\rangle=-\lambda\int d\mathbf{r}d\mathbf{r}'A(\mathbf{r}-\mathbf{r}')\phi_1[\overline{c_0(\mathbf{r})}]\phi_1[\overline{c_0(\mathbf{r}')}], \tag{19}$$

where $\overline{c_0(\mathbf{r})}$ is the optimum order parameter fluctuation in the uniform medium (at $A=0$) given by the standard Cahn-Hilliard theory. Substituting the latter into Eq. (17) leads to Gaussian statistics for the nucleation barrier height:

$$S(W)=\frac{(W-\langle W\rangle)^2}{2\Delta}, \tag{20}$$

where the dispersion is

$$\Delta=2\int d\mathbf{r}'d\mathbf{r}A(\mathbf{r}-\mathbf{r}')\phi_1[\overline{c_0(\mathbf{r})}]\phi_1[\overline{c_0(\mathbf{r}')}]. \tag{21}$$

The latter integral can be estimated as the square of the characteristic free energy fluctuation in the nucleus volume. It is independent of $\langle W\rangle$ and can be very small, $\Delta\ll\langle W\rangle^2$. In particular, there is a range of values for W over which

$$\sqrt{\Delta}\ll|W-\langle W\rangle|\ll W,$$

in which case the exponent in Eq. (20) is much larger than unity, in spite of the fact that it describes relatively small deviations from the average barrier. It follows from the above that the barrier distribution function $\rho(W)=\rho_0\exp[-S(W)]$ reaches its maximum at the average barrier $\langle W\rangle$ and in the proximity of the maximum is a Gaussian distribution with root-mean-square fluctuation of the order of the characteristic free energy fluctuation in the nucleus volume.

Nothing is known about the form of the ''interaction'' function $\phi_1(c)$ in the general case. In the absence of more specific information we take the simplest conceivable form

$$\phi_1(c)=c^2, \tag{22}$$

corresponding to the first nonvanishing term in the expansion of $\phi_1(c)$ (the linear term in the expansion disappears when integrated over space because of particle number conservation).

For the average change in free energy density we shall use the phenomenological Landau-Ginzburg approximation

$$\overline{\phi(c)}=\alpha c^2+\beta c^3+\gamma c^4, \tag{23}$$

which allows for the existence of more than one stable phase. The condition that the two phases have the same energies is

$$\beta=-2\sqrt{\alpha\gamma},\quad \alpha>0,\ \gamma>0. \tag{24}$$

To describe the difference between the phases one can put $-2\sqrt{\alpha\gamma}<\beta<0$.

Near the spinodal the approximation in Eq. (23) represents the first two nonvanishing terms of a Taylor series if we put

$$\gamma=0,\quad \beta<0,\quad \text{and}\quad \alpha=-3c_s\beta, \tag{25}$$

where $c_s(=n_s-\langle n\rangle)$ is the difference between the order parameter at the spinodal and its actual average value.[5]

On the other hand, near the binodal, where the two phases have almost the same free energies, the capillarity approximation is applicable[5] and gives

$$R=R_c\equiv\frac{2\sigma}{\mu c_b}\quad \text{and}\quad W=W_c\equiv\frac{4\pi}{3}\sigma R^2, \tag{26}$$

where $c_b(=n_b-\langle n\rangle)$ is the difference between the order parameter at the binodal and its actual average value, σ is the surface tension, and μ is a constant determined by the properties of the second phase. The capillarity approximation will be used to describe the barrier fluctuations near the binodal.

The most delicate point of the above approach is the assumption of Gaussian statistics for the random functional in Eq. (10). This applies when the fluctuation in energy is determined by a large number of random contributions. In glasses and noncrystalline films where the structural parameters fluctuate in each elemental cell and the critical nucleus typically contains many cells the above is certainly the case. For doped crystals, Gaussian statistics is applicable only if the average number of impurity atoms in the critical nucleus is considerably greater than unity. This takes place in the important limiting cases of nucleation near the spinodal or the binodal, where the critical radius turns out to be large.[5] However, the nucleus radius may not be very large for the case of second-phase nucleation in crystals with small impurity concentration so that the average number of impurity atoms in a nucleus is less than or of the order of unity. In this case the above equations are not valid, although the idea of optimum fluctuations may still survive. This latter case will be analyzed separately in Sec. IV below.

We end this section with a remark concerning possible fluctuations of another energy parameter of phase transitions in systems with static disorder. Because of the fluctuations in structural material parameters, the free energies of the two stable (metastable) phases will fluctuate from one local region to another in a disordered system. The characteristic binodal and spinodal lines, on the phase diagram (in the ''temperature–order-parameter'' plane), then transform into regions of finite widths. Fluctuations in free energies of the two phases are described by the same probability distributions as that derived above for the barrier height. Indeed, the underlying Eqs. (3), (6), and (7) remain the same for both the minima and the maximum of the effective double-well potential representing the energy diagram of a first-order phase transition. We shall see in what follows that in some intervals near the binodal and spinodal the fluctuations in barrier height are comparable to its average value. These same intervals determine the width of the binodal and spinodal smearing in the phase diagram.

III. UNCORRELATED AND STRONGLY CORRELATED DISORDER

In some cases, such as that of noninteracting frozen impurity atoms in a crystal, the disorder is uncorrelated while in other cases there may be some correlation between fluctuations in different elemental cells of a material. As an example of correlated disorder we mention the medium-range order observed in a variety of glasses by means of neutron and x-ray scattering.[31–34] Medium-range order implies that the arrangements of structural units in a glass are not completely random but have correlations on a scale r_c larger than the characteristic interatomic length (typically, $r_c \sim 10-30$ Å).

The existence of this characteristic correlation range means that the correlation function $A(\mathbf{r})$ is a maximum at $r=0$ and decreases rapidly (presumably exponentially) for $r \gg r_c$. Two limiting cases are independent of the particular shape of $A(\mathbf{r})$. The first is uncorrelated disorder for which the correlation range is small compared to the characteristic nuclear radius R. In that case we may take

$$A(\mathbf{r}) = A_1 \delta(\mathbf{r}) \quad \text{for} \quad r_c \ll R, \tag{27}$$

where $\delta(\mathbf{r})$ is the Dirac delta function. In the opposite limiting case of strongly correlated disorder we may take

$$A(\mathbf{r}) = \text{const} \equiv A_2 \quad \text{for} \quad r_c \gg R. \tag{28}$$

The two parameters A_1 and A_2 are related by $A_1 \sim A_2 r_c^3$

Equations (27) and (28) imply that the disorder is isotropic, and so the optimum fluctuations are expected to be spherically symmetric. This suggestion about the symmetry of the optimal fluctuation is the usual one for the optimum fluctuation method. It is understood in this context that, although a pure symmetric fluctuation rarely appears in a random system, small deviations from the symmetric shape produce only small corrections to the equations for the optimum symmetric fluctuation [Eqs. (14), (15), (16), and (17)]. Hence, these equations remain approximately valid when applied to slightly asymmetric fluctuations, which have a nonzero phase volume and thus appear in a random system with nonzero probability. The problem of describing such slightly asymmetric fluctuations in the proximity of the optimal one, however, appears in calculating the preexponential factor in Eq. (18) which represents the effective phase volume. Although the standard optimum fluctuation method enables one to calculate the preexponential as well, and the same can be extended to the problem under consideration, we do not do so in the present work. The reason is that the probability function $\rho(W)$ typically enters physical quantities in combination with the nucleation exponential $\exp(-W/kT)$. The latter dominates any preexponential power dependence, and will only compete with the probability exponent $S(W)$.

Rather than calculate the preexponential ρ_0 we give a simple order-of-magnitude estimate. Supposing the characteristic energy decay scale of the exponent $S(W)$ (root-mean-square barrier fluctuation) is $\sqrt{\Delta}$ and taking into account the normalization condition $\int \rho(W) dW = 1$, we get $\rho_0 \sim 1/\sqrt{\Delta}$.

A. Uncorrelated disorder

For the case of uncorrelated disorder, substituting Eqs. (22) and (27) into Eqs. (14), (15), (16), and (17) gives, respectively,

$$-\kappa \nabla^2 c + \alpha c + \tfrac{3}{2} \beta c^2 + (2\gamma - \lambda A_1) c^3 = 0, \tag{29}$$

$$J = \int d\mathbf{r} \{ \kappa (\nabla c)^2 + \alpha c^2 + \beta c^3 + (\gamma - \lambda A_1/2) c^4 \}, \tag{30}$$

$$W = \int d\mathbf{r} \{ \kappa (\nabla c)^2 + \alpha c^2 + \beta c^3 + (\gamma - \lambda A_1) c^4 \}, \tag{31}$$

and

$$S = \frac{\lambda^2 A_1}{2} \int d\mathbf{r} c^4. \tag{32}$$

As has been noted in Sec. II above, the barrier probability distribution is Gaussian when the disorder is small. Particular expressions for the dispersion of the Gaussian distribution are given below.

1. Phenomenological description

In accordance with Eq. (24) we put $|\beta| \lesssim 2\sqrt{\alpha\gamma}$ in Eq. (29). As long as the term proportional to β is close to that given in Eq. (24), one can reduce Eq. (29) to dimensionless form by choosing the characteristic amplitude and radius of nucleation to be, respectively,

$$c = \sqrt{\frac{\alpha}{2\gamma - \lambda A_1}} \quad \text{and} \quad R = \sqrt{\frac{\kappa}{\alpha}}. \tag{33}$$

Then, the barrier to nucleation can be estimated as

$$W = \frac{\kappa^{3/2} \alpha^{1/2}}{2\gamma - \lambda A_1} \left(\frac{5\gamma - 3\lambda A_1}{2\gamma - \lambda A_1} \right)$$

to within a numerical factor. The latter equation simplifies for both $|\lambda A_1| \ll \gamma$ and $|\lambda A_1| \gg \gamma$. On solving for λ into Eq. (32) we find a Gaussian distribution [Eq. (20)] with dispersion

$$\Delta = \frac{A_1 \langle W \rangle^2}{\alpha^{1/2} \kappa^{3/2}}, \tag{34}$$

which changes by 20% between the cases of small and not small $|W - \langle W \rangle| / \langle W \rangle$. If α is small enough (near the critical point),

$$\alpha \lesssim A_1^2 / \kappa^3,$$

the dispersion in barriers becomes comparable with the average barrier.

2. Properties near the spinodal

In the absence of disorder near the spinodal [Eq. (25)] the maximum concentration in the center of a nucleus is known[5] to be of the order of c_s. Therefore the last term (the one due to disorder) in Eq. (29) can be neglected provided that $|\lambda A_1| \ll \beta/c_s$. With that, Eq. (29) reduces to a dimensionless form by choosing the characteristic nuclear radius and amplitude as

$$R=\sqrt{\frac{\kappa}{\beta c_s}} \quad \text{and} \quad c=c_s. \tag{35}$$

Correspondingly, the integral in Eq. (32) is estimated as $\int c^4 d\mathbf{r}=c^4R^3=(\kappa/\beta)^{3/2}c_s^{5/2}$ and $W-\langle W\rangle=\lambda A_1\int c^4 d\mathbf{r}$. From that we get Gaussian statistics $S(W)=(W-\langle W\rangle)^2/\Delta$ with dispersion

$$\Delta\approx A_1\left(\frac{\kappa}{\beta}\right)^{3/2}(c_s)^{5/2} \tag{36}$$

(to within a numerical multiplier). It follows then that the characteristic width of the peak in the barrier distribution, $\sqrt{\Delta}\propto c_s^{5/4}$, decreases with c_s more slowly than the average barrier $\langle W\rangle\sim\alpha c^2R^3\propto c_s^{3/2}$. Since the underlying inequality $|\lambda A_1|<\beta/c_s$ is valid provided that $|W-\langle W\rangle|<\langle W\rangle$, we can assert that, in the close proximity of the spinodal,

$$c_s \lesssim \left(\frac{A_1}{\langle W\rangle^2}\right)^{2/5},$$

the disorder makes the barrier to nucleation a random quantity dispersed in a wide band $\sqrt{\Delta}\sim\langle W\rangle$. Note that as long as $R\rightarrow\infty$ with $c_s\rightarrow 0$, the above nucleation barrier fluctuations in the close proximity of the spinodal do correspond to the case of uncorrelated disorder.

3. Properties near the binodal

Following the results in Ref. 5 we use the capillarity approximation in which the order parameter changes abruptly and the concept of surface free energy applies. Therefore, the functions in the integrands of the functionals J, W, and S are considered as constants and the gradient term $\int d\mathbf{r}\kappa(\nabla c)^2$ is estimated as $4\pi R^2\sigma$, where R is the nucleus radius and σ is the surface free energy per unit area. Hence, for the case of uncorrelated disorder

$$J=4\pi R^2\sigma-\frac{4\pi R^3}{3}\left(\mu+\frac{\lambda A_1c^4}{2}\right),$$

$$W=4\pi R^2\sigma-\frac{4\pi R^3}{3}(\mu+\lambda A_1c^4),$$

$$S=\frac{2\pi\lambda^2A_1c^4R^3}{3}. \tag{37}$$

Optimizing J with respect to R and substituting R into $W(R)$ gives

$$R=\frac{R_c}{1+\lambda A_1c^4/2\mu}, \quad W=W_c\frac{1-\lambda A_1c^4/2\mu}{(1+\lambda A_0c^4/2\mu)^3}, \tag{38}$$

where R_c and W_c are given in Eq. (26). For the case of small disorder ($|\langle W\rangle-W|\ll\langle W\rangle$) Eq. (37) leads to Gaussian statistics with dispersion

$$\Delta=\frac{4\pi}{3}A_1R_c^3c^4. \tag{39}$$

Note that although the dispersion diverges with $R_c\rightarrow\infty$ (near the binodal), the corresponding root-mean-square fluctuation is proportional to $R_c^{3/2}$, while the average barrier $\langle W\rangle\propto R_c^2$. Therefore the nucleation barrier fluctuations become relatively small near the binodal. For both the cases of small and large W/W_c the statistics is not Gaussian and the distribution is asymmetric with respect to the average barrier.

B. Strongly correlated disorder

For the case of strongly correlated disorder Eqs. (14), (15), (16), and (17) become

$$-\kappa\nabla^2c+\left(\alpha-\lambda A_2\int d\mathbf{r}c^2\right)c+\frac{3}{2}\beta c^2+2\gamma c^3=0, \tag{40}$$

$$J=\int d\mathbf{r}\left\{\kappa(\nabla c)^2+\left(\alpha-\frac{\lambda A_2}{2}\int d\mathbf{r}c^2\right)c^2+\beta c^3+\gamma c^4\right\}, \tag{41}$$

$$W=\int d\mathbf{r}\left\{\kappa(\nabla c)^2+\left(\alpha-\lambda A_2\int d\mathbf{r}c^2\right)c^2+\beta c^3+\gamma c^4\right\}, \tag{42}$$

and

$$S=\frac{\lambda^2A_2}{2}\left(\int d\mathbf{r}c^2\right)^2. \tag{43}$$

1. Phenomenological description

Based on Eq. (23) one can proceed along the same lines as for the case of uncorrelated disorder in Sec. III A 1 above. Omiting all the routine details we note that this again leads to Gaussian statistics with dispersion

$$\Delta=\frac{A_2\langle W\rangle^2\alpha}{\kappa^3}. \tag{44}$$

As opposed to the case of uncorrelated disorder [Eq. (34)], this dispersion goes to zero as $\alpha\rightarrow 0$ (near the critical point). The average barrier decreases as $\langle W\rangle\propto\alpha^{1/2}$ and thus the relative root-mean-square fluctuation remains finite with approach to the critical point in this regime.

2. Properties near the spinodal

Putting into Eqs. (41), (42), and (43) the parameters determined in Eqs. (25) and (35) for the case of small disorder ($|W-\langle W\rangle|\ll W$) leads to Gaussian statistics with dispersion

$$\Delta=\frac{A_2\kappa^3c_s}{\beta^3}. \tag{45}$$

As in the case of uncorrelated disorder the width of the distribution $\sqrt{\Delta}$ decreases with c_s more slowly than the average barrier $\langle W\rangle$ does. Close to the spinodal, at

$$c_s\lesssim\frac{\sqrt{A_2}}{\beta},$$

the root-mean-square fluctuation $\sqrt{\Delta}$ becomes comparable to the average barrier. Meanwhile, it should be remembered that the regime of correlated disorder is restricted to the region $c_s \gtrsim k/(\beta r_c^2)$ corresponding to the condition $R < r_c$.

3. Properties near the binodal

Employing the capillarity approximation for the case of strongly correlated disorder gives [in place of Eqs. (37)]

$$J = 4\pi R^2 \sigma - \frac{4\pi R^3 \mu}{3} - \frac{\lambda A_2}{2}\left(\frac{4\pi R^3 c}{3}\right)^2, \tag{46}$$

$$W = 4\pi R^2 \sigma - \frac{4\pi R^3 \mu}{3} - \lambda A_2\left(\frac{4\pi R^3 c}{3}\right)^2, \tag{47}$$

$$S = \frac{8\pi \lambda^2 A_2 c^4 R^6}{9}. \tag{48}$$

For the case of small fluctuations $|W - \langle W\rangle| \ll \langle W\rangle$ the Gaussian distribution has dispersion

$$\Delta = A_2\left(\frac{4\pi}{3} R^3 c_0\right)^2. \tag{49}$$

We note that, as opposed to the case of uncorrelated disorder, the mean-square fluctuation ($\sqrt{\Delta} \propto R_c^3$) diverges near the binodal more strongly than the average barrier ($W_c \propto R_c^2$). Therefore in the regime of strongly correlated disorder the characteristic fluctuation in the nucleation barrier exceeds its average value near the binodal (it should be remembered, however, that this regime is restricted to the case $R < r_c$ and thus inevitably fails in the nearest proximity of the binodal). Beyond the region of small fluctuations the barrier distribution is asymmetric and not Gaussian.

IV. NON-GAUSSIAN FLUCTUATIONS

As has been mentioned at the end of Sec. II, the disorder cannot be considered Gaussian for the case of nuclei that contain on average less than or of the order of one impurity atom. To tackle the latter problem we use Poisson statistics which leads to the following expression[30,35] for the logarithm of the probability (entropy) of a given impurity concentration fluctuation $m(\mathbf{r})$:

$$S = -\int d\mathbf{r}\left\{[\langle m\rangle + m(\mathbf{r})]\ln\left[\frac{\langle m\rangle}{\langle m\rangle + m(\mathbf{r})}\right] + m(\mathbf{r})\right\}, \tag{50}$$

where $\langle m\rangle$ is the average impurity concentration. The latter reduces to Gaussian statistics for the case of small fluctuations $m \ll \langle m\rangle$.

Note that taken as $m(\mathbf{r})$ the impurity concentration in Eq. (50) implies the number of impurity atoms in an optimum nucleus to be considerably larger than unity in spite of the fact that the average number $\langle m\rangle$ is small. Therefore we consider very strong fluctuations causing the barriers far in the tail of probability distributions. Although the alternative conceivable case of non-Gaussian fluctuations with a small number of impurities in an optimum nucleus seems to be realistic, this case cannot be described analytically in the framework of the standard optimum fluctuation method, which is based on a continuity approximation that leads to integro-differential equations. Aimed at treating the problem analytically and extending the optimum fluctuation method to the case of phase transitions, the present paper does not cover that alternative case.

Assuming that the interaction with impurities has the form suggested in Sec. II, the free energy functional will take the form [cf. Eq. (9)]

$$F = \int [\overline{\phi(c)} + \kappa(\nabla c)^2 - \xi m \phi_1] d\mathbf{r}, \tag{51}$$

where ξ is a coupling parameter and we consider the case $\xi > 0$ in which the barrier to nucleation is decreased due to impurities. Proceeding along the same lines as in Sec. II we optimize the functional

$$\Phi = S + \lambda F,$$

where λ is the undetermined Lagrange multiplier. This leads to the equations

$$m = \langle m\rangle (e^{\lambda\phi_1} - 1), \tag{52a}$$

$$-2\kappa\nabla^2 c + \frac{\partial\overline{\phi}}{\partial c} - \xi m \frac{\partial \phi_1}{\partial c} = 0. \tag{52b}$$

$$W = \int d\mathbf{r}[\kappa(\nabla c)^2 + \overline{\phi} - \xi m \phi_1], \tag{52c}$$

$$S = \langle m\rangle \int d\mathbf{r}[e^{\lambda\phi_1}(\lambda\phi_1 - 1) + 1]. \tag{52d}$$

It follows from the above equations that the capillarity approximation is suitable for fluctuations that differ considerably from Gaussian ones. The reasoning behind this statement is that assuming the opposite is true [that is, $m(\mathbf{r})$ and $c(\mathbf{r})$ are slowly varying functions of coordinates] will lead to a contradiction. Indeed, the average number of impurity atoms per nucleus is small, while the number of impurity atoms in optimum nuclei is taken to be larger than unity. Since $m \gg \langle m\rangle$, it follows from Eq. (52a) that the exponential $\exp(\lambda\phi_1)$ is large. If $c(\mathbf{r})$ is a slowly varying function of coordinates, then in accordance with the inequality $\exp(\lambda\phi_1) \gg 1$ and with Eq. (52a), $m(\mathbf{r})$ will change in space much more drastically than $c(\mathbf{r})$. Because the functions $m(\mathbf{r})$ and $c(\mathbf{r})$ have exponentially different coordinate dependences, Eq. (52b) cannot be satisfied. To get around this contradiction we have to assume that both the order parameter $c(\mathbf{r})$ and the impurity concentration $m(\mathbf{r})$ are not slowly varying smooth functions. We may assume instead that these functions are almost constant in some region and simultaneously decrease at the boundary of that region. This picture corresponds to the capillarity approximation.

In the capillarity approximation we get

$$J = 4\pi R^2 \sigma - \frac{4\pi}{3} R^3 (\mu - \lambda^{-1} \xi \langle m\rangle e^{\lambda\phi_1}), \tag{53a}$$

$$W = 4\pi R^2 \sigma - \frac{4\pi}{3} R^3 (\mu - \phi_1 \xi \langle m\rangle e^{\lambda\phi_1}), \tag{53b}$$

$$S=\frac{4\pi}{3}R^3\langle m\rangle\lambda\phi_1 e^{\lambda\phi_1}, \tag{53c}$$

where ϕ_1 is a constant inside the nucleus whose value is determined by the properties of the nucleated phase. In the limiting case of strong deviations from Gaussian statistics, at $\lambda\phi_1 \gg 1$, the correction due to disorder in Eq. (53a) is much smaller than the one in Eq. (53b). As a result the probability exponent becomes

$$S(W)=\frac{\langle W\rangle - W}{\xi\phi_1}\ln\left(\frac{\langle W\rangle - W}{\xi\phi_1 R^3\langle m\rangle}\right). \tag{54}$$

V. NUCLEATION RATE

Since the barrier to nucleation is a random quantity characterized by its probability distribution function $\rho(W)$, the steady-state nucleation rate

$$I_s(W)=I_0\exp\left(-\frac{W}{kT}\right) \tag{55}$$

also becomes a random quantity. If we divide the material into a set of local regions, the nucleation rates will vary exponentially between these regions. In what follows we first consider the kinetics of nucleation in the subset of regions characterized by a given rate I_s and then average the results over different regions.

Letting n_I be the fraction of nucleated regions characterized by the rate I, the nucleation kinetics will be described by the equation

$$\frac{dn_I}{dt}=IV_I f(t)(1-n_I), \tag{56}$$

whose solution is

$$n_I=1-\exp\left[-IV_I\int_0^t f(t)dt\right]. \tag{57}$$

Here $f(t)$ describes the transient nucleation regime during which the nucleation rate changes from zero to its steady-state value I (that is, $0<f<1$) and V_I is the minimum volume required to create a nucleus at the rate I. The latter volume can be estimated as $4\pi R^3/3$, where R is the characteristic nucleus radius corresponding to the rate I. We note that, since the nucleation rate depends on the nucleus parameters, such as R, exponentially, both R and V_I are logarithmically weak functions of I. In the first approximation one can neglect the dependence $V_I=V(I)$ as compared to the multiplier I. Another point to note is that the multiplier $1-n_I$ in Eq. (56) describes the effect of saturation arising from the dwindling of local regions corresponding to the rate I. This multiplier describes the saturation in the mean-field approximation, neglecting the possibility of fluctuations that are free from nuclei and thus determine the nucleation rate at the late stage of nucleation. Because of the latter remarks, our consideration of late stage nucleation in what follows can serve at best as a rough approximation.

In some approaches[36] $f(t)$ has been phenomenologically assumed to have a shape

$$f(t)=1-\exp(-t/\tau), \tag{58}$$

where τ is the characteristic induction time. As derived in the framework of the classic nucleation theory[37,38] the explicit form of $f(t)$ is

$$f(t)=\exp\left[-\exp\left(-2\frac{t-\lambda_g\tau}{\tau}\right)\right], \tag{59}$$

with

$$\lambda_g=g^{-1/3}-1+\ln[3(1-g^{-1/3})/\epsilon],$$

where g is the number of molecules in the critical nucleus,

$$\epsilon=\left(-\frac{g^2}{kT}\frac{\partial^2 F}{\partial g^2}\right)^{-1/2},$$

and with the induction time

$$\tau=\frac{g^2\epsilon^2}{2D},$$

where D is the rate of collisions between monomers and a g-mer. Unfortunately, the results for $f(t)$ in Eq. (59) are restricted to classical nucleation theory and it is not clear how they can be extended to the density functional model underlying the present approach. Yet, since the problem of transient nucleation in the density functional approach as such is beyond the scope of this work, we shall employ the above equations (58) and (59). An important qualitative feature of $f(t)$ is that its parameters τ and λ_g do not depend on the nucleation barrier exponentially, as does the nucleation rate. It is therefore possible to neglect fluctuations in $f(t)$ as compared to those in I.

To obtain the number of nuclei as a function of time we average the result in Eq. (57) over the disorder configurations,

$$N(t)=V_I^{-1}\int dW\rho(W)\left\{1-\exp\left[-I(W)V_I\int_0^t f(t')dt'\right]\right\}, \tag{60}$$

with the barrier probability distribution $\rho(W)$ given in the previous sections. Since the exponent in the integrand in Eq. (60) is in turn the exponential of W, it is convenient to integrate over the variable I rather than W. Its probability distribution function is

$$\psi(I)=\rho[W(I)]\left|\frac{dW}{dI}\right|$$

$$\approx\frac{kT}{I_0\sqrt{\Delta}}\exp\{-S[kT\ln(I_0/I)]+\ln(I_0/I)\}. \tag{61}$$

Then Eq. (60) becomes

$$N(t)=V_I^{-1}\int \psi(I)\left\{1-\exp\left[-IV_I\int_0^t f(t')dt'\right]\right\}dI. \tag{62}$$

The effective nucleation rate measured in experiments can be expressed as

$$I_{\mathrm{eff}} \equiv \frac{dN}{dt} = f(t) \int \psi(I) I \exp\left[-I V_I \int_0^t f(t')dt' \right] dI. \tag{63}$$

In order to analyze the physical quantities $N(t)$ and I_{eff} it is worth noting some properties of the probability distribution $\psi(I)$ that appears in Eqs. (62) and (63). As long as the barrier distribution is Gaussian [Eq. (20)] (near its maximum, at least), we can reduce $\psi(I)$ to log-normal form

$$\psi(I) \approx \frac{kT}{I_m \sqrt{\Delta}} \exp\left\{ -\frac{(kT)^2}{2\Delta} \left[\ln\left(\frac{I}{I_m} \right) \right]^2 - \frac{\Delta}{2(kT)^2} \right\}. \tag{64}$$

Fluctuations in nucleation barriers are important provided that the characteristic width of the barrier distribution is large,

$$\sqrt{\Delta} > kT.$$

The latter inequality is assumed to hold in what follows and will be justified in the next section where we estimate the parameters of the theory. Since the ratio $\Delta/(kT)^2$ is in the exponent, the above inequality does not have to be strong in order for the effects of static disorder to be important. The distribution $\psi(I)$ is a maximum at the nucleation rate

$$I_m = I_0 \exp\left[-\frac{\langle W \rangle}{kT} - \frac{\Delta}{(kT)^2} \right], \tag{65}$$

which is smaller than the nucleation rate

$$I(\langle W \rangle) = I_0 \exp(-\langle W \rangle / kT)$$

corresponding to the average barrier. One can also calculate the average nucleation rate

$$\langle I \rangle = \int_0^\infty \psi(I) I dI = I_0 \exp\left[-\frac{\langle W \rangle}{kT} + \frac{\Delta}{2(kT)^2} \right], \tag{66}$$

which is exponentially larger than both $I(\langle W \rangle)$ and I_m. Note that the expression for $\langle I \rangle$ corresponds to the optimum nucleation barrier

$$W_{\mathrm{opt}} = \langle W \rangle - \frac{\Delta}{kT}, \tag{67}$$

which arises from the competition of two exponential factors: the increase in the nucleation rate and the decrease in the probability as the barrier decreases. This also can be expressed as

$$\langle I \rangle \sim \max_W [\rho(W) I_0 \exp(-W/kT)].$$

The latter agrees with the preliminary discussion in Sec. I and with the interpretation in Fig. 1. One other characteristic of the distribution $\psi(I)$ is its dispersion, which can be calculated to give

$$\langle (\delta I)^2 \rangle = \int (I - \langle I \rangle)^2 \psi(I) dI \approx \langle I^2 \rangle = \langle I \rangle^2 \exp\left[\frac{3\Delta}{2(kT)^2} \right]. \tag{68}$$

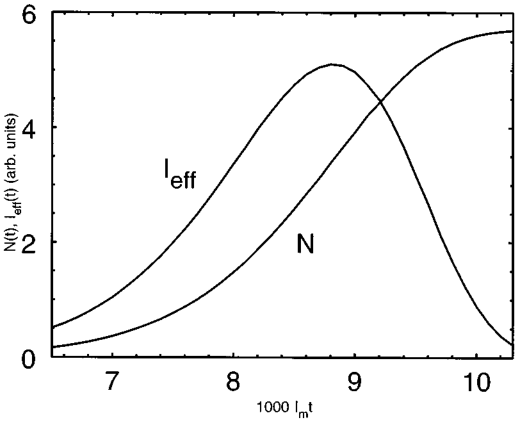

FIG. 3. Nucleus concentration N and effective nucleation rate $I_{\mathrm{eff}} = dN/dt$ depending on the dimensionless time tI_m, where I_m is the most probable nucleation rate. These curves are obtained by numerical integration with the parameters $\exp(2\lambda) = 30$, $I_m \tau_{\mathrm{ind}} = 0.005$, and $(kT)^2/2\Delta = 0.1$.

We are now in a position to describe the nucleation kinetics. As is seen from Eqs. (62) and (63), the dependence $N(t)$ is superlinear in t at small $t < \tau$ and saturates at long times such that $\langle I \rangle t \gg 1$. In other words, $N(t)$ has an S shape, as is shown in Fig. 3. For the sake of definiteness and because it is of primary interest for experimental studies of nucleation, we restrict ourselves to considering the quasilinear region of $N(t)$ for which the time of experiment is considerable longer than τ but still far from saturation. Because of the latter condition one can set exponentials to unity in the integrands of Eqs. (62) and (63), while the condition $t > \tau$ enables one to put $f = 1$. With that we get simply

$$I_{\mathrm{eff}} = \langle I \rangle, \tag{69}$$

where $\langle I \rangle$ is given by Eq. (66). Note that the disorder changes both the absolute value and the temperature dependence of the nucleation exponent. The numerical estimate in Sec. VI below shows that this change may not be small and may be comparable to the exponent itself.

To be more precise we should examine the position of inflection point t_i in the S shape of $N(t)$ that corresponds to the maximum in $I_{\mathrm{eff}}(t)$. In order to determine t_i we first equate the derivation dI_{eff}/dt to zero and then set the exponential in the corresponding integrands close to the unity. With that we get

$$\frac{dI_{\mathrm{eff}}}{dt} \approx \langle I \rangle V_I \frac{df}{dt} - f^2 \langle I^2 \rangle V_I^2 = 0. \tag{70}$$

Substituting Eqs. (66) and (68) gives

$$\frac{1}{f^2} \frac{df}{dt} = I_0 V_I \exp\left(-\frac{\langle W \rangle}{kT} + \frac{2\Delta}{(kT)^2} \right). \tag{71}$$

Using either Eq. (58) or (59) leads to approximately the same result for the inflection point t_i:

$$t_i = \tau \left[-\ln(I_0 V_I \tau) + \frac{\langle W \rangle}{kT} - \frac{2\Delta}{(kT)^2} \right]. \tag{72}$$

Here the logarithm on the right-hand side is relatively small since both the induction time τ and the characteristic kinetic time $(V_I I_0)^{-1}$ are determined by the same diffusion processes and are thus of the same order of magnitude.

If we examine t_i in Eq. (72) as a function of temperature putting $\tau \propto \exp(E_D/kT) \gg 1$, then we find that $t_i(T)$ is a maximum,

$$(t_i)_{\max} = \tau \left(\frac{\langle W \rangle}{4\sqrt{\Delta}} \right)^2 \gg \tau \quad \text{at} \quad kT = \frac{4\Delta}{\langle W \rangle}. \tag{73}$$

Summarizing, we can say that the dependence $N(t)$ has an S shape. In the transient region where the number of nuclei is linear in time, the observed nucleation rate is predicted to have a maximum at a time t_i that is considerably larger than the induction time, and it reaches this maximum at a temperature determined by the disorder characteristics. It follows from the above that experimental investigations of the inflection point in the dependence $N(t)$ may give information about the effects of disorder in nucleation kinetics.

Two comments are in order regarding the above conclusion about the maximum in nucleation rate. First, it has been assumed in the course of the derivation that the inequality $IV_I \int_0^t f(t) dt < 1$ holds, allowing one to omit the exponentials in the corresponding integrands. That assumption may not be valid for some local regions possessing very high nucleation rates and violating the above inequality. Such fast regions can be swept out by annealing the material prior studying the nucleation kinetics.

The second comment is that because the dependence $I_{\text{eff}}(t)$ is nonmonotonic, the linear approximation for $N(t)$ may be sensitive to the choice of the interval in which that approximation is applied. In particular, extrapolating superlinear (sublinear) time dependence $N(t)$ at $t \ll t_i$ ($t \gg t_i$) by a straight line and interpreting its slope as the nucleation rate may lead to results that are considerably larger (smaller) than the real nucleation rate. Since t_i is nonmonotonic in temperature, such an extrapolation may even lead to a conclusion that the nucleation rate depends nonmonotonically on temperature. Therefore, care should be taken in the interpretation of experimental results on nucleation in disordered systems.

VI. CONCLUSIONS

Let us summarize the main results of the investigation presented. First, we have shown that in materials with static disorder the local barrier to nucleation is a random quantity varying considerably between different local regions of the system. Second, an optimum fluctuation method is developed to describe the probability distribution of nucleation barriers. This method extends the well-known density-functional Cahn-Hilliard approach to the case of disordered systems. Third, it is shown that local nucleation rates in a disordered medium form a wide distribution whose position and dispersion depend exponentially on temperature. The measured concentration of nucleus is predicted to be nonlinear in time (possessing an S shape) and exponentially different from the classical theory prediction in both its absolute value and temperature dependence. The latter conclusion is in general agreement with the experimental results quoted above.

Our approach is equally applicable to fluctuations in nucleation barriers and in stationary minima of the local free energy density. Because of the fluctuations in these minima, the lines (spinodal and binodal) that would separate different regions in phase diagrams of homogeneous materials will smear into corresponding quasilinear regions for the case of disordered systems. The above results can be used to estimate the characteristic widths of these regions.

We now estimate numerically the effects of disorder upon the nucleation. In accordance with the above results the disorder enters the nucleation rate in an exponential $\exp[\Delta/(kT)^2]$. An estimate to serve as a rough guide is based on Eqs. (34) and (33):

$$\frac{\Delta}{(kT)^2} = \frac{\Delta}{W^2} \left(\frac{W}{kT} \right)^2 \sim \frac{A_1 a}{\kappa^2} \frac{R}{a} \left(\frac{W}{kT} \right)^2, \tag{74}$$

where a is the characteristic atomic length in a solid. The ratio $A_1 a/\kappa^2 \sim A_1 a^3/E_{\text{at}}$ can be estimated as the squared relative fluctuation in atomic energies E_{at}. In turn, the latter can be estimated as the relative dispersion in microscopic structural parameters.

For the case of amorphous solids this gives a number of the order of 10^{-3} that corresponds to characteristic fluctuations of the order of several percent in valence angles, bond length, etc.[39–41] As a result we get

$$\frac{\Delta}{(kT)^2} \sim 10^{-3} \frac{R}{a} \left(\frac{\langle W \rangle}{kT} \right)^2 \tag{75}$$

for the case of amorphous solids. Putting $R/a \sim 10$ and $\langle W \rangle \sim 50kT$ (which is typical of glasses[12,14,16]) we get the estimate $\Delta/(kT)^2 \sim 25$. Therefore, the contribution to the nucleation exponent due to disorder may be comparable to the exponent itself. This may at least partly explain the many order-of-magnitude differences between the measured nucleation rates in silica glasses and those predicted by classical nucleation theory[14] (alternative explanations are based on the assumptions of temperature-dependent surface energy and/or failure of the Stokes-Einstein relation between viscocity and diffusion coefficient.[13,17]). Another prediction that agrees with experimental results on glasses concerns low-temperature annealing of the material prior to studying the nucleation kinetics. As was mentioned in Sec. V, this may sweep out some fast local regions and thus provide conditions for a maximum in the nucleation rate. Such a maximum in preannealed glassy materials has indeed been observed.[16]

For the case of doped crystals the squared relative fluctuation in atomic energies can be estimated as the relative impurity concentration n_i, which quantity should be used instead of the factor 10^{-3} in Eq. (75). Bearing in mind the impurity concentration $n_i \gtrsim 10^{-3}$, we conclude that the ratio $\Delta/(kT)^2$ for the case of doped crystals may be even larger than that of glasses. That the disorder contribution is predicted to be proportional to the impurity concentration for the case of nucleation in crystals offers scope to verify our theory.

Overall, our approach emphasizes a considerable difference between the nucleation kinetics in homogeneous and disordered systems. So far the prevailing hypothesis has been that data on nucleation in disordered solids can be interpreted by properly choosing the parameters in the equations of classical nucleation theory. For example, a linear temperature dependence of the surface free energy has been proposed, corresponding to a negative entropy term of unknown origin, for the classical theory to describe the observed nucleation rates.[13,17] In contrast, in our theory the effective nucleation barrier given by Eq. (67) increases as the temperature increases, so that the suggestion of a negative entropy term in surface energy may not be required.

In conclusion, let us note that our theory can easily be modified to the two-dimensional case of nucleation and/or evaporation at random surfaces. Effects of disorder can be shown to increase as the dimensionality decreases.

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