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Nucleation in disordered media

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A theory of the nucleation of crystalline particles in disordered media is proposed accounting for small statistical fluctuations in microscopic structural parameters, which are shown to affect considerably the thermodynamic barrier to nucleation. As a result, the classical nucleation-rate exponent $-W/kT$ takes the correction $\Gamma\,(W/kT)^3$ at high temperatures, where Γ depends both on the correlation radius of the disorder and its amplitude; this correction may be significant. At low temperatures the nucleation-rate exponent remains finite in the case of uncorrelated disorder, while it is proportional to $T^{-1/3}$ at $T \to 0$ in the case of strongly correlated disorder. The implications of these findings for nucleation in glasses are discussed.

The classical nucleation theory largely evolved in the 1920s–1940s (Refs. 1–4) remains practically unchanged until the present. According to this theory the steady-state nucleation rate I may be expressed as a function of temperature T by

$$I = A\,\exp\left(-\frac{W+G}{kT}\right), \tag{1}$$

where A is a constant approximately independent of temperature, W and G are the thermodynamic and kinetic barriers to nucleation, respectively, and k is Boltzmann's constant. The kinetic barrier is usually related to the viscosity η so that Eq. (1) becomes

$$I = \frac{A'}{\eta}\,\exp\left(-\frac{W}{kT}\right), \tag{2}$$

where A' is a constant. As expressed in terms of the free energy difference between the two phases per unit volume $\mu\,(>0)$, and the interfacial energy per unit area σ, the thermodynamic barrier in forming a spherical embryo of radius R is given in the capilarity approximation by

$$W = \max\{F_c\,(R)\} = \max\left\{-\frac{4\pi R^3}{3}\mu + 4\pi R^2\sigma\right\} = \frac{16\pi\sigma^3}{3\mu^2}, \tag{3}$$

where $F_c\,(R)$ is the change in the free energy due to the embryo formation. The latter change reaches its maximum at the critical radius $R_c \equiv 2\sigma/\mu$. Since only the nuclei of radii $R \geq R_c$ are stable, the thermodynamic barrier coincides with the maximum value of $F_c\,(R)$, as is reflected in Eq. (3).

During the last decade the above theory was applied to describe crystal nucleation rates in glasses.[5–7] Based on these studies a conclusion has been made that the steady-state crystal nucleation rates calculated by the theory are many orders of magnitude smaller than the experimental values in inorganic glasses. Even though the theory allows for a justification of the activation temperature dependences of nucleation rates, the corresponding absolute values are in some cases 20 orders of magnitude smaller than the measured quantities. The discrepancy could be explained by postulating a temperature-dependent interfacial energy $\sigma\,(T)$. However, the above postulate can hardly be theoretically substantiated.[8]

It is the main purpose of this work to discuss the role of a disorder in nucleation processes like crystal nucleation in glasses. The idea is that there are some locally favorable inhomogeneities in randomly disordered media, which effectively decrease thermodynamic nucleation barriers and thus increase nucleation rates exponentially. This increase will be shown to depend both on the correlation radius of the disorder and on its amplitude.

While the short-range order topology in the ensemble of structural units ("elemental cells") of a glass is conserved, their microscopic parameters (valence angles, bond lengths, etc.) fluctuate, leading to the corresponding fluctuations in atomic energies. Associated with the above are local fluctuations in the free energy difference between the two phases and in the interfacial energy. These fluctuations are of static nature: Their lifetimes are much longer than the time of the nucleation process. That is why the nucleation rates are expected to be different in different local region of a glass. (Note that the above arguments fail as applied to nucleation in flexible, liquidlike systems where fluctuations are short-lived.)

Following the standard nucleation theories we consider the change in the free energy F in forming a spherical nucleus of radius R as composed of two contributions: the energy gain due to a new phase formation and the energy lost due to the interface formation. Each of the contributions can be in turn regarded as a sum of fluctuating (random) and nonfluctuating (average) terms in the case of a disordered medium. Taking only nonfluctuating terms into account we would have F of exactly the same form, as in the classical nucleation theory [see Eq. (3)]. Adding the fluctuating terms gives

$$F = -\frac{4\pi R^3}{3}\langle\mu\rangle + 4\pi R^2\langle\sigma\rangle + X_R + Y_R = F_c\,(R) + X_R + Y_R. \tag{4}$$

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Here $\langle\mu\rangle$ and $\langle\sigma\rangle$ stand for nonfluctuating parts of the corresponding quantities, while X_R and Y_R are random parts of the free energy difference between the two phases and the interfacial energy for the nuclei of a given radius R, respectively, possessing zero average value $\langle X_R\rangle = \langle Y_R\rangle = 0$.

To establish the probability distributions for the above random quantities, we note that a nucleus is supposed to consist of a large number of molecules and, thus, both X_R and Y_R can be regarded as a sum of large number of random contributions corresponding to individual elemental cells in a system. These numbers are approximately equal to $N_x = 4\pi R^3/3V$ and $N_y = 4\pi R^2/V^{2/3}$, where V is the characteristic volume of elemental cell in a random system. Assuming microscopic cell fluctuations are small they can be considered as Gaussian ones, characterized by the corresponding dispersions δ_x and δ_y. Consequently, the above mentioned sums of such fluctuations also obey Gaussian statistics with the dispersions $\Delta_x = N_x\delta_x$ and $\Delta_y = N_y\delta_y$. As a result the probability distribution for random quantity F has the form

$$\rho(F) = (2\pi D)^{-1/2}\exp\left\{-\frac{[F-F_c(R)]^2}{2D}\right\}, \qquad (5)$$

with the dispersion $D = N_x\delta_x + N_y\delta_y$.

Let us consider first the limiting case of a very small disorder $D \to 0$, so that $\rho(F)$ is close to the δ function and, thus, $F \approx F_c(R)$. To be considered as the thermodynamic nucleation barrier the latter energy must be the maximum one among all the energies $F_c(R)$ referring to different radii R, that is, $F = \max\{F_c(R)\} = W$, in accordance with Eq. (3). Thus, based on the probability distribution in Eq. (5) the above approach reduces to the standard nucleation theory in the limiting case of a very small disorder .

We now turn to the case of a finite disorder. The solution we are looking for implies the nucleation barrier F to be considerably smaller than W owing to some favorable static fluctuations. Even though such fluctuations appear with small probabilities $P(F) \ll 1$, they are expected to increase the effective nucleation rate exponentially. In other words, there are some optimal fluctuations resulting from the competition between an exponential increase in the nucleation rate and an exponential decrease in the probability $P(F)$ with the barrier F decrease. Taking $P(F)$ in the form $P(F) \propto \exp[-\varphi(F)]$, one can represent the average nucleation rate as

$$\langle I\rangle = \int \frac{A'}{\eta}\exp\left(-\frac{F}{kT}\right) d[P(F)] = I_0\exp[-S(T)],$$

$$S(T) = \min_F\left[\varphi(F) + \frac{F}{kT}\right] = \varphi(F_0) + \frac{F_0}{kT}, \qquad (6)$$

where the barrier F_0 corresponds to the optimal fluctuation.

To find the probability $P(F)$ of the nucleation barrier not exceeding a given value $F < W$, we first calculate the conditional probability $P(F,R)$ of the minimum work needed to create a nucleus (stable or unstable) of a given radius R not exceeding a given value F:

$$P(F,R) = \int_0^F \rho(F)\,dF \approx \exp\left\{-\frac{[F-F_c(R)]^2}{2D}\right\}. \qquad (7)$$

It has been taken into account in the last equality that the probability under consideration is to be small. Another reading of Eq. (7) is that the condition $F = F_c(R)$ determines two characteristic radii R_1 ($< R_c$) and R_2 ($> R_c$), such that $P(F;R)$ is close to the unity at $R < R_1$ and at $R > R_2$. One can say that the minimum work needed to form a nuclear of radius R does not exceed F with the probability close to the unity if $R < R_1$ or $R > R_2$, while this probability turns out to be much less than unity if $R_1 < R < R_2$. Since the nuclear radius R changes in a wide range, from $R \ll R_c$ to $R \gg R_c$, in the course of its growing, one can expect the region $R_1(F) < R < R_2(F)$ to play the role of a bottleneck in forming a nucleus with a barrier F (less than W). Therefore, the probability to form a nucleus with a barrier less than F can be estimated as a product of the probabilities $p(R_i)$ that the minimum energy needed to form a nucleus of radius R_i does not exceed F for all R_i ranging from R_1 to R_2. In its turn, $p(R_i)$ can be defined as the conditional probability that the minimum work $f(R_i)$ needed to form a spherical atomic layer of radius R_i is negative provided that all the previous layers (of smaller radii R) beginning from $R = R_1$ have been created without a loss in energy. Bearing in mind that at $R > R_c$ atomic layers can be created with negative average changes in free energy and, thus, no fluctuations are needed to make these changes negative, only layers with $R < R_c$ are to be included in the above mentioned product of probabilities. The minimum energy needed to create an atomic layer with radius R_i and width $a = V^{1/3}$ is given by

$$\begin{aligned} f(R_i) &= -4\pi\langle\mu\rangle R_i^2 a + 8\pi\langle\sigma\rangle R_i a + x_i + y_i \\ &\equiv f_c(R_i) + x_i + y_i, \end{aligned} \qquad (8)$$

where x_i and y_i are Gaussian random quantities with the dispersions $\delta_x 4\pi R_i^2/V^{2/3}$ and $\delta_y 4\pi R_i^2/V^{2/3}$. When small, the probability that this layer can be created without a loss in free energy takes the form

$$p(R_i) \approx \exp\left\{-\frac{[f - f_c(R_i)]^2}{2\Delta(R_i)}\right\} \quad \text{at} \quad f = 0, \qquad (9)$$

where

$$\Delta(R) = \frac{4\pi R^2}{V^{2/3}}(\delta_x + \delta_y) \equiv \frac{4\pi R^2}{V^{2/3}}\delta. \qquad (10)$$

Combining the above gives

$$\begin{aligned} P(F) = \prod_i p(R_i) &\approx \prod_i \exp\left\{-\frac{[f_c(R_i)]^2}{2\Delta(R_i)}\right\} \\ &\approx \exp\left\{-\int_{R_1}^{R_c}\frac{[f_c(R)]^2}{2\Delta(R)}d\left(\frac{R}{a}\right)\right\}. \end{aligned} \qquad (11)$$

We are now in a position to determine the average nucleation rate defined in Eq. (6). In order to find the exponent $S(T)$ it is convenient to express the quantity to be minimized in terms of R_1:

$$S(T) = \min_{R_1} \left\{ \int_{R_1}^{R_c} \frac{[f_c(R)]^2}{2\Delta(R)} d\frac{R}{a} + \frac{F_c(R_1)}{kT} \right\}. \quad (12)$$

Since $dF_c(R)/dR = f_c(R)/a$, in accordance with the definitions for $F_c(R)$ and $f_c(R)$ in Eqs. (4),(8), the equation for R_1 takes the form

$$\frac{f_c(R_1)}{2\Delta(R_1)} = \frac{1}{kT}. \quad (13)$$

Expressing R_1 from Eq. (13) and substituting it in Eq. (11) leads to the final result

$$S(T) = \frac{W}{kT}\left[\frac{1+3\xi+\xi^2}{(1+\xi)^3}\right], \quad \xi \equiv \frac{\delta}{\langle\sigma\rangle a^2 kT}\frac{R_c}{a}. \quad (14)$$

In the limiting cases Eq. (14) reduces to

$$S(T) = \frac{W}{kT}\left(1-2\xi^2\right) \quad \text{at} \quad \xi \ll 1, \quad (15a)$$

$$S(T) = \frac{W\langle\sigma\rangle a^2}{\delta}\frac{a}{R_c}\left(1-\frac{2}{\xi^2}\right) \quad \text{at} \quad \xi \gg 1. \quad (15b)$$

Note that although nonlinear in $1/T$ over a wide temperature interval, the dependences in Eqs. (14),(15) can be approximated by the linear form $W_{\rm eff}/kT$ within narrow temperature intervals $\Delta T \ll T$ which are normally of interest in the experimental investigations of nucleation. Therefore, the above results do not contradict the experimentally observed temperature dependences of nucleation rates in glasses. At the same time the absolute value of $S(T)$ can be strongly reduced due to a disorder [say, $S(T)$ is approximately 2 times smaller than the classical result W/kT at $\xi = 2$]. Note also that $S(T)$ remains finite at low temperatures (that is, the effective thermodynamic barrier to nucleation $W_{\rm eff}$ is proportional to T at low temperatures). The predicted phenomenon of zero temperature nucleation can show up in a multicomponent glass provided the diffusion remains finite at low temperatures, which may be in principle achieved by the exposure of a glass to penetrating radiation or intense light.

We have been tacitly assuming above the disorder to be uncorrelated. There is ample evidence in the literature[9–12] that the arrangements of structural units in a glass are not completely random but have some correlation on a scale of $r_c \sim$ 10–30 Å, varying between different glasses. The above consideration can be relevant only if the critical radius R_c is considerably greater than the correlation radius r_c. As a matter of fact the equality $R_c = a$ has been used in the course of the preceding analysis, although the results can be shown to hold true in the general case of uncorrelated disorder $R_c \gg r_c > a$.

We now turn to the opposite limiting case of strongly correlated disorder $r_c \gg R_c$ which also allows analytical consideration. We note that the probability distribution for any microscopic fluctuating parameter z_i has the Gaussian form

$$\exp\left(-\sum_{ij}\beta_{ij}z_i z_j\right), \quad (16)$$

provided that the fluctuations are small and $\langle z_i\rangle = 0$, where the indices i and j denote elemental cells in the system under consideration. A possible correlation is characterized by the coefficients β_{ij}, so that $\langle z_i z_j\rangle = \beta_{ij}^{-1} \equiv \alpha_{ij}$. The latter quantity depends on the distance r_{ij} between cells i and j, that is, $\alpha_{ij} = \alpha(r_{ij})$. In particular, α_{ij} reduces to the Kronecker δ in the case of uncorrelated disorder, while α_{ij} is almost independent of r_{ij} in the case of strongly correlated disorder. The distribution in Eq. (16) is associated with the probability distribution for a sum of the random quantities $\sum_1^N z_i$, of the type representing the random variables X_R, Y_R in Eq. (4) and x_i, y_i in Eq. (8). The latter sum can be easily proved[13] to obey Gaussian statistics with the dispersion $\sum_1^N \alpha_{ij}$. In the case of uncorrelated disorder the latter dispersion transforms to the cell's (microscopic) dispersion multiplied by the number N of terms in the sum, a property which has been already used in Eqs. (9),(12) above. In the opposite limiting case of strongly correlated disorder the number of terms in the sum becomes equal to $N^2/2$. Therefore, to describe the nucleation in the case of strongly correlated disorder one should insert the additional multiplier $N/2 = 2\pi R^2/a^2$ into the expression for the dispersion in Eq. (10). After that Eqs. (12) and (13) can be used to obtain the final result for the average nucleation rate. The result cannot be represented in the analytical form within the whole range of its applicability. In the limiting cases of small and large fluctuations one gets

$$S(T) = \frac{W}{kT}\left(1-4\varsigma^2\right) \quad \text{at} \quad \varsigma \ll 1, \quad (17a)$$

$$S(T) = \frac{9}{2}\frac{W}{kT}\varsigma^{-2/3} \quad \text{at} \quad \varsigma \gg 1, \quad (17b)$$

where

$$\varsigma = \frac{2\pi\delta}{\langle\sigma\rangle a^2 kT}\left(\frac{R_c}{a}\right)^3. \quad (18)$$

Note that $\varsigma = 2\pi\left(R_c/a\right)^2\xi \gg \xi$ and, thus, correlations in the static disorder lead to an exponential increase in the nucleation rate as compared with that of the uncorrelated disorder case, at least at not very low temperatures. Which of the two cases (strongly correlated or uncorrelated disorder) is relevant depends on the relationship between the critical radius R_c and the correlation radius r_c in a particular glass.

Let us estimate the parameters ξ and ς which govern the nucleation rate exponent in Eqs. (14) and (17). We note that $\langle\sigma\rangle a^2$ is typically of the order of characteristic bound energies for atoms in a solid, while δ_x and δ_y represent fluctuations in these energies due to a disorder. The quantities $\sqrt{\delta_x}/\langle\sigma\rangle a^2$ and $\sqrt{\delta_y}/\langle\sigma\rangle a^2$ may not be very small in amorphous solids, since atomic potentials are extremely sensitive to random changes in microscopic structural parameters like valence angles, bond lengths, etc. For instance, associated with the above quantities, relative dispersions in microscopic spring constants are estimated as ~ 0.1 by means of the computer modeling of different glassy structures.[14,15] The same order of magnitude estimate can be extracted from the comparison of atomic kinetics data with the theory based on accounting for statistical fluctuations in atomic potentials in glasses.[16] Putting also $\sqrt{\delta}/kT \sim 1$ one can roughly estimate $\xi \sim 0.1\,(R_c/a)$ and $\varsigma \sim 0.1\,(R_c/a)^3$. For a typical ratio $R_c/a \sim 10$ in glasses[5–7] the latter estimates give $\xi \sim 1$ and $\varsigma \sim 100$. With these parameters Eqs. (14), (17) predict the nucleation-rate exponent $S\,(T)$ in a disordered system to be few times smaller than in a crystal with the same average parameters. Such a decrease in $S\,(T)$ may correspond to an increase in nucleation rates within 10–20 orders of magnitude for typical $S\,(T) \sim 50$.

Two comments with regard to the underlying concepts of the above theory are in order. The first is that fluctuations in the diffusion coefficient in a disordered media have not been taken into account. The reasoning behind this approximation is that diffusion barriers in random media are normally characterized by the dispersion δ related to fluctuations in microscopic atomic potentials, while fluctuations in thermodynamic barriers are governed by the dispersion of the order of $\delta\,(R_c/a)^2 \gg \delta$ and, thus, are expected to be much more important. The second comment is that an assumption of a nucleus remaining spherical in spite of a disorder in a random medium can be substantiated in the case of a small disorder. Indeed, supposing deviations from a spherical shape are relatively small, $R'/R \ll 1$, they can be taken into account by the correspondingly small renormalizing of the parameters δ, $\langle\sigma\rangle$, and $\langle\mu\rangle$ above. This procedure leads to the conclusion that the nucleation-rate exponent $S\,(T)$ increases with R'/R decrease, and, thus, the spherical shape wins over all other ones. However, the question remains open about a nucleus shape in the case of an arbitrary disorder.

In summary, a theory of nucleation in disordered media is proposed which is based on accounting for small statistical fluctuations of microscopic structural parameters. The fluctuations are shown to increase the nucleation rate exponentially and to change its temperature dependence. The correction to the exponent of the classical nucleation theory due to a disorder may not be small depending both on the correlation radius of the disorder and its amplitude.

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