Nucleation as motion along a trajectory in order-parameter space

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A statistical approach to the theory of nucleation is developed. The size distribution function of the nuclei is introduced on the basis of the concept of the most probable trajectory in the space of the order parameters—the smoothed concentrations of the particles. It is shown that in the limit of large sizes of the nuclei the results of an analysis of the trajectory equations coincide in form with the results of the classical theory of nucleation. As an illustration the dependence of the frequency of nucleus formation on the parameters of the system in nucleation near a critical point is considered.

The classical theory of nucleation is applicable principally to nuclei of a size such that the energy of formation of a nucleus can be divided into a volume part and a surface part.[1,2] To calculate the latter in this case one uses macroscopic concepts (surface tension, the chemical potentials of the homogeneous phases, etc). For small nuclear sizes this division of the energy is not justified, and the parameters of the nucleus are found by direct calculation of the partition function of many-particle complexes, without allowance, as a rule, for their interaction with the medium.[1] In the general case the interaction of a nucleus with the medium can be taken into account for systems admitting the use of model Hamiltonians. Such an approach has been used, e.g., in Refs. 3 and 6, in the description of the process of nucleation near a critical point. Lying at its basis are dynamical equations describing the change of the order parameter with time with allowance for a random force. This approach, however, requires some refinement, since the manner in which the nuclear-size distribution function is introduced in these papers is not sufficiently general.

In the present paper we analyze the process of nucleation of spherical nuclei in application to first-order phase transitions of the gas-liquid type. The starting point is the Fokker-Planck equation for the distribution function ρ of a defined subsystem with a nucleus with respect to the order parameters

$$n_{\mathbf{k}}=V^{-1}\int d^3r\,n(\mathbf{r})\exp i\mathbf{kr},$$

where $n(\mathbf{r})$ is the local density at the point $\mathbf{r}$, V is the volume of the subsystem, and $k<k_0$ (k_0^{-1} is the characteristic length scale of the smoothing[7]). The size distribution function of the nuclei is introduced on the basis of the concept of the most probable trajectory, in the space of the parameters $n_{\mathbf{k}}$, along which the transition of the subsystem from the initial unstable state of the old phase to the more stable new phase can occur. From analysis of the equation of the trajectory in the limit of large nuclear sizes we obtain expressions for the energy of formation of the nucleus and for the other parameters determining the nucleation process. As an example we consider the dependence of the frequency of nucleus formation on the parameters of the system in nucleation near a critical point.

1. THE STARTING EQUATIONS

In the local approximation in $n_{\mathbf{k}}$ the Fokker-Planck equation for the distribution function $\rho(\{n_{\mathbf{k}}\})$ can be represented in the form[2,8]

$$\frac{\partial\rho}{\partial t}=\sum_{\mathbf{k},\mathbf{k}'}\frac{\partial}{\partial n_{\mathbf{k}}}\Gamma_{\mathbf{kk}'}\rho_e\frac{\partial}{\partial n_{\mathbf{k}'}}\frac{\rho}{\rho_e},\qquad(1)$$

where $\Gamma_{\mathbf{kk}'}$ is the matrix of the kinetic coefficients (dependent, in the general case, on $n_{\mathbf{k}}$), $\rho_e=\exp(-\beta H)$ is the equilibrium distribution, β^{-1} is the temperature, and $H=H(\{n_{\mathbf{k}}\})$ is the Hamiltonian. In the framework of the squared-gradient approximation of the thermodynamics of inhomogeneous systems the Hamiltonian H is determined by the expression[9]

$$H=\int d^3\mathbf{r}\left[\frac{c}{2}|\nabla n|^2+W(n)\right],\quad W(n)=w(n)-\mu n,$$

where $n=n(\mathbf{r})$, c is the influence parameter, $w(n)$ is the free energy of the homogeneous liquid, and μ is the specified chemical potential of the particles in the system. For simplicity we shall suppose that the function $W(n)$ has one local maximum at $n=n_c$ and two local minima at $n=n_g$ and $n=n_l$ ($n_g<n_c<n_l$), corresponding to the homogeneous states of the old phase and the new phase.

Using the given expression for H, we shall consider the consistency of the solution of (1) in application to a subsystem consisting of old phase and a nucleus of the new phase. We introduce a set of parameters $x=x_1,\ldots,x_s$ by which the state of the nucleus can be characterized, and the corresponding phase functions $X=X_1,\ldots,X_s$, which depend on the $n_{\mathbf{k}}$. The solution of (1) can then be sought in the form

$$\rho=\rho_e\exp\beta\left[\mu(X)+\sum_\alpha\mu_\alpha(X)n_\alpha+\ldots\right],\qquad(2)$$

where $\mu(x)$ and $\mu_\alpha(x)$ are certain functions of x, and the n_α are linear combinations of the parameters $n_{\mathbf{k}}$ (not expressable in terms of X). Confining ourselves in (2) to those terms of the expansion in n_α that have been written out and determining $\mu(x)$ and $\mu_\alpha(x)$ from the condition for synchronization of first moments—the distribution function $f(x)$ of the nuclei with respect to the parameters x, and the distribution $n_\alpha(x)$:

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$$f(x)=\langle\delta(x-X)\rangle, \quad n_\alpha(x)=f^{-1}(x)\langle\delta(x-X)n_\alpha\rangle,$$

where

$$\delta(x-X)=\prod_i \delta(x_i-X_i),$$

and the angular brackets denote averages over ρ, it is not difficult to obtain from (1) a closed system of equations for $f(x)$ and $n_\alpha(x)$. Neglecting terms associated with fluctuation of the kinetic coefficients, we can write these equations in the form

$$\frac{\partial f(x)}{\partial t}+\sum_i \frac{\partial}{\partial x_i} u_i f(x)=0,$$

$$\frac{\partial n_\alpha(x)}{\partial t}+\sum_i u_i \frac{\partial n_\alpha(X)}{\partial x_i}=-\sum_{\alpha'} L_{\alpha\alpha'}(x)\beta\mu_{\alpha'}(x) \tag{3}$$

$$-\sum_i L_{\alpha i}(x)\left[\left(\frac{\partial\beta\Omega(x)}{\partial x_i}\right)_\mu+\frac{\partial \ln f(x)}{\partial x_i}\right], \tag{4}$$

where

$$u_i(x)=-\sum_\alpha L_{i\alpha}(x)\beta\mu_\alpha(x)$$

$$-\sum_j L_{ij}(x)\left[\left(\frac{\partial\beta\Omega(x)}{\partial x_j}\right)_\mu+\frac{\partial \ln f(x)}{\partial x_j}\right]$$

$$\Omega(x)=-\beta^{-1}\ln\int d\{n_{\mathbf{k}}\}\delta(x-X)\exp\beta\left[\sum_\alpha \mu_\alpha(x)n_\alpha-H\right],$$

$$\left(\frac{\delta\Omega(x)}{\partial x_i}\right)_\mu=\left(\frac{\partial\Omega(x)}{\partial x_i}\right)_{\{\mu_\alpha(x)\}}, \quad n_\alpha(x)=-\frac{\delta\Omega(x)}{\delta\mu_\alpha(x)},$$

and the kinetic coefficients $L_{\alpha\alpha'}(x)$, $L_{\alpha i}(x)=L_{i\alpha}(x)$, and $L_{ij}(x)$ are determined as averages over $f^{-1}(x)\delta(x-X)\rho$ of the expressions

$$\sum_{\mathbf{k},\mathbf{k}'}\frac{\partial n_\alpha}{\partial n_{\mathbf{k}}}\Gamma_{\mathbf{k},\mathbf{k}'}\frac{\partial n_{\alpha'}}{\partial n_{\mathbf{k}'}^*}, \quad \sum_{\mathbf{k},\mathbf{k}'}\frac{\partial n_\alpha}{\partial n_{\mathbf{k}}}\Gamma_{\mathbf{k}\,\mathbf{k}'}\frac{\partial X_i}{\partial n_{\mathbf{k}'}^*},$$

$$\sum_{\mathbf{k},\mathbf{k}'}\frac{\partial X_i}{\partial n_{\mathbf{k}}}\Gamma_{\mathbf{k}\,\mathbf{k}'}\frac{\partial X_j}{\partial n_{\mathbf{k}'}^*},$$

respectively. The terms

$$\sum_\alpha \frac{\partial}{\partial x_i} f(x)\frac{\delta L_{ij}(x)}{\delta\mu_\alpha(x)}\frac{\partial\mu_\alpha(x)}{\partial x_i}$$

omitted in (3) are important only for large deviations of $\mu_\alpha(x)$ and $\partial\mu_\alpha(x)/\partial x_i$ from zero, and will not be considered henceforth. An analogous remark also applies to (4).

Introducing the formal parameter ε determining the relative order of magnitude of the kinetic coefficients and replacing

$$L_{\alpha\alpha'}(x)\to\varepsilon^2 L_{\alpha\alpha'}(x), \quad L_{\alpha i}(x)\to\varepsilon L_{\alpha i}(x),$$

we shall seek the solution of (3), (4) in the form of a series in powers of ε^{-1}. Taking into account only the first nonvanishing terms of the expansion in ε^{-1}, we obtain the following equations for $f(x)$ and $\mu_\alpha(x)$:

$$\frac{\partial f(x)}{\partial t}=\sum_{i,j}\frac{\partial}{\partial x_i}D_{ij}(x)f_e(x)\frac{\partial}{\partial x_j}\frac{f(x)}{f_e(x)}, \tag{5}$$

$$\mu_\alpha(x)=-\beta^{-1}\sum_{\alpha',i}L_{\alpha\alpha'}^{-1}(x)L_{\alpha' i}(x)\left[\frac{\partial\beta F(x)}{\partial x_i}+\frac{\partial \ln f(x)}{\partial x_i}\right], \tag{6}$$

where

$$f_e(x)=\exp\left[-\beta F(x)\right], \quad F(x)=\Omega(x)|_{\{\mu\ (x)\}=0},$$

$$D_{ij}(x)=L_{ij}(x)-\sum_{\alpha,\alpha'}L_{i\alpha}(x)L_{\alpha\alpha'}^{-1}(x)L_{\alpha' j}(x).$$

Here $L_{\alpha\alpha'}^{-1}(x)$ is the inverse of the matrix $L_{\alpha\alpha'}(x)$, and the parameter ε is not written out explicitly. The kinetic coefficients in (5), (6) are calculated in the zeroth approximation in $\mu_\alpha(x)$. The given equations describe the nucleation process in conditions of slow relaxation of the distribution $f(x)$ and fast relaxation of $n_\alpha(x)$.

2. NUCLEATION OF SPHERICAL NUCLEI

The basic parameters x_i by which the state of the nucleus is characterized are the sizes. To introduce the phase functions $X_i=X_i(\{n_{\mathbf{k}}\})$ corresponding to these parameters we shall consider the most probable trajectory, in the space of the parameters $n_{\mathbf{k}}$, along which the subsystem can undergo a transition from the initial unstable state of the old phase to the more stable new phase. This trajectory passes through a saddle point of the function H in the direction of steepest descent, and can be found from the condition that the vectors $dn_{\mathbf{k}}$ and $\partial H/\partial n_{\mathbf{k}}^*$ be collinear, i.e., from the equation

$$\frac{\partial n(\mathbf{r})}{\partial\tau}=-\frac{\delta H}{\delta n(\mathbf{r})}, \tag{7}$$

where τ is a real parameter. Using the solution $n(\mathbf{r},\tau)$ of (7), we can construct a set of vectors orthogonal to the trajectory, and also the tangent vector $\partial n(\mathbf{r},\tau)/\partial\tau$, and use these to determine the required set of phase functions.

Henceforth we shall confine ourselves to analyzing the process of nucleation of spherical nuclei. In this case the connection between the parameter τ and the radius $x_1=a$ of the nucleus, and also the dependence of the phase function $X_1=R$ on $n_{\mathbf{k}}$, can be determined by the relations

$$n(a,\tau)=n_c, \tag{8}$$

$$\Phi(R)\equiv\int d^3\mathbf{r}\frac{\partial n(r,R)}{\partial R}\left[n(r,R)-n(\mathbf{r})\right]=0, \tag{9}$$

where $n(r,\tau)$ is a spherically symmetric solution of (7), describing the subsystem with the nucleus, $n(r,a)=n(r,\tau(a))$, and $\tau(a)$ is the solution of (8). In accordance with (9), for $F(x)=F(a)$ we shall then have the expression

$$F(a)=-\beta^{-1}\ln\int d\{n_{\mathbf{k}}\}\delta(a-R)\exp(-\beta H)$$
$$=-\beta^{-1}\ln\int d\{n_{\mathbf{k}}\}\left|\frac{\partial\Phi(a)}{\partial a}\right|\delta[\Phi(a)]\exp(-\beta H). \tag{10}$$

The integral in (10) is determined principally by the value of the factor $|\partial\Phi(a)/\partial a|\exp(-\beta H)$ at the point of the conditional extremum of H, which can be found from the equations

$$\frac{\delta H}{\delta n(\mathbf{r})}-\dot{a}\frac{\delta\Phi(a)}{\delta n(\mathbf{r})}=0, \quad \Phi(a)=0, \tag{11}$$

where $\dot{a}$ is a Lagrange multiplier. The solution (11) has the form $\dot{a}=da/d\tau$ and $n(\mathbf{r})=n(r,a)$, since, by definition, the trajectory $n(r,a)$ minimizes H in the plane orthogonal to the vector $\partial n(r,a)/\partial a$. Consequently,

$$F(a) \approx H(a) - \beta^{-1} \ln \int d^3\mathbf{r} \left| \frac{\partial n(r,a)}{\partial a} \right|^2, \tag{12}$$

where $H(a)$ is the value of H for $n(\mathbf{r}) = n(r,a)$. This approximation corresponds to the mean-field approximation. We note that, in accordance with (7), $H(a)$ can be represented in the form

$$H(a) = -\int^a da\, \dot{a} \int d^3\mathbf{r} \left| \frac{\partial n(r,a)}{\partial a} \right|^2. \tag{13}$$

We now consider the expression for the size-diffusion coefficient $D_{11}(x) = D(a)$ of the nucleus, which appears in the equation for $f(x) = f(a)$:

$$\frac{\partial f(a)}{\partial t} = \frac{\partial}{\partial a} D(a) f_e(a) \frac{\partial}{\partial a} \frac{f(a)}{f_e(a)}, \tag{14}$$

where $f_c(a) = \exp[-\beta F(a)]$. We shall define the parameters n_α by the relations

$$n_\alpha = \int d^3\mathbf{r}\, \varphi_\alpha(\mathbf{r}, R)\, n(\mathbf{r}),$$

where $\varphi_\alpha(\mathbf{r},a)$ is the set of all unit vectors orthogonal to the vector

$$\varphi(r,a) = \lambda(a)^{-1/2} \frac{\partial n(r,a)}{\partial a}, \quad \lambda(a) = \int d^3\mathbf{r} \left| \frac{\partial n(r,a)}{\partial a} \right|^2.$$

In addition, we shall use operator notation for the projector

$$P(\mathbf{r}, \mathbf{r}') = \varphi(r,a)\varphi(r',a),$$

the matrix $\Gamma(\mathbf{r},\mathbf{r}')$ in (1), and

$$D(\mathbf{r}, \mathbf{r}', a) = D(a) P(\mathbf{r}, \mathbf{r}'),$$

using bold print for the operators. By analogy with the above, the averages over $\delta(a-R)\exp\beta[F(a) - H]$ that appear in $D(a)$ can be replaced in this case by their values at the point $n(\mathbf{r}) = n(r,a)$, and, with allowance for the equalities

$$\frac{\partial \Phi(R)}{\partial R} \frac{\delta R}{\delta n(\mathbf{r})} = \frac{\partial n(r,R)}{\partial R},$$

$$\frac{\delta n_\alpha}{\delta n(\mathbf{r})} = \varphi_\alpha(r,R) + \frac{\delta R}{\delta n(\mathbf{r})} \int d^3\mathbf{r}' n(\mathbf{r}') \frac{\partial \varphi_\alpha(r',R)}{\partial R}$$

$\mathbf{D}(a)$ can be represented in the form

$$\mathbf{D}(a) \approx \lambda^{-1}(a) \mathbf{P} \left[\mathbf{\Gamma} - \mathbf{\Gamma} \left(1 - \delta a \frac{\partial \mathbf{P}}{\partial a}\right) \times \mathbf{Q} (\mathbf{Q} \tilde{\mathbf{\Gamma}} \mathbf{Q})^{-1} \mathbf{Q} \left(1 - \delta a \frac{\partial \mathbf{P}}{\partial a}\right) \mathbf{\Gamma} \right] \mathbf{P}, \tag{15}$$

where

$$\tilde{\mathbf{\Gamma}} = \left(1 - \delta a \frac{\partial \mathbf{P}}{\partial a}\right) \Gamma \left(1 - \delta a \frac{\delta \mathbf{P}}{\partial a}\right),$$

$$\delta a = \lambda^{-1}(a) \int d^3\mathbf{r}\, n(r,a) \frac{\partial n(r,a)}{\partial a}$$

and $\mathbf{Q} = 1 - \mathbf{P}$. Using the operator equality

$$\mathbf{Q}(\mathbf{Q}\tilde{\mathbf{\Gamma}}\mathbf{Q})^{-1}\mathbf{Q} = \tilde{\mathbf{\Gamma}}^{-1} - \tilde{\mathbf{\Gamma}}^{-1}\mathbf{P}(\mathbf{P}\tilde{\mathbf{\Gamma}}^{-1}\mathbf{P})^{-1}\mathbf{P}\tilde{\mathbf{\Gamma}}^{-1},$$

we transform (15) to the form

$$\mathbf{D}(a) = \lambda^{-1}(a) \mathbf{P} \left(1 - \delta a \frac{\partial \mathbf{P}}{\partial a}\right)^{-1} \mathbf{P} (\mathbf{P} \tilde{\mathbf{\Gamma}}^{-1} \mathbf{P})^{-1} \mathbf{P} \left(1 - \delta a \frac{\partial \mathbf{P}}{\partial a}\right)^{-1} \mathbf{P},$$

and then, by direct expansion in powers of δa, to the following expression:

$$\mathbf{D}(a) = \lambda^{-1}(a) \mathbf{P} \left[\mathbf{P} \left(1 + \delta a \frac{\partial \mathbf{P}}{\partial a}\right) \mathbf{\Gamma}^{-1} \left(1 + \delta a \frac{\partial \mathbf{P}}{\partial a}\right) \mathbf{P} \right]^{-1} \mathbf{P}. \tag{16}$$

Calculating the matrix elements (in the basis $\varphi(a,r)$) of the latter expression, we obtain

$$D(a) = \left[\int d^3\mathbf{r} \int d^3\mathbf{r}'\, \psi(r,a) \Gamma^{-1}(\mathbf{r}, \mathbf{r}') \psi(r',a) \right]^{-1}, \tag{17}$$

where $\Gamma^{-1}(\mathbf{r},\mathbf{r}')$ is the inverse of the matrix $\Gamma(\mathbf{r},\mathbf{r}')$, and

$$\psi(r,a) = \frac{\partial n(r,a)}{\partial a} + \delta a \left[\frac{\partial^2 n(r,a)}{\partial a^2} - \frac{1}{2} \frac{\partial n(r,a)}{\partial a} \frac{\partial \ln \lambda(a)}{\partial a} \right].$$

In the following we shall use the approximation

$$\Gamma_{\mathbf{k}\mathbf{k}'} = \delta_{\mathbf{k},\mathbf{k}'} k^2 \Gamma_0 V^{-1},$$

where $\Gamma_0 = \text{const}$, and, consequently, in (17) we shall set

$$\Gamma^{-1}(\mathbf{r}, \mathbf{r}') = (4\pi\Gamma_0)^{-1} |\mathbf{r} - \mathbf{r}'|^{-1}.$$

3. THE FREQUENCY OF NUCLEUS FORMATION

We shall consider approximate solutions of (7) that have as $a \to \infty$ the form of a travelling wave $n(r,a) = n(r-a)$. Assuming the parameter c to be independent of $n(\mathbf{r})$, we represent (7) in the form

$$\dot{a} \frac{\partial n(r,a)}{\partial a} - c\nabla^2 n(r,a) + \Psi(n(r,a)) = 0, \tag{18}$$

where $\Psi(n) = \partial W(n)/\partial n$, and rewrite $\partial n(r,a)/\partial a$ as follows:

$$\frac{\partial n(r,a)}{\partial a} = -\frac{\partial n(r,a)}{\partial r} + \left[\frac{\partial n(r,a)}{\partial a} + \frac{\partial n(r,a)}{\partial r} \right]. \tag{19}$$

We shall treat the term in the square brackets in (19) as a perturbation. Then for $n(r,a)$ in the zeroth approximation in the perturbation we obtain from (18) the equation

$$\dot{a} \frac{\partial n(r,a)}{\partial r} + c\nabla^2 n(r,a) - \Psi(n(r,a)) = 0. \tag{20}$$

The boundary conditions for (20) are determined by the expressions

$$\left. \frac{\partial n(r,a)}{\partial r} \right|_{r=0} = 0, \quad n(r,a) \xrightarrow[r \to \infty]{} n_g,$$

and Eq. (8) serves to determine the dependence of $\dot{a}$ on a. The values of $F(a)$ and $D(a)$ in the given approximation are calculated using the formulas (12), (13), and (17) after the replacement of $\partial n(r,a)/\partial a$ by $-\partial n(r,a)/\partial r$. More accurate expressions for $F(a)$ and $D(a)$ can be obtained directly from the solution of (18) with initial conditions that can be found from an analysis of the dependence of H on $n_\mathbf{k}$ near the saddle point.

Equation (20) is simplified considerably for $d \ll a$, where d is the characteristic size of the interphase region. In this case we can introduce the variable $z = r - a$ and, omitting terms $\sim d/a$, represent Eq. (20) in the form

$$c\frac{\partial^2 n(z)}{\partial z^2} + v\frac{\partial n(z)}{\partial z} - \Psi(n(z)) = 0, \tag{21}$$

where $v = \dot{a} + 2c/a$. The boundary conditions and Eq. (8) for (21) can be written in the form

$$n(z) \xrightarrow[z\to-\infty]{} n_l, \quad n(z) \xrightarrow[z\to\infty]{} n_g, \quad n(0) = n_c,$$

and the parameter v is considered as an eigenvalue. Substituting the solution of (21) into the expressions for $F(a)$ and $D(a)$, to the same accuracy in d/a we shall have

$$F(a) = -\frac{4\pi a^3}{3}\Delta P + 4\pi a^2\sigma - \beta^{-1}\ln 4\pi a^2, \tag{22}$$

$$D(a) = (4\pi a^3)^{-1}(n_l - n_g)^{-2}\left(1 - \frac{\delta a}{a}\right)^{-2}\Gamma_0, \tag{23}$$

where $\Delta P = W(n_g) - W(n_l)$ is the difference of the pressures of the new and the old phase, $\sigma = v^{-1}c\Delta P$ is the surface-tension coefficient, and $\delta a = (2\sigma)^{-1}c(n_l^2 - n_g^2)$. In the general case, Eq. (21) can have several eigenvalues v. They are all positive, i.e., according to (21),

$$v\int dz \left|\frac{\partial n(z)}{\partial z}\right|^2 = \Delta P$$

and, by definition, $\Delta P > 0$. Obviously, into (22) and (23) we must substitute the largest eigenvalue, since in this case the energy of formation of a nucleus of critical size will be a minimum.

Approximating $\Psi(n)$ in (21) by the third-degree polynomial

$$\Psi(n) = B(n - n_g)(n - n_c)(n - n_l),$$

we obtain the familiar (from diffusion theory) solution describing the profile of a travelling wave with a concentration drop[10]:

$$n(z) = n_g + (n_l - n_g)\left[\exp\left(\frac{z + z_0}{d}\right) + 1\right]^{-1}, \tag{24}$$

and the following expressions for the parameters in (22) and (23):

$$\Delta P = \frac{B(n_l - n_g)^3}{12}(n_l + n_g - 2n_c), \quad \sigma = \frac{1}{6}\left(\frac{cB}{2}\right)^{1/2}(n_l - n_g)^3,$$
$$v = \left(\frac{cB}{2}\right)^{1/2}(n_l + n_g - 2n_c), \quad \delta a = 3d\frac{n_l + n_g}{n_l - n_g}, \tag{25}$$

where

$$d = \left(\frac{2c}{B}\right)^{1/2}(n_l - n_g)^{-1}, \quad z_0 = d\ln\frac{n_l - n_c}{n_c - n_g}.$$

The expressions (22), (23), and (25) differ from the corresponding expressions of the classical theory of nucleation in two respects: first, in the dependence, albeit weakly expressed, of the surface tension on the supersaturation, and second, in the different dependence of $D(a)$ on a from that adopted in the theory of nucleation in Ref. 1. For $\delta a \ll a$ our dependence $D(a)$ coincides with that cited in Ref. 3.

We shall use the given expressions to calculate the dependence of the frequency J of nucleus formation on μ and β near a critical point. The frequency J is determined by the stationary solution of (14) with the boundary conditions

$$f(a) \xrightarrow[a\to 0]{} Cn_l f_e(a), \quad f(a) \xrightarrow[a\to\infty]{} 0,$$

which leads to[1]

$$J = Cn_l\left\{\int_0^\infty da[D(a)f_e(a)]^{-1}\right\}^{-1}$$

$$\approx Cn_l 4\pi a^{*2} D(a^*)\left(\frac{4\beta\sigma}{\pi}\right)^{1/2}\exp(-\beta\Delta F), \tag{26}$$

where C is a parameter having the meaning of the number density of nuclei of zero size, $a^* = 2\sigma/\Delta P$, and $\Delta F = 4\pi a^{*2}\sigma/3$. The dependence of the parameters in (26) on μ and β is determined from the expansion[7,9]

$$\Psi(n) = -A(1 - \beta^{-1}\beta_{\text{cr}})(n - n_{\text{cr}})$$
$$+ B(n - n_{\text{cr}})^3 - \Delta\mu,$$

where n_{cr} and β_{cr} are the values of n and β at the critical point, $\Delta\mu = \mu - \mu_\infty$, and μ_∞ is the equilibrium value of the chemical potential (for a planar interphase boundary). Representing (in accordance with this expansion) the parameters in (26) in the form of series in powers of $\Delta\mu$, and confining ourselves to the first terms of the series, we shall have

$$J = J_{\text{cr}}(1 - \beta^{-1}\beta_{\text{cr}})^{-5/4}\exp[-\beta_{\text{cr}}\Delta F_{\text{cr}}(1 - \beta^{-1}\beta_{\text{cr}})^{7/2}], \tag{27}$$

where

$$\Delta F_{\text{cr}} = \left(\frac{4}{3}\right)^4\frac{\pi}{\Delta\mu^2}\left(\frac{cB}{2}\right)^{3/2}\left(\frac{A}{B}\right)^{7/2}$$

$$J_{\text{cr}} = Cn_{\text{cr}}\Gamma_0\frac{\Delta\mu}{4}\left(\frac{2}{cB}\right)^{1/4}\left(\frac{B}{A}\right)^{5/4}.$$

The expression (27) differs from the corresponding expression for J in Ref. 3 only in the pre-exponential factor (in Ref. 3 the pre-exponential factor is $\sim\Delta\mu^3(1 - \beta^{-1}\beta_{\text{cr}})^{-11/14}$). Basically, this difference is connected with the fact that in (12) we took the logarithmic term into account. The region of applicability of (27) is limited by the conditions imposed on the chemical potential $[\Delta\mu \ll (4AB/3)^{1/2} \times n_{\text{cr}}^2(1 - \beta^{-1}\beta_{\text{cr}})^{1/2}]$ and on the size of the interphase region $[d \ll a^*]$.

Thus, introduction of the concept of the most probable trajectory in the space of the order parameters n_k makes it possible to introduce the concept of the sizes a of the nuclei and the size distribution function $f(a)$ of the nuclei, and to obtain from (1) the equation (14) without resorting to a macroscopic analysis of the nucleation process. The results of an analysis of the equation of the trajectory in the limit of large sizes of the nuclei agree in form with the results of the classical theory of nucleation. In the limit of small sizes of the nuclei, in accordance with the structure of Eq. (18) we should expect deviations from the results of the classical theory. In this case it is also necessary to make more consistent allowance (i.e., going beyond the framework of the mean-field approximation) for the influence of fluctuations on the character of the dependence of $F(a)$ on a.

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