Kinetics of nucleation at first-order phase transitions

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A study is made of the nucleation stage in the decomposition of a supersaturated two-dimensional solution. This problem is distinctive in that the concentration around a quasisteadily growing nucleus has a logarithmic behavior, making it necessary to consider a multidimensional Fokker-Planck equation in all the macroscopic variables characterizing the nuclei and the concentration field. The size distribution function of the nuclei and the rate of nucleation are found. The results are applied to the kinetics of layered crystal growth. It is noted that the distribution function over the unstable variable (in this case the size of a nucleus) has the universal property that it is independent of the kinetic coefficients.

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The problem of determining the rate of nucleation at a first-order phase transition usually reduces to that of solving the Fokker-Planck equation for the size distribution function of the new-phase nuclei and the macroscopic problem of the growth of the transcritical nuclei without allowance for fluctuations. This approach, which was suggested by Zel'dovich,[1] (see also Ref. 2), is justified in the case of sufficiently fast relaxation of the remaining degrees of freedom (e.g., the concentration field around the nucleus in a supersaturated solution). This condition, however, is not always satisfied. In particular, Voronkov[3] has pointed out that it can be violated for two-dimensional nucleation on the face of a crystal during layered growth.

In the present paper we investigate the decomposition of a two-dimensional supersaturated solution. In this problem the approximation of a one-dimensional Fokker-Planck equation is also inapplicable if diffusion in the solution is important. Similar cases requiring the introduction of additional variables were considered by Kramers,[4] by Landauer and Swanson,[5] and, in the most general form, by Langer.[6] We shall obtain the Fokker-Planck equation for the distribution function over all the thermodynamic degrees of freedom of the system under consideration, and, solving it, we shall find the size distribution function of the nuclei and express the nucleation rate in terms of the thermodynamic probability for the formation of a critical nucleus. We shall apply the results to the kinetics of layered crystal growth.

1. NUCLEATION IN THE DECOMPOSITION OF A TWO-DIMENSIONAL SOLUTION

Suppose that the concentration $\bar{c}$ of a weak two-dimensional solution is slightly greater than the solubility limit c_k, so that the supersaturated γ is small:

$$\gamma=(\bar{c}-c_k)/c_k\ll 1.$$

The state of the system at an arbitrary time is determined by the position, size, and shape of the nuclei of the precipitating phase and by the concentration field $c(\mathbf{r})$ in the solution. For a small supersaturation the number of nuclei is small, and they develop independently, so it is sufficient to consider a system consisting of one nucleus. The probability of a given state of the system is determined by the minimum work W necessary to attain it. The latter is made up of the work of creating the concentration field.

$$W_1=\frac{T}{\bar{c}}\int(c-\bar{c})^2 d^2r$$

and the work of formation of the nucleus

$$W_2=\alpha P+n_0(\mu_0-\mu)S,$$

where T is the temperature, P and S are the perimeter and area of the nucleus, α is the energy per unit length of the phase boundary, and n_0 is the number of atoms per unit area of the nucleus. The difference in the chemical potentials of the atoms in the nucleus and in solution is

$$\mu_0-\mu=T\ln(c_k/\bar{c})\approx -T\gamma.$$

The saddle point—the extrememum of W—corresponds to a nucleus in the form of a circle of radius

$$R_k=\alpha/n_0T\gamma. \tag{1}$$

In a polar coordinate system with origin at the center of this (critical) nucleus, we represent the shape of the boundary $\rho(\theta)$ in the form of an expansion

$$\rho(\theta)=R_k+\sum_{m=-\infty}^{+\infty}\rho_m Y_m(\theta) \tag{2}$$

in the orthogonal system of functions

$$Y_0(\theta)=1,\quad Y_m(\theta)=\sqrt{2}\begin{cases}\cos m\theta & \text{for } m\geqslant 1\\ \sin m\theta & \text{for } m\leqslant -1\end{cases}. \tag{3}$$

In the neighborhood of the saddle point the ρ_m are small, and to quadratic accuracy we have

$$W_2=\pi T n_0\gamma\left[R_k^2+\sum_{m=-\infty}^{+\infty}(m^2-1)\rho_m^2\right].$$

The equilibrium distribution function over the states of the nucleus is obtained by integrating the complete distribution function $\exp[-(W_1+W_2)/T]$ over the possible realizations of the concentation field $c(\mathbf{r})$. Here, strictly speaking, the integration should be carried out under the auxiliary condition that the total number of particles in the system be conserved:

$$n_0S+\int c\,d^2r=\text{const}.$$

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However, if the area of the system is large enough this condition is unimportant, and the distribution function over the states of the nucleus is simply $\exp(-W_2/T)$. When the invariance of the problem with respect to translations of the nucleus as a whole ($m = \pm 1$) and the stability with respect to changes in shape ($|m| \geqslant 2$) are taken into account, the equilibrium distribution function of the nuclei over their dimensions $R = R_k + \rho_0$ is

$$f_0(R)=f_0(R_k)\exp[\pi n_0\gamma(R-R_k)^2], \tag{4}$$

where

$$f_0(R_k)=\text{const}\exp(-\pi n_0\gamma R_k^2) \tag{5}$$

[$f_0(R)dR$ is the number of nuclei per unit area having dimensions in the interval from R to $R+dR$].

The kinetics of nucleation and nuclear growth is governed by diffusion in the solution and by the processes of attachment and escape of particles at the phase boundary. Diffusion in the solution in the presence of δ-function-correlated fluctuational flows,

$$\langle J_\alpha(\mathbf{r},t)J_\beta(\mathbf{r}',t')\rangle=2D\bar{c}\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{6}$$

is described by the equation

$$\dot{c}=D\Delta c-\operatorname{div}\mathbf{J}, \tag{7}$$

where D is the diffusion coefficient. Conservation of matter in the system leads to a boundary condition of the form

$$n_0V_n=(D\nabla c-\mathbf{J})_n, \tag{8}$$

where V_n is the normal velocity of the phase boundary, and the quantity on the right-hand side is the normal component of the total flux. For the time being, let us assume for the sake of simplicity that the phase boundary has fast kinetics, so that at each point on the boundary a local equilibrium is established:

$$c_b=c_k(1+\gamma R_k\varkappa), \tag{9}$$

where $\varkappa$ is the curvature of the boundary.

Equations (6)–(9) form a complete system of Langevin equations, which is equivalent to an infinite-dimensional Fokker-Planck equation. To obtain this equivalent equation, let us perform a separation of variables.

The rotational part of the fluctuational flows is not important, and we shall therefore treat them as potential flows:

$$\mathbf{J}=-D\nabla\varphi.$$

Since we are interested in nuclei which are close to critical, let us linearize boundary conditions (8) and (9). Substituting $c(\mathbf{r})$ and $\varphi(\mathbf{r})$ in the form of an expansion in the circular harmonics (3)

$$c(r,\theta)-\bar{c}=\sum_{m=-\infty}^{+\infty}c_m(r)Y_m(\theta),\quad \varphi(r,\theta)=\sum_{m=-\infty}^{+\infty}\varphi_m(r)Y_m(\theta)$$

and describing the shape of the nucleus by expansion (2), we obtain from (7)–(9) the following system of equations:

$$\dot{c}_m=D\Delta_m(c_m+\varphi_m),\quad \Delta_m\equiv\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}-\frac{m^2}{r^2}, \tag{10}$$

$$\dot{\rho}_m=\frac{D}{n_0}\frac{\partial}{\partial r}(c_m+\varphi_m)\Big|_{r=R_k},$$

$$c_m|_{r=R_k}=\frac{c_k\gamma}{R_k}(m^2-1)\rho_m.$$

Eliminating ρ_m from the last two equations yields the following boundary condition

$$\dot{c}_m=\frac{Dc_k\gamma}{n_0R_k}(m^2-1)\frac{\partial}{\partial r}(c_m-\varphi_m)|_{r=R_k}$$

for equation (10)

Let us now introduce a system of functions $\Phi_m^\lambda(r)$ satisfying Bessel's equation

$$\lambda\Phi_m^\lambda=D\Delta_m\Phi_m^\lambda$$

with the boundary conditon

$$\lambda\Phi_m^\lambda(R_k)=\frac{Dc_k\gamma}{n_0R_k}(m^2-1)\frac{\partial\Phi_m^\lambda(r)}{\partial r}\Big|_{r=R_k}. \tag{11}$$

For $|m|\geqslant 1$ only a continuous spectrum $\lambda<0$ exists, while for $m=0$ there is also a split-off positive eigenvalue $\lambda=\lambda_0$ in addition to the continuous spectrum. The eigenfunction corresponding to λ_0 is of the form

$$\Phi_0^{\lambda_0}(r)=K_0\left(\sqrt{\frac{\lambda_0}{D}}r\right), \tag{12}$$

while the eigenvalue λ_0 itself is given by the equation

$$z=\frac{c_k\gamma}{n_0}\frac{K_1(z)}{K_0(z)},\quad z\equiv\sqrt{\frac{\lambda_0}{D}}R_k, \tag{13}$$

which is obtained by substituting (12) into boundary condition (11) (K_0 and K_1 are Macdonald functions).

Expanding $c_m(r)$ and $\varphi_m(r)$ in the basis Φ_m^λ:

$$c_m(r)=\int c_m^\lambda\Phi_m^\lambda(r)\,d\lambda,\quad \varphi_m(r)=\int\varphi_m^\lambda\Phi_m^\lambda(r)\,d\lambda,$$

we obtain the Langevin equations in the separated variables:

$$\dot{c}_m^\lambda=\lambda(c_m^\lambda+\varphi_m^\lambda). \tag{14}$$

The correlators of the random forces

$$\langle\varphi_m^\lambda(t)\varphi_{m'}^{\lambda'}(t')\rangle=D_m^\lambda\delta_{mm'}\delta_{\lambda\lambda'}\delta(t-t'),$$

can be found from (6).

The system of equations (14) is equivalent (see, e.g., Ref. 7) to the Fokker-Planck equation for the distribution function $F(c_m^\lambda)$

$$\dot{F}=-\frac{\partial}{\partial c_0^{\lambda_0}}\left[\lambda_0c_0^{\lambda_0}F-\lambda_0^2D_0^{\lambda_0}\frac{\partial F}{\partial c_0^{\lambda_0}}\right]$$

$$-\sum_{m=-\infty}^{+\infty}\int_{-\infty}^{0}d\lambda\frac{\partial}{\partial c_m^\lambda}\left[\lambda c_m^\lambda F-\lambda^2D_m^\lambda\frac{\partial F}{\partial c_m^\lambda}\right], \tag{15}$$

in which the variables c_m^λ are separated. Saddle-point linearized Fokker-Planck equations of the type in (15) were studied in Refs. 4–6. The item of interest to us, viz., the size distribution of the nuclei, is obtained by the appropriate integration of the stationary distribution function $F(c_m^\lambda)$. This integration for the Fokker-Planck equation is done in general form in the Appendix. It turns out that the distribution function over the unstable variable is uniquely determined by the equilibrium distribution function and does not depend on the kinetic coefficients.

In our case the unstable variable is the size of the nucleus, and the distribution function $f(R)$ which we seek is of the form [see (A.5)]

$$f(R)=f_0(R_k)\,(n_0\gamma)^{1/2}\exp[\pi n_0\gamma(R-R_k)^2]\int\limits_{R-R_k}^{\infty}\exp(-\pi n_0\gamma\xi^2)\,d\xi. \tag{16}$$

In the region of subcritical dimensions of the nucleus, $R_k - R \gg (n_0\gamma)^{-1/2}$, the distribution function (16) goes over to the equilibrium function (4).

The rate of nucleus formation (the flow through the saddle) is governed by the growth rate of the unstable mode (see Appendix). To find this growth rate one must solve the fluctuationless problem, which, in the variables c_m^λ is of the form

$$\dot{c}_m^\lambda=\lambda c_m^\lambda$$

[Eq. (14) without the fluctuation terms φ_m^λ. The unstable mode corresponds to the single positive value $\lambda=\lambda_0$ determined by Eq. (13). Since $c_k\gamma/n_0 \ll 1$, the quantity z in (13) is small, and, to logarithmic accuracy, we find the following expression for λ_0:

$$\lambda_0=\frac{2Dc_k\gamma}{R_k^2 n_0}\left(\ln\frac{n_0}{c_k\gamma}\right)^{-1}. \tag{17}$$

This formula is valid in the limit of infinitely fast kinetics at the phase boundary. For a finite rate of attachment and escape of particles, the boundary condition is no longer (9) but rather (without the fluctuation term)

$$n_0V_n=\Gamma[c_b-c_k(1+\gamma R_k\varkappa)],$$

where Γ is the corresponding kinetic coefficient. For the growth rate λ_0 of the unstable mode we obtain, in place of (17),

$$\lambda_0=\frac{\Gamma c_k\gamma}{n_0R_k}\left[1+\frac{\Gamma R_k}{2D}\ln\frac{1+D/\Gamma R_k}{c_k\gamma/n_0}\right]^{-1}, \tag{18}$$

which goes over to (17) under the condition

$$D/\Gamma R_k \ll \ln(n_0/c_k\gamma). \tag{19}$$

This inequality is always satisfied in the limit $\gamma\to 0$. If, instead of (19), the opposite inequality holds, the kinetics is limited by the processes occurring at the boundary of the nucleus, and λ_0 does not depend on the diffusion coefficient in the solution:

$$\lambda_0=\Gamma c_k\gamma/R_kn_0.$$

The nucleation rate I (the number of transcritical nuclei arising in a unit area per unit time) is, according to (A.9),

$$I=f_0(R_k)\lambda_0/2\pi(n_0\gamma)^{1/2}, \tag{20}$$

where $f_0(R_k)$ is the thermodynamic probability for the formation of a critical nucleus [Eq. (5)], and λ_0 is given in the general case by Eq. (18). The nucleation rate (20) is governed mainly by the exponential factor appearing in $f_0(R_k)$. The problem of determining the pre-exponential factor in $f_0(R_k)$ is an independent problem which, as far as we know, has never been solved. Therefore, our results (as in Refs. 1–3) in fact amounts to an evaluation of the kinetic pre-exponential in the expression for the nucleation rate.

2. TWO-DIMENSIONAL NUCLEATION DURING LAYERED CRYSTAL GROWTH

The problem of this section is analogous to the previously considered problem of the decomposition of a two-dimensional solution. A nucleus on an atomically smooth face is a multiatom terrace bounded by a ring-shaped step. The concentration of atoms n_0 in the nucleus is the surface density of lattice sites in the corresponding crystallographic plane. The gas of adsorbed atoms responsible for the growth of the nucleus is distributed with concentration $c(\mathbf{r})$ over the entire surface of the face, including the area of the nucleus.

The dimension R_k of the critical nucleus and the size distribution function of the nuclei are given by expressions (1) and (16), respectively. In place of (7), the diffusion equation (both outside the nucleus and on it) is of the form

$$\dot{c}=D\Delta c-(c-\bar{c})/\tau_0, \tag{21}$$

where the additional term describes the input of material to the face from the interior, with characteristic time τ_0. Under the condition of conservation of matter, we must include the diffusion fluxes from both sides of the nuclear boundary, and in place of (8) we have

$$n_0V_n=D(\nabla c|_{r=R+0}-\nabla c|_{r=R-0})_n \tag{22}$$

(the fluctuation term, as in (21), has been dropped). Boundary conditions (9) remains unchanged. The distribution of adatoms corresponding to the unstable mode is described by Macdonald functions: by $K_0([(\lambda_0+1/\tau_0)/D]^{1/2}r)$ outside the nucleus and by $I_0([(\lambda_0+1/\tau_0)/D]^{1/2}r)$ on the nucleus. The equation for λ_0 obtained from boundary conditions (9) and (22) is

$$\lambda_0K_0([(\lambda_0+1/\tau_0)/D]^{1/2}R_k)\,I_0([(\lambda_0+1/\tau_0)/D]^{1/2}R_k)=Dc_k\gamma/n_0R_k^2. \tag{23}$$

To determine the nucleation rate one must substitute the value for λ_0 obtained from (23) into formula (20).

Let us discuss the limiting cases in which the solution of the transcendental equation (23) can be written in explicit form. In the limit of small supersaturation γ, when $\tau_0 \ll R_k^2/D$, the argument of the functions K_0 and I_0 is large, and

$$\lambda_0=(2c_k\gamma/n_0)(D/R_k^2\tau_0)^{1/2}.$$

In the opposite case ($\tau_0 \gg R_k^2/D$) the expression for λ_0 is

$$\lambda_0=\frac{2Dc_k\gamma}{R_k^2n_0}\left|\ln\left(\frac{R_k^2}{D\tau_0}+\frac{2c_k\gamma}{n_0}\right)\right|^{-1}, \tag{24}$$

which goes over to (17) at a sufficiently high (but still small compared to unity) degree of supersaturation γ, when

$$\tau_0 \gg R_k^2n_0/Dc_k\gamma.$$

3. DISCUSSION

In this paper the size distribution function (16) of the nuclei is found by integrating the exact solution of the multidimensional Fokker-Planck equation over all the stable variables. We note that this same result could have been obtained by assuming, in analogy with Ref. 1, that the nuclear size R is a Markov variable and writing the corresponding (one-dimensional) Fokker-Planck equation for this variable. However, as was pointed out by Voronkov,[3] such an approximation is justified only in those cases when either the concentration variables are not at all important (kinetics limited at the nuclear boundary) or the concentration field at a fixed

R relaxes sufficiently rapidly to some steady (dependent only on R) distribution, i.e., the quasisteady approximation is valid.1)

In the three-dimensional case[1] there are in fact grounds for assuming that the size of the molecules is a Markov variable. The quasisteady concentration field falls off with distance as r^{-1}. The relaxation time of such a field, $\tau_c \sim R_k^2/D$, is small compared to the characteristic time for changes in the quantity $R - R_k$ (the deviation of the nuclear size from critical)

$$\lambda_0^{-1} \sim (R_k^2/D)\,(n_0/c_k\gamma).$$

In the two-dimensional case the quasisteady approximation does not exist, since the stationary solution of the diffusion equation ($\ln r$) diverges at large distances. In the problem of layered crystal growth the input of material from the interior alters the diffusion equation in such a way [see (21)] that the stationary solution is nondivergent at infinity. The quasisteady approximation is not always applicable,[3] however, but only for

$$\tau_0 \ll \frac{R_k^2 n_0}{D c_k \gamma} \ln \frac{D\tau_0}{R_k^2} \tag{25}$$

[the results obtained in Ref. 3 agree with (24) within the limits of their applicability (25)].

In summary, the problem of two-dimensional nucleation does not in general reduce to the one-dimensional Fokker-Planck equation in the size of the nucleus. However, as follows from the analysis given in the Appendix, in all cases the use of this equation gives the correct stationary nuclear size distribution function, having a universal form (16).

APPENDIX

Let us consider the general form of a Fokker-Planck equation linearized about a saddle point:

$$\dot{F} = M_{ij} \frac{\partial}{\partial x_i}\left[F H_{jk} x_k + T \frac{\partial F}{\partial x_j} \right]. \tag{A.1}$$

Here $F(\mathbf{x})$ is the distribution function over the variables x_i and the temperature T. The matrix H determines the quadratic form of the energy:

$$\mathscr{H} = {}^1\!/_2 x_i H_{ij} x_j,$$

which is not positive definite at the saddle point. The negative eigenvalue of the martrix H is assumed to be unique, so that in any diagonal representation of the energy $\mathscr{H}$ one of the coefficients is negative. We shall call the variable corresponding to this coefficient "unstable."

The matrix M in the case of purely dissipative systems is the positive definite symmetric matrix of kinetic coefficients. In dynamical systems (in this case $\mathbf{x}$ is the set of coordinates and momenta and $\mathscr{H}$ is the Hamiltonian) the matrix M contains, in addition to the symemtric kinetic part M^+ ($M_{ij}^+ \neq 0$ only for indices i, j corresponding to the momenta), an antisymmetric dynamic part M^-, which is made up of ones and minus ones in such a way that the Hamiltonians of the equation of motion are of the form

$$\dot{x}_i = -M_{ij}^- H_{jk} x_k.$$

The equilibrium solution of equation (A.1) is of the Gibbs form

$$F_0 = \text{const} \exp(-\mathscr{H}/T).$$

We are interested in the stationary solution of equation (A.1) corresponding to the leakage of particles from the region on one side of the saddle, where equilibrium is assumed to be established, through the saddle to the other side. Following Langer,[6] we seek this solution in the form

$$F(\mathbf{x}) = F_0(\mathbf{x}) \int_0^\infty \exp\left[-\frac{1}{2}(\xi + u_i x_i)^2 \right] d\xi, \tag{A.2}$$

where $\mathbf{u}$ is a constant vector. Substitution of (A.2) into (A.1) yields an equation for $\mathbf{u}$:

$$H_{ij} M_{jk} u_k + T(u_j M_{jk} u_k)\, u_i = 0. \tag{A.3}$$

Suppose equation (A.1) is written in one of the bases which diagonalize $\mathscr{H}$. We shall assume that in the diagonal representation of the energy

$$\mathscr{H} = \frac{1}{2} \sum_i H_i x_i^2$$

the unstable variable corresponds to the index $i = 0$, i.e., $H_0 < 0$. The distribution function with respect to the variable x_0 is obtained by integrating the complete distribution function (A.2) over all the stable variables x_i ($i \neq 0$) under the condition $x_0 = \text{const}$:

$$f(x_0) = \text{const} \int_0^\infty d\xi \int \exp\left[-\frac{1}{2T} \sum_i H_i x_i^2 - \frac{1}{2}(\xi + u_i x_i)^2 \right] \prod_{i \neq 0} dx_i. \tag{A.4}$$

The inside integral is Gaussian and so can be evaluated simply by finding the maximum argument of the exponential with respect to the variables x_i ($i \neq 0$). The position of the maximum is determined by the equation

$$H_i x_i + T(\xi + u_j x_j)\, u_i = 0 \qquad (i \neq 0),$$

the solution of which, with allowance for (A.3), is of the form

$$x_i = \frac{(x_0 + \xi/u_0)}{M_{0k} u_k} M_{ij} u_j \quad (i \neq 0).$$

Substituting the expressions found for x_i into (A.4), we obtain

$$f(x_0) = f_0(x_0) \left(\frac{|H_0|}{2\pi T} \right)^{1/2} \int_{x_0}^\infty \exp\left(-\frac{|H|\xi^2}{2T} \right) d\xi, \tag{A.5}$$

where

$$f_0(x_0) = \text{const} \exp\left(\frac{|H_0| x_0^2}{2T} \right)$$

is the equilibrium x_0 distribution function reached by $f(x_0)$ in the limit $-x_0 \gg (T/|H_0|)^{1/2}$.

This result has the important property that the stationary distribution over the unstable variable x_0 is independent of the kinetic coefficients, while the expression for the complete distribution function (A.2) contains the kinetic matrix M in an important way [see Eq. (A.3)]. This property does not depend on the particular means used to diagonalize the energy.

To evaluate the total flow of particles through the saddle, let us make use of the following simple considerations (which are analogous to some extent with Ref. 1). Far from the saddle point the fluctuations are unimportant, and the particles which have passed through the saddle move in accordance with the equation of motion

$$\dot{x}_i = -M_{ij}H_{jk}x_k. \tag{A.6}$$

In conformity with the presence of a single unstable variable, the matrix $(-MH)$ has one positive eigenvalue λ, leading to the presence of a single exponentially growing solution of equation (A.6). Since the remaining solutions are exponentially damped, far from the saddle point the particles which have passed through it asymptotically obey

$$x_i = A_i e^{\lambda t}, \tag{A.7}$$

where A_i is the eigenvector corresponding to the positive eigenvalue λ of the matrix $(-MH)$. The distribution functions $f(x_0)$ for $x_0 \to \infty$ has the asymptotic form

$$f(x_0) = f_0(0)\,(T/2\pi|H_0|)^{1/2}x_0^{-1}. \tag{A.8}$$

Evaluating the flow of particles through the plane $x_0 = \text{const}$ and choosing x_0 sufficiently large, we obtain from (A.7) and (A.8)

$$I = \dot{x}_0 f(x_0) = \lambda (T/2\pi|H_0|)^{1/2} f_0(0). \tag{A.9}$$

This result agrees with the result[6] obtained by direct integration of the complete distribution function (A.2).

[1)] The rate of relaxation of the variables describing the distortion of the nuclear shape and the angular dependence of the concentration field is not important, since in the linear approximation the angular harmonics in the Fokker-Planck equation always separate, and the nuclear dimension in this case is correlated only with the isotropic part of the concentration field.

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