Microscopic Reversibility and the Nonlinear Einstein–Onsager Relation in Macroscopic Description of Nucleation

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We investigate the possibility of describing fluctuational decay of a metastable phase macroscopically, without a detailed knowledge of the microscopic kinetics. Using the ideas of microscopic reversibility, we construct a hydrodynamic-type equation which describes the buildup of fluctuations in the region of subcritical sizes. An equation of Ornstein–Uhlenbeck type is used to bridge this equation with the one describing unstable growth of larger (overcritical) fluctuations. An explicit time-dependent solution to the proposed system of equations is derived in the spirit of the singular perturbation technique. It is shown that this solution also accurately approximates the solution of the Farkas–Becker–Döring master equation, so that the macroscopic level of description is consistent with the underlying models.

KEY WORDS: Metastable system; large fluctuations; time-dependent nucleation; singular perturbations; master equation; random walk.

1. INTRODUCTION

In fundamental applications of the principle of microscopic reversibility (MR) there are two major trends. The first is related to the understanding of the origin of macroscopic (hydrodynamic) laws from the first-principle reversible microscopic kinetics (for a recent review see ref. 1). The second trend is to start with macroscopic equations and use MR to (a) understand their symmetry and (b) include fluctuations as a first step beyond the hydrodynamic description. It is this trend where some of the most

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impressive results of Lars Onsager were obtained.[2, 3] What remained unsolved after Onsager is mainly related to *large* fluctuations; a relatively recent review can be found in ref. 4.

In the present study we apply the principle of microscopic reversibility to describe fluctuation-induced onset of a new phase (nucleation). Fluctuations here are not only large (they have to exceed some critical size in order to become unstable), but they are also crucial, as without them the metastable phase would never decay. We are going to construct *macroscopic* equations which correctly describe either the decay or the buildup of fluctuations (Section 2). Further, in Section 3 we derive an explicit time-dependent solution to these equations for an arbitrary distribution of subcritical fluctuations. An important point is that this macroscopic solution turns out to be consistent with the solution of a master equation[5, 6] which models nucleation on a mesoscopic level. This is discussed in Section 4. Another, more formal aspect of the problem considered is that up to the form of the boundary conditions the mentioned master equation describes a typical random walk problem. In this sense the macroscopic level of description is related to "continuous approximation of a random walk"—a well-known topic since the classical papers of Kramers and Moyal.[7] This problem still attracts much attention—see, e.g., ref. 8 and references therein—and several approximation schemes were proposed.[9, 10] Remarkably enough, for the specific problem considered, the ideas of MR allow one to approximate the time-dependent solution of the master equation *directly*, without an intermediate Fokker–Planck approximation, although identification with an appropriate approximation scheme can be performed *a posteriori*. This is briefly discussed in Section 5, while a more detailed study of the relation between the nucleation and the random walk problem is contained in ref. 11.

2. MACROSCOPIC DESCRIPTION OF NUCLEATION

Consider the entropy reduction $\Delta S(n)$ associated with the reversible formation of a spherical "droplet" of a new phase which contains n molecules. In a metastable system this entropy will have a characteristic minimum at some value n_*, known as the "critical size." If the droplets are to be treated as fluctuations, one can formally introduce their (unnormalized) "equilibrium" distribution $f_n^{eq} \propto \exp\{\Delta S(n)\}$, which is the well-known Einstein probability formula. Of course, this distribution is unphysical at $n > n_*$, where $\Delta S(n)$ increases unboundedly. Nevertheless, one may suspect that well below the critical size, fluctuations are "unaware" of their potential instability and are in local equilibrium with monomers. As the equilibrium distribution is defined up to a prefactor, one can require $f_1^{eq} = f_1$, where f_1

is the number of monomers in the system. On a macroscopic level the decay rate (or growth rate for $n > n_*$) of a dropletlike fluctuation is given by a phenomenological expression $\dot{n}(n)$ which changes its sign at the critical size. Decay of a distribution of such fluctuations $f(n, t)$ can be described by a continuity equation

$$\partial f/\partial t = -\partial j/\partial n \qquad (1a)$$

$$j = \dot{n} f \qquad (1b)$$

Every subcritical fluctuation of size n will vanish after a characteristic decay time $t_{\text{dec}}(n) = -\int_0^n dn/\dot{n}$. We deliberately do not distinguish between $n = 1$ and $n = 0$ on the lower limit of integration, as such differences must not affect the macroscopic picture. Naturally, the integral in the above expression for the decay time is expected to converge on this limit. This really turns out to be the case for typical nucleation models, where due to surface tension effects, small fluctuations rapidly decay. From the principle of MR one would expect that the same time $t_{\text{dec}}(n)$ is required to build up a fluctuation of size n. In this case the only possible *first-order* differential equation which would be automatically satisfied by the equilibrium distribution is given by

$$\partial v/\partial t = \dot{n} \, \partial v/\partial n \cdot \qquad (2)$$

with $v(n, t)$ being the ratio of the kinetic distribution f to the equilibrium distribution f_n^{eq}. Note that unlike $f_n^{\text{eq}} \sim \exp(\Delta S)$ (and f in the region of buildup of equilibrium), which may change on a microscopic scale due to large values of $\Delta S(n)$, the function $v(n, t)$ is expected to be *smooth*.[12] The latter property allows a hydrodynamic-type description given by Eq. (2). Alternatively, the standard equation (1) which will be used later for description of deterministic growth of fluctuations at $n > n_*$ assumes a smooth function $f(n, t)$.

Both Eqs. (1) and (2) fail near the critical size n_* in a region characterized by the width $\delta = [(1/2) \, \partial^2 \Delta S/\partial n^2]^{-1/2}$. In this region fluctuational corrections to the deterministic growth rate become important. Since in the macroscopic limit the barrier $-\Delta S(n_*)$ increases slower than n_* (like $n_*^{2/3}$ in classical nucleation theory), the value of δ remains large, i.e., $1 \ll \delta \ll n_*$. On the other hand, the change of entropy in this region is of the order of unity, so that all the functions can be treated as smooth, and the conventional Fokker–Planck description is valid. The latter is given by Eq. (1a) with the diffusional correction $-D \, \partial f/\partial n$ added to the flux j in Eq. (1b). The coefficient D can be determined from the conventional Einstein–Onsager relation $\dot{n} \approx D \, \partial \Delta S/\partial n$.[6] One can show that the change of the

diffusion coefficient in the near-critical region is negligible, which leads to the Ornstein–Uhlenbeck equation

$$\tau \frac{\partial f}{\partial t} = \frac{\delta^2}{2} \frac{\partial^2 f}{\partial n^2} - \frac{\partial}{\partial n}(n - n_*) f, \qquad \tau^{-1} \equiv \frac{d\dot{n}}{dn}\bigg|_{n = n_*} \qquad (3)$$

Equations (1)–(3) describe the problem in the singular perturbation sense. Below we will illustrate the technique of solution more explicitly after specifying the initial and boundary conditions. Note that when obtaining these equations, unlike previous treatments,[12, 13] we did not assume any specific form of the underlying microscopic kinetics. Also, the conventional Einstein–Onsager relation was employed solely near the equilibrium point where it is guaranteed to be valid. Otherwise—if one would wish to relate $\dot{n}$ to microscopic properties at *any* values of n—this relation may have a completely different form (see Section 4).

3. SOLUTION OF THE MACROSCOPIC EQUATIONS

Consider the following initial conditions: $f(n, 0) = N\delta(n - n_1)$, $n_1 < n_*$. Physically, this means that initially there are no large size fluctuations, except for N artificially inserted droplets of a subcritical size n_1. We switch to Laplace transforms of Eqs. (1) and (2) with respect to time (luckily, the resulting expression can be inverted) and obtain, at $n_1 < n < n_*$, $V(n, p) \sim \exp\{-pt_{\text{dec}}(n)\}$. Here $V(n, p)$ is the transform of $v(0, t)$, and the prefactor can be obtained from the standard boundary condition $v(0, t) \equiv 1$ [i.e., $V(0, p) = 1/p$], which means that small fluctuations have an equilibrium distribution. In the direct vicinity of n_* the decay time diverges. Here the second-order equation—the Laplace transform of Eq. (3)—should be incorporated. The inner solution is given by $V^{\text{in}}(n, p) \sim i^m \operatorname{erfc}[(n - n_*)/\Delta]$ with $m \equiv p\tau$ and $i^m \operatorname{erfc}(z)$ being the repeated error integral.[14] The proportionality coefficient is derived in a standard manner by matching the inner and outer solutions.[12] To the other side of the barrier the dropletlike fluctuations grow deterministically and can be described by Eq. (1). Up to an n-independent factor, one has here for the Laplace transform of the flux $J(n, p) \sim \exp[-pt_{\text{gr}}(n_0, n)]$, where $t_{\text{gr}}(n_0, n)$ is the time of deterministic (macroscopic) growth from some value $n_0 > n_*$ to n. This value n_0, as well as the proportionality coefficient, can be derived from matching with the right-hand asymptote of the inner solution. The result reads

$$J(n > n_*, p) = \tau j_{\text{st}} \Gamma(m) \exp\{-pt_i(n)\} \left\{ 1 - \frac{Np}{\dot{n}_1 f_{n_1}^{\text{eq}}} \exp[pt_{\text{dec}}(n_1)] \right\} \qquad (4)$$

Here j_{st} is the steady-state flux over the barrier[6]

$$j_{st} = \frac{\delta}{2\tau\sqrt{\pi}} f_1 \exp[\Delta S(n_*)] \tag{5}$$

and $t_i(n)$ is the "incubation time"[15]

$$t_i(n) = t_{dec}(n_* - \delta/\sqrt{2}) + t_{gr}(n_* + \delta/\sqrt{2}, n)$$

$$= 2\tau \log \frac{n_* \sqrt{2}}{\delta} - 2\tau \int_0^{n_*} dn \left(\frac{1}{\tau\dot{n}} - \frac{1}{n-n_*}\right) + \int_0^n \frac{dn}{\dot{n}} \tag{6}$$

(the principal value of the integral is assumed).

Asymptotically (i.e., $\delta/n_* \to 0$), the inversion of the Laplace transform given by Eq. (4) can be performed through summation of residues located in the *finite* part of the complex p-plane. This gives[11]

$$j(n, t) = j^0(n, t) - \frac{N}{\dot{n}_1 f_{n_1}^{eq}} \frac{\partial}{\partial t} j^0(n, t + t_{dec}(n_1))$$

with

$$j^0(n, t) = j_{st} \exp\{-\exp[(t_i(n) - t)/\tau]\} \tag{7}$$

corresponding to the flux of nucleated particles in the absence of pre-existing droplets.[12, 15]

Strictly speaking, description of nucleation given by Eqs. (5)–(7) is not completely macroscopic, since, in principle, mesoscopic corrections to $\Delta S(n_*)$ may be important. Though one can expect that relative values of such corrections (and their derivatives) to be small, their absolute values may not be, leading to dramatic changes in the values of j_{st}. Consider, e.g., the logarithmic term discussed in ref. 16, or the "Lothe–Pound" correction.[17] Nevertheless, the expression for the *reduced* flux, $j(n, t)/j_{st}$, is completely macroscopic: It is determined by the kinetics $\dot{n}(n)$ and by the thermodynamics—the second derivative of the entropy, which enters through δ, being insensitive to the details of the microscopic behavior. We will now illustrate this by choosing a specific type of microscopic kinetics and demonstrating that Eq. (7) approximates the solution of the corresponding master equation.

4. NUCLEATION FROM A MASTER EQUATION

The classical model[5, 6] assumes the following master equation:

$$\partial f_n/\partial t = j_n - j_{n+1}, \qquad j_n = \beta_{n-1} f_{n-1} - \alpha_n f_n \tag{8}$$

Here the gain β_n is usually taken from simple kinetic model of collisions of molecules with the surface of the nucleus. The loss coefficient α_n is constructed from the detailed balance condition $\beta_{n-1} f_{n-1}^{eq} = \alpha_n f_n^{eq}$ with supposedly known equilibrium distribution f_n^{eq}. The left-hand boundary condition of the same type as discussed above is assumed: $f_1 = f_1^{eq} = \text{const}$. This condition can be considered for time scales which are smaller than the lifetime of the metastable state. Otherwise, the depletion of monomers is to be taken into account.[18] In the leading approximation the deterministic growth rate $\dot{n}$ can be associated with the difference of the gain and loss coefficients $\beta_n - \alpha_n$. The objective is, however, to obtain a macroscopiclike expression which would not contain any kind of finite differences. This can be done if one notes that the functions β_n, $\Delta S(n)$, etc. (but not f_n^{eq}!) are expected to be smooth. Thus, from the detailed balance condition one obtains[13]

$$\dot{n} \approx \beta_n \{ 1 - \exp(-\partial \Delta S / \partial n) \} \tag{9}$$

The latter can be considered as a nonlinear (or maybe more accurately, discrete) form of the Einstein–Onsager relation with β_n associated with the diffusion coefficient D (see also ref. 19). Note that despite the smoothness of the entropy as a function of n, its derivative is not necessarily small, as the values of $\Delta S(n)$ are large (macroscopic), so that in a general case Eq. (9) cannot be linearized. More explicitly, consider the standard expression

$$\Delta S(n) = a \cdot n - l \cdot n^{2/3}, \qquad a \equiv \Delta \mu / kT \tag{10}$$

with $\Delta \mu$ being the difference of chemical potentials between phases and l the reduced "surface tension." Substituting this in Eq. (9), one obtains $\dot{n} = \beta_n \{ 1 - \exp[a((n_*/n)^{1/3} - 1)] \}$. The parameter a describes the effect of discreteness of sizes n.[12, 20] The conventional Einstein–Onsager relation, which would have the form $\dot{n} = \beta_n a[1 - (n_*/n)^{1/3}]$, is recovered at all sizes only for $a \ll 1$. However, physically one typically encounters larger values of a unless nucleation is observed very close to the critical temperature.

We now expect that the time-dependent solution of the master equation (8) can be approximated by Eq. (7) with the growth rate given by the above expression. In Fig. 1 we illustrate this by comparing Eq. (7) with the numerical solution of the master equation for $\beta_n \sim n^{2/3}$. We consider that the accuracy is quite good (no matching parameters were used)—recall that the master equation has nonlinear coefficients and that the discreteness parameter in the example considered was larger than unity—i.e., $a \approx 1.2$. For example, the standard Kramers–Moyal truncation procedure in this case would lead to an exponentially large error even for the steady-state
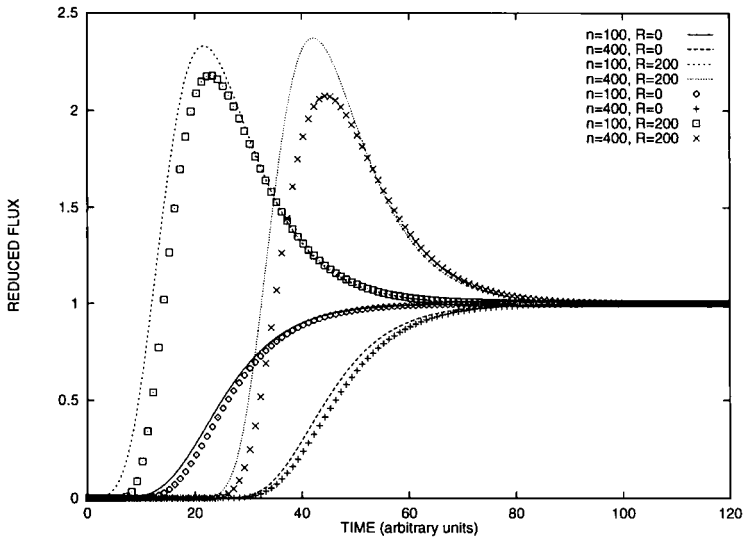
Fig. 1. Time dependence of the reduced nucleation flux $j(n, t)/j_{st}$ at different sizes n and for different values of the ratio $R \equiv N/f_{n_1}^{eq}$ (N is the number of dropletlike fluctuations with size $n_1 = 20$ created at $t = 0$, and $f_{n_1}^{eq}$ is their equilibrium concentration). Lines: macroscopic solution (7) with the growth rate (9); symbols: numerical results from the master equation (8). Other parameters: $\tau = 7.96$ (when measured in the same units as "time"), $-\Delta S(n_*) = 29.9$, $n_* = 50.1$.

flux j_{st}, not to mention the more delicate time-dependent behavior. At present we cannot prove in a general form that Eq. (7) approximates the time-dependent solution of the master equation with asymptotic accuracy for $\delta/n_* \to 0$, although we suspect that this is the case. Nevertheless, we can demonstrate that this solution is accurate in a sense of a specific criterion, namely the so-called *time lag*, being defined as

$$t_L(n) = \int_0^\infty dt \left\{ 1 - j(n, t)/j_{st} \right\} \tag{11}$$

The mathematical convenience of this criterion is due to the possibility of its direct derivation from the master equation *both* exactly and asymptotically.[20] Physically, it can be directly measured in an experiment[21] and is often the only observable indicator of time-dependent effects. From the macroscopic solution—Eq. (7)—one has

$$t_L(n) = t_i(n) + \gamma\tau + N/(f_{n_1}^{eq}\dot{n}_1) \tag{12}$$

where $\gamma = 0.5772...$ is the Euler constant. An asymptotic study of the exact expression for the time lag from the master equation in the absence of preexisting droplets $(N = 0)$ was performed in ref. 20, and its extension to account for such droplets[11] gave precisely Eq. (12). This proves that at least for the mentioned criterion (the time lag) the macroscopic description is asymptotically equivalent to the one given by the master equation. Note that the expression for the time lag contains, in fact, *three* free parameters, namely n_1 (the size of inserted subcritical droplets), N (their number), and n (the overcritical size at which the flux is observed). Thus, the level of comparison is rather detailed.

5. THE FOKKER–PLANCK EQUATION AND HIGHER APPROXIMATIONS

It is possible to construct a unique Fokker–Planck equation with correct outer branches given by Eqs. (1) and (2), which has been done in ref. 11. Such an equation accurately approximates the underlying microscopic kinetics, which in reality may not have a Fokker–Planck form—recall the master equation of Section 4. For the master equation (8) this Fokker–Planck equation can be also obtained in the leading order of the general approximation scheme proposed by Hänggi *et al.*[10] With asymptotic accuracy such an equation will be satisfied by the same solution (7), which means that in the sense of the mentioned criterion of comparison—the time lag—it provides an accurate approximation to the random walk master equation (8). On a less formal level, however, a Fokker–Planck equation will hardly be an advantage compared to macroscopic equations of Section 2, which are incomparably simpler for solution.

In case one would wish to improve the accuracy beyond the macroscopic level of description, one simply has to replace carefully the finite differences in Eq. (8) by derivatives, up to the second order, and treat the "extra" terms as corrections. An important point, however, is that when considering *subcritical* sizes—this is required to refine the constants in Eq. (7)—one has first to switch from Eq. (8) to an equation for the reduced distribution $v(n, t)$,[12] as it is this function [and not $f(n, t)!$] which is a smooth with respect to n in this region.

6. CONCLUSION

The principle of microscopic reversibility allows one to describe the fluctuation-induced nucleation by hydrodynamic-type equations without a detailed knowledge of the underlying microscopic kinetics. As shown both

numerically and analytically, the solution of these macroscopic equations is consistent with predictions of the Farkas–Becker–Döring master equation which models nucleation on a mesoscopic level.

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