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Continuous approximation of a random walk

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We consider the problem of nucleation affected by pre-existing nuclei which can be treated as a one-step random process described by a nonlinear master equation (ME). We construct a nontrivial time-dependent expression for the flux of nucleated particles and demonstrate that in the sense of a specific criterion—the time lag of transient nucleation—this expression satisfies the ME with asymptotic accuracy. A Fokker-Planck approximation to the ME which describes correctly both nucleation and growth is also constructed.

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The approximation of a random-walk master equation (ME) by a differential equation of a Fokker-Planck (FP) type is a classical problem [1] which attracts much attentions in modern literature as well [2–4]. It is impossible to enumerate even a small part of the related physical situations (see, e.g., Ref. [2(c)]), but typically they include mesoscopic objects which can be characterized by a discrete random variable n representing the number of molecules in a small droplet [5], number of monomers in a polymer chain [6], or the number of excess unit charges in a tunnel-diode circuit [7]. From a physical point of view the main characteristics of a FP equation are the equilibrium distribution $f_n^{\rm eq}$ and the deterministic growth rate, $\dot{n}$. Intuitively, for a "good" FP approximation these two properties should correspond to those of the ME. This imposes very rigid conditions on the choice of the FP coefficients [3(a)]. Violation of the equilibrium condition which is encountered, e.g., in the well-known Kramers-Moyal truncation procedure, can lead to an exponentially large overestimation of the activation flux for barrier crossing problems [3(a), 7(b)]. The error produced by the violation of the growth condition is not so pronounced, but it increases unboundedly if the approximation is applied for arbitrary large n. Anyway, as the continuous equation cannot be identical to the ME, one needs an integral criterion of comparison, preferably one that can be derived exactly, which would "smooth" the unimportant differences. In addition, this criterion should also have a distinct physical meaning, so that an adequate FP equation can be considered as "experimentally indistinguishable" from the ME. For the standard random-walk problems, the natural choice for such a criterion is the mean first-passage time (MFPT) [3(a)]; in the following study we shall use a mathematically similar quantity, adjusted to the physical situation discussed.

From the above it should be clear that the validity of a particular FP approximation cannot be evaluated *a priori*. Moreover, even after the criterion of comparison is introduced, the approximation problem will remain somewhat academic until the solution, or at least a clear outline of the analytical method, is presented. Otherwise, if one would wish to solve the equations numerically, the ME could be much more convenient than its FP approximation. For that reason in the present paper, we stress the *analytical solution*, presenting first the general method and the results, and then demonstrating that these results are asymptotically accurate for the ME. Only then do we construct an adequate FP approximation the validity of which is thus proven "automatically." On the basis of this treatment we are able to point out the adequate approximation scheme among those reported previously [3(a)].

As a particular physical example we shall consider the ME of the nucleation theory in its classical version [5], which is a "nonlinear" ME in terms of Ref. [2(c)]. The well-known Zeldovich continuous approximation [5(b)] correctly accounts for the equilibrium distribution and for the growth rate in the direct vicinity of the critical size n_*. These properties are sufficient to predict the steady-state flux of nucleated particles over the barrier. The time-dependent solutions of the Zeldovich equation, however, are very sensitive to the values of the growth rate at all sizes [8]. Thus, the application of this approximation scheme far from n_* can, in principle, lead to unboundly large errors [9]. Alternatives to the Zeldovich approximation were discussed in Ref. [10]. However, a FP equation which would predict correctly both $f_n^{\rm eq}$ and $\dot{n}$, or in more physical terms both nucleation and growth, has not been obtained up to this date.

In the present paper we obtain the time-dependent expression for the nucleation rate affected by pre-existing nuclei. Furthermore, we prove the asymptotic accuracy of the obtained expression for ME using as a criterion of comparison the so-called time lag of transient nucleation which, mathematically, is similar to MFPT. In a derivation of the time lag from the ME we follow the outline of Ref. [9], although we also include the effects of the pre-existing nuclei. Formally, this means more general initial conditions, and, in view of the available experimental data for glasses [11], accounting for such nuclei is, probably, the only possibility of remaining in the borders of classical nucleation theory [12]. Finally, we are going to construct a FP equation which correctly accounts for both nucleation and growth, and demonstrate that the solution to this equation is the same time-dependent expression mentioned above.

The time dependence of the distribution function f_n is determined by [5]

$$\frac{\partial f_n}{\partial t}=j_n-j_{n+1}\ ,\quad j_n=\beta_{n-1}f_{n-1}-\alpha_n f_n\ . \tag{1}$$

The gain β_n is usually taken from some simple kinetic model of collisions of monomers with the surface of a nucleus; typically, it is a power-law function of n. Alternatively, the loss α_n is not implemented in the ME *a priori* but is reconstructed from the detailed balance condition with $f_n^{\rm eq}\propto\exp\{-U(n)/kT\}$. Here, $U(n)$ is the minimal work to form a nucleus, given by the well-known difference of surface ($\sim n^{2/3}$) and volume ($n\delta\mu$) terms with $\delta\mu$ being the difference of chemical potentials. For a metastable system the equilibrium distribution $f_n^{\rm eq}$ is non-normalizable and should be considered solely as an auxiliary construction. Note that this function is defined accurately to a constant factor which one can specify to obtain at $n=1$ the number of monomers.

Due to the smoothness of β and U as functions of n the deterministic growth rate $\dot n=\beta_n-\alpha_n$ is given by [4(a)]

$$\dot n\approx\beta_n\{1-\exp(U'/kT)\}\ . \tag{2}$$

The prime in Eq. (2) denotes a derivative with respect to n. For the specific form of $U(n)$ considered, one has $U(n)=U_*[3(n/n_*)^{2/3}-2(n/n_*)]$ with $U_*\gg kT$ being the nucleation barrier and n_* denoting the critical nucleus. In this case Eq. (2) leads to $\dot n=\beta_n(1-\exp\{a[(n_*/n)^{1/3}-1]\})$ with $a=\delta\mu/kT$. The above expression is the generalized Einstein relation, and for small a it reduces to its conventional form $\dot n=-\beta U'/kT$. Thus, the quantity a can be identified as the "discreteness parameter" [8(a), 9]. More accurately, terms with β' should also be incorporated in the above expressions for $\dot n$. We will show, however, that in the leading approximation discussed such terms do not contribute to the solution.

Equation (1) is valid on a semi-infinite interval $1\le n<\infty$. Following Ref. [5] we expect the number of monomers f_1 to remain constant during the nucleation process [13]. In the large-time limit this inhomogeneous boundary condition leads to a nonequilibrium steady-state distribution with a nonzero flux $j_{\rm st}$. In what follows we attempt to construct a time-dependent solution to Eq. (1). We shall use the small parameter $\varepsilon^2=-2kT/[n_*^2U''(n_*)]=3kT/U_*$ and consider the asymptotic limit $\varepsilon\to0$. Other parameters of the problem, particularly the discreteness parameter a, can be arbitrary, though finite. Note that the transition probabilities in Eq. (1) satisfy van Kampen's scaling assumptions [2(c)] with $n_*\sim1/(a\varepsilon^2)$ playing the role of the large parameter Ω (the "size of the system"). However, in the present case one cannot expand the solution in the vicinity of deterministic trajectory. Rather, at $n<n_*$ we will need a "ghost" of such a trajectory describing an "uphill" motion of particles against a deterministic force.

We will discuss the approximation in terms of $F(n,p)$, the Laplace transform of $f_n(t)$, and $V(n,p)$, the Laplace transform of $v_n(t)=f_n(t)/f_n^{\rm eq}$. The main assumption [4,8(a)] is that for the simplest initial conditions the function $V(n,p)$ is smooth in the region of uphill motion of the particles, while in the region of downhill motion the smooth function is $F(n,p)$. For smooth functions the finite differences can be replaced by derivatives, so that the ME can be approximated as [4(a)]

$$pV-f_n(0)/f_n^{\rm eq}=\frac{d}{dn}\beta\frac{dV}{dn}+\dot n\frac{dV}{dn}\ ,\quad n\lesssim n_* \tag{3}$$

$$pF=\frac{d}{dn}\beta\frac{dF}{dn}-\frac{d}{dn}(\dot nF)\ ,\quad n\gtrsim n_*\ . \tag{4}$$

Here, $f_n(0)$ is the distribution at $t=0$ ("pre-existing nuclei"). We consider a monodisperse distribution of N subcritical nuclei, so that at $n>1$, $f_n(0)=N\delta(n-n_1)$ with $1\ll n_1<n_*$. The number of molecules contained in these nuclei, Nn_1, is expected to be much smaller than the number of monomers f_1, otherwise the validity of the left-hand boundary condition could be disputed. The results can be readily extended to an arbitrary $f_n(0)$ with n confined to $n<n_*$. The leading asymptotic solution which we are going to construct is not affected by terms containing β' [we remind the reader that such terms have been already neglected in Eq. (2)]. Thus, another form of the second-order term, say $(\beta F)''$ in Eq. (4), will lead to the same result—in what follows we show this more explicitly. The particular forms of Eqs. (3) and (4) have been chosen in such a way that they become equivalent to each other in the "true continuous limit" with $\dot n=-\beta U'/kT$. For higher approximations in ε these equations require corrections.

We solve Eqs. (3) and (4) using matched asymptotic expansions [14]. At $n_1<n<n_*$ we neglect the second-order term in Eq. (3) and obtain the outer solution. Near n_* in a standard manner [14, 8(a)] we match it with the inner solution $i^m erfc(z)$ (the repeated error function [15]) with $m=p\tau$, $\tau^{-1}=d\dot n/dn$ at $n=n_*$, and $z=(n-n_*)/\varepsilon n_*$. Despite small values of ε the solution is still smooth in terms of n as the inner region contains a large number of integer points: $\varepsilon n_*\sim(a\varepsilon)^{-1}\gg1$. One could argue that due to small values of $\dot n$ in the inner region the neglected corrections with β' may become important. However, although the input of such corrections really increases upon approach to the inner region (from $\sim a\varepsilon^2$ to $\sim a\varepsilon$ [8(a), 9]), it still remains small and can be disregarded in the leading approximation discussed. To the other side of the barrier, the right-hand asymptote of the inner solution as $z\to+\infty$ can be matched with the outer solution of Eq. (4) which describes deterministic growth. Thus, for $J=\dot nF$, being the Laplace transform of the flux in growth region, one obtains

$$J(n>n_*,p)=\tau j_{\rm st}\Gamma(m)\exp\{-pt_i(n)\}\times\left\{1-\frac{Np}{\dot n_1 f_{n_1}^{\rm eq}}\exp[pt_{\rm dec}(n_1)]\right\}\ . \tag{5}$$

Here, the deterministic decay time is defined as $t_{\rm dec}(n_1)=-\int_0^{n_1}dn/\dot n$ and $t_i(n)$ is the "incubation time" [8(b)],

$$t_i(n)=2\tau\ln\frac{\sqrt2}{\varepsilon}-2\tau\int_0^{n_*}dn\left[\frac{1}{\tau\dot n}-\frac{1}{n-n_*}\right]+\int_0^n\frac{dn}{\dot n} \tag{6}$$

(the principal value of the integral is indicated).

So far the derivation was straightforward as *ordinary* differential equations were considered. Before using the obtained Laplace transform to extract the *time dependence* of the solution, one should note that due to the asymptotic nature of the above derivation, Eq. (5) is valid for finite, nonasymptotic values of p. Thus, one should not expect an accurate time dependence for very small times. If, however, one is interested in larger time scales, one still can invert (5) through summation over the residues of $J(n,p)\exp(pt)$ located only in the *finite* part of the left half-plane. Summation over the residues of the γ function is elementary and yields

$$j(n,t)=j^0(n,t)-\frac{N}{\dot{n}_1 f_{n_1}^{\rm eq}}\frac{\partial}{\partial t}j^0[n,t+t_{\rm dec}(n_1)] \tag{7}$$

with

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

describing the flux in the absence of the pre-existing nuclei [8(a), 8(b)]. Note that the expected accuracy of the Laplace transform [Eq. (5)], from which we derived the last expression, is of the order of $\max\{a\varepsilon^2,\varepsilon^2\}$; this can be verified by estimation of the neglected terms. The accuracy of the inverse Laplace transformation is less controlled, but nevertheless one can expect that in a certain sense Eq. (7) is an accurate approximation to the solution of the ME for not too small times. To make this statement somewhat more rigorous we introduce a criterion of comparison, the "time lag" which is defined as

$$t_L(n)=\int_0^\infty dt\{1-j(n,t)/j_{\rm st}\}\ . \tag{8}$$

In other words, we are going to compare the areas under the transient curves $j(n,t)$. Integration of Eq. (7) gives

$$t_L(n)=t_i(n)+\gamma\tau+N/(f_{n_1}^{\rm eq}\dot{n}_1)\ , \tag{9}$$

where γ is Euler's constant. If one is able to show that the ME predicts (asymptotically) the same value of $t_L(n)$ for arbitrary values of parameters n_1, N, and n, one can conclude that Eq. (7) is "asymptotically close" (in the sense of the mentioned criterion, of course) to the solution of the ME.

The formal reason for choosing the time lag as a criterion of comparison is that it can be deduced directly from the ME *both* exactly and asymptotically—see Ref. [9] and the forthcoming discussion. At the same time, when making this choice we were also keeping in mind the experimental studies of Ref. [11]. In such studies a *large* number of nucleated particles is detected simultaneously and the time lag is the most adequate (and often the only observable) indicator of transient effects. In case, however, a *single* nucleus can be detected, the situation is more close to the first-passage time problem. Particularly, the flux $j(n,t)$ may not manage to achieve a noticeable fraction of the steady-state value before the first nucleus is detected. In this case an accurate description of relaxation to $j_{\rm st}$ (which is indicated by the time lag) becomes less pertinent. Here, alternative criteria and (for small passage times [16]) alternative methods of solution may be more adequate.

From the definition of the time lag [Eq. (8)] and the ME one has

$$\alpha_n t_L(n+1)-(\alpha_n+\beta_{n-1})t_L(n)+\beta_{n-1}t_L(n-1)=-1+j_n(0)/j_{\rm st}\ ,$$

where $j_n(0)$ is the flux at $t=0$. In the absence of pre-existing nuclei, $j_n(0)\equiv 0$, this equation, up to the form of boundary conditions and the shifted index of β_n, just coincides with the equation for the MFPT [see 2(c), 3(b) and references therein]. Thus, the time lag can be evaluated *exactly*, which is also true in the case of pre-existing nuclei. The possibility of exact evaluation of $t_L(n)$ was first indicated by Frisch [17] and was examined in more detail in subsequent papers [9,18]. For the initial distribution considered the result reads as

$$t_L(n>n_1)=t_L^0(n)-N\sum_1^{n_1-1}(\beta_k f_k^{\rm eq})^{-1}\ ,$$

where $t_L^0(n)$ is the time lag in the absence of pre-existing nuclei ($N=0$). In the above expression the sum is dominated by terms with k close to n_1. Due to the smoothness of β and U as function of n, this sum can thus be reduced to a geometric series which, together with (2) yields $-1/(f_{n_1}^{\rm eq}\dot{n}_1)$. Using this approximation, and the asymptotic approximation for $t_L^0(n)$ which was obtained from the ME in a similar manner in Ref. [9], one recovers Eq. (9) for *every* n in the growth region.

Physically, the approximation of the ME by two differential equations can be explained in the following manner. When describing particles moving "downhill" (in the deterministic direction) we apply the standard continuity equation, i.e., $\partial f/\partial t=-\partial j/\partial n$ with $j=\dot{n}f$, which corresponds to the outer solution of Eq. (4). On the other hand, if one wishes to describe the buildup of equilibrium—the "uphill" motion of particles—and at the same time satisfy the principle of microscopic reversibility, one has to consider the equation $\partial v/\partial t=\dot{n}\partial v/\partial n$, which corresponds to the outer solution of Eq. (3). An asymptotic approximation to the Green's function of the ME can be constructed from the "smooth" solutions of the homogeneous part of Eqs. (3) and (4), similarly to the "true continuous limit" [8(c)] when these two equations are identical to each other.

We now construct a single FP equation for the entire region of sizes. To ensure the correct equilibrium distribution, the flux should be proportional to $\partial v/\partial n$ [5(b)]. The coefficient, however, should be taken not as $-\beta f^{\rm eq}$, but should be adjusted to give the correct drift term. This leads to $j=-\beta f^{\rm eq}(\dot{n}/\dot{n}_c)\partial v/\partial n$ with the continuous growth rate $\dot{n}_c$ defined as $\dot{n}_c=-\beta U'/kT$. Thus, the required Fokker-Planck equation has the form

$$\frac{\partial f}{\partial t}=\frac{\partial}{\partial n}\beta f^{\rm eq}\frac{\dot{n}}{\dot{n}_c}\frac{\partial}{\partial n}\frac{f}{f^{\rm eq}}\ . \tag{10}$$

This equation is equivalent to the one that arises within the general approximation scheme proposed by Hänggi and co-workers [3(a)]. The Laplace transform of Eq. (10) is also asymptotically equivalent, however, to each of the differential equations (3) and (4) in the corresponding re-

gions. Thus, the time-dependent solution constructed above will "automatically" satisfy the FP equation (10), and asymptotic correctness of the latter follows from the correct prediction for the time lag. Note that unlike Eqs. (3) and (4), which allow a certain flexibility in the choice of the second-order terms, within Eq. (10) this term is fixed. In this sense this equation provides a unique (leading-order) FP approximation for the entire region of sizes for not too small times. On the other hand, when applying to the Laplace transform of Eq. (10) the technique described above, one should recall that this equation contains nonsmooth functions. Hence, one has to be able to predict regions with f smooth and regions with f/f^{eq} smooth, and one has to consider these regions separately thus recovering Eqs. (3) and (4).

We have considered the leading-order asymptotic approximation to the MF for not too small times. We have shown the asymptotic equivalence in this situation of the approximations by a *single* FP equation (10) and by a *pair* of simpler Eqs. (3) and (4). A nontrivial time-dependent solution to the differential equations [Eq. (7)] was constructed using the singular perturbation technique. This solution predicts asymptotically accurate values of the time lag for every size in the growth region, proving in this sense the validity of the proposed approximations.

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