Transient nucleation distributions and fluxes at intermediate times and sizes

Vitaly A. Shneidman
Department of Physics, New Jersey Institute of Technology, Newark, New Jersey 07102

(Received 6 June 2001; accepted 15 August 2001)

General interpolating expressions, valid for near- and arbitrary overcritical sizes of clusters, are proposed for the nucleation fluxes and distributions. Results are expressed in terms of the deterministic growth rates, and are characterized by a non-Gaussian dependence on the size of nuclei. In a sense, the proposed approximations combine the positive aspects of the parabolic model by Trinkaus and Yoo [Philos. Mag. A **55**, 269 (1987)] and of the boundary layer (''matched asymptotic'') solution earlier described by the author [Sov. Phys. Tech. Phys. **32**, 76 (1987); **33**, 1338 (1988)]. Specifications of the general results are made for several mainstream nucleation models via selection of appropriate growth rates. Examples include surface- and diffusion-limited nucleation in the continuous (Zeldovich–Frenkel) and discrete (Becker–Döring, Turnbull–Fisher) versions of the nucleation equation. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1409366]

I. INTRODUCTION

The physical problem of transient nucleation can be formulated as follows. An initially stable system is rapidly quenched into a metastable region, after which its thermodynamic parameters (temperature, pressure, etc.) are held constant. Nuclei of the new phase are formed due to thermal fluctuations and one is interested in the rate of their formation and distribution over sizes.

For many fluid systems, such as one-component supersaturated vapor or non-glass forming undercooled liquid, the actual transient period, typically, will be unobservably short and the nucleation process can be treated as steady state. (Eventually, the metastable phase will be exhausted by the growing nuclei, and the steady state will be destroyed, but this happens much later in time, and will not be part of the present study.) For solids, on the other hand, the time interval before the steady-state nucleation regime can be appreciable, and can range, for example, from minutes to days in case of crystal nucleation in glasses.[1–3] Similar effects are of interest in amorphous silicon.[4]

The classical picture views nucleation as a random walk of nuclei in the space of their sizes via random gain or loss of monomers. The master equation (the ''Becker–Döring equation'') was originally formulated in the steady-state version[5,6] which can be treated exactly.[5] Zeldovich[7] considered the time-dependent version of the master equation and gave some semiquantitative estimations for the transient problem. Nevertheless, in the absence of relevant experiments, the main attention was devoted to the steady state for which, in present terminology, an asymptotic analysis was performed. A numerical survey of early studies on transient nucleation which followed Ref. 7 until the early 1980s can be found, e.g., in Ref. 8.

The time-dependent Becker–Döring equation cannot be solved exactly.[9] There are a few features which can make even an asymptotic treatment a challenging task. First, coefficients of this equation are nonlinear functions of the size of a nucleus n. Second, the difference of the gain and loss coefficients changes sign at the critical size n_*. This feature is most natural from a physical point of view, describing transition from decay at $n<n_*$ to growth at $n>n_*$, but mathematically it leads to a rather complex boundary layer structure of the solution. Next, the standard methods of analysis are often hard to apply to a discrete equation, and one has to worry about constructing an adequate continuous approximation.[10–15] Still, a realistic continuous equation (e.g., the one due to Zeldovich and Frenkel) will retain the aforementioned nonlinear and boundary layer aspects.

Most of such aspects were ignored in early treatments of the transient problem. Kaschiev,[16] for example, replaced the nucleation equation by a diffusion equation in the near-critical region when evaluating the Green's function. This makes the problem exactly solvable, but the key feature of transition from nucleation to growth is lost, and many other aspects of nucleation are not reproduced.

In case one intends to mimic nucleation by a standard exactly solvable differential equation, the choice should be not the diffusion but the so-called unstable Ornstein–Uhlenbeck equation. This equation is well studied (especially in its stable version) in connection with random processes,[17] and the Green's function is known exactly. The Ornstein–Uhlenbeck equation has linear coefficients and homogeneous boundary conditions which makes it different from the Zeldovich–Frenkel equation, but the change of sign near n_* is properly reproduced.

The Ornstein–Uhlenbeck equation appears in the parabolic nucleation model employed by Trinkaus and Yoo[18] (TY). An inhomogenous boundary condition of the nucleation problem, formally, ruins the exact solvability, but most likely the standard Green's function of that equation is still a reasonable approximation and, within the model, the TY expressions are sufficiently close to the exact ones. Limitations

of the TY results come not so much from the solution itself, but rather from the parabolic model which is not accurate away from n_*, in the region of large sizes.

About the time of the TY paper, it was shown by the present author[19] that the general nucleation equation (with nonlinear coefficients) can be solved asymptotically if the nucleation barrier W_* is large compared to the thermal energy, T (Boltzmann constant is taken as unity). The method is based on a combination of matched asymptotic (MA) technique (which is standard in boundary layer analysis[20]) and the technique of Laplace transformations, and is briefly outlined in the Background section. The Laplace transform of an analog of the Ornstein–Uhlenbeck equation is indeed recovered as part of the solution, but only in the vicinity of n_*. In the growth region the resulting nucleation flux is described by a characteristic ''double-exponential'' function[19] with a non-Gaussian dependence on size.

Compared to the TY solution, the MA results can be applied to arbitrary sizes in the growth region[21] and to a general nucleation model, including the discrete Becker–Döring equation. In contrast to TY, however, the original MA solution predicted an asymptotic, not an exact zero at $t=0$, causing a certain surprise in some of the later publications. More importantly, the time-dependent flux[19] (and the resulting distribution) could not be used in the direct vicinity of n_*. Klimenko,[22] using a technically different asymptotic method, further showed that the solution[19] can be extended into the near-critical domain of sizes, although the problem at $t=0$ remained and, in fact was enhanced compared to the growth region. Subsequently, the MA approach was generalized[23] to construct a nucleation flux with an exact rather than an asymptotic zero at $t=0$; this was done, however, only at $n=n_*$, which prevented matching with the growth region. There were other related studies for the near-critical region—see references in Refs. 24 and 25—or for the growth region (e.g., in the contexts of pre-existing nuclei[23,26] or continuous quench[19,27]), but a unified approximation which would combine the positive aspects of the TY and MA approaches at all sizes has not been constructed.

The importance of such a unification can be substantiated by the fact that while the TY or the MA solutions can be accurate in the regions of sizes for which they are designed, naive attempts to extend them beyond their natural domains can be disastrous. For example, the growth-region distribution of the MA solution[19,21] diverges if extrapolated to $n=n_*$. Alternatively, the erfc-type near-critical approximation for the distribution of nuclei (which in the time-dependent version was suggested by TY and which with minor modifications enters all later relevant studies) can lead to an ''asymptotic catastrophe'' [25] if applied straightforwardly, without matching of asymptotes, towards large sizes. In addition, a single interpolation for the time dependence can clarify the nature of the asymptotic zero near $t=0$.

The goal of the present paper is thus to construct an expression for the distribution of nuclei which would bridge the sizes in the near critical and growth regions, and which would be applicable, at least formally, for arbitrary times, including $t=0$. This is achieved by Eq. (37), which is expected to be valid for various types of nucleation models, including discrete models of the Becker–Döring type.

Hopefully, the availability of a single unifying formula will consolidate the somewhat fragmented current state of the transient nucleation theory. However, the same general expression can have multiple simplified representations in various domains of times and sizes, and for specific nucleation models, which (together with clarification of some methodical issues) determines the overall volume of the paper.

Possible applications are related to analysis of time-dependent cluster distributions which span the near- and the overcritical sizes. Available examples of such distributions include computer experiments for nucleation in Ising systems.[28] Similar effects can be of potential interest for real-life experiments with a sufficiently large n_* (e.g., in polymers). In other situations the simpler MA expressions can be equally accurate, but the intent of the proposed general expressions is not to replace the earlier results, but rather to establish their interconnections and clarify the limits of applicability.

Results also can be useful in connection with numerical transient solutions of the Becker–Döring equations.[8,29,30] Such solutions, in principle, can have unlimited precision, playing the role of exact results for a specific nucleation model. It is often a challenge for an analytical treatment to reproduce numerical data with sufficient accuracy. At the same time, analytics can complement numerical treatments by a more general, ''*trans*-model'' view of the nucleation picture.

The paper has the following structure.

The Background section emphasizes the role of deterministic growth rate, $\dot{n}$ in the nucleation problem.[7] The TY solution and a recent attempt by Maksimov *et al.*[25] to extend it into the growth region, are also briefly analyzed here. Some insight into the structure of the MA solution is given. Remarkably, much of the understanding can be obtained already from the steady-state case, where a possibility of an exact treatment[5] provides additional help.

The transient flux is obtained in Sec. III via inversion of the Laplace transform derived earlier in Ref. 23. The result resembles the TY expression but with a non-Gaussian dependence on size described by a function $z(n)$. The latter, in turn, is determined by $\dot{n}$. The MA solution[19,21] is recovered in the growth region at larger times.

In Sec. IV the cluster distribution is obtained via integration of the flux. The result interpolates between the known erfc-type approximations in the near-critical region and the double-exponential expression at larger sizes, and has a proper steady-state limit. The number of nuclei also is evaluated in this section; interestingly enough, despite the different form of the result compared to the earlier MA expression, the time-lag[21] remains unchanged.

In Sec. V the general expressions are specified for several mainstream nucleation models via evaluation of the nonlinear function $z(n)$. Results can be expressed as elementary functions for the standard Zeldovich–Frenkel equation and for diffusion-limited nucleation. The situation is more involved for the discrete nucleation models, but simple interpolations are possible.

Section VI contains the discussion, and Appendixes A

and B, respectively, present some formal derivations and generalizations for the case of pre-existing nuclei, and the solution of the Becker–Döring equation in the strict limit $t \to 0$.

II. BACKGROUND

A. Thermodynamics, kinetics and the nucleation equation

In the classical theory of nucleation the minimal work which is required to form a nucleus of n monomers is given by

$$W(n) = W_* \left\{ 3\left(\frac{n}{n_*}\right)^{2/3} - 2\frac{n}{n_*} \right\}. \tag{1}$$

Here W_* is the work to form a critical nucleus with size n_*; according to Gibbs, W_* represents the barrier to nucleation. To ensure marginal stability of a metastable phase, this value should be large compared to the thermal energy T.

The growth rate $\dot{n}$ is determined by the kinetics of mass exchange between the nucleus and the matrix. The best known examples are the ballistic (surface-limited) and the diffusion-limited mass exchange mechanisms. Growth rates look simpler in terms of reduced radii r (with $\dot{r} = \dot{n}\, dr/dn$) and with neglect of discreteness effects are given by

$$\dot{r} = \frac{1}{\tau r^{\theta}}\left(1 - \frac{1}{r}\right), \quad r \equiv \left(\frac{n}{n_*}\right)^{1/3} \tag{2}$$

with $\theta = 0$ and $\theta = 1$ for the ballistic- and diffusion-limited cases, respectively. With $\theta = -1$, Eq. (2) corresponds to cavitation.[7] In all cases the parameter τ has a dimension of time and will be defined below. Growth rates which account for the discrete nature of n are also available, as described in Sec. V.

The actual model of nucleation requires evolution of the nuclei distribution function, $f_n(t)$. The corresponding master equation, the general "Becker–Döring equation" (BD), is given in Appendix B. At this point it should be sufficient to note that the key kinetic parameter of the master equation is the gain probability $\beta(n)$ (which specifies a *model* within the general BD scheme), and that the relation to experimentally observed "nucleation rate" is given by the flux $j(n,t)$. The BD equation is constructed in such a manner that the flux is identically zero for the (quasi) equilibrium distribution $N_n \propto \exp\{-W(n)/T\}$, which is equivalent to the detailed balance. The continuous version of that equation has the form[7]

$$\frac{\partial f}{\partial t} = -\frac{\partial j}{\partial n}, \quad j = -\beta(n) N \frac{\partial}{\partial n}\frac{f}{N}. \tag{3}$$

For surface-limited nucleation with $\beta(n) \propto n^{2/3}$, Eq. (3) is the standard Zeldovich–Frenkel equation.

There exists a fundamental connection between the "microscopic" coefficient $\beta(n)$ and the deterministic ("macroscopic") growth rate in continuous models[7]

$$\dot{n}^{\mathrm{cont}}(n) = -(\beta(n)/T) dW/dn \tag{4}$$

which leads to Eqs. (2) for $\beta(n) \propto n^{(2-\theta)/3}$. A generalized version of Eq. (4), appropriate for the BD scheme,

$$\dot{n}^{\mathrm{BD}}(n) = \beta(n)\{1 - \exp[T^{-1} dW/dn]\} \tag{5}$$

was discussed in Refs. 19 and 15 in connection with discreteness effects; specific growth rates for the mainstream nucleation models were known earlier—see Sec. V.

The parameter τ can be equivalently represented as

$$\tau^{-1} = \left.\frac{d\dot{n}}{dn}\right|_{n=n_*} = \frac{2\beta(n_*)}{\Delta^2} \tag{6}$$

with

$$\Delta^{-2} = -(2T)^{-1} d^2W/dn^2 \quad \text{at } n = n_*. \tag{7}$$

Connection between $\beta(n)$ and $\dot{n}$ can be useful in two ways. First, the macroscopic models for growth and decay are often based on well-studied deterministic equations of hydrodynamic type, and are better understood compared to their microscopic (stochastic) nucleation counterparts. Equation (6) allows one to estimate $\beta(n_*)$ and thus to evaluate the steady-state nucleation rate[7] (see next section). Second, even if one starts from a purely microscopic model of nucleation with a specified $\beta(n)$, an asymptotic time-dependent solution still will be expressed in terms of $\dot{n}$ rather than $\beta(n)$.[19,21] In particular, a general solution of a simpler continuous equation can be applied to the discrete BD equation if $\dot{n}^{\mathrm{cont}}$ is replaced by $\dot{n}$ in accord with Eq. (5).

As a preliminary example, consider the "incubation time" which appears in the MA solution, and which is the time it takes the flux to reach $1/e$ of its steady-state value. This time is given by[21]

$$t_i(n) = t_{\mathrm{dec}}(n_* - \Delta/\sqrt{2}) + t_{\mathrm{gr}}(n_* + \Delta/\sqrt{2}, n). \tag{8}$$

Here t_{dec} and t_{gr} are positive deterministic decay and growth times (i.e., integrals $\int dn/\dot{n}$) with indicated initial sizes $n_* \mp \Delta/\sqrt{2}$, respectively. The final size is the indicated size n for growth, while for decay this size is the smallest size $n_{\min}$ present in the system. Selection of a model will affect the value of $t_i(n)$ but not the shape of the transient flux.

In other words, the deterministic rate $\dot{n}$ allows one to construct general time-dependent solutions to the nucleation equation, prior to the specification of a concrete form or coefficients of that equation. A specification can be subsequently achieved by substitution into the general results an appropriate growth rate, and evaluation of the aforementioned integrals $\int dn/\dot{n}$.

B. Steady-state distribution and flux

Formally, the steady-state nucleation equation allows for an exact solution.[5] In case of the Zeldovich–Frenkel equation, for example, the exact expression is given by[7]

$$f_s(n)/N(n) = j_s \int_n^{\infty} dn'/\beta(n')N(n') \tag{9}$$

with the steady-state flux, j_s determined from the lower boundary condition

$$f_n = N_n \quad \text{at } n = n_{\min}.$$

One should keep in mind, however, that the above boundary condition is already asymptotic, neglecting the

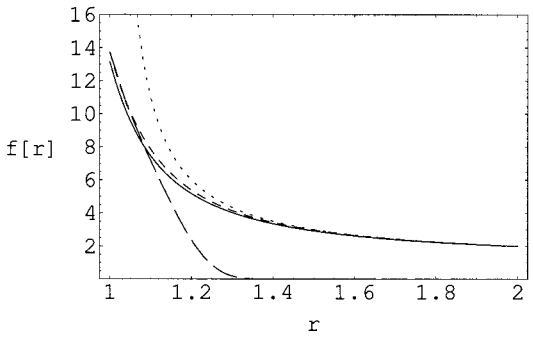

FIG. 1. The reduced steady-state distribution $f_s(r)/\tau j_s$ of the standard Zeldovich–Frenkel equation in the above-critical region of sizes for $W_*/T=20$. Solid line, exact Eq. (9). Dotted line, asymptotic Eq. (14). Long-dashed line, the erfc-approximation, Eq. (12). Short-dashed line, steady-state limit of the proposed interpolating approximation, Eq. (38).

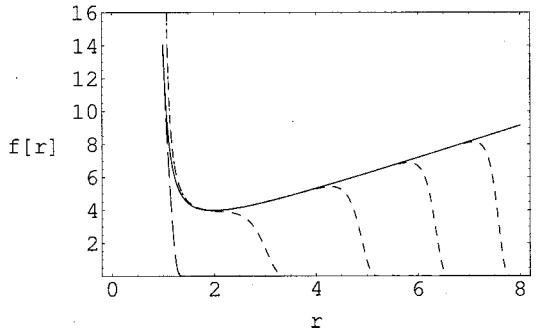

FIG. 2. Reduced steady-state and transient distributions in case of diffusion-limited nucleation and growth for $W_*/T=20$. Solid line, exact steady-state distribution, Eq. (9) with $\beta(n)\propto n^{1/3}$. Long-dashed line, the erfc-approximation, Eq. (12) (same as in Fig. 1). Short-dashed lines, asymptotic transient distributions given by Eqs. (15), (18), and (52) for $t/\tau=10$, 20, 30, and 40 (from left to right).

depletion of the matrix by growing nuclei. Otherwise, an integral conservation law should be employed.[31] Neglect of depletion is equivalent to large values of W_*/T, with an exponentially small nucleation rate and a correspondingly large lifetime of a metastable state. For that reason, more instructive (and more appropriate in view of time-dependent generalizations) is the asymptotic steady-state solution,[7] although exact results remain useful for verification purposes. A large barrier is equivalent to small Δ/n_*.

In the vicinity of n_* the barrier is parabolic and the equilibrium distribution is approximated as

$$N(n)=N(n_*)\exp\{(z_{\rm lin})^2\}, \quad |z_{\rm lin}|\ll n_*/\Delta \tag{10}$$

with $z_{\rm lin}$ linearly depending on n

$$z_{\rm lin}\equiv(n-n_*)/\Delta. \tag{11}$$

The steady-state distribution is given by[7]

$$f_s(n)=\tfrac{1}{2}N(n)\,{\rm erfc}(z_{\rm lin}) \tag{12}$$

with an associated flux $j(n)=\text{const}\equiv j_s$:

$$j_s\simeq\frac{\Delta}{2\tau\sqrt{\pi}}N(n_*). \tag{13}$$

Equation (13) is valid for the flux at *any* size, while Eq. (12) (and thus the time-dependent generalizations of the erfc-approximation) is strictly valid only in the parabolic region (the "boundary layer"). In particular, Eq. (12) does not predict a proper distribution of nuclei in the growth region $n-n_*\gg\Delta$, which should be of drift form

$$f_s(n)=j_s/\dot{n}. \tag{14}$$

[The drift form is well known in physical kinetics;[32] in the specific nucleation context it also can be deduced directly from the exact expression for $f_s(n)$ both in the continuous[33(a)] and discrete[33(b)] cases for $W_*\gg T$].

Figure 1 (solid line) shows exact steady-state distributions over radii, $f_s(r)=f_s(n)dn/dr$ for the standard Zeldovich–Frenkel equation. The erfc-approximation (long-dashed lines) works reasonably in the near-critical region, but fails dramatically away from r_*. The asymptotic Eq. (14) shown by dotted lines in Fig. 1, on the other hand, blends in with exact results in the growth region but diverges at the critical size $r=1$. An interpolation obtained as the steady-state limit of the general transient expression in Sec. IV, bridges the two limits and is shown by a short-dashed line. The difference from the exact distribution at any size is minor for the chosen value of $W_*/T=20$ (which is small by most experimental standards); a more realistic value of $W_*/T=30$ would make the two curves practically indistinguishable.

Failure of the erfc-approximation is even more spectacular in case of diffusion-limited growth, Fig. 2, where a similar scaled distribution $f_s(r)/\tau j_s$ is plotted. Here Eq. (12) with a full (non-Gaussian) $N(n)$ describes an exponential decay into the growth region instead of a linear *increase* at $r\gg1$. The error can be reduced if the erfc-approximation is used more consistently together with the approximate Eq. (10) (not shown in the figure), but even in that case the result would be a power-law decay for $r\gg1$. This is in distinct contrast with increasing distribution, as in Fig. 2 or with saturation, as in Fig. 1. [Not being able to distinguish between the surface- and diffusion-controlled nucleation is another drawback of the erfc-approximation. These limitations, however, do not affect the correct value of j_s which is sensitive exclusively to the near-critical region. Note also that asymptotes of Eqs. (12) and (14) coincide in the common region of applicability; this is an important preview of the matched asymptotic ideas described below.]

C. The growth region transient solution (Refs. 19 and 21) and distribution of nuclei

The method of solution (see the Appendix in Ref. 19) involves the Laplace transform of the nucleation equation, which makes it an ordinary differential equation; after that standard matched asymptotic technique[20] can be applied. In the "outer region" below n_* a nonlinear first order differential equation is considered which is solved in terms of the decay time $t_{\rm dec}(n)$. Alternatively, near n_* ("inner region") a second-order linear differential equation is recovered which is solved in terms of the repeated error integrals[34] (see also Appendix A below), which generalize the standard erfc of Eq. (12). The asymptote of the outer solution at $n\to n_*$ can

be matched with the subcritical asymptote of the inner solution, giving the proportionality coefficient of the latter. The other, above-critical inner asymptote has a relatively simple structure and, after the inversion of the Laplace transform, determines the asymptote of the growth distribution and the corresponding flux.[19] This flux is replicated in time (with correction for retardation) by any flux in the growth region[21] and is given by

$$j(n,t)=j_s\exp\{-e^{-x}\},\quad x=(t-t_i(n))/\tau. \tag{15}$$

The incubation time $t_i(n)$ is determined by Eq. (8) above or by an integral representation, Eq. (7) of Ref. 21.

The number of nuclei with size exceeding a given value of n (which is usually measured in experiments[1–3]) is given by[21]

$$\rho(t)=\tau j_s E_1(e^{-x}). \tag{16}$$

Here E_1 is the first exponential integral.[34] In some of the latter studies it was suggested to subtract from this expression a constant $\tau j_s E_1(e^{t_i/\tau})$ in order to ensure an exact rather than an asymptotic zero at $t=0$. Strictly speaking, this would be incorrect, even though the added constant is negligibly small both asymptotically and numerically. It will be shown below that if one wishes to refine the solution near $t=0$, a different functional form of Eq. (16) will appear which automatically satisfies the initial condition.

At large times $t-t_i(n)\gg\tau$ one has $\rho(t)\sim j_s[t-t_L(n)]$ with[21]

$$t_L(n)=t_i(n)+\gamma\tau, \tag{17}$$

$\gamma=0.5772...$ being Euler constant, and $t_L(n)$ known as the ''time-lag'' (also, ''induction time''). Alternatively, an exact expression for the time-lag also can be constructed both for the discrete and continuous versions of the nucleation equation.[12,35] With a certain effort one can show[33] that in each case the asymptotes of the exact expressions indeed coincide with $t_i(n)+\gamma\tau$, testifying to the validity of the matched asymptotic solution.

The transient distribution in the growth region is related to the flux by the same standard relation

$$f(n,t)=j(n,t)/\dot{n} \tag{18}$$

as discussed above in the steady-state context. Examples of such distributions for diffusion-limited growth at different times are shown in Fig. 2 by dotted lines. (Similar curves were observed in Ref. 36 from numerical solutions of a diffusion version of the Turnbull–Fisher equation, although no direct identification has been performed.) One should keep in mind, however, that Eq. (18) is also asymptotic, and in generalizations of Eq. (15) for smaller times and sizes described below, relations between the distribution and the flux also will become more complex.

D. The parabolic model (Ref. 18)

Consider a parabolic approximation for the barrier

$$W^{\mathrm{par}}=W_*-T(z_{\mathrm{lin}})^2 \tag{19}$$

which is expected to be valid at all sizes. With a size-independent $\beta(n)$, the growth rate in Eq. (4) is a linear function

$$\dot{n}_{\mathrm{lin}}=\frac{n-n_*}{\tau}. \tag{20}$$

In that case, Eq. (3) is reduced to a standard unstable Ornstein–Uhlenbeck equation, albeit with an inhomogeneous boundary condition at $n=n_{\min}$, which prevents an exact solubility. Still, a rather accurate solution to this equation was constructed by Trinkaus and Yoo (TY)[18] via a minor perturbation of the condition on the lower boundary. To simplify identification of the results, let us introduce a function

$$\alpha(t)=1/\sqrt{1-\exp(-2t/\tau)} \tag{21}$$

as in Ref. 23, and rewrite the TY results in present notations as

$$f^{\mathrm{TY}}(n,t)=\tfrac{1}{2}N(n)\mathrm{erfc}\{\alpha(t)z_{\mathrm{lin}}(n)-\sqrt{\alpha^2(t)-1}z_{\mathrm{lin}}(0)\}, \tag{22}$$

$$j^{\mathrm{TY}}(n,t)/j_s=\alpha(t)\exp\{-\alpha^2(t)[z_{\mathrm{lin}}(n)-\sqrt{1-1/\alpha^2(t)}z_{\mathrm{lin}}(0)]^2+z_{\mathrm{lin}}^2(n)\}. \tag{23}$$

[Herewith $z_{\mathrm{lin}}(0)$, not $z_{\mathrm{lin}}(n_{\min})$, will be used for brevity of notations; in fact in most situations treating the lowest size $n_{\min}$ as zero is an excellent approximation, especially for the Zeldovich–Frenkel equation.]

If one accepts the parabolic model from the start, than the TY solution is a rather accurate one. In particular, it predicts an exact zero at $t=0$. On the other hand, the parabolic model itself is not a good representation of the nucleation problem away from n_*, especially in the growth region. In particular, at $n\gg n_*$ even in the steady-state limit the TY distribution deviates from the proper result by an exponentially large factor. A similar problem is recovered in other similar erfc-type approximations discussed by Maksimov *et al.*[25] and could be labeled an ''asymptotic catastrophe'' if one uses the terminology of that paper (although the latter discussed the ''catastrophe'' in terms of the flux).

At the same time, the TY solution can be remarkably accurate near n_* where a parabolic approximation for the barrier or a linear approximation for growth are reasonable. Non-linearity will affect only decay and will result in a slight difference between $z(0)$ and $z_{\mathrm{lin}}(0)$. Since this difference is a nonasymptotic constant (a number) it can be treated as a minor correction. Moreover, in case of the continuous ballistic model (*standard* Zeldovich–Frenkel equation) this number is exceptionally small—see Sec. V—and errors produced by the TY approximation near n_* can be hard to detect even in numerical studies.

E. Nonlinear transformation of coordinates and interpolation of the critical flux (Ref. 23)

In the vicinity of the critical size a natural variable is $z_{\mathrm{lin}}(n)$. On the other hand, in the growth region the natural variable should have a form of $\mathrm{const}\exp(t_i(n)/\tau)$, in order to

ensure the simplest structure of the exponential in the transient solution, Eq. (15). The required compromise is achieved by using[23]

$$z(n)=-\exp\left[\int_{n_*-\Delta}^{n}\frac{dn}{\tau\dot{n}+i0}\right]. \tag{24}$$

Here i is the imaginary unity, and despite the somewhat unusual structure, the above expression is reduced to elementary functions for some of the mainstream nucleation models—see Sec. V. Near n_* the new variable $z(n)$ indeed coincides with $z_{\rm lin}$, in particular $z(n)$ changes sign at $n=n_*$. Away from n_*, it is related to the incubation and decay times introduced earlier

$$t_i(n)/\tau=\ln\{-2z(n)z(0)\},\quad n>n_*, \tag{25}$$

$$z(0)=-\exp\{-t_{\rm dec}(n_*-\Delta)/\tau\}. \tag{26}$$

[Note that $|z(0)|$ is large as $O(n_*/\Delta)$.]

Using the z variables allows one to construct a more general (compared to the original MA treatment) Laplace transform of the flux which is valid at arbitrary sizes and which, upon inversion, ensures an exact zero at $t=0$. The critical flux is given by[23]

$$j_*(t)=j_s\alpha(t)\exp\{-(\alpha^2(t)-1)\exp[2t_{\rm dec}(n_*-\Delta)/\tau]\}. \tag{27}$$

Inversion of the Laplace transform at arbitrary sizes will be part of the present work.

F. Generalizations of Eq. (23) for the growth region (Ref. 25) and open questions

Recently, Maksimov *et al.*[25] suggested, among several other options, that the TY expression for the flux also could be used for the Zeldovich–Frenkel equation at arbitrary sizes if the variable $z_{\rm lin}$ (in current notations) is replaced by some nonlinear function $B(n)$ while $A=-B(1)$ is substituted for $z_{\rm lin}(0)$. The value of $B(n)$ is given by[25]

$$B(n)\simeq\sqrt{\frac{2W_*}{T}}\frac{(n/n_*-1)\Psi(n_*/n)}{(n/n_*)^{1/2}-1+\sqrt{6}\Psi(n_*/n)} \tag{28}$$

with

$$\Psi(y)=1-3y^{1/3}+\sqrt{6y}-9y^{2/3}/32.$$

The assumption about a possibility of nonlinear generalization of size in the TY expression, most likely is justified for the flux (but not for the distribution), as will be described below. However, an attempt to evaluate $B(n)$ without matching the asymptotes lead to Eq. (28), which does not describe correctly the region of large sizes. Indeed, the time-lag[25]

$$t_L(n)\simeq\tau\ln(AB(n))$$

increases logarithmically with n as $n\to\infty$. This can be true, however, only for a strictly linear growth.[21] For other models, including the standard Zeldovich–Frenkel equation, the time-lag should increase with size as a power law.[21] Similarly, the ''asymptotic catastrophe'' of the erfc-approximation for the distribution function remains, and one of the goals of the present work is to overcome this problem.

III. TRANSIENT FLUX AND LIMITS

Inversion of the Laplace transform of the flux—see Appendix A—gives the following result

$$j(n,t)/j_s=\alpha(t)\exp\{-(\alpha^2(t)-1)(z(0)^2+z(n)^2)\}\times\exp\{-\phi(n,t)\} \tag{29}$$

with

$$\phi(n,t)=2|z(0)|z(n)\sqrt{\alpha^2(t)[\alpha^2(t)-1]}. \tag{30}$$

Equation (29) is valid if at least one of $|z(0)|$ or $z(n)$ is large. To isolate the large parameter in $|z(0)|$ one can write

$$z(0)=-\frac{n_*}{\Delta}e^C \tag{31}$$

with C being a model-dependent constant[19] of the order of unity

$$C=-\lim_{\delta\to 0}[t_{\rm dec}(n_*-\delta)/\tau+\ln(\delta/n_*)]. \tag{32}$$

(If the lower boundary is selected at negligibly small values of $n_{\rm min}$, the constant C equals zero for strictly linear growth, as in the TY case, and is $1-\ln 3$ for the standard Zeldovich–Frenkel equation.[19])

The other parameter of the solution, $z(n)$ is large if n is in the growth region. More precisely, if deviation of n from n_* is of the order of n_*, (say, $n=2n_*$), one has $z(n)$ comparable to $|z(0)|$. Further into the growth region $z(n)$ increases exponentially with size, dramatically increasing the accuracy of the asymptotic results.

In the vicinity of n_* the Gaussian form of Eq. (29) could be anticipated, and it should be treated as a unifying expression for earlier results. For example, the parabolic limit of TY is recovered from Eq. (29) if $z(n), z(0)$ are replaced, respectively, by $z_{\rm lin}(n), z_{\rm lin}(0)$. Alternatively, for $z(n_*)=0$ and a general $z(0)$, Eq. (29) gives

$$j_*(t)/j_s=\alpha(t)\exp\{-(\alpha^2(t)-1)z^2(0)\}. \tag{33}$$

This is the critical flux of Ref. 23, Eq. (27) above. Next, for $t\gg\tau$ and $z(n)$ replaced by $z_{\rm lin}$, the form of Eq. (29) becomes similar to the one by Klimenko,[22] and several other approximations of Gaussian-type mentioned in Ref. 25 also follow from Eq. (29) after linearization of $z(n)$ and specification of the time scales.

Applicability of Eq. (29) away from n_* is less obvious, although a similar time dependence (with a rather different dependence on size) was recently suggested by Maksimov *et al.*[25] The dependence is Gaussian in terms of the nonlinear function $z(n)$. The width of the maximum unboundedly increases with time, when $\alpha(t)$ tends to 1. In terms of the physical variable n, however, the structure of the solution is very different due to an exponential dependence of $z(n)$. After a short initial period, the flux is practically steady state for all n smaller than some $n_F(t)$—a front which propagates with the growth rate. At $n>n_F(t)$ the flux decays with size extremely rapidly (with a ''double-exponential'' rate—see below). Location of the front, approximately, is given by the solution of the equation $t=\tau\ln\{2z(n_F)|z(0)|\}\equiv t_i(n_F)$. The width of the front is of the order of $\tau\dot{n}_F$.

The double-exponential limit, which describes the aforementioned front, is recovered from Eq. (29) in the growth region, albeit in a less straightforward manner. For small times, $t \lesssim \tau$, the limit of Eq. (29)—see below—is different from Eq. (15). However, for $W_* \gg T$, the flux at such times is anyway exceptionally close zero due to large values of $|z(0)|$ and $z(n)$ [or, equivalently, due to large $t_i(n)/\tau$ in the double-exponential expression]. Flux becomes nonzero at larger times with $t \sim \tau \ln(|z(0)|z(n))$. Here the function $\alpha(t)$ approaches 1, but the small difference $\alpha(t)-1$ is multiplied by a large factor containing $|z(0)|$ and $z(n)$. This leads to an intermediate asymptote with the leading dependencies on time and size combined in a dependence on a single parameter x, as in Eq. (15). The dominant dependence on x, and the corrections, become explicit if Eq. (29) is cast in mixed notations as

$$j(n,t)/j_s = \exp\left\{ -e^{-x} - \frac{1}{4} e^{-2x} \left(\frac{1}{z(0)^2} + \frac{1}{z(n)^2} \right) + \ln \alpha(t) - (\alpha^2(t)-1) \left[e^{-x} + \frac{1}{4} e^{-2x} \left(\frac{1}{z(0)^2} + \frac{1}{z(n)^2} \right) \right] \right\}. \tag{34}$$

For finite (nonasymptotic) values of x with $\alpha^2(t)-1 \sim 1/(z(0)z(n))^2$, corrections to the double-exponential limit are asymptotically small; the largest one is given by $e^{-2x}/4z(0)^2$. [Strictly speaking, when considering finite x, the value $\alpha^2(t)-1$ should be replaced by its asymptote $\exp(-2t/\tau)$ while the exponential with corrections should be expanded, but it is tempting to keep the form which ensures an exact zero at $t=0$.]

Consider now the limit of Eq. (29) for $t \ll \tau$ with $\alpha(t) \sim 1/\sqrt{2t/\tau} \gg 1$. Neglecting 1 compared to $\alpha^2(t)$ in Eqs. (29) and (30) one obtains

$$j/j_s = \frac{1}{\sqrt{2t/\tau}} \exp\left\{ -\frac{(z(n)-z(0))^2}{2t/\tau} \right\}. \tag{35}$$

This is a diffusionlike behavior, in qualitative agreement with the early suggestion by Zeldovich[7] (a similarity also noted by Maksimov[25]). The exponential size dependence of $z(n)$—see Sec. V—is different, however, from earlier power-law expectations. No specific role is played by the critical size at such small times.

A note of caution on this limit should be added. Although Eq. (35) correctly predicts $j=0$ at $t=0$, it still should be treated as a small-time interpolation (see the Discussion section) rather than a strict result. In particular, the solution of the Becker–Döring equation in the limit $t \to 0$ has a structure which is different from Eq. (35), as described in Appendix B.

IV. THE DISTRIBUTION FUNCTION AND THE NUMBER OF NUCLEI

From the continuity equation one has

$$f(n,t) = -\int_0^t dt' \frac{\partial j(n,t')}{\partial n}. \tag{36}$$

Using Eqs. (13) and (29) for the steady state and transient fluxes, respectively, one obtains after integration

$$f(n,t) = \frac{1}{2} N(n_*) \exp[z^2(n)] \frac{z(n)\Delta}{\tau \dot{n}} \operatorname{erfc}\{\alpha(t) z(n) - \sqrt{\alpha^2(t)-1}\, z(0)\}. \tag{37}$$

Introducing $p(n) \equiv z(n)\Delta/\tau\dot{n}$ and $q(n) \equiv N(n_*) \times \exp[z^2(n)]/N(n)$, one notes that for any nucleation model $p(n), q(n) \simeq 1$ near the critical size. For a strictly linear growth and a parabolic barrier these approximations are exact at any size. Thus, with $z(n), z(0)$ replaced, respectively, by $z_{\rm lin}(n)$ and $z_{\rm lin}(0)$, Eq. (37) becomes identical to the one by TY. Similarly, restricting Eq. (37) to the vicinity of n_* where $z(n) \simeq z_{\rm lin}(n)$ and where the above equalities for p and q are approximately valid, one recovers at larger times the functional form of the near-critical distribution by Klimenko,[22] and several other erfc-type approximations mentioned in Ref. 25 also can be reproduced with appropriate specifications.

The major novelty of the result is associated with the region away from n_* where $p(n), q(n) \neq 1$ and where the erfc function acquires a size-dependent prefactor which is exponentially large and which qualitatively changes the structure of the distribution. As will be shown below, with the new prefactor a proper drift-type structure of the distribution, Eq. (18) is recovered in this region, after a short initial transient period. In particular, there is now no "asymptotic catastrophe" in the steady-state limit. For $t \to \infty$, Eq. (37) takes the form

$$f_s(n) = \frac{1}{2} N(n_*) \exp[z^2(n)] \frac{z(n)\Delta}{\tau \dot{n}} \operatorname{erfc}\{z(n)\}. \tag{38}$$

This converges either to the Zeldovich limit, Eq. (12) near n_*, or goes asymptotically to Eq. (14) in the growth region with $z(n) \gg 1$. For these reasons, Eq. (38) can be numerically close to the exact distribution at all sizes—see Fig. 1.

An important simplification of the general time-dependent expression is possible if one notes that the argument of the exponential function can be large not only for large $z(n)$ in the growth region, but also for a large product $\sqrt{\alpha^2-1}|z(0)|$ for arbitrary $z(n)$ (i.e., for not too large times). In this case one has a generalization of Eq. (18),

$$f(n,t) \approx \frac{j(n,t)}{\dot{n}} \frac{1}{\alpha(t) + \sqrt{\alpha^2-1}|z(0)|/z(n)}. \tag{39}$$

The distribution is smaller than predicted by the drift expression due to the diffusion component of the flux. In particular, at $n \gg n_*$ with $z(n) \gg |z(0)|$ one has

$$f(n,t) \approx \frac{j(n,t)}{\alpha(t)\dot{n}}, \tag{40}$$

which, together with Eq. (29) for the flux, determines the distribution at any time. It is interesting to note that the drift-type distribution which corresponds to $\alpha(t)=1$ in Eq. (40), is observed early, at $t \gtrsim \tau$, well before the double-exponential limit of Eq. (15) is established at $t \sim \tau \ln(|z(0)|z(n)) \gg \tau$.

Equation (39) is also valid near n_*, although for a limited time. At $n=n_*$ the singularity of $\dot{n} \to 0$ disappears since $z(n)$ also tends to zero, and one has

$$f_*(t) \simeq \frac{j_*(t)\tau}{\Delta} \frac{1}{\sqrt{\alpha^2(t)-1}|z(0)|}, \quad t \lesssim \frac{\tau}{2} \ln \frac{W_*}{T} \tag{41}$$

with $j_*(t)$ given by Eq. (27). Indicating the restrictions on time is necessary since the above expression has no steady-state limit. [Nonrigorously, adding a small constant $1/\sqrt{\pi}$ to the denominator could validate Eq. (41) at $t \to \infty$ without much effect on transient behavior.]

Returning to the general distribution, Eq. (37) one can evaluate the number of particles with size exceeding n

$$\rho(n,t) = \int_n^\infty dn'\, f(n',t). \tag{42}$$

Performing the integration with asymptotic accuracy one obtains

$$\rho(n,t) \approx \tau j_s \exp[-(\alpha^2(t)-1)(z(0)^2+z(n)^2)] \times E_1[\phi(n,t)(1+\sqrt{1-1/\alpha^2(t)}|z(0)|/z(n))] \tag{43}$$

with the function $\phi(n,t)$ defined in Eq. (30). Note that there is no singularity at $n=n_*$ since $\phi(n,t)$ crosses zero together with $z(n)$.

In the growth region for $t \gtrsim \tau \ln(|z(0)|z(n))$, $\phi(n,t)$ takes the asymptotic form of e^{-x}; in other parts of the expression $\alpha(t)$ can be replaced by 1, leading to Eq. (16). The time-lag

$$t_L(n) = \lim_{t \to \infty} \{t - \rho(n,t)/j_s\} \tag{44}$$

remains unchanged, and is given by Eq. (17).

V. SPECIFICATION OF THE MODELS

A. The standard Zeldovich–Frenkel (ZF) equation

The standard ZF equation corresponds to surface-limited nucleation with a gain coefficient

$$\beta_n = \beta(n_*)(n/n_*)^{2/3}, \quad \beta(n_*) = \Delta^2/2\tau \tag{45}$$

and with the growth rate [in terms of radii $r \equiv (n/n_*)^{1/3}$] given by Eq. (2) with $\theta=0$. The incubation time is given by[21]

$$t_i^{\mathrm{ZF}}(r) = \tau\{r - 2 + \ln(r-1) + \ln(6W_*/T)\}. \tag{46}$$

The nonlinear function $z(n)$ is obtained by integration of Eq. (24)

$$z^{\mathrm{ZF}}(r) = \frac{r-1}{\epsilon_r} \exp(r-1), \quad \epsilon_r \equiv \frac{\Delta}{3n_*} \ll 1 \tag{47}$$

($\epsilon_r = \Delta\, dr/dn$ at $n=n_*$ is the width of the barrier in the r space). This is consistent with Eqs. (25) and (46).

In Fig. 3 $z^{\mathrm{ZF}}(r)$ (solid line) is shown together with the parameter $B(r)$ by Maksimov *et al.*[25] (dotted line). The short-dashed line corresponds to z_{lin} by TY (z_{lin} looks nonlinear since r, not n is used as a variable). All of these functions are multiplied by ϵ_r, so that there are no free parameters, which simplifies the comparison.

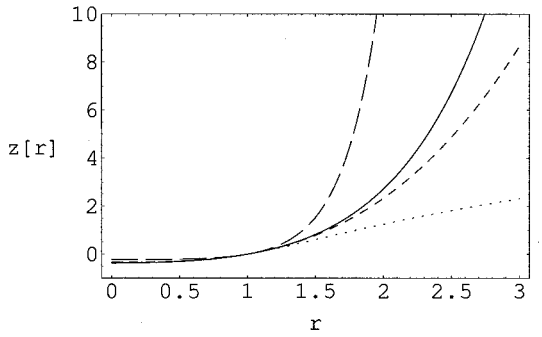

FIG. 3. The nonlinear parameter $z(r)$, Eq. (47), for the standard Zeldovich–Frenkel (ZF) equation (solid line), and alternative approximations. Short-dashed lines, $z_{\mathrm{lin}}(r)$; dotted line, parameter $B(r)$ by Maksimov *et al.* Long-dashed line, $z(r)$ for diffusion-limited growth, Eq. (51). All parameters are multiplied by ϵ_r, see the text.

In the vicinity of $r_*=1$ the functions $z_{\mathrm{lin}}(r)$ and $z(r)$ coincide with each other; the difference is cubic in $r-1$. As a result, one has

$$z_{\mathrm{lin}}(0) = z^{\mathrm{ZF}}(0)\exp(1-\ln 3) \approx 0.906 z^{\mathrm{ZF}}(0)$$

which is close to $z^{\mathrm{ZF}}(0)$. Thus the TY expressions will provide good numerical approximations for the transient distribution and flux near r_*. At larger sizes, however there is a strong deviation between a power-law $z_{\mathrm{lin}}(r)$ and exponential $z^{\mathrm{ZF}}(r)$, and the TY expression is inapplicable even for the flux; error in the distribution is still larger due to the prefactor of the erfc-expression, and does not vanish as $t \to \infty$.

Maksimov's expression for $B(r)$ is close to the correct values of $z^{\mathrm{ZF}}(r)$ near $r=1$, although not as close as z_{lin} since the difference in $B(r)-z^{\mathrm{ZF}}(r)$ is quadratic (not cubic) in $r-1$. At larger r, Maksimov's expression exponentially deviates from $z^{\mathrm{ZF}}(r)$.

B. The Becker–Döring (BD) and Turnbull–Fisher (TF) models

The BD and TF models are the two major discrete models for surface-limited nucleation. In the BD case the gain coefficient is the same as in Eq. (45), while in the TF case it is multiplied by $\exp\{[W(n)-W(n+1)]/2T\}$.

The growth rates for these models are known—see, e.g., Ref. 37 for growth in the Turnbull–Fisher model, or Refs. 33 for a general survey. One has

$$\dot{r}^{\mathrm{BD}} = 1/a\tau \ \{1-\exp[a(1/r-1)]\} \tag{48}$$

$$\dot{r}^{\mathrm{TF}} = 2/a\tau \ \{\sinh[(a/2)(1-1/r)]\} \tag{49}$$

with

$$a = 2W_*/Tn_* = \delta\mu/T$$

being the ''discreteness parameter'' which is responsible for deviations of Eqs. (48) and (49) from Eq. (2); $\delta\mu$ is the difference of chemical potentials between phases.

For both models the integral $\int dr/\dot{r}$ cannot be evaluated in elementary functions and, strictly speaking, the value of $z(n)$ is to be evaluated numerically. In practice, however, even for not very small a, deviation from the ZF growth rate is not that large and for moderate sizes the elementary expression for $z^{\mathrm{ZF}}(r)$, Eq. (47), can work. In the simpler double-exponential limit, accuracy of the elementary predictions in case of the TF model was verified numerically by Spinella *et al.*[4]

For large $r \gg 1$ one has to account for a different limiting growth rates $\dot{r}_\infty$ in the discrete models compared to $\dot{r}_\infty^{\mathrm{ZF}} = 1/\tau$ (otherwise even a minor discrepancy will store unboundedly as $r \to \infty$). One could use

$$z(r) \simeq \frac{r-1}{\epsilon_r} \exp(r/\tau\dot{r}_\infty - 1) \tag{50}$$

which is similar to corrections suggested for the incubation time.[38] Numerical accuracy of such corrections to t_i was examined recently by Granasy and James.[30] One should keep in mind, however, that Eq. (50) is accurate only in its leading exponential term and a more detailed study of the limit $r \to \infty$ will be presented elsewhere.[39]

C. Diffusion-limited nucleation and growth

Integration of Eqs. (2) and (24) with $\theta = 1$ gives

$$z^{\mathrm{diff}}(r) = \frac{r-1}{\epsilon_r} \exp\{r^2/2 + r - 3/2\}. \tag{51}$$

Together with Eq. (25) this is consistent with the incubation time obtained earlier[21]

$$\frac{1}{\tau} t_i^{\mathrm{diff}}(r) = (r-1)^2/2 + 2(r-1) - 3/2 + \ln(r-1) + \ln\frac{6W_*}{T}. \tag{52}$$

The values of $\epsilon_r z^{\mathrm{diff}}(r)$ are shown in Fig. 3 by a long-dashed line. Due to slower growth, $z^{\mathrm{diff}}(r)$ increases with size much faster than its counterpart for surface-limited nucleation, Eq. (47). Larger values of $z(r)$ imply weaker small-time transient effects, before the double-exponential regime is established.

In the growth region with large $z(r)$ transient distributions (37) and (51) would be numerically indistinguishable from those obtained from the double-exponential solution, which were shown in Fig. 2. The difference, nevertheless, can become important near n_*.

VI. DISCUSSION

In the present work a general expressions for the distribution of nuclei, Eq. (37) was proposed. Relevant expressions for the flux and the number of nuclei also can be of interest. ''Generality'' implies applicability to arbitrary nucleation model after the nonlinear function of size $z(n)$ in Eq. (24) (which depends exclusively on the deterministic growth rate) is calculated. It is helpful that for the some of the mainstream models, including the standard Zeldovich–Frenkel equation, $z(n)$ evaluates to elementary functions (Sec. V).

In the obtained expression time can be arbitrary; sizes of nuclei span near- and over-critical regions. There is no upper bounds for time or sizes as long as the original Becker–Döring formulation which neglects the depletion of monomers by nucleation and growth is considered.

Simplifications achieved by using the z variables can be explained as follows. One can show that in these variables the Zeldovich–Frenkel equation becomes asymptotically close to the exactly solvable Ornstein–Uhlenbeck (OU) equation not only in the vicinity of n_*, but in the decay and growth regions as well. In the Becker–Döring case two different continuous approximations are required[15,19] for the subcritical region (smooth function $v = f_n/N_n$, the ratio of kinetic to equilibrium distribution) and for the growth region (smooth f_n). Nevertheless, in z variables each of the two differential representations approach a corresponding form of the OU equation. It is not surprising that results are Gaussian in terms of the variable z, which is typical for the OU case.

Most of relevant earlier expressions are reproduced by the obtained results in appropriate limits. For example, the double-exponential matched asymptotic (MA) solution[19,21] is recovered in the growth region for $t \gg \tau$ [where τ is defined in Eq. (6)]. Similarly, the Trinkaus and Yoo (TY)[18] expressions for the distribution and the flux are obtained for a linear $z(n) = z_{\mathrm{lin}}(n)$ and a parabolic nucleation barrier. Kaschiev's results, however, are not reproduced in any limit since he, in effect, was solving a diffusion rather than a nucleation equation.

The main applied value of the proposed distribution is associated with spanning of the regions of sizes since previous expressions worked either near the critical size (e.g., the TY results[18]) or in the growth region (e.g., the MA solution[19,21]). The domain of small times covered by the present results seems to be of less practical significance, although it allows one to trace the establishment of the double-exponential regime starting from $t = 0$, and to estimate the corrections.

The limit $t \to 0$ requires a separate consideration. The obtained expressions for the flux, distribution, etc., produce an exact zero at $t = 0$, which could be considered as an advantage compared to the double-exponential MA solution where this zero is asymptotic. Nevertheless, the present results should be treated as an interpolation. In contrast to the MA solution the asymptotic structure of which is well understood, it is unclear if Eqs. (29) and (37) are unique, or if it is possible to construct an alternative approximation which bridges the instant $t = 0$ and the double-exponential limit at later times.

The reason for the uncertainty is that the MA ideas are straightforward if W_*/T is the *only* large asymptotic parameter of the problem. Other parameters also can be large, but they are either directly linked to the barrier (as the parameter n_*/Δ), or these parameters are expected to form finite, non-asymptotic combinations with the barrier. This is best exemplified by the parameter x, Eq. (15), which is a combination of the logarithm of the barrier and possibly large time and

size, but which is finite and which is the only argument of the asymptotic solution. When time gets small, however, there appears a competing large function, $\alpha(t)$. Analysis suggests that time in the nucleation problem has a complex multizone boundary layer structure near $t=0$ with each zone requiring a different approximation. Getting a single expression which would be reasonable on every scale of time in this situation becomes almost a matter of luck. In particular, higher-order terms in the expansion of the solution can be anticipated. Such terms appear, for example, in the Laplace transform of the near-critical flux,[33(b)] although a full transient expression is yet unavailable.[39]

To emphasize the problem, in Appendix B a small-time solution to the Becker–Döring (BD) equation has been constructed without the assumption of a high nucleation barrier. This solution satisfies the initial conditions, but its structure is very different from the small-time limit of Eq. (37). In fact, it is unlikely that any differential approximation to the BD equation can produce a time-dependent solution of type (B3), which could be an important reminder in view of the search for "the best" differential version of the nucleation equation.[11–15]

However, with all the intriguing mathematics of the BD equations at very small times, which still requires clarification, for most physical problems the region $t \lesssim \tau$ is often of no practical interest since at such times the flux is anyway indistinguishable from zero (whether this zero is treated as an exact or as an asymptotic one). Observable results, such as the time-lag of transient nucleation, remain unchanged.

APPENDIX A: INVERSION OF THE LAPLACE TRANSFORM FOR THE FLUX

In the inner region near n_* the Laplace transform of the nucleation equation (written in terms of the reduced distribution $v=f_n/N_n$) is solved by a repeated error integral $i^m \operatorname{erfc}(z_{\rm lin})$.[19] Here $m=p\tau$, with p being the Laplace index (in the remaining part of this section time will be measured in the units of τ, so that m and p will not be distinguished). The function i^m erfc is defined as[34]

$$i^m \operatorname{erfc}(z)=\frac{2}{\sqrt{\pi}\Gamma(m+1)}\int_z^\infty (x-z)^m \exp(-x^2)dx \qquad \text{(A1)}$$

with a power-law and exponential asymptotes for $z\to\mp\infty$, respectively. Inversion of the asymptote of the inner solution into the growth region allows one to find the corresponding distribution and the flux, Eq. (15)—see Appendix of Ref. 19 for detail.

A more general Laplace transform was suggested in Ref. 23 in connection with pre-existing nuclei. If $f_n(0)$ is the initial distribution, and $v(n,0)\equiv f_n(0)/N_n$, one has the transform of the flux

$$J(n,p)=-j_s\frac{\pi}{4p}\Gamma(m+1)2^m i^{m-1}\operatorname{erfc}[z(n)] \times\int_0^n dw\,\frac{dv(w,0)}{dw}\exp[z^2(w)]i^{m-1} \times\operatorname{erfc}[-z(w)]\exp[z^2(n)] \qquad \text{(A2)}$$

(the last exponential factor was accidentally omitted in Ref. 23; otherwise the reader is referred to that paper for technical detail of the derivation).

Inversion of the Laplace transform does not affect the m-independent term $dv(w,0)/dw$. If the inverse of the remaining part of Eq. (A2) is labeled as $\delta j(n,w,t)$, the total flux will be expressed as

$$j(n,t)=\int_0^n dw\,\frac{dv(w,0)}{dw}\,\delta j(n,w,t). \qquad \text{(A3)}$$

The function $\delta j(n,w,t)$, which is related to a Green's function, will determine the partial contribution to the flux at size n at time t from the initial distribution near size w.

In order to obtain $\delta j(n,w,t)$, one can express $\Gamma(m+1)$ in Eq. (A2) through a product of $\Gamma(m/2)$ and $\Gamma(m/2+1/2)$.[34] Each of the resulting gamma functions is further combined with one of the erfc functions, and known[40] expressions are used to invert

$$\Gamma(m/2+\nu)i^{m-1}\operatorname{erfc}(z)$$

for $\nu=0$ and $\nu=1/2$. The convolution theorem leads to

$$\delta j(n,w,t)/j_s=\frac{2}{\sqrt{\pi}}\exp(z_1^2+z_2^2)z_2\int_0^t d\,e^{-u}\alpha(t-u)\alpha^3(u) \times\exp\{-z_1^2\alpha^2(t-u)-z_2^2\alpha^2(u)\}, \qquad \text{(A4)}$$

where z_1 and z_2 stand for $z(n)$ and $z(w)$, respectively, and $\alpha(t)$ is defined in Eq. (21). Introducing a new integration variable

$$y=z_2\sqrt{\alpha^2(u)-\alpha^2(t)}$$

one can cast Eq. (A4) as

$$\delta j(n,w,t)/j_s=\frac{2\alpha(t)}{\sqrt{\pi}}\exp\{-(\alpha^2(t)-1)(z_1^2+z_2^2)\} \times\int_0^\infty dy\,\exp\left\{-\frac{Q}{y^2}-y^2\right\} \qquad \text{(A5)}$$

with

$$Q\equiv z_1^2z_2^2\alpha^2(t)[\alpha^2(t)-1].$$

The integral evaluates to $\sqrt{\pi}/2\exp(-2\sqrt{Q})$. This gives an asymptotic expression for $\delta j(n,w,t)$. With $v(w,0)=\Theta(n_{\min}-w)$ one returns to conventional transient nucleation (no pre-existing nuclei), obtaining Eq. (29) in the text.

APPENDIX B: THE BECKER–DÖRING EQUATION AT SMALL TIMES

The classical master equation of the nucleation problem has the form

$$\partial f_n/\partial t=j_n-j_{n+1},\quad j_n=\beta_{n-1}f_{n-1}-\alpha_n f_n \qquad \text{(B1)}$$

with the loss coefficient $\alpha_n=\beta_{n-1}N_{n-1}/N_n$ determined by detailed balance. At very small times one can consider only gain; losses can be neglected due to condition $f_{n+1}\ll f_n \ll N_n$. This gives

$$\frac{\partial f_n}{\partial t} \approx \beta_{n-1} f_{n-1} \tag{B2}$$

or, with $n_{\min}=1$ and $f_1=\text{const}$,

$$f_{n+1}=\frac{1}{n!} f_1 \beta_1 \beta_2 \cdots \beta_n t^n + O(t^{n+1}). \tag{B3}$$

The critical size (which is due to competition of gain and the neglected loss) does not play any special role at such small times.

In the standard case of β_n given by Eq. (45) one has

$$f_{n+1}^{\mathrm{BD}}(t) \approx f_1 (t/\tau)^n (\Delta^2/2)^n n_*^{-2n/3} (n!)^{-1/3}. \tag{B4}$$

This result describes analytical properties of the solution in the limit $t \to 0$, but otherwise the region of its applicability is exceptionally short, smaller than $1/\alpha_2$—the time it takes f_2 to approach its near-equilibrium value.

[1] P. James, Phys. Chem. Glasses **15**, 95 (1974).
[2] V. M. Fokin, A. M. Kalinina, and V. N. Filipovich, Fiz. Khim. Stekla **6**, 148 (1980).
[3] J. Deubener, R. Brükner, and M. Sternizke, J. Non-Cryst. Solids **163**, 1 (1993); J. Deubener, *ibid.* **274**, 195 (2000).
[4] C. Spinella, S. Lombardo, and F. Priolo, J. Appl. Phys. **84**, 5383 (1998).
[5] L. Farkas, Z. Phys. **25**, 236 (1927).
[6] R. Becker and W. Döring, Ann. Phys. (Paris) **24**, 719 (1935).
[7] Ya. B. Zeldovich, Acta Physicochim. URSS **18**, 1 (1943).
[8] K. F. Kelton, A. L. Greer, and C. V. Thompson, J. Chem. Phys. **79**, 6261 (1983).
[9] Exact results are available only for selected characteristics of the Becker–Döring equation, such as the time-lag.
[10] An approximation is often sought in the form of a single Fokker–Planck equation (Refs. 7,11–14), or as a two different equations for the sub- and overcritical regions of sizes (Ref. 15).
[11] F. C. Goodrich, Proc. R. Soc. London, Ser. A **277**, 167 (1964); C. F. Clement and M. H. Wood, J. Nucl. Mater. **89**, 1 (1980).
[12] B. Shizgal and J. C. Barrett, J. Chem. Phys. **91**, 6505 (1989).
[13] D. T. Wu, J. Chem. Phys. **97**, 1922 (1992); "Nucleation theory," in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich and F. Spaepen (Academic, San Diego, 1996), pp. 37–187.
[14] V. A. Shneidman and P. Hänggi, Phys. Rev. E **49**, 894 (1994).
[15] V. A. Shneidman, Phys. Lett. A **143**, 245 (1990).
[16] D. Kaschiev, Surf. Sci. **14**, 209 (1969); *Nucleation: Basic Theory with Applications* (Buttersworth–Heinemann, Oxford, 2000).
[17] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, New York, 1985).
[18] H. Trinkaus and M. H. Yoo, Philos. Mag. A **55**, 269 (1987).
[19] V. A. Shneidman, Sov. Phys. Tech. Phys. **32**, 76 (1987).
[20] A. H. Nayfeh, *Introduction to Perturbation Techniques* (Wiley, New York, 1981), Chap. 12.
[21] V. A. Shneidman, Sov. Phys. Tech. Phys. **33**, 1338 (1988).
[22] A. Y. Klimenko, Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza **1**, 163 (1988).
[23] V. A. Shneidman, Phys. Rev. A **44**, 2609 (1991).
[24] G. Wilemski and B. E. Wyslouzil, J. Chem. Phys. **105**, 1090 (1996).
[25] I. L. Maksimov, M. Sanada, and K. Nishioka, J. Chem. Phys. **113**, 3323 (2000).
[26] V. A. Shneidman and P. Hänggi, J. Chem. Phys. **101**, 1503 (1994); V. A. Shneidman, Phys. Rev. E **59**, 4441 (1999).
[27] V. A. Shneidman, Sov. Phys. JETP **64**, 306 (1986); J. Chem. Phys. **103**, 9772 (1995); Phys. Rev. Lett. **75**, 4634 (1995).
[28] V. A. Shneidman, K. A. Jackson, and K. M. Beatty, Phys. Rev. B **59**, 3579 (1999).
[29] A. L. Greer, P. V. Evans, R. G. Hamerton, and D. K. Shangguan, J. Cryst. Growth **99**, 38 (1990); A. L. Greer and K. F. Kelton, J. Am. Ceram. Soc. **74**, 1015 (1991).
[30] L. Granasy and P. James, J. Chem. Phys. **113**, 9810 (2000).
[31] O. Penrose, J. Stat. Phys. **89**, 305 (1997).
[32] E. M. Lifshits and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, New York, 1981).
[33] (a) V. A. Shneidman and M. C. Weinberg, J. Chem. Phys. **97**, 3621 (1992); (b) **97**, 3629 (1992).
[34] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
[35] R. Andreas and M. Boudart, J. Chem. Phys. **42**, 2057 (1965); H. L. Frisch and C. Carlier, *ibid.* **54**, 4326 (1971); G. Wilemski, *ibid.* **62**, 3772 (1975).
[36] J. Bartels, U. Lembke, R. Paskova, J. Schmelzer, and I. Gutzow, J. Non-Cryst. Solids **136**, 181 (1991).
[37] K. F. Kelton and A. L. Greer, J. Non-Cryst. Solids **79**, 295 (1986).
[38] V. A. Shneidman and M. C. Weinberg, Mater. Res. Soc. Symp. Proc. **398**, 99 (1996).
[39] V. A. Shneidman (in preparation).
[40] H. Bateman and A. Erdelyi, *Tables of Integral Transformations* (McGraw-Hill, New York, 1954), Vol. 1.