Universal Distributions Generated in a Nucleation Pulse

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Asymptotic analysis of the nucleation-growth equations describing a nucleation pulse of arbitrary duration is performed. It is discovered that after extended growth an asymptotic distribution is established, which is not of any standard form (Gauss, log-normal, etc.). Regardless of the mass exchange mechanism between the nucleus and the metastable phase, in the extremes of long and short pulses the shapes of the distribution become universal, with additional insensitivity of either the maximum or, respectively, the width to the duration of the pulse.

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Homogeneous nucleation is of enormous interest in connection with condensing vapors [1,2], crystallizing liquids [3], glasses [4] and amorphous solids [5], colloidal [6] and biological [7] systems, etc. Applications to the description of ferroelectric [8] and ferromagnetic domains [9], or to nucleation and growth of quantum dots [10], could also be mentioned. The standard technique for nucleation studies is the nucleation pulse [2] ("two-step annealing" [4]), when after a brief nucleation period the supersaturation is abruptly decreased, terminating nucleation but allowing further growth of subnanoparticles to optically visible sizes. Of main interest are the distributions of nuclei over sizes. An understanding of their structure would allow us, on the one hand, to extract accurate nucleation information from growth measurements and, on the other hand to increase control over the microstructure of the material, which is determined by those distributions, via modification of the nucleation and growth conditions.

In the past, significant numerical and analytical effort was devoted to analysis of the classical time-dependent Becker-Döring nucleation equations (see, e.g., Refs. [1,5,11,12] and Refs. [1,13], and references therein, respectively). Many of the predicted dependences, in particular, those for the distribution function [14], can be applied to nucleation in nonclassical models as well, as observed in large-scale simulations and related computer-assisted studies of lattice systems [14,15], in molecular dynamics [16], or in phase field models [17]. However, in most of the *real* experiments the observed distribution will be extremely different, undergoing dramatic changes once particles are grown to large sizes. The goal of this Letter is to describe those changes analytically in a general form, applicable to arbitrary nucleation-growth mechanism, and to find the asymptotic shape of the distribution once particles grow to large sizes. The accuracy of the results is confirmed by exact numerics for classical-type nucleation models, similar to the one used in Refs. [11,12,18], and it is conjectured that results will hold for nonclassical models (e.g., phase field [19–21]) due to similarities in the growth laws, as described below.

It could be useful to distinguish the current problem from the one due to Lifshits, Slyozov, and Wagner (LSW) [22]. In their case the supersaturation is continuously decreasing with time due to depletion of monomers by growing particles, and scale-free asymptotic distributions are formed for each type of the mass exchange. Those exhibit remarkable insensitivity to fine detail of the initial conditions determined by the nucleation stage, and in practice the LSW regime is commonly used to study later stages of a phase transformation. In contrast, an abrupt drop in supersaturation following a nucleation pulse is due to external control [2,4]. Although particles do grow to large sizes, the depletion of monomers (or direct interactions between nuclei) is assumed to remain negligible and, despite certain universality features described below, a detailed memory of the initial nucleation conditions is preserved. Indeed, for a high nucleation barrier $\Phi_* \gg kT$ the above assumption is valid on an exponential time scale, allowing for the establishment of the asymptotic distributions described below (which requires a large, but nonexponential, time). On a still larger time scale the described solution has the meaning of an *intermediate asymptote* before depletion becomes important, eventually leading to the LSW regime.

It is convenient to start with the deterministic evolution of the distribution due to growth or decay of particles with a rate $\dot{R}(R)$, and then to specify the nucleation part, which determines initial conditions. Indices "n" and "g" will distinguish the nucleation and the growth stages, and the dimensionless $\Lambda = R_*^g/R_*^n > 1$, the ratio of critical radii, will describe the relative depth of the nucleation quench. Time t will be measured from the start of growth; functions of time which have a discontinuity at that instant will be distinguished by $t = 0^-$ and $t = 0^+$.

Consider a typical

$$\dot{R} = \frac{R_*}{\tau}\left(\frac{R_*}{R}\right)^{\theta}\left(1 - \frac{R_*}{R}\right) \tag{1}$$

with the time scale τ defined as the inverse of $d\dot{R}/dR$ at $R = R_*$ (which should be specified separately for the nucleation and the growth stages, with, e.g., $\tau^g = 1$ to

simplify notations). The power index θ depends on the type of mass exchange, with $\theta = 0$ and 1 corresponding to interface- and diffusion-limited growth, respectively, and $\theta = -1$ to the case of cavitation [23]. Identical expressions are encountered in field-theoretic models with $\theta = 0$ and 1 corresponding to nonconserved (Ginzburg-Landau) and conserved (Cahn-Hillard) order parameter, respectively, and appearing in various combinations in phase field models [19–21]; $\theta = -1$ corresponds to the inflation scenario.

Evolution of the distribution $f(R, t)$ due to deterministic growth is described by a continuity equation

$$\partial f/\partial t + \partial j/\partial R = 0, \qquad j \simeq \dot{R} f. \tag{2}$$

Introducing a full (''total'') derivative with respect to time, $D/Dt = \partial/\partial t + \dot{R}\partial/\partial R$, one can cast the above equation as

$$D \ln|j|/Dt = \partial \ln|\dot{R}|/\partial t. \tag{3}$$

Since for any $t > 0$ the growth rate has no explicit time dependence, the flux is conserved along the growth path, and in terms of a dimensionless $r = R/R_*^g$ is given by $j(r, t) = j(r_0, 0^+)$, where $r_0(r, t)$ is the ''nascent size,'' which achieves the value of r at time t. The exception is $t = 0$, where integration of Eq. (3) across the discontinuity gives $j(r, 0^+) = j(r, 0^-)\dot{r}^g/\dot{r}^n$, which is an equivalent representation of the continuity of the distribution, i.e., $f(r, 0^-) = f(r, 0^+)$. The flux $j(r_0, 0^-)$, which determines the initial distribution, must be obtained from the solution of the *nucleation* equation, further denoted as $j_0(\Lambda r_0)$ to comply with present notations. The general result at arbitrary growth time t thus takes the form

$$f(r, t) = j_0(\Lambda r_0)\frac{\dot{r}_0^g}{\dot{r}_0^n \dot{r}^g}, \qquad \int_{r_0}^{r} \frac{dr}{\dot{r}^g} = t. \tag{4}$$

Note that singularity at $r = 1$ with $\dot{r}^g = 0$ is fictitious since $r_0(1, t) = 1$ and a similar zero appears in the numerator. More accurately, for $r \to 1$ one has $r_0 - 1 \sim (r - 1)e^{-t}$, leading to an exponential decay of the distribution at the new critical size: $f(1, t) \simeq f(1, 0)e^{-t}$. This results in separation of the decay and the growth regions, and to formation of a maximum in the latter region even if the initial distribution was monotonic. On the other hand, the singularity corresponding to $\dot{r}_0^n = 0$ (with $r_0 = 1/\Lambda$) can be ''real,'' reflecting a rapid increase of the initial distribution towards the old critical size. This singularity, however, will disappear into $r = 0$ after a finite decay time $t_d = -\int_0^{1/\Lambda} dr/\dot{r}^g$, and will be described in more detail once the flux and the growth rates in the general equation (4) are specified.

In order to account for nucleation, one needs to include a fluctuational correction $-\beta\partial f/\partial R$ to the drift flux in Eq. (2), which leads to a Fokker-Planck-type equation [23]. If $\Phi = \Phi_*[3(R/R_*)^2 - 2(R/R_*)^3]$ is the minimal work required to form a nucleus, one has [23]

$$\beta = -kT\frac{\dot{R}}{d\Phi/dR} = \frac{R_*^2}{\tau}\frac{kT}{6\Phi_*}\left(\frac{R_*}{R}\right)^{\theta+2}. \tag{5}$$

For a high barrier β is small, which allows one to use singular perturbation methods to solve the time-dependent Fokker-Planck equation [24]. This leads to Eq. (6), below, for the transient flux, with the incubation time (for selected growth rates) given by Eq. (7). Furthermore, since β decays with size, fluctuational corrections to the *growth* solution are negligible at large times with a characteristic $r \gg 1$.

One has for $\Lambda r > 1$

$$j_0(\Lambda r) = j_s \exp(-e^{-x}), \qquad x \equiv [t_n - t_i(\Lambda r)]/\tau^n. \tag{6}$$

Here t_n is the duration of the nucleation pulse and t_i is the ''incubation time'' determined by the type of mass exchange. The number of particles which will grow to large sizes is given by $N(t_n) = \tau^n j_s E_1(e^{-x})$ [24(b)], where E_1 denotes the first exponential integral [25] and x from Eq. (6) is evaluated at the new critical size $r = 1$. Equations (4) and (6) thus provide a general parametric representation of the distribution in terms of r_0; evaluation of $r_0(r, t)$ will relate the distribution to physical variables. A similar double-exponential shape of the transient flux is observed empirically in nonclassical systems as well [15,16], potentially further increasing the generality of the solution.

For integer θ the incubation time is evaluated in elementary functions [24(b)]. One has

$$\frac{1}{\tau^n} t_i(r) = \ln\left[\frac{6\Phi_*}{kT}(r-1)\right] + r - 2 + \theta\left(\frac{r^2}{2} - 1\right), \quad \theta = 0, 1, \tag{7}$$

and only the logarithmic term is present for $\theta = -1$. The distribution in Eq. (4) at $t = 0$ is then an elementary function too [recall that $r_0(r, 0) = r$], which decays monotonically with r in the ballistic case, and which can have a local maximum for diffusion-limited growth if the pulse is sufficiently long.

To obtain the distribution at $t > 0$ one needs to evaluate $r_0(r, t)$, which can be done in elementary functions only for

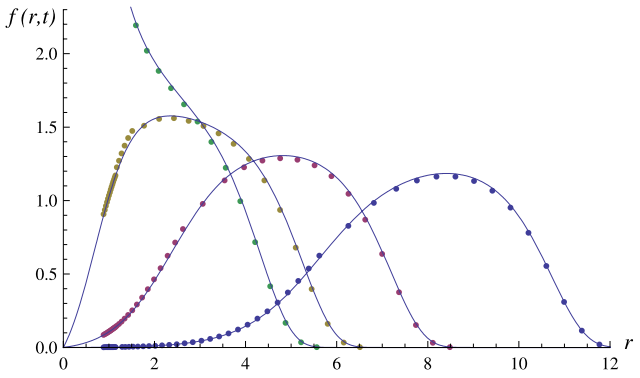

FIG. 1 (color online). Postnucleation transformations of the ballistic distribution with $t_n/\tau^n \simeq 10$, $\Lambda \simeq 1.3$. Symbols are exact numerics; lines are Eqs. (4) and (8). Dimensionless growth times, from left to right: $t/\tau^g = 0.57$ (descending) and (bell shaped) 1.7, 4.0, and 7.9.

cavitation, $\theta = -1$, with a linear growth rate. Otherwise, e.g., in the more challenging case of interface-limited growth, the dependence is expressed in terms of a special function. One has

$$r_0(r, t) = 1 + W((r-1)e^{r-t-1}), \tag{8}$$

where $W(z)$, the Lambert W function, is defined as the root of an equation $z = W(e^W)$ [26].

Typical evolution of the distribution is shown in Fig. 1. Initial singularity at the old critical size $r = 1/\Lambda$ disappears after a short $t_d = \ln[\Lambda/(\Lambda-1)] - 1/\Lambda$. At small r and for t close to t_d, the distribution is approximated by

$$f(r, t) \simeq \tau^n j_s \frac{r}{r^2/2 + t - t_d}, \tag{9}$$

and two distinct situations are possible. For $t > t_d$ the distribution is defined for all $r \geq 0$, and linearly tends to zero for $r \to 0$ (the latter reflects the fact that nucleation is expected to be negligible on the growth stage, so that there is no source in the continuity equation). For $t < t_d$, however, the distribution is defined only for $r > \sqrt{2(t_d - t)}$ and is singular when r approaches the lower boundary. Physically, disappearance of the singularity indicates an abrupt dissolution of a large number of particles which were formed on the nucleation stage but did not survive growth. It is unclear, though, whether this will have observable consequences since those particles are so small.

One also notes from Fig. 1 that at large times, well after the initial singularity disappears, the distribution approaches an asymptotic shape. The latter is best described in a reference frame moving together with the growing particles.

Consider first a not-too-short nucleation pulse and define the initial location of the "front" (sharp cutoff of the distribution) r_0^f from the condition $j_0(r_0^f) = j_s/e$, i.e., $x = 0$ in Eq. (6). As the front r^f moves towards large sizes, the dependence $r_0(r, t)$ in the general solution is asymptotically reduced to its dependence on a *single* parameter ρ, the dimensionless distance from the front:

$$\int_{r_0^f}^{r_0} \frac{dr}{\tau^g \dot{r}^g} \sim \frac{r - r^f}{\tau^g \dot{r}^f} \equiv \rho/\nu, \qquad \nu = \lim_{r\to\infty} \frac{\tau^g \dot{r}^g}{\tau^n \dot{r}^n}. \tag{10}$$

In terms of ρ the distribution takes a time-independent asymptotic form $F(\rho) = j_0(\Lambda r_0)\tau^g \dot{r}_0^g/(\nu \tau^n \dot{r}_0^n)$ for any type of mass exchange.

Further simplifications and emergence of universal behavior are observed for a long pulse with $r_0^f \gg 1$. Here the rational and the double-exponential factors in the general expression for $F(\rho)$ are well separated, and one can write

$$F(\rho) \simeq \frac{1 - 1/r_0}{1 - 1/\Lambda r_0} \exp(-e^\rho). \tag{11}$$

For r_0 close to 1 ($\rho \to -\infty$) the dependence is exponential, $r_0 \sim 1 + \exp(\rho/\nu + \text{const})$, with the constant determined by the nonlinear part of growth during the nucleation pulse, while $\exp(-e^\rho) \simeq 1$. On the other hand, in the vicinity of the front the rational part approaches unity, so that the front's shape is determined exclusively by $\exp(-e^\rho)$, regardless of the growth type.

In between the cutoffs the distribution will have a flat top, which appears especially surprising for diffusion-limited growth with a very different structure of initial conditions. For an extra long pulse when not only the double-exponential front is sharp, but even the exponential cutoff at small sizes becomes near vertical, the distribution approaches a boxlike shape for *any type of growth*, as in Fig. 2.

In the opposite case of an ultrashort pulse the "front" is not a convenient reference point since the rapidly decaying distribution does not have one from the start. Subsequently, however, a well-pronounced *maximum* will be developed (this is in contrast with the long-pulse scenario where the distribution is exceptionally broad and flat). Introducing

$$\zeta \sim (r - r^{\max})/\dot{r}^{\max}, \tag{12}$$

one obtains the asymptote of the dimensionless distribution for $r^{\max}(t) \to \infty$

$$F(\zeta) = \frac{e^{-\alpha}}{\alpha} \exp(\zeta - e^\zeta), \quad \alpha = \exp\left[\frac{t_i(\Lambda) - t_n}{\tau^n}\right] \gg 1. \tag{13}$$

The accuracy of the absolute value of the maximum $F^{\max} \simeq e^{-(\alpha+1)}/\alpha$ is not expected to be too high due to extreme sensitivity to α (and thus to initial conditions), but the ζ dependence is accurate and is remarkably similar for all types of growth and for all (short) pulse durations, as in Fig. 3. In terms of r, however, the distributions will be sensitive to growth type, with $\dot{r}^{\max} \sim (r^{\max})^{-\theta}$ in Eq. (12) implying either a constant width ($\theta = 0$) or an expanding and narrowing distribution for $\theta < 0$ and $\theta > 0$, respectively.

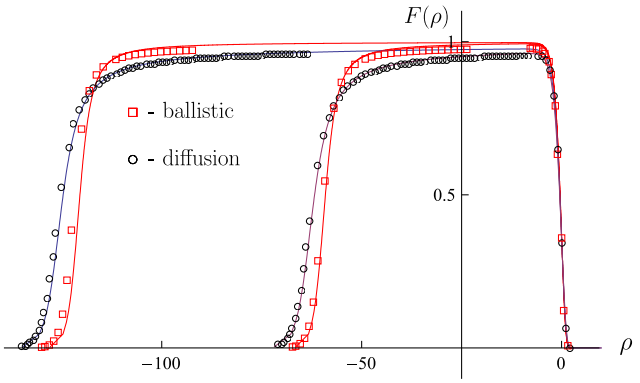

FIG. 2 (color online). Boxlike asymptotic distributions originating from long nucleation pulses t_n for ballistic and diffusion mechanisms. Durations of each pair of pulses were matched to ensure a similar number of nuclei. Shorter pulses: $t_n/\tau^n = 61.32$ (ballistic) and 61.16 (diffusion); longer pulses: $t_n/\tau^n = 122.47$ (ballistic) and 122.32 (diffusion). Symbols are exact numerics (not shown for the flat part); lines are Eqs. (10) and (11).

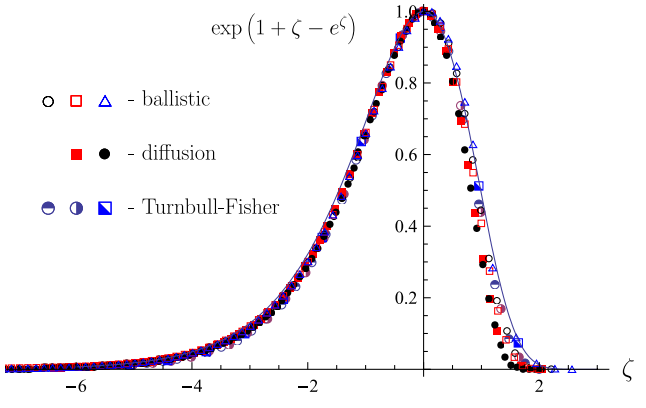

FIG. 3 (color online). Universal distribution $F(\zeta)/F^{\max}$, Eqs. (12) and (13), formed in short nucleation pulses of different durations t_n. Symbols are exact numerics. From left to right (legend): $t_n/\tau^n \simeq 1$, 2, and 3 (ballistic); 1.22 and 2.45 (diffusion); 0.75, 1, and 2.5 (Turnbull-Fisher). Note that the width of all distributions emerges near same for all types of growth and all pulse durations.

In order to verify that the conclusion above is not an artifact of a continuos nucleation equation, the Turnbull-Fisher version [11,12,18,27] of the discrete Becker-Döring equation was considered. The associated growth rate is given by $(2/a\tau)\sinh[\frac{a}{2}(1-1/r)]$ [18]; $a = 2\Phi_*/(kTn_*)$ is the "discreteness parameter" [28] and n_* the critical cluster number. The general numerical approach was described by Kelton *et al.* [11,18] and the MATHEMATICA realization of the nucleation update scheme is discussed in Ref. [15]. Parameters [29] were close to that of lithium disilicate nucleated and grown at 730 and 840 K, respectively (which is typical for corresponding experiments [4]), with $n_*^n \simeq 18$, $n_*^g \simeq 40$, and $\Phi_* \simeq 37kT^n$. The deterministic (growth) part of the distribution was represented by a histogram with a variable number of bins (and a similar approach, with artificially reduced values of a, was used to test the continuous description); computational detail will be provided elsewhere [30]. Numerical results are still in good agreement with the universal curve in Fig. 3.

In summary, despite the complicated structure of the time-dependent nucleation-growth equations, it is possible to construct an accurate general expression for the distribution of nuclei formed during a pulse of arbitrary length. At small growth times, which follow the pulse, the distribution undergoes dramatic changes, including an intriguing disappearance of the "nucleation singularity" at subcritical sizes. At larger times changes are moderated and the distribution, in appropriate variables, approaches an asymptotic shape. In both limits of long and short pulses that shape exhibits universal features, turning insensitive to the physical mechanism of mass exchange or the mathematical structure of the underlying nucleation model. Most remarkably, in those limits even the pulse duration can have no effect on either the maximum of the distribution or even on its width. Results are expected to have direct applications to vapor condensation and, especially, to two-step annealing crystallization studies, but can be of more general validity due to the ubiquitous nature of the technique of a nucleation pulse.

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