Nonuniversality of nucleation kinetics following a finite rate quench

Vitaly A. Shneidman
Department of Materials Science and Engineering, The University of Arizona, Tucson, Arizona 85721
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Nucleation fluxes and numbers of nuclei are evaluated as functions of time and the quench rate, q, using asymptotic technique. In contrast to predictions of conventional (adiabatic) nucleation descriptions with the number of quenched-in nuclei scaling as q^{-1}, a different scaling $q^{-\alpha}$ is observed with nonuniversal, model-dependent values of $\alpha<1$. [S1063-651X(99)08704-8]

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It is well known [1,2] that a rapid quench can bring a physical system into a metastable state which is characterized by a prolonged lifetime. The latter is determined by the intensity of nucleation and growth of the stable phase, before the system settles in thermodynamic equilibrium. Experimental examples include supersaturated vapor [1], undercooled or overheated liquids [2], binary fluids [3], glass-forming melts [4,5], amorphous solids [6], electron-hole liquid [7], to mention only a few. In view of the enormous variety of nucleation models (both ''classical'' [8–12] or ''nonclassical,'' e.g., [2,13]), which are used to explain or predict the observed behavior, one requires an understanding of the sensitivity of the description to the selection of a specific type of a nucleation mechanism, and, on the other hand, an understanding of its universality.

As a first step to understand the differences between various nucleation models, one can consider a much simpler deterministic growth of nuclei, which neglects fluctuations. A typical growth rate is given by

$$v(r)=\tau^{-1}r^{-\nu}(1-1/r), \tag{1}$$

with $r\equiv R/R_*$ (R_* being the critical size) and τ some characteristic time scale which will be described shortly. The value of the power index, ν, depends on the mass exchange mechanism between the nucleus and the metastable phase, with $\nu=0,\pm 1$ corresponding to surface- [11] or diffusion-limited [14] growth or cavitation [10], respectively. Similar expressions also appear in field-theoretic descriptions for a nonconserved ($\nu=0$ [15]) or conserved ($\nu=1$ [16]) order parameter, with $\nu=-1$ corresponding to inflation models. Combinations of several types of dynamics can be encountered both within classical [17] and nonclassical descriptions [13], but the main feature of the changing sign at $R=R_*$ (equivalently, the presence of a single unstable mode [18]) is typical, and determines the universality of the kinetic part of the description. The nonlinear off-critical dynamics, on the other hand, is model-sensitive.

The parameter τ in Eq. (1), which formally can be defined as $(dv/dr)^{-1}$ at $r=1$, provides a link between growth and nucleation [10], with τ^{-1} corresponding to the increment of the unstable mode in field-theoretic descriptions [18]. Nucleation—the possibility of a nucleus to go against the drift prescribed by Eq. (1)—becomes feasible due to thermal fluctuations. This leads either to a Fokker-Plank-type equation [10,11] (discrete master equation [8,9,12]) for the distribution of nuclei $f(r)$ in the classical picture, or to functional equations for the order parameter in field-theoretic (nonclassical) descriptions.

The key characteristic of the nucleation problem is the minimal work, $W(R)$, which is required to create a given nucleus. Its maximum, W_* (saddle point in the multidimensional case), determines the barrier to nucleation. In specific problems evaluation of W_* can be quite a nontrivial task [13,19]. Nevertheless, once this parameter is known and τ is determined from macroscopic kinetics, the steady-state flux of nuclei over the barrier under rather relaxed assumptions is given by [10]

$$j_s=\delta^2/2\tau\sqrt{\pi}f_{\rm eq}(R_*), \tag{2}$$

with $f_{\rm eq}\propto\exp(-W/T)$ being the (quasi)equilibrium distribution (temperature is measured in units of the Boltzmann constant), and δ is the width of the fluctuational region near the critical size. The above expression is asymptotically accurate for a high nucleation barrier, $W_*\gg T$, a condition which also will be crucial for generalizations described below.

The remarkable feature of Eq. (2) is that it is model-independent; in particular, it does not include the power index ν which distinguishes models in Eq. (1). Moreover, consider an experimentally more realistic situation of nucleation after a finite rate quench with $q=-dT/dt>0$. In the adiabatic approximation, i.e., with the nucleation rate determined in accordance with Eq. (2) with $R_*=R_*(T)$, the number of quenched-in nuclei will scale as q^{-1}, again independently of the model considered.

One can expect that the difference between models will show itself for faster, nonadiabatic processes where the nonlinear off-critical growth or decay of nuclei is important. On the other hand, the contribution of the near-critical region where models are equivalent to each other is still expected to be considerable (even if not dominating, as in the adiabatic case) providing a certain degree of universality.

The intent of the present paper is to provide a general nonadiabatic solution of the aforementioned problem of transient nucleation following a finite-rate quench. Although attention will be focused on analytics (in particular, on the elucidation of the connection between universality and model dependence), one also should keep in mind experimental studies [4,6,20] where some effects are in qualitative disagreement with the homogeneous nucleation description, with no quenched-in nuclei. For example, in glass-to-crystal

nucleation [4,20] the early-time numbers of nuclei appear to be systematically larger [20,21], and the time lags smaller [22] than conventional expectations. Similarly, exponential-type tails in the distributions of grains in amorphous silicon [6] contradict the homogeneous nucleation description, and the quenched-in nuclei (where such tails do appear—see below) can provide at least one possible explanation.

Formally speaking, the derivations below are restricted to models within the classical approach. Nevertheless, the area of applicability of the results is expected to be wider, since in the scaled form they turn out to be sensitive only to the growth/decay rates, which are similar in both classical and nonclassical cases, as suggested by Eq. (1).

Let us characterize quench by a dimensionless rate of the barrier change

$$n = -\tau q (W_*/T)'_T, \tag{3}$$

with the prime indicating the derivative with respect to temperature. In Refs. [23,24] it was shown that asymptotically (i.e., for finite n and large W_*/T) a distribution $f(r) = f_{\rm eq}(r)\exp\{-n\zeta(r)\}$ is established in the subcritical region of sizes. The function $\zeta(r)$ is given by $-\int_0^r dr\, r^3/\tau v(r)$, and the above distribution will serve as an initial condition at $t=0$ for the subsequent isothermal problem. At the same time, the effect of quenched-in *overcritical* nuclei can be neglected for a reasonably fast quench [25]. Similarly, the quenched-in distribution of nuclei from a higher equilibrium temperature [which would replace the above $f(r)$ in the limit $n\to\infty$] can be shown to have no observable effects for $W_* \gg T$.

In the absence of an initial distribution, the reduced flux $j^0(r,t)/j_s \equiv \phi_0$ at an arbitrary observation size $r>1$ would be given by

$$\phi_0(x) = \exp(-e^{-x}), \quad x \equiv [t - t_i(r)]/\tau, \tag{4}$$

which is the transient flux of homogeneous nucleation [24]. The functional shape of the solution is independent of the model, but a specific growth rate enters via the incubation time, $t_i(r) \gg \tau$, which contains both growth and decay [21]. This time weakly (logarithmically) depends on the barrier, and explicit expressions are available for $\nu = 0, \pm 1$ [21]; at large r the incubation time increases as $r^{\nu+1}$ for $\nu > -1$ or as $\ln r$ for $\nu = -1$ in Eq. (1). This nonuniversality of $t_i(r)$ can be eliminated by switching to the scaling parameter x in Eq. (4), and mostly will be of no interest in the present context. On the other hand, the model dependence of the function $\zeta(r)$, which determines the quenched-in initial distribution, cannot be eliminated by simple scaling transformations.

When quenched-in nuclei are added, there is a chance that some of them will cross the barrier, effectively increasing the nucleation rate. With an appropriate scaling, the *trans*-barrier asymptote of a corresponding Green's function is expressed through the derivative of $\phi_0(X)$ with a shifted argument $X = x + t_d(r_1)/\tau$, and with $t_d(r_1) = -\int_0^{r_1} dr/v(r)$ being the positive decay time for a nucleus initially placed at $r_1 < 1$ [26]. Although the nucleation equation has an inhomogeneous boundary condition, $f(r) \to f_{\rm eq}(r)$ for $r \to 0$, asymptotically the superposition principle holds, and the total flux can be determined as a sum of the transient flux, j^0, and a correction, δj, due to quenched-in nuclei. With the above-mentioned initial distribution, the reduced correction $\delta j/j_s \equiv I$ is given by

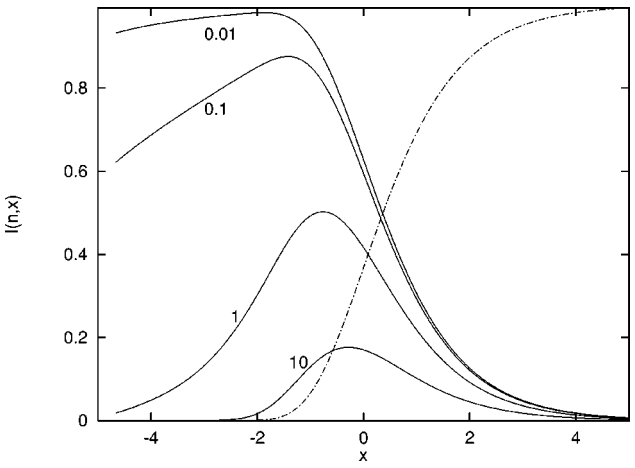

FIG. 1. The scaled excess flux due to quenched-in nuclei, Eq. (6), as a function of $x = (t - t_i)/\tau$ for different values of n. For $n \gg 1$ the shape of the curves approaches $\phi_0'(x)$ with the area scaling as $n^{-2/5}$. The function $\phi_0(x)$, Eq. (4), is shown by a dashed line and corresponds to the flux due to homogeneous nucleation.

$$I(n,x) = -\int_0^1 \frac{dr_1}{\tau v(r_1)} e^{-n\zeta(r_1)} \phi_0'(X). \tag{5}$$

In the analysis of the above expression one notes the singularity of the integrand as $r_1 \to 1$; this turns out to be important for a proper limit of small n. The large-n limit is sensitive to the divergency of $v(r_1)$ as $r_1 \to 0$. The function $t_d(r)$, which enters the argument X, and the function $\zeta(r)$ can be evaluated in elementary functions for integer ν in Eq. (1), but mostly only the asymptotes near the singular points will be required. For arbitrary $\nu \geqslant -1$, those asymptotes are given by $t_d \sim r^{\nu+2}/(\nu+2)$, $\zeta \sim r^{\nu+5}/(\nu+5)$ for $r \to 0$, and $t_d \sim \ln(1-r) + \psi(2+\nu) - \psi(1)$, $\zeta \sim \ln(1-r) + \psi(5+\nu) - \psi(1)$ for $r \to 1$ with ψ being the digamma function [27].

Making a substitution $Z = e^{-x}$ and switching to a new integration variable $y = \exp(-t_d/\tau)$, one obtains after some transformations

$$I(n,x) = Z \int_0^1 dy\, \exp\{-n\zeta[r(y)] - yZ\}. \tag{6}$$

This result is expected to be valid for arbitrary (though non-asymptotic) values of the quench index n and the parameter Z which describes the dependence on the observation size and time. Equation (6) corresponds to bell-shaped curves which are skewed for small n (see Fig. 1). Corrections to the distribution function in the growth region are given by $I(n,x)/v(r)$ and have similar shapes which are more model-sensitive due to an additional explicit size dependence. The tail of the distribution at large sizes is determined by the asymptote of $t_i(r)$: $f(r) \propto r^\nu \exp[-nr^{\nu+1}/(\nu+1)]$ (or $f \propto r^{-(n+1)}$ for $\nu = -1$) with a time-dependent prefactor.

In the limit of small n the function ζ can be replaced by its logarithmic asymptote, and the integral in Eq. (6) approaches the incomplete gamma function $\gamma^*(n+1, Z)$ [27].

In the formal limit $n=0$, one has $I(0,x)=1-\phi_0(x)$ implying that the total flux, i.e., the sum of the fluxes due to quenched-in nuclei and due to transient homogeneous nucleation, should correspond to j_s. Here, the distribution $f(r)$ acquires a power-law tail, $f(r)\propto r^{\nu}$ for $r\gg 1$, which is typical for the steady-state nucleation regime.

In the most interesting case of large n (fast quench), the Z and n dependences are factorized. Here one obtains $I(n,x)=\phi_0'(x)\,\delta\rho_\infty(n)/j_s\tau$, with $\delta\rho_\infty(n)$ being the total number of the observed quenched-in nuclei

$$\delta\rho_\infty(n)\approx\delta\rho_a[n/(\nu+5)]^{1-\alpha}\Gamma(\alpha). \tag{7}$$

In the above, $\delta\rho_a\approx\tau j_s/n$ is the number of nuclei quenched-in adiabatically; the model-dependent parameter α is defined as $\alpha=(\nu+2)/(\nu+5)$, and $\Gamma(\alpha)$ is the gamma function. Once the correction due to quenched-in nuclei is small, the total flux, which is proportional to $I(n,x)+\phi_0(x)$, can be approximated as

$$j(r,t)\approx j_s\phi_0[x+\delta\rho_\infty(n)/j_s\tau], \tag{8}$$

i.e., as the transient flux with the time shifted by $\delta\rho_\infty(n)/j_s$.

For intermediate n the general Eq. (6) should be used for the flux, while the number of quenched-in nuclei is given by

$$\delta\rho=\delta\rho_a n\int_0^1 dy\, y^{-1}\,\exp\{-n\zeta[r(y)]\}. \tag{9}$$

For small n one has, as expected, $\delta\rho\approx\delta\rho_a$.

The striking feature of the solution is that $\delta\rho$ is *larger* than its adiabatic counterpart. This sharply contrasts with higher moments of the distribution function which are suppressed by nonadiabatic effects [28]. Furthermore, in contrast to $\delta\rho_a$, the value of $\delta\rho$ explicitly depends on the chosen model via the function $\zeta(r)$, which is sensitive to nonuniversal, nonlinear decay. Most clearly, this is seen from the asymptotic Eq. (7): Instead of the universal dependence $\delta\rho_a\propto q^{-1}$ of the adiabatic approximation, one has $\delta\rho\propto q^{-\alpha}$ with α determined by the power index ν in Eq. (1).

In the discrete nucleation models [8,9,12] another asymptotic parameter, the critical cluster number, g_*, enters the problem. The discreteness effects modify the growth/decay rate $v(r)$ and thus the function $\zeta(x)$ in the above expressions; the asymptotes in Eq. (7) can be modified too. Generally speaking, the neglect of such effects is possible only for very large values of $g_*\gg W_*/T$ [29], which correspond to high temperatures. Nevertheless, the qualitative conclusions of $\delta\rho>\delta\rho_a$ and of model sensitivity of the results are expected to hold even for smaller $g_*\gg 1$, and for $g_*\gtrsim W_*/T$ a reasonable numerical accuracy of the results based on the continuous growth rates, Eq. (1), is anticipated.

To verify these analytical predictions, a master equation [12] was solved numerically, similar to the works by Kelton *et al.* [30,31]. This master equation corresponds to surface-limited kinetics; diffusion-limited nucleation was simulated by multiplying the rate coefficients of the master equation by r^{-1}. To isolate the effect of quenched-in nuclei the transient flux of homogeneous nucleation was subtracted from the full flux observed at $r=1.7$.

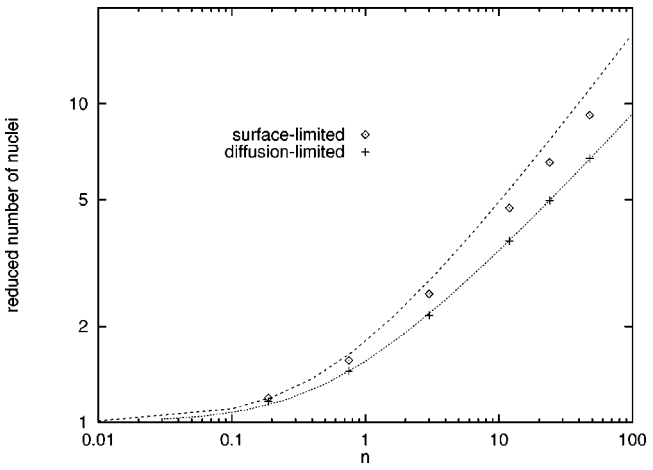

FIG. 2. Nonuniversality (model dependence) in the number of quenched-in nuclei, $\delta\rho/\delta\rho_a$. Symbols, from numerical solutions of the nucleation master equation; dashed and dotted lines, Eq. (9) with $\nu=0$ and $\nu=1$, respectively. Note that for small n (adiabatic regime) the difference between models disappears.

Parameters of lithium disilicate were considered with $T=900$ K. The latter is larger than the temperatures of the actual experimental measurements [4,5], but it gives reasonably high values of $g_*\approx 65$ and $W_*/T\approx 78$, with moderate discreteness effects.

Strictly speaking, the obtained analytical results should be applied with caution to glass-forming melts which are characterized not only by the change of the barrier, but also by an increase in τ in the course of a quench. In particular, already in the adiabatic approximation $\delta\rho_a$ can be larger than $\tau j_s/n$. Nevertheless, as long as one remains at temperatures higher than that of the maximum nucleation rate (higher than the glass transition temperature), results are expected to remain qualitatively correct, and reasonably accurate if scaled by $\delta\rho_a$. (This was verified by bringing the temperature down to 730 K.) For the higher temperature of 900 K (Fig. 2) the results are not only qualitatively but also numerically accurate. In accord with the analytical conclusion, contributions of quenched-in nuclei are larger than the adiabatic expectation. The predicted model dependence of the corrections is also observed, although the difference is somewhat smaller than between the analytical expressions. The latter is likely due to the discrete nature of the boundary condition for the master equation which removes the region of very small r, where the difference between the two models is the largest. For the same reason, analytical predictions turn out to be more accurate in the diffusion case—faster decay of small nuclei reduces the contribution of the corresponding region of sizes, and thus reduces the role of discreteness effects.

In summary, the first analytical (asymptotic) study of the full transient nucleation problem, including the conditions of preliminary quench, was performed. Results distinctly contain universal (model-independent) and model-sensitive components. Although the treatment was strictly justified (and verified numerically) only for models within the classical nucleation picture, results are expected to be of broader

validity due to archetypal structure of the growth rate expressions. In particular, it was found that the observed number of quenched-in nuclei scales nonuniversally with the quench rate, being determined by the peculiarities of the nonlinear decay. For fast quenches, the number of such nuclei is determined by the type of singularity in the decay of smallest nuclei, which is model-specific. Surprisingly, the value of this number turns out to be larger (not smaller) than conventional predictions based on universal, adiabatic approximations.

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