Heating rate effects in the transient nucleation problem

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The matched asymptotic (singular perturbation) treatment of the nucleation equation [V. A. Shneidman, Sov. Phys. Tech. Phys. **32**, 76 (1987); **33**, 1338 (1988)] is modified to include finite heating rate effects, which follow the isothermal transient stage. Despite the complicated mathematical structure of the discrete Becker-Döring equation, the obtained analytical solution is shown to be accurate numerically. The described situation is typical for two-step annealing crystallization studies and can lead to reinterpretation of some of the classical experiments. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2768032]

Theoretical interest in the problem of transient nucleation can be traced to the early classical work of Zeldovich.[1] The interest only grew over time due to the nontrivial mathematical structure of the underlying equations (especially if taken in the discrete, "Becker-Döring" form[2,3]) and even to a greater extent, due to novel challenges provided by experiments. Specifically, effects of transient nucleation were shown to be important in crystallization of silicate glasses and amorphous silicon[5] or during nucleation and growth of quantum dots.[6] The increased precision of modern molecular dynamics[7] and Monte Carlo[8] nucleation studies also indicated the inevitable presence of such effects, which extend far beyond the original classical theory.[9]

Probably, the most detailed account for transient nucleation in real-life experiments is provided by "two-step annealing" studies,[4] when a system is allowed to nucleate for some time at a nucleation temperature T_N, which is then rapidly increased to a temperature T_D where microscopic nuclei can be developed and counted. The derivative of their number with respect to the nucleation time will determine the quantity of the main interest, the nucleation rate or "flux."

Within the steady-state treatment interpretation of the flux j_{st} is straightforward: It should not depend either on the nucleation time t or on the development conditions. With this simplicity, however, only limited information about the properties of the microscopic nuclei can be revealed. A deeper insight can be provided by the transient nucleation studies, but in that case not only will the flux acquire a time dependence but the development conditions will also have a significant effect. Theoretical understanding is required here for a proper interpretation of the experiments and, since the two-step annealing is a state-of-the-art process for many industrial glass-ceramic products, can be useful for applications. The problem is also of a broader interest for the chemical physics community, emphasizing the inherent connection between nucleation and growth and representing a new mathematical challenge in the general topic of time-dependent nucleation.

The steady-state solution of the Becker-Döring equation can be obtained either exactly[10] or asymptotically[1] for a high nucleation barrier. The flux j_{st} does not depend on size R where it is observed. In the transient case a full exact solution is impossible, but still the flux can be obtained asymptotically[11,12] and efficient numerical solutions are also available.[13,14] In both types of approaches transient flux exhibits a distinct R dependence. If, as commonly assumed in interpretation of the classical experiments, the heating rate H between the nucleation and the development stages is infinitely fast, and the size R in the transient flux $j(R,t)$ corresponds to the critical size R_* at the development temperature T_D. Dependence on T_D is then used to extract further quantitative information, such as the interfacial tension between the crystal nucleus and the melt (see, e.g., Ref. 15 and references therein). Recently, the assumption of infinite H was questioned by Davis[16] and was shown to lead to undercounting of the number of nuclei. However, without consistent analytical studies there remains a confusion in literature not only with respect to quantitative interpretation of the effect but also on the very status of transient nucleation in the aforementioned classical experiments.[17]

The goal of this communication is thus to construct an accurate expression for the transient flux as a function of the subsequent heating rate H. As it turns out, results may or may not be sensitive to T_D depending on heating conditions. Comparison with exact numerics will provide an independent test of the analytical approach.

The singular perturbation solution to the Becker-Döring equation can be obtained using a combination of matched asymptotic and Laplace transformation techniques.[11,12] In the growth region $R > R_*$ the result is given by

$$j(R,t) = j_{st} \exp\{-\exp[(t_i(R) - t)/\tau]\}. \tag{1}$$

Here, τ is the "relaxation time," the same as appears in the preexponential of j_{st} (Ref. 1) and defined through the deterministic growth rate $u(R)$ as $\tau^{-1} = du/dR$ at $R = R_*$. The "incubation time" $t_i(R)$ depends on off-critical $u(R)$ and thus depends on the selection of the model. In a general case one has (**P** indicates the principal value of the integral, recall that $u(R)$ changes sign at $R = R_*$) (Ref. 11)

TABLE I. The survival size R_s at the end of nucleation annealing for different values of subsequent heating rate H. The development temperature T_D is 840 K with $R_*(T_D) \simeq 0.991$ nm for selected parameters; the nucleation temperature T_N is 730 K with $R_*(T_N) \simeq 0.762$ nm. The Turnbull-Fisher (TF) R_s corresponds to numerical solution of Eqs. (6) and (4). The approximate R_s is from Eq. (13). The last row gives the crossover temperature T_c as the solution of Eq. (11).

H (K/s)	0.01	0.1	1	10	100	1000
TF R_s (nm)	0.774	0.802	0.848	0.910	0.973	0.989
Approximate R_s (nm)	0.767	0.794	0.840	0.901	0.961	0.982
T_c (K)	732.4	754.5	780.5	811	848	893

$$t_i(R) = \tau \ln \frac{6W_*}{T} + \mathbf{P} \int_0^R \frac{dR'}{u(R')} - 2\tau C,$$

$$C = \int_0^{R_*} dR \left(\frac{1}{\tau u(R)} - \frac{1}{R - R_*} \right). \tag{2}$$

Here, W_* is the barrier to nucleation and Boltzmann constant is taken as 1.

Note that the solution is not sensitive to a specific form of the general master equation of the nucleation problem, but once j_{st} has been evaluated, it depends only on the associated growth rate $u(R)$. For example, in the continuous "Zeldovich-Frenkel" (ZF) (Refs. 1 and 18) equation $u(R)$ is given by $\tau u(R) = R_*(1 - R_*/R)$, which allows one to evaluate the above integrals in elementary functions[11]

$$t_i^{ZF}(R) = \tau\{r - 2 + \ln(6W_*/T) + \ln(r-1)\}, \quad r \equiv R/R_*. \tag{3}$$

For the discrete form of the master equation, with Turnbull-Fisher selection of the coefficients, the growth rate was given by Kelton and Greer.[19] In the present notations,

$$u(R) = \frac{2R_*}{a\tau} \sinh\left\{ \frac{a}{2}\left(1 - \frac{1}{r}\right) \right\}, \tag{4}$$

where $a = 2W_*/(Tn_*)$ is the "discreteness parameter"[20] (the ZF limit is recovered for $a \to 0$) and n_* is the number of monomers in the critical nucleus. When substituted into the general equation (2) this growth rate leads to integrals which cannot be simplified unless some assumptions are made about the values of R and a.[21]

Nevertheless, in order to provide a compact and accurate expression, which can be used later both for comparison with exact numerics and, potentially, with experiment, one notes that in two-step annealing, typical R only slightly exceeds R_*. For such R the growth rates $u(R)$ and $u^{ZF}(R)$ are close and the major difference in incubation times comes from the decay region $R < R_*$,

$$t_i(R) \approx t_i^{ZF}(R) - \tau[C(a) - C(0)], \tag{5}$$

with $C(0) = 1$. In the present study only a single nucleation temperature will be used, with $a \simeq 4.06$ and $C(a) - C(0) \simeq 0.25$. The neglected first size-dependent correction is given by $\tau(a^2/24)(\ln r - r + 1)$.

The remaining question, which is central in the study, is to establish the meaning of size R in the above expression. This requires consideration of growth/decay of nuclei during heating; the growth rate $u(R, T)$ will also be a function of temperature, which will be further indicated explicitly.

Consider a nucleus with size $R > R_*(T_N)$ at the end of the nucleation part of experiment. If, by the end of the heating stage (when temperature reaches T_D), the nucleus is still larger than $R_*(T_D)$, it will further increase its size during the development stage and will be counted as "nucleated." Otherwise, the nucleus will decay. For a constant heating rate H between the nucleation and the development stages the limiting "survival size" R_s follows from the equation

$$\frac{dR_s}{dT} = \frac{1}{H} u(R_s, T). \tag{6}$$

This equation should be solved backward in time (temperature) with the initial condition $R_s(T_D) = R_*(T_D)$. Once the solution is obtained, the value $R_s(T_N)$ will determine the size R in the transient solution discussed above. For simplicity, H will be treated as constant, although at this stage of the treatment that assumption is not crucial and qualitative conclusions will remain valid as long as H changes little compared to $\ln \tau$.

Numerical values of R_s for different heating rates are given in Table I; dimensional growth rates were selected as approximately corresponding to lithium disilicate, a prototype nucleating system studied in great detail (parameters will be given below). However, before comparing the full transient solution with numerics it could be instructive to gain some additional insight into the structure of R_s.

Equation (6) with $u(R, t)$ from Eq. (4) is equivalent to a nonlinear Riccati equation, which is known to possess no analytical solution.[22] However, during most of the growth process the size R_s remains close to the current value of $R_*(T)$ [and during the initial low-temperature stage, when that condition is not satisfied too well, nuclei practically do not grow anyway]. This allows one to use a linearization,

$$u(R_s, T) \simeq [R_s - R_*(T)]/\tau(T), \tag{7}$$

and Eq. (6) can be solved.

Introducing a dimensionless "time,"

$$\tilde{t} = \frac{1}{H} \int_{T_N}^T \frac{dT}{\tau}, \tag{8}$$

one obtains after some transformations

$$R_s(T_N) = R_*(T_N) + \int_{T_N}^{T_D} \frac{dR_*}{dT} dT \exp(-\tilde{t}). \tag{9}$$

Consider the limits. For $H \to \infty$ the value of $\tilde{t}$ approaches zero, and one recovers the standard result $R_s = R_*(T_D)$. In the more formal limit $H \to 0$ one has $\tilde{t} \to \infty$ with $R_s \to R_*(T_N)$.

For further simplifications note that τ rapidly decays with temperature, in an exponential approximation,

$$\tilde{t} \simeq (-H d\tau/dT)^{-1}. \tag{10}$$

For each temperature one can define a critical heating rate $H_c(T) = (-d\tau/dT)^{-1}$ with $\tilde{t} \simeq 1$, and the inversion of that definition gives a crossover temperature T_c for a given heating rate H,

$$H_c(T_c) = H. \tag{11}$$

The value of the integral in Eq. (9) depends mainly on the relation between T_c and T_D. For fast heating, with $T_c > T_D$, the value of $\tilde{t}$ remains small. The exponential in Eq. (9) can be expanded, while the remaining integral is mainly determined by the upper limit and can be calculated in exponential approximation,

$$R_s \simeq R_*(T_D) - \frac{1}{H\tau} \left(\frac{d \ln \tau}{dT} \right)^{-2} \left. \frac{dR_*}{dT} \right|_{T=T_D}. \tag{12}$$

This provides a small negative correction to the conventional expression.

To get an explicit dependence on the heating rate in the intermediate region $T_N < T_c \lesssim T_D$ the integral in Eq. (9) can be evaluated by parts,

$$R_s(T_N) = R_*(T_D) e^{-\tilde{t}_d} + \int_{T_N}^{T_D} R_*(T) \frac{d\tilde{t}}{dT} e^{-\tilde{t}} dT,$$

with $\tilde{t}_d \equiv \tilde{t}(T_D)$. The integrand will have a broad maximum near $T = T_c$. Switching to a new integration variable $\tilde{t}$ and using the fact that in a narrow region its temperature dependence is approximately exponential, one can write $T \simeq T_c + \ln t/b$ with $b = -d \ln \tau/dT$ at $T = T_c$. After linearizing $R_*(T)$ near T_c and performing the integration, one obtains

$$R_s = R_*(T_c)(1 - e^{-\tilde{t}_d}) + R_*(T_D) e^{-\tilde{t}_d}$$
$$- \left. \frac{dR_*}{d \ln \tau} \right|_{T=T_c} [Ei(-\tilde{t}_d) - e^{-\tilde{t}_d} \ln \tilde{t}_d - \gamma]. \tag{13}$$

Here, Ei is the exponential integral[23] and γ is Euler constant. Since $\ln R_*$ typically changes with temperature much slower than $\ln \tau$, corrections due to the last term in the above equations are small, with R_s being close to either $R_*(T_c)$ or to $R_*(T_D)$ depending on the value of $\tilde{t}_d$.

Accuracy of this additional approximation is illustrated in Table I, which also lists the values of crossover temperature T_c for selected parameters. The condition of "fast" heating, traditionally expected when analyzing annealing experiments, corresponds to $T_c > T_D$, which is realized only for unrealistically high H.

In order to verify the accuracy of the obtained transient flux, the nucleation master equation was solved numerically.
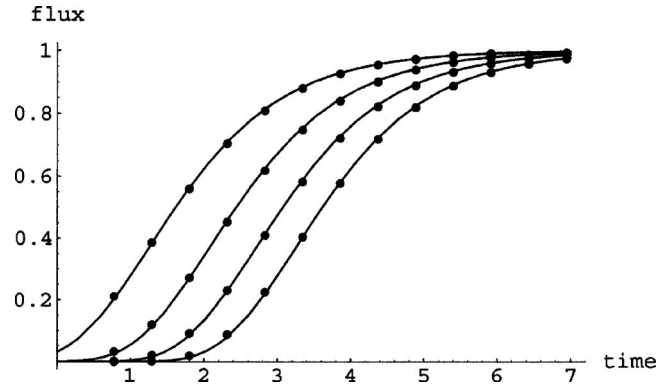

FIG. 1. Reduced transient flux $j/j_{st}(T_N)$ as a function of reduced annealing time $t/\tau(T_N)$ for various values of the subsequent heating rate H. From left to right (in K/s): $H = 0.1$, 1, 10, and ∞. Solid lines, analytical results; and symbols, numerical solutions of the Becker-Döring equations. Parameters of lithium disilicate with $\tau(T_N) \sim 20$ min were used.

The effect of lower boundary, which is not included in Eqs. (2) and (3) (see, however, Ref. 21) was minimized by placing that boundary at the smallest $n = 1$, n is the number of monomers in a cluster. During isothermal nucleation stage the solution followed the general outline by Kelton et al.[13] In *Mathematica* realization of the approach a matrix form of the equations was used, similar to Ref. 9. After time t, the "nucleation annealing time," the isothermal part of the run was terminated and the distribution of clusters served as initial conditions for subsequent heating. The nonisothermal stage was described as a sequence of small isothermal steps with temperature instantaneously increased at the end of each step.[19,24] More detail will be provided elsewhere.[25]

The nucleation flux was evaluated at $n = n_*(T_D)$. The integral of the flux gave the number of particles ρ by the end of the heating stage. For a given heating rate the numbers $\rho_1, \rho_2, \ldots$, were obtained for a collection of nucleation annealing times $t_1, t_2, \ldots$, and the resulting "experimental" flux was defined as $(\rho_k - \rho_{k-1})/(t_k - t_{k-1})$ with corresponding annealing time $t = (t_{k-1} + t_k)/2$. (This is not the most efficient approach from a computational point but it mimics the real experiment.[4]) Note that for a sufficiently slow heating ρ includes secondary nuclei formed during the heating stage.[25] However, the number of such nuclei turns out to be independent of the nucleation annealing time and will not affect the derivative of ρ with respect to this time when evaluating the flux.

Parameters which specify the Turnbull-Fisher nucleation model, and which are close to those conventionally used in describing lithium disilicate,[26] were selected the same as in Ref. 27 with T_0 in the approximation for growth rate replaced by a correct value of 460.15 K.

Numerical results are shown by symbols in Fig. 1. Solid lines represent Eqs. (1), (3), and (5), with the size R given by the Turnbull-Fisher survival size R_s (Table I). A small nonzero value of the analytical expression at $t = 0$ for the slowest heating serves as a reminder that this is an asymptotic rather than an exact result, but otherwise the agreement is good, and the account for the difference between the discrete (TF) and the continuous (ZF) forms of the nucleation master equation is important. Neglect of the constant in Eq. (5) would

lead to a noticeable shift of the curves in Fig. 1.

In summary, the first analytical expression for the transient nucleation flux as a function of postnucleation heating rate (as in two-step annealing) has been obtained. Despite the complicated mathematical structure of the underlying discrete master equation, the solution is accurate, testifying to the power of asymptotic approaches in the nucleation problem.

The heating rate dependence enters the solution through a survival size R_s, which may or may not be close to critical size at the development temperature. Generally speaking, in order to achieve the level of accuracy shown in Fig. 1, R_s should be evaluated numerically from the growth equation. For practical applications linearization of the growth rate (which allows one to integrate the growth equation in quadratures) and subsequent evaluation of the integrals in exponential approximation could be sufficient, giving an expression that is explicitly independent of the nucleation temperature and of the development temperature if it exceeds a certain crossover temperature $T_c(H)$.

With respect to interpretations of the classical, as well as of more recent experimental data (which conventionally assumed an infinite H), the obtained results can significantly alter the deduced temperature dependences of the critical size and of the interfacial tension. Future progress here mainly depends on one's ability to control the magnitude of the heating rate.

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