The Journal of Chemical Physics

RESEARCH ARTICLE | JULY 15 1994

Initiation of a phase transition by preexisting nuclei

Vitaly A. Shneidman; Peter Hänggi

Check for updates

J. Chem. Phys. 101, 1503–1512 (1994)
https://doi.org/10.1063/1.467773

View Online
Export Citation

25 September 2024 13:41:25

Nanotechnology & Materials Science
Optics & Photonics
Impedance Analysis
Scanning Probe Microscopy
Sensors
Failure Analysis & Semiconductors

Unlock the Full Spectrum.
From DC to 8.5 GHz.
Your Application. Measured.
Find out more
Zurich Instruments

AIP Publishing

Initiation of a phase transition by preexisting nuclei

Vitaly A. Shneidman[a] and Peter Hänggi
Institute of Physics, University of Augsburg, Memminger Str. 6, D-86135 Augsburg, Germany

(Received 17 March 1994; accepted 7 April 1994)

Preexisting nuclei are often invoked in situations where the observed kinetics of a phase transition is much faster than one would expect from the classical theory of homogeneous nucleation. We examine analytically the time-dependent effects produced by such nuclei. Corrections to the number of nucleated particles, the time lag, and the transient rate of homogeneous nucleation are derived. For a high nucleation barrier the results are expected to be asymptotically accurate, both for the continuous ("Zeldovich–Frenkel") and the discrete ("Becker–Döring") nucleation models. This is confirmed by comparison with exact expressions available for a parabolic barrier in the continuous case, and with numerical solutions of the discrete Master equation. The probability formulation of the nucleation problem is also considered and the distribution of waiting times to detect the first "successful" nucleus is obtained.

I. INTRODUCTION

The classical nucleation theory (CNT)[1–5] has been remarkably successful in explaining various experimental data. Nevertheless, in certain cases the CNT seems to overestimate dramatically the limits of stability of a metastable phase. One could mention the metastable classical liquid,[6] or the undercooled helium-III[7] where the CNT predicts an unrealistically small rate of the phase transition. Another example is nucleation in glasses.[8] Here the discrepancy between the CNT and experiment may look not so striking—particularly because there are no independent data for the interfacial tension.[9] Nevertheless, there seems to exist a systematic overestimation of the time lag as predicted by the CNT.[10]

To go beyond the CNT one requires a more detailed understanding of the thermodynamic properties of small clusters—see, e.g., Ref. 11 and references therein. On the other hand, in many of the above-mentioned situations the CNT can be "saved" if one assumes the presence of some preexisting nuclei which reduce the stability of the metastable phase. Such nuclei can be either "quenched in" during preparation of the metastable phase,[12] or can be produced by a permanently acting source, such as cosmic radiation.[7] In some experimental studies[13,14] preexisting nuclei are deliberately produced. In such cases one can examine the sensitivity of nucleation to variation of initial conditions.[14]

In the present study we are not going to discuss various mechanisms to produce the preexisting nuclei. Such mechanisms can be rather intricate—consider, e.g., the "baked alaska" model put forward in Ref. 7(a)—and they are very specific in each particular experimental situation. Rather, we assume instead that such nuclei have already entered the system, and we examine the resulting corrections to homogeneous nucleation. We will mainly consider *subcritical* nuclei which still have to cross the barrier in order to grow into the stable phase, and for this situation a detailed analytical treatment is presented. On the other hand, in the context of the present study the effects induced by *overcritical* nuclei are simpler, and they are only briefly discussed in the Appendix. We organize our work into six sections:

In Sec. II we consider the correction to the time lag of homogeneous nucleation—its precise definition is given below. This quantity is of special importance for the nucleation problem, being often the *only* experimentally accessible indicator of transient effects.[8,13] Moreover, it is the only physically meaningful quantity related to transient nucleation which can be directly derived from the Master equation, *both* exactly and asymptotically.[15] We show that preexisting nuclei add new unexpected aspects to the time lag problem. First, the correction due to such nuclei can be derived from elementary considerations, which is by itself surprising taking into account the general complexity of the problem. Second, even minor concentrations of preexisting nuclei can cause the time lag to assume *negative* values. In such cases a reconsideration of the conventional definition of this quantity is required.

In Sec. III we derive the correction to the transient nucleation rate, and discuss the "scaling" form of the result for a monodisperse distribution of preexisting nuclei. Actually, the low-noise asymptote of the Green's function describing barrier crossing is derived in this section. This quantity is useful for other (nonnucleation) problems which include noise-assisted barrier crossing.[16]

In Sec. IV the results are used to evaluate the total number of the nucleated particles. Also, for a specific example of the Zeldovich–Frenkel nucleation equation, we explicitly obtain the correction to the distribution of particles over their sizes. This section is more oriented towards potential applications. Particularly, in view of experimental data,[8] we evaluate the reliability of estimations which to a first approximation treat the nucleation process as being homogeneous.

In Sec. V we demonstrate the high accuracy of the obtained results by comparing them with numerical solutions of the Master equation of the CNT. Actually, we expect that the significance of a highly accurate approximation to the solution of a Master equation extends beyond the nucleation problem. We do not discuss here the mathematical aspects of this fact, as it deserves a separate study.[17] Nevertheless, the

[a]Present address: Department of Materials Science and Engineering, The University of Arizona, Tucson, AZ 85721.

25 September 2024 13:41:25

 0021-9606/94/101(2)/1503/10/$6.00 © 1994 American Institute of Physics

numerical comparisons in this section provide an important complement for the more formal proofs given in the aforementioned reference.

Section VI is devoted to the probabilistic formulation of the nucleation problem. Such a consideration stands somewhat apart from the other sections of our paper. It becomes important, however, if one is able to detect a *single* nucleus when nucleation should be described as a random process. We show that the results which were obtained from the conventional nucleation picture can be directly incorporated into the probability problem. We obtain the distribution of random waiting times to detect the first overcritical nucleus, and separate the effects produced by preexisting nuclei from those due to homogeneous nucleation.

Note that in the course of the treatment we shall encounter *three* different types of the nucleation flux. To avoid confusion with notations, we note from the start that $j^{(0)}$ will denote the flux of homogeneous nucleation and δj—the flux due to preexisting nuclei originally present in the system. The total flux, i.e., the sum of the two aforementioned fluxes, will be denoted as j. Similar notations will be used for the number of nucleated particles, n and for the time lag, t_L. The flux due to a *permanent* source of nuclei of unit intensity will be denoted as J, although it will be considered solely for auxiliary purposes. The stationary values of corresponding fluxes are indicated by a subscript "st."

II. THE TIME LAG

A. The probability for a nucleus to cross the barrier

Consider a nucleus of a subcritical size $g_1<g_*$ (the asterisk indicates the critical value). This nucleus tends to decay with a deterministic (macroscopic) rate $\dot{g}_1<0$, but there is also a small probability that, via activation, it will cross the barrier, and grow to large sizes. To assess this probability we shall consider the following auxiliary problem (cf. also Ref. 18).

Let us insert one nucleus per second at size g_1. After some transition period a steady-state regime will be established: The majority of inserted particles will go to small sizes, while an exponentially small fraction, $J_{\rm st}$, will go into the growth region. The numerical value of $J_{\rm st}$ will just coincide with a probability for a single nucleus to cross the barrier. To estimate this value recall that in the region of deterministic decay, $g\leqslant g_1$ a distribution $f(g)\cong -1/\dot{g}$ is established. On the other hand, the Zeldovich expression for the steady-state homogeneous flux $j_{\rm st}^{(0)}$ can be represented in the form

$$j_{\rm st}^{(0)}=\frac{\Delta}{2\tau\sqrt{\pi}}N(g_*), \tag{2.1}$$

where, with kT denoting the thermal energy,

$$\Delta=\left\{-\frac{1}{2kT}\frac{\partial^2\phi}{\partial g^2}\bigg|_*\right\}^{-1/2},\quad \tau=\left\{-\frac{d\dot{g}}{dg}\bigg|_*\right\}^{-1}, \tag{2.2}$$

and $N(g_*)$ is the equilibrium distribution at the critical size. In the CNT the latter is estimated as $N(g_*)\approx N_1\exp\{-\phi(g_*)/kT\}$, with N_1 being the number of monomers and $\phi(g)$ the minimal work required to form a nucleus of size g. The only difference between homogeneous nucleation and the present problem is that instead of the distribution $f(g=1)\cong N_1$ of the CNT one now has $f(g_1)\cong -1/\dot{g}_1$ and the barrier to cross is reduced by $\phi(g_1)$. Thus one obtains

$$J_{\rm st}=\frac{\Delta}{2\tau\sqrt{\pi}}\frac{1}{-\dot{g}_1}\exp\left\{\frac{\phi(g_1)-\phi_*}{kT}\right\}, \tag{2.3}$$

which is the correction to homogeneous nucleation rate due to a permanent source of unit intensity placed at $g_1<g_*$. Moreover, it is also the probability for a single nucleus to cross the barrier. Obviously, upon approaching the barrier this probability increases. This is due to the effective reduction of the barrier height as well as to the smaller values of the decay rate $\dot{g}_1$. The latter implies that the nucleus spends more time at large sizes with better chances to overcome the barrier. The region of validity of Eq. (2.3) is restricted to $J_{\rm st}\ll 1$. Equivalently, this means that initially the nucleus is placed not too close to the top of the barrier, i.e., $g_*-g_1\gg\Delta$, implying that the fluctuational corrections to the deterministic decay rate are negligible. The alternative situation which can arise for g_1 within the immediate neighborhood of g_* is considered in Appendix A.

B. Correction to the time lag

The time lag (also, "induction time") of transient nucleation is defined as

$$t_L(g)=\lim_{t\to\infty}[t-n_g(t)/j_{\rm st}^{(0)}]. \tag{2.4}$$

This is equivalent to the operational definition used in experimental studies.[8(a)–8(c),13] In the above expression $n_g(t)$ is the total number of nucleated particles with size exceeding the observation size $g>g_*$. At large times the input to $n_g(t)$ due to a single preexisting nucleus approaches a constant (2.3), and the correction to the time lag is given by

$$\delta t_L=-J_{\rm st}/j_{\rm st}^{(0)}\leqslant 0. \tag{2.5}$$

For an arbitrary initial subcritical distribution $f_0(g_1)$, one thus has

$$\delta t_L=-\int_0^{g_1^{\max}}\frac{f_0(g_1)}{N_1|\dot{g}_1|}\exp\left[\frac{\phi(g_1)}{kT}\right]dg_1. \tag{2.6}$$

Here $g_1^{\max}<g_*$ is the size of the largest nucleus initially present in the system. Despite its elementary derivation this result is expected to be asymptotically accurate for $\phi(g_*)-\phi(g_1^{\max})\gg kT$ (or equivalently, for $g_*-g_1^{\max}\gg\Delta$). The exponential factor in Eq. (2.6) means that the effect of preexisting nuclei on the time lag may be dramatic even for extremely small concentrations. In particular, the absolute values of the correction in Eq. (2.6) may easily exceed the time lag of homogeneous nucleation, making the total time lag *negative*. This is discussed more explicitly in Sec. V below. Negative values of the total time lag, though, do not have any essential physical consequences. This simply means that in this case the time lag, as defined by Eq. (2.4), is not an adequate physical characteristic, and alternative

25 September 2024 13:41:25

quantities (e.g., the mean waiting time to detect the first nucleus—see Sec. VI) should be considered. However, here one needs the full time dependence of the flux of nuclei. This is the topic of Sec. III.

III. TRANSIENT NUCLEATION RATE WITH PREEXISTING NUCLEI

A. Correction to the nucleation flux

We again start with the auxiliary problem discussed in Sec. II A: A nucleus with size $g_1<g_*$ is inserted each second at $g=g_1$ but now we do not wait until the steady-state flux J_{st} over the barrier is established, but consider the time dependence $J(g,t)$ at an arbitrary observation size $g>g_*$. This flux is composed by superposition of effects of each inserted nucleus. Thus, the effect of a *single* nucleus can be derived as

$$\delta j(g,t)=\frac{\partial}{\partial t}J(g,t). \tag{3.1}$$

Now compare the transient flux $J(g,t)$, which is due to inserted particles, with the transient flux of homogeneous nucleation, $j^{(0)}(g,t)$. Upon an abrupt "switch-on" of the homogeneous nucleation at $t=0$ the equilibrium distribution $N(g)$ will gradually build up at subcritical sizes. According to the microscopic reversibility principle, this equilibrium distribution will be established at the size g_1 precisely after the same time t_1 which is required for a nucleus of size g_1 to decay. Later, the system will not "know" the origin of the distribution at $g\leqslant g_1$, and it will evolve in time in the same manner as it would evolve in case of a distribution created artificially. This immediately implies

$$J(g,t-t_1)=[f(g_1)/N(g_1)]j^{(0)}(g,t). \tag{3.2}$$

Here, $f(g_1)$ is the distribution caused by preexisting nuclei which was estimated in Sec. II A as $-1/\dot{g}_1$. As mentioned, the time t_1 can be evaluated as the decay time

$$t_1=t_{dec}(g_1)\equiv-\int_0^{g_1}dg/\dot{g}. \tag{3.3}$$

Substituting this value into Eq. (3.2) and using the explicit expression for $f(g_1)$ and $N(g_1)$ of Sec. II, one obtains

$$\delta j(g,t)=\int_0^{g_1^{max}}\frac{dg_1}{-\dot{g}_1}\frac{f_0(g_1)}{N_1}\exp[\phi(g_1)/kT]$$

$$\times\frac{\partial}{\partial t}j^{(0)}[g,t+t_{dec}(g_1)], \tag{3.4}$$

where g_1^{max} is the maximal (subcritical) size present in the system. One can show that in case g_1^{max} is well separated from g_*, i.e., $g_*-g_1^{max}\gg\Delta$, which is actually the region of validity of the above equation, integration over time leads to Eq. (2.6) for the time lag.

For a single inserted nucleus $f(g_1)=\delta(g-g_1)$ Eq. (3.4) multiplied by $\dot{g}^{-1}$ determines the transbarrier asymptote of the Green's function—an explicit expression will be discussed in Sec. IV below. Recall that in the derivation of Eq. (3.4) we did not assume specific forms of the barrier, the growth rate, or even the nucleation equation. Particularly, this expression is expected to be valid for the discrete form of the nucleation equation as we shall demonstrate numerically in Sec. V, and as was discussed analytically in Ref. 17. We also verified that in the corresponding limit [Eq. (3.4)] coincides with the exact expression available for a parabolic barrier (cf. Appendix B), and that in case $f_0(g_1)$ corresponds to the steady-state distribution of homogeneous nucleation it will not evolve in time (cf. Appendix C).

From a mathematical point of view, the possibility of relating δj and $j^{(0)}$ is by no means trivial as we have a superposition of two problems with different boundary conditions. Recall that in CNT one assumes $f(g=1)=N_1$ and adding preexisting nuclei *must not* change this condition. On a formal level this means that when discussed separately, preexisting nuclei assume an absorbing boundary at $g=1$, in contrast to the "nonuniform" boundary condition characteristic for homogeneous nucleation. Generally speaking, this leads to a qualitatively different solution. What helps is that in the asymptotic limit considered an influence of a different boundary extends only on a very short distance ("boundary layer"), but otherwise the solution remains unchanged.

The expression for the homogeneous transient flux $j^{(0)}(g,t)$ was previously obtained in Ref. 19 using singular perturbation technique. The result reads

$$j^{(0)}(g,t)=j_{st}^{(0)}\exp[-\exp(-x)],\quad x=[t-t_i(g)]/\tau. \tag{3.5}$$

Here the "relaxation time" τ is the same as defined in Eq. (2.2), while $t_i(g)$ is the "incubation time" (i.e., the time for the homogeneous flux to achieve the value of $j_{st}^{(0)}/e$). This latter time is smaller than the homogeneous time lag by a value $\gamma\tau$, with $\gamma=0.5772...$ being the Euler's constant. In general form, i.e., for arbitrary growth rate $\dot{g}(g)$, the incubation time is given by

$$t_i(g)=2\tau\ln\frac{\sqrt{2}g_*}{\Delta}-2\tau\int_0^{g_*}dg\left(\frac{1}{\tau\dot{g}}-\frac{1}{g-g_*}\right)+\int_0^{g}\frac{dg}{\dot{g}}. \tag{3.6}$$

The principal value of the last integral which accounts for the growth of nucleated particles is indicated. In many specific cases the integrals in Eq. (3.6) can be evaluated in terms of elementary functions.[19(b)] We, however, postpone the discussion of an "elementary" example until Sec. IV, and focus on the general properties of the solution which are independent of the specific form of the growth rate $\dot{g}(g)$.

B. Scaling form of the result

Consider a monodisperse distribution of subcritical nuclei:

$$f_0(g)=N(g)V\delta(g-g_1) \tag{3.7}$$

with V denoting the ratio between the number of inserted particles and the equilibrium number of particles with the same size. Let us introduce a scaling variable

$$\hat{x}=[t-t_i(g)+t_{dec}(g_1)]/\tau\equiv x+t_{dec}(g_1)/\tau \tag{3.8}$$

with x defined in Eq. (3.5). In this case the solution of Sec. III A for the correction $\delta j(g,t)$ can be represented in the form

25 September 2024 13:41:25

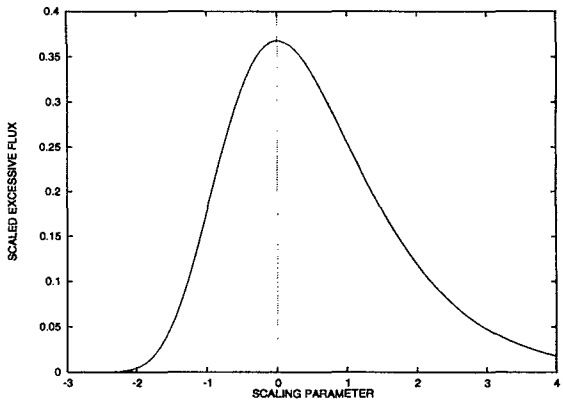

FIG. 1. The scaled excessive flux [the left-hand side of Eq. (3.9)] as a universal function of the scaling parameter $\hat{x}$.

$$\delta j(g,t)\,\frac{\tau|\dot{g}_1|}{V j_{\rm st}^{(0)}}=\exp[-\hat{x}-\exp(-\hat{x})]. \tag{3.9}$$

It is remarkable that three (!) independent variables, namely the time t, the observation size g, and the size of the inserted nuclei g_1 collapse to form a *single* scaling variable $\hat{x}$. The universal function on the right-hand side of Eq. (3.9), which contains no parameters, is plotted in Fig. 1. Note the asymmetry of the function with respect to $\hat{x}$ and, hence, with respect to time. The transbarrier asymptote of the Green's function $G(g_1,g;t)$ coincides with $\delta j(g,t)/\dot{g}$ for $V=1/N(g_1)$, i.e., when a single nucleus is inserted. The scaling variable $\hat{x}$ remains constant on the growth trajectory, i.e., the solution is carried in a drift-like manner to large sizes.

IV. THE NUMBER OF NUCLEATED PARTICLES AND THEIR DISTRIBUTION OVER SIZES

Formally, the flux of nucleated particles $j(g,t)$ which was described above provides the complete solution of the nucleation problem. We wish, however, to discuss certain consequences which bring the results somewhat closer to realistic experimental situations[8(a),8(b)] in which one measures not the nucleation rate but rather the number of nucleated particles with size exceeding some well-defined size g. We shall also consider the time-dependent distribution of particles over their sizes for the specific example of the Zeldovich–Frenkel nucleation equation where this distribution is given by an *elementary function*.

A. Number of nucleated particles

The total number of particles $n_g(t)$ with a size exceeding a given overcritical value g is given by $\int_0^t dt'\, j(g,t')$. Again we split $n_g(t)$ into a homogenous part, $n_g^{(0)}(t)$ and the correction $\delta n_g(t)$. For simplicity we consider a monodisperse initial distribution (3.7). Integrating the corresponding expressions for the nucleation rate one obtains:

For the homogeneous nucleation [cf. Ref. 19(b)],

$$n_g^{(0)}(t)=j_{\rm st}^{(0)}\tau E_1(e^{-x}), \tag{4.1}$$

where $x=x(g,t)$ is defined in Eq. (3.5), and τ in Eq. (2.2); E_1 is the first exponential integral.[20] The correction due to preexisting nuclei is given by

$$\delta n_g(t)=Q\,\exp[-\exp(-\hat{x})],\quad Q\equiv-\delta t_L\cdot j_{\rm st}^{(0)}, \tag{4.2}$$

where $\hat{x}$ is given in Eq. (3.8), and $Q=N_1V/(-\dot{g}_1)$ is the total number of preexisting nuclei that cross the barrier. One can introduce a reduced value $q=Q/\tau j_{\rm st}$—the reduced correction to the time lag, $-\delta t_L/\tau$. In this case, in the "scaling form," one has

$$n_g(t)/\tau j_{\rm st}^{(0)}=E_1(e^{-x})+q\,\exp[-\exp(-\hat{x})]. \tag{4.3a}$$

Note the following. The difference of the "scaling parameters" x and $\hat{x}$ is given by $t_{\rm dec}(g_1)/\tau$, being small if g_1 is noticeably smaller than g_*. Within a crude approximation this difference can be neglected. If, in addition, one considers *small* $q\ll 1$, and recalls that the double exponenta in Eq. (4.3a) is the derivative of the first exponential integral, one obtains

$$n_g(t)/\tau j_{\rm st}^{(0)}\approx E_1(e^{-x-q})+O(q^2)+O(q\cdot t_{\rm dec}/\tau). \tag{4.3b}$$

Thus, the *small* correction due to preexisting nuclei results simply in the time shift of the number of nucleated particles. This shift is, of course, the same as the shift of the time lag δt_L. For $n_g(t)$ evaluated at the time corresponding to the *total* time lag t_L, one thus finds

$$n_g(t_L)/\tau j_{\rm st}^{(0)}=E_1(e^{-\gamma})+O(q^2)+O(q\cdot t_{\rm dec}/\tau)\cong 0.49, \tag{4.4}$$

where, we remind the reader, $\gamma\approx 0.5772$ is the Euler's constant. In the leading approximation this reduces to the same result as in case of homogeneous nucleation.[19(b)] The importance of the above relation is that it allows one to extract the values of τ from the measured values of $n_g(t)$ and $j_{\rm st}^{(0)}$ without *any* assumptions concerning the nucleation mechanism.[10,19(b)] One can see that with reasonable accuracy this relation can also be applied in the presence of preexisting nuclei—there is no first-order corrections in Eq. (4.4). Moreover, one can show that the higher corrections are of opposite sign, so that Eq. (4.4) may be valid even for $q\sim 1$, i.e., in situations where the effects of preexisting nuclei are otherwise already strong. This is illustrated in Fig. 2 where we plot Eq. (4.3) for different values of q and for $t_{\rm dec}(g_1)/\tau=0.785$. (The latter corresponds to $g_1=g_*/2$ for the model that will be discussed below in Sec. IV B.) One can deduce from this plot that even for $q\sim 1$ the main effect of preexisting nuclei is a shift in time for the values of $n_g(t)$ compared to $n_g^{(0)}(t)$. Thus, at $t=t_L$ the value $n_g(t)$ is indeed very weakly sensitive to preexisting nuclei, and is close to its "homogeneous value," approximately giving $0.5\,\tau j_{\rm st}^{(0)}$. Only for larger values of q ($q=3$ in Fig. 2) does the quantity $n(t=t_L)$ acquire much smaller values, but in this case the qualitative difference from the typical "homogenous" behavior is evident: For large q the transient curve approaches its large-time asymptote from a different side. Thus, one concludes that an application of the homogeneous relation [Eq. (4.4)] to deduce τ from experimental data[8] may be quite

25 September 2024 13:41:25

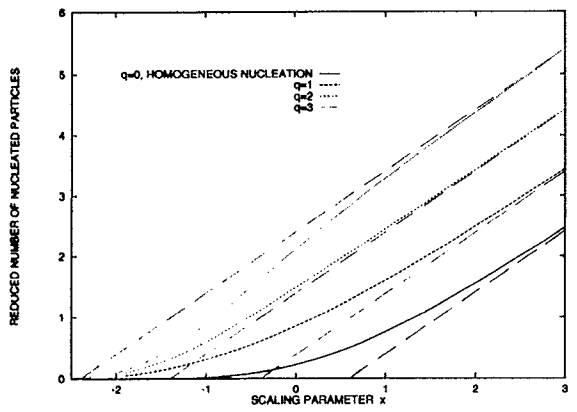

FIG. 2. Time dependence of the reduced total number of nucleated particles $n_g(t)/\tau j_{st}^{(0)}$ for different concentrations of preexisting nuclei—Eq. (4.3a). The scaling parameter x is related to time in Eq. (3.5). The numerical values of q define the reduction of the time lag, i.e., $q=-\delta t_L/\tau$. Straight (long-dashed) lines correspond to the large-time asymptotes of the corresponding curves $n_g(t)\sim j_{st}^{(0)}(t-t_L)$. Note the qualitatively different way of approaching the large-time asymptote for small and large q. For small q the curve $n_g(t)$ is simply shifted in time compared to its homogeneous values, being in accord with Eq. (4.3b).

reasonable as a first approximation, unless the effects of preexisting nuclei are so strong that they can be detected from "naked eye."

B. The distribution function. An example

In the growth region the distribution function $f(g,t)$ is given by $j(g,t)/\dot{g}$. The growth rate $\dot{g}$ and thus the distribution (even the steady-state one!), depends on the specific nucleation model considered. It is more convenient to discuss specific examples in terms of the radial distribution $f(R,t)=f(g,t)\cdot dg/dR$, as the growth law $\dot{R}(R)$ generally looks more compact than $\dot{g}(g)$. Using for the flux the results of Sec. III, one obtains the correction to the distribution function due to a *single* nucleus injected at $t=0$ at the size $R(g_1)\equiv R_1$:

$$\delta f(R,t)=\frac{j_{st}^{(0)}\nu}{4\pi R_1^2\tau N_1|\dot{R}(R_1)|\dot{R}(R)} \times\exp\left[\frac{\phi(R_1)}{kT}-\hat{x}-\exp(-\hat{x})\right]. \tag{4.5}$$

Here ν is the molecular volume of the new phase, N_1 is the number of monomers, and in accord with Eq. (2.2), τ^{-1} equals $d\dot{R}/dR$ at $R=R_*$. Equation (4.5) also explicitly gives the transbarrier asymptote of the Green's function. For further specification one needs to relate the scaling parameter $\hat{x}$ to the physical quantities t, τ, R, and R_1 which requires an *explicit* expression for $\dot{R}(R)$—see Eqs. (3.8) and (3.5). A frequently used expression for the growth rate is the one that follows from the Zeldovich–Frenkel nucleation equation,[5] i.e.,

$$\dot{R}(R)=(R_*/\tau)[1/R_*-1/R]. \tag{4.6}$$

This corresponds to the "continuous ballistic model" in classification of Ref. 15; on other occasions this growth rate emerges when the growth of nuclei is determined by reactions on their surfaces, or for a "nonconserved order parameter".[21] As shown in Refs. 15 and 22, this model is also very close to the Turnbull–Fisher model which is often discussed [see, e.g., Ref. 12(b), and references therein] in view of the mentioned experiments. For this growth rate the integrals in Eq. (3.6) can be elementary evaluated [see Eq. (12) in Ref. 19(b)], and the expression for the decay time can also be integrated explicitly.[15(a)] For the "scaling parameter" $\hat{x}$ in Eq. (4.5) one thus finds after some transformations:

$$\hat{x}=\frac{t}{\tau}-\ln\frac{6\phi_*}{kT}+2-\frac{R_1+R}{R_*}-\ln\frac{(R-R_*)(R_*-R_1)}{R_*^2}. \tag{4.7}$$

Note that despite the general complexity of the problem, the solution in Eq. (4.5) is now given by an *elementary* function. At large times this solution describes a hump with the shape shown in Fig. 1, which propagates towards large sizes with a constant rate R_*/τ.

V. COMPARISON WITH NUMERICAL SOLUTIONS OF THE MASTER EQUATION: RESULTS AND DISCUSSION

The Master equation of the CNT can be represented in the form

$$\frac{\partial f_g}{\partial t}=j_g-j_{g+1},\quad j_g=\beta_{g-1}N_{g-1}\left(\frac{f_{g-1}}{N_{g-1}}-\frac{f_g}{N_g}\right) \tag{5.1}$$

with $\beta_g\sim g^{2/3}$ being the gain coefficient and N_g the equilibrium distribution; i.e.,

$$N_g=N_1\exp\{-\phi(g)/kT\},\qquad \phi(g)=\phi_*\{3(g/g_*)^{2/3}-2g/g_*\}. \tag{5.1'}$$

At some small $g=g_<\ll g_*$ the kinetic distribution $f_g(t)$ coincides with the equilibrium distribution N_g, and this is used as the left-hand boundary condition. The second boundary condition is taken as $f_g(t)\equiv 0$ at some overcritical size $g_>$. In the steady-state version, Eq. (5.1) was introduced into the nucleation theory and solved by Farkas.[2] He, however, hesitated to extend the macroscopic expression (5.1′) into the region of the smallest clusters, considering quite reasonably that here a microscopic treatment is required. Nevertheless, not having at our disposal a better expression for N_g, we shall follow Becker and Döring[3] in extending Eq. (5.1′) to *all* sizes. This defines the problem completely, and allows a comparison with the analytical treatment given above.

The parameters $g_<$ and $g_>$ have no direct physical meaning and thus must not affect the results. Recall that $g_<$ and $g_>$ did not enter the asymptotic solutions of Secs. III and IV—and as shown below, upon reasonable choice they really do not influence the results numerically.

The numerical method to solve Eq. (5.1) is close to the one described by Kelton *et al.*,[23] although the Turnbull–Fisher Master equation considered in that paper had a different form for the gain coefficient, and we also added a monodisperse distribution of preexisting nuclei at $g_1<g_*$.

25 September 2024 13:41:25

To relate the numerical results to the asymptotic solution, one has to specify the deterministic growth rate $\dot{g}$. It was shown[15,19] that for the model considered the growth rate is given by

$$\dot{g}=\frac{3g_*}{a\tau}(g/g_*)^{2/3}(1-\exp\{a[1-(g_*/g)^{1/3}]\}) \qquad (5.2)$$

with $a = 2(\phi_*/kT)g_*^{-1}$ (in case of vapor condensation a is the logarithm of supersaturation). In the limit $a\to 0$ Eq. (5.2) is reduced to Eq. (4.6). We, however, considered large values of $a\cong 1.2$. The general expression (5.2) is substituted into Eqs. (3.6) and (3.3) to calculate $t_i(g)$ and $t_{\rm dec}(g_1)$, respectively. This in turn determines the scaling variables x and $\hat{x}$ in Eqs. (3.5) and (3.8). The total flux $j^{(0)}(g,t)+\delta j(g,t)$ is then obtained as a sum of Eqs. (3.5) and (3.8).

The following parameters are held constant. The critical size $g_*=50.1$, the nucleation barrier $\phi_*/kT=29.9$, and the size of inserted nuclei $g_1=20$.

In Fig. 3(a) we plot the transient flux for different concentrations of preexisting nuclei. In accord with the discussion of Sec. II A, even minor concentrations of such nuclei may be very important, leading to a substantial "overshot" of the nucleation rate. For example, the upper curve in Fig. 3(a) corresponds to $g_1 f(g_1)/N_1\approx 4\times 10^{-10}$. According to Ref. 24, such concentrations, which are smaller than 10^{-6}, are currently far beyond the limit of experimental resolution. On the other hand, the time lag is given by the area between the transient curve and the steady-state line $j/j_{\rm st}\equiv 1$—see Fig. 3(a). This geometric interpretation follows from the definition (2.4). For small values of the flux $j/j_{\rm st}<1$ the area is positive, while in case of an overshot $j/j_{\rm st}>1$ the corresponding area is negative—see the lower and upper shaded areas in Fig. 3(a), respectively. In case the overshot is sufficiently large—as in the depicted example—the total time lag becomes negative.

When solving the Master equation (5.1) for the largest concentration of preexisting nuclei [upper points in Fig. 3(a)] we verified the insensitivity of the results to the position of boundaries by shifting $g_<$ from 1 to 6 and $g_>$ from 102 to 402. All these results are shown using the same symbols (diamonds) and they practically overlap, so that the solution is really insensitive to "unphysical" parameters. As discussed in Ref. 15, to account in the homogeneous asymptotic solution for artificially large values of $g_<$, one simply has to reduce the time lag (and, equivalently, the incubation time) by $t_{\rm dec}(g_<)$. The shift of $g_<$, however, is not expected to affect the correction $\delta j(g,t)$, provided of course, $g_<$ remains smaller than g_1.

In Fig. 3(b) we plot the flux at different sizes with and without preexisting nuclei. The "hump" moves to the large sizes with the same rate, $\dot{g}(g)$, as the front in case of homogeneous nucleation. Compared to the homogeneous case, the impact of preexisting nuclei can be detected somewhat earlier, since homogeneous nucleation is retarded by the decay time $t_{\rm dec}(g_1)$. The slight lowering of the "hump" predicted by the Master equation is due to diffusional spreading, which in the leading approximation is not included in the asymptotic solution. In principle, it is not too difficult to include this effect in the asymptotic solution as a correction, but one

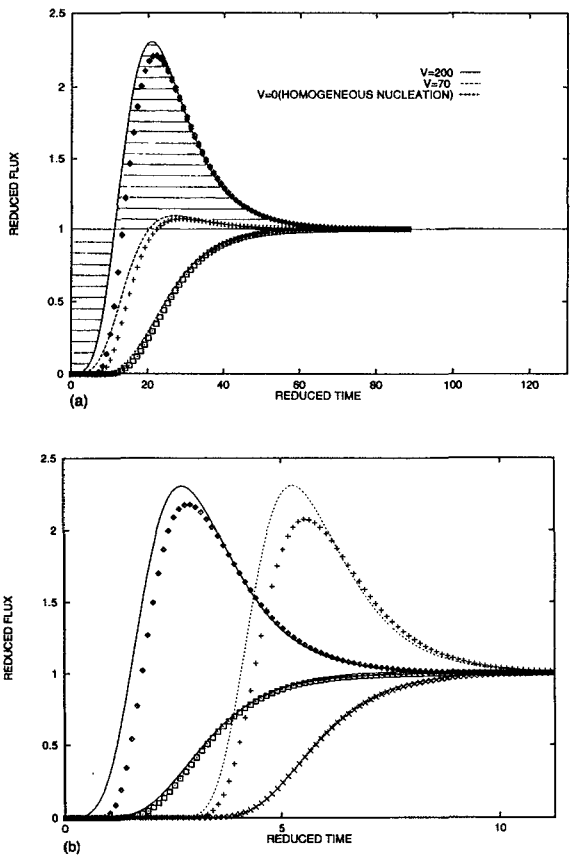

FIG. 3. (a) Reduced flux $j(g,t)/j_{\rm st}^{(0)}$ at the observation size $g=96$ for different concentrations of preexisting nuclei initially placed at $g_1=20$. Curves—asymptotic solution of Sec. III, symbols—numerical solutions of the Farkas–Becker–Doering Master equation for the same parameters (see the description in the text). The difference between the shaded areas below and above the steady-state line $j/j_{\rm st}^{(0)}\equiv 1$ determines the time lag (being negative for the example depicted). (b) Reduced flux at different observation sizes g with and without preexisting nuclei. Lines—asymptotic solution of Sec. III, symbols—numerical solutions of the Master equation (5.1). Lower (sigmoidal) curves—homogeneous flux ($V=0$). Upper (bell-shaped) curves—the flux with preexisting nuclei ($V=200$). From left to right (both upper and lower curves): $g=100$ (solid lines and diamonds) and $g=400$ (dashed lines and crosses). The critical size $g_*=50.1$, other parameters are given in the text.

can show that the diffusion lowering is small, up to arbitrary large sizes. Employing the aforementioned geometric interpretation of the time lag, one can see from Fig. 3(b) that for a sufficiently large size the time lag will become positive. Indeed, the time lag of homogeneous nucleation increases with size while the input of preexisting nuclei remains constant. Nevertheless, in practice the overshot shown in Fig. 3(b) can be exponentially large, which would mean a negative time lag for every physically reasonable size.

We also wish to note that the proposed asymptotic solution is not only qualitatively correct, but is also rather accurate numerically. Recall that Eq. (5.1) is a Master equation with essentially nonlinear coefficients and no matching parameters were used for comparison in Figs. 3(a) and 3(b). The accuracy of the homogeneous solution is slightly higher. This is due to a "better" (larger) asymptotic parameter g_*/Δ, compared to $(g_*-g_1)/\Delta$ in case of preexisting nuclei.

25 September 2024 13:41:25

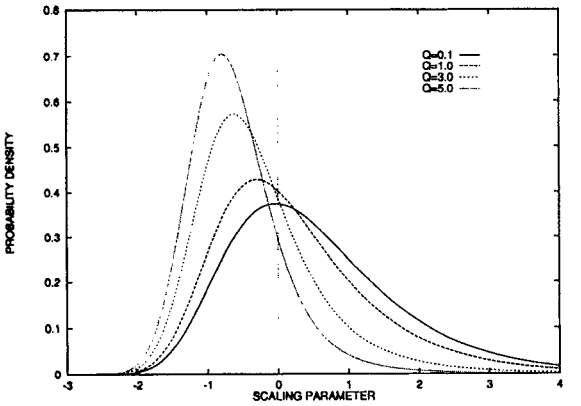

FIG. 4. The probability density $\partial\tilde{P}_g/\partial\hat{x}$, cf. Eq. (6.4). The parameter Q is the average number of preexisting nuclei which successfully cross the barrier. For small values of Q (solid line) this density coincides with the scaled correction to the nucleation flux of Fig. 1.

VI. PROBABILITY INTERPRETATION OF THE SOLUTION AND THE WAITING TIME TO DETECT THE FIRST NUCLEUS

In certain experiments such as the studies of bubble nucleation,[6] a detection of a *single* nucleus is claimed to be possible. In this case, nucleation should be considered as a stochastic process which may be characterized by a *random* time interval $t(g)$ required to observe the first nucleus with size g. Note that this time does not coincide with the standard "first-passage time" discussed in the theory of random processes:[25] In contrast to the first-passage time situation, in the nucleation problem one has *many* subcritical nuclei which are *not conserved* being able to dissolve into monomers.

The probability aspects of the nucleation problem were, probably, for the first time discussed by Kolmogorov.[26] He had shown that (a) nucleation flux can be understood as the probability flux in a corresponding reformulation of the problem, and that (b) an independent event is the one *not to detect* a nucleus during a small time interval dt. The probability of such an event is $(1-jdt)$, and these independent probabilities multiplied for events at different times lead to a well-known result:[26]

$$P_g(t)=1-\exp\left\{-\int_0^t j(g,t)dt\right\} \tag{6.1}$$

for the probability to detect at least one nucleus with size exceeding g at time t. Actually, a "detector" of particles at size g means an absorbing boundary, so that the flux $j(g,t)$ in Eq. (6.1) is not precisely the flux of the nucleation equation, where no such boundary is assumed. However, it is intuitively obvious (and it can be demonstrated explicitly[27(a)]), that in the growth region (away from g_*!) the boundary does *not* change the flux within asymptotic accuracy.

Thus, when evaluating the integral in the exponent of Eq. (6.1) one is able to employ Eqs. (4.1)–(4.3) for $n_g(t)$. This completely determines the probability density $\partial P_g(t)/\partial t$ for the distribution of the waiting times to detect the first nucleus. The *average* waiting time is thus given by

$$\bar{t}(g)=\int_0^\infty dt\; t\partial P_g/\partial t. \tag{6.2}$$

The homogenous nucleation rate $j_{\rm st}^{(0)}$ is proportional to the size of the system. The same is true for the average number Q of preexisting nuclei which cross the barrier if their concentration $f(g_1)/N_1$ is held fixed. If the system is not large, i.e., if both $j_{\rm st}\tau$, $Q\ll 1$, the average waiting time can be easily evaluated. In this case the maximum input in the integral in Eq. (6.2) is given by large $x\gg 1$ and $\hat{x}\gg 1$, so that $n_g^{(0)}(t)$ can be approximated as $j_{\rm st}[t-t_L^{(0)}(g)]$, while $\delta n_g(t)$ simply coincides with Q—the average number of particles which cross the barrier. From Eq. (6.2) on thus finds

$$\bar{t}(g)=1/j_{\rm st}^{(0)}+t_L^{(o)}(g)-Q/j_{\rm st}^{(0)}\equiv 1/j_{\rm st}^{(0)}+t_L^{(0)}(g)+\delta t_L, \tag{6.3}$$

where Eq. (4.2) relating Q to the correction for the time lag has been invoked. Negative values of the total time lag, $t_L\equiv t_L^{(0)}(g)+\delta t_L$, simply mean that the average waiting time is *smaller* than the one predicted by the steady-state nucleation theory, i.e., $\bar{t}(g)<1/j_{\rm st}^{(0)}$.

From Eq. (6.3) one can see that for vanishingly small probability of homogeneous nucleation (i.e., $j_{\rm st}^{(0)}\to 0$), one is hardly able to detect the time lag effects, and thus the effects of preexisting nuclei. This difficulty, however, is due to the definition of $\bar{t}(g)$ as the average time over *all* events. Indeed, on certain occasions all preexisting nuclei will decay without ever having crossed the barrier, and one will have to wait for the first homogeneous nucleus to emerge. This takes a very long time, $\sim 1/j_{\rm st}^{(0)}$. Thus, an "unsuccessful" event which has no physical meaning in view of preexisting nuclei gives a major input to the average waiting time. One can avoid these difficulties by registering only *successful* events. If the first nucleus emerges sufficiently fast, such a successful event is due to preexisting nuclei. If the nucleus does not emerge at all ($1/j_{\rm st}^{(0)}$ may well exceed the time of experimental observation), or emerges after a very long time, the event is disregarded. The above expressions can be easily adjusted to this situation by neglecting the homogeneous term in the expression for $n_g(t)$ and introducing the correct normalization. For the conventional probability, $\tilde{P}_g(t)$, to detect the *first successful preexisting nucleus*, one thus obtains

$$\tilde{P}_g(t)=\{1-e^{-Q}\}^{-1}(1-\exp\{-Q\,\exp[-\exp(-\hat{x})]\}). \tag{6.4}$$

Here we remind the reader that the scaling variable $\hat{x}$ is a function of time t, overcritical observation size g, and the size of the inserted subcritical nucleus, g_1—see Eq. (3.8). Equation (6.4) constitutes a single-parametric function of $\hat{x}$[28] and the corresponding probability density is plotted in Fig. 4. For small Q (solid-like in Fig. 4) the density corresponds to the "scaled flux" depicted in Fig. 1. This has a simple explanation. If in a single measurement the probability to detect a nucleus is small, i.e., $Q\ll 1$, one has to perform *many* measurements (of the order of $1/Q$) to obtain good statistics. Upon averaging over a large number of data, the probability aspect of the problem is lost, and it becomes equivalent to

25 September 2024 13:41:25

the conventional one. In the opposite limit of large Q, the maximum of the probability density shifts towards negative values of $\hat{x}$ (small times). This shift occurs very slowly, proportional to $\ln(\ln Q)$, so that the dependence on the number of preexisting nuclei $f_0(g_1)$ (or, on the size of the system) becomes extremely weak, although formally it never saturates. For moderate values of Q the maximum in the probability density approximately corresponds to $\hat{x}=0$, so that the average time is given by

$$\langle t(g)\rangle = t_i(g) - t_{\rm dec}(g_1) + \tau \int_{-\infty}^{\infty} d\hat{x}\ \hat{x}\ \frac{\partial \tilde{P}_g(\hat{x})}{\partial \hat{x}} \tag{6.5}$$

with $t_i(g)$ and $t_{\rm dec}(g_1)$ defined by Eqs. (3.6) and (3.3), respectively. This average time $\langle t(g)\rangle$, unlike the time $\bar{t}(g)$ in Eq. (6.2), remains finite if the homogeneous nucleation is improbable (i.e., $j_{\rm st}^{(0)}\to 0$). The different method of averaging is indicated by the angle brackets. For moderate values of Q the integral is small compared to the difference of the first two terms, and with accuracy $\tau O(1)$ one has

$$\langle t(g)\rangle \sim \tau \ln \frac{\phi_*}{kT} + \int_{g_1}^{g} \frac{dg}{\dot{g}}\,. \tag{6.6}$$

VII. CONCLUSIONS

The key results of our study are the explicit corrections to the homogeneous nucleation rate which are induced by preexisting nuclei, Eq. (3.9), as well as the corrections for number of nucleated particles, Eq. (4.2), and the time lag, Eq. (2.6). The obtained expressions are expected to be accurate not only for the continuous (Zeldovich–Frenkel) form of the nucleation equation, but also (with a corresponding modification of the deterministic growth rate $\dot{g}$) for the Master equation introduced by Farkas, Becker, and Doering. A surprising fact is the ease with which preexisting nuclei, even in minor concentrations can completely overshadow the effect of homogenous nucleation. Particularly, the total time lag may become *negative*. This also indicates the limitation of the conventional definition of this quantity given by Eq. (2.4). This definition puts a very strong emphasis on homogeneous nucleation, and it is not surprising that the time lag may loose its physical meaning when homogeneous nucleation is practically negligible. A probabilistic formulation of the nucleation problem (see Sec. VI) allows one to consider nucleation by successful inserted nuclei, without a reference to homogeneous nucleation. In this case the role of the time lag is played by the mean waiting time to detect the first nucleus, which, of course, is always positive. Applicability of the probability formulation in a realistic physical situation depends on the experimental possibility to detect a *single* nucleus. As to other results of the present study, there seems to be no obstacles to their application, but one still has to know the initial distribution $f_0(g_1)$ of preexisting nuclei. This distribution is very sensitive to the history of preparation of the experimental sample [quench rate, annealing time, etc., see, e.g., Ref. 12(b)]. Thus, we expect that further development of the theory can be done only in connection with specific experimental situations.

ACKNOWLEDGMENTS

One of us (V. S.) wishes to thank M. C. Weinberg for multiple discussions and the Alexander von Humboldt Foundation for support. P. H. acknowledges the support of the Volkswagen Stiftung.

APPENDIX A: CORRECTION TO THE TIME LAG BY A NEAR-CRITICAL NUCLEUS

Similar to the treatment of Sec. II A we first consider a steady-state problem with a unit source of nuclei at $g=g_1$. The inserted flux will split into two parts—J_+, towards large sizes $g>g_1$, and $J_-<0$ towards the small ones, $g<g_1$. The Zeldovich–Frenkel nucleation equation for the corrections to the homogenous distribution $\delta f(g,t)$ and flux $J(g,t)$ has the conventional form on both sides of the source

$$\frac{\partial \delta f}{\partial t} = -\frac{\partial J}{\partial g}\,, \quad J = -DN\,\frac{\partial}{\partial g}\,\frac{\delta f}{N} \tag{A1}$$

with N being the equilibrium distribution and $D=\dot{g}/(\partial \ln N/\partial g)$. The boundary conditions for δf are, however, different. Its ratio $\delta f/N$ should decay on *both* sides of the barrier, and it should be continuous at $g=g_1$. In the steady-state case (i.e., $J=J_\pm$ at $g\gtrless g_1$) the latter condition leads to

$$J_+ \int_{g_1}^{\infty} \frac{dg}{DN} = -J_- \int_{-\infty}^{g_1} \frac{dg}{DN}\,. \tag{A2}$$

Formally, we extend the region of integration to negative sizes, as the major input to the integral on the right-hand side of Eq. (A2) is expected to come from the vicinity of g_1 which is expected to be large (macroscopic). Together with the conservation condition

$$J_+ = 1 + J_-\,, \tag{A3}$$

Eq. (A2) allows the elementary evaluation of J_+. In case g_1 is well below g_* the integral on the left-hand side of Eq. (A2) is asymptotically large compared to the one on the right-hand side which, in turn is determined mainly by its upper limit and equals $-1/[\dot{g}_1 N(g_1)]$. This means $J_+ \ll |J_-|$ and from Eq. (A3), $J_- \cong -1$. In this case one recovers the results of Sec. II A. If, on the other hand, g_1 is close to g_*, i.e., $|g_1 - g_*| \ll g_*$ [although the parameter $Z_1 \equiv (g_1-g_*)/\Delta$ can be of arbitrary value and sign], one can use a parabolic approximation near the top of the barrier to evaluate the integrals in Eq. (A2). In this case the result is

$$J_+ = \frac{1}{2}\,\mathrm{erfc}[-Z_1], \quad Z_1 \equiv \frac{g_1 - g_*}{\Delta}\,. \tag{A4}$$

The growth probability rapidly approaches unity for an overcritical nucleus, $g_1 > g_*$. One can easily check that Eq. (A4) overlaps with Eq. (2.3) for subcritical nuclei with $\Delta \ll g_* - g_1 \ll g_*$. Thus, similar to Ref. 27(b), one can construct a formal interpolation:

$$J_+ \cong \frac{1}{2}\,\frac{\Delta Z_1}{\tau \dot{g}_1}\,\mathrm{erfc}(-Z_1)\exp\left(Z_1^2 + \frac{\phi_* - \phi(g_1)}{kT}\right). \tag{A5}$$

This interpolation covers the whole subcritical and near-critical regions, including the overcritical sizes up to

25 September 2024 13:41:25

$g_1 - g_* \ll g_*$ [for larger g_1 Eq. (A5) is to be replaced by 1]. Such an interpolation may be useful if the initial location of preexisting nuclei is unclear. As discussed in Sec. II B, the correction to the time lag is obtained by multiplying $-J_+$ by the actual number of inserted particles and reducing it by j_{st}.

APPENDIX B: COMPARISON WITH AN EXACT EXPRESSION FOR A PARABOLIC BARRIER

In case of a parabolic barrier,

$$\phi^{pb}(g) = \phi_*\{1-(g/g_*-1)^2\}, \quad \phi_*/kT \equiv (g_*/\Delta)^2 \tag{B1}$$

and $D=$const, Eq. (A1) becomes the well-known Ornstein–Uhlenbeck equation for an overdamped unstable harmonic oscillator. For an unrestricted region of sizes this equation can be solved *exactly* even for an arbitrary time dependence of its coefficients.[29] In the nucleation context the situation is somewhat aggravated by the necessity to restrict g to positive values.[30] Nevertheless, as should be clear from the discussion in Sec. III, in case a nucleus is placed at $1 \ll g_1 < g_*$ it is "almost the same" whether this nucleus will be absorbed at $g=1$, or be allowed to proceed to negative sizes. Anyway, the chances for a "negative" nucleus to cross the barrier are exponentially small. Without the reference to preexisting nuclei the exact solubility was exploited in our previous study[31] to test the asymptotic solution obtained for a time-dependent (periodically modulated) barrier. In the present case we are interested in a more simpler, transient case. A single nucleus with size g_1 is inserted into the system at $t=0$. For the drift part of the flux the result reads

$$\delta j^{pb}(g,t) = \frac{\Delta \exp\{[\phi^{pb}(g_1)-\phi_*]/kT\}\alpha(t)}{2\tau^2\sqrt{\pi}|\dot{g}_1^{pb}|} \times \exp\left\{-\hat{x}^{pb} - \alpha^2(t)\left[\exp(-\hat{x}^{pb}) + \frac{1}{4}\left[\frac{\Delta^2}{g_*^2} + \frac{\Delta^2}{(g-g_*)^2}\right]\exp(-2\hat{x}^{pb})\right]\right\}. \tag{B2}$$

Here $\alpha(t)$ is defined by

$$\alpha(t) = [1-\exp(-2t/\tau)]^{-1/2}, \tag{B3}$$

while the growth rate corresponds to

$$\dot{g}^{pb} = (g-g_*)/\tau. \tag{B4}$$

The scaling parameter $\hat{x}$, as follows from Eqs. (3.6) and (3.8), is now given by

$$\hat{x}^{pb} = t/\tau - \ln(2\phi_*/kT) - \ln[(g-g_*)/(g_*-g_1)], \tag{B5}$$

and in Eq. (B2) we choose $g_1=0$. Note the presence of two essentially different time scales.[27(b)] At $t \ll \tau$ the parameter $\hat{x}$ has large negative values, which means vanishingly small values for the flux in Eq. (B2). Only for much larger times, namely for $t > \tau \ln(\phi_*/kT)$, does the flux acquire noticeable values. At such times, $\alpha(t)$ in Eq. (B3) already equals unity; and hence one recovers the "scaling expression" (3.9) within asymptotically negligible corrections.

APPENDIX C: THE EFFECT OF OVERCRITICAL NUCLEI AND THE STEADY-STATE LIMIT

An important test of the validity of the obtained results is to verify that in case the initial distribution corresponds to the steady-state distribution of homogeneous nucleation, the solution will not evolve in time. Since we are interested in the growth region $g > g_*$, the overcritical nuclei will become important in this case. Although we have not discussed such nuclei so far—their inclusion is straightforward. Overcritical nuclei simply grow to large sizes with the drift flux $\dot{g}f(g,t)$ remaining constant along the trajectories of growth.

Consider now the initial distribution produced by the steady-state homogeneous nucleation

$$f_0(g_1) \approx \begin{cases} N(g_1), & g_* - g_1 \gg \Delta, \quad \text{(C1)} \\ j_{st}^{(0)}/\dot{g}_1, & g_1 - g_* \gg \Delta, \quad \text{(C2)} \end{cases}$$

in the sub- and overcritical regions, respectively. In the direct vicinity of g_* the distribution is given by $(1/2)N(g)\mathrm{erfc}[(g-g_*)/\Delta]$,[4] which bridges the two branches given by Eqs. (C1) and (C2).

Upon the (formal) switch-on of the nucleation process at $t=0$ the distribution (C1) and (C2) is to be treated as *preexisting* nuclei with an input $\delta j(g,t)$, and the transient homogeneous flux, $j^{(0)}(g,t)$ should be added. At first, up until $t \sim \tau \ln(g_*/\Delta)$, the overcritical nuclei will grow, preserving the value of their flux so that their input is given by $j_{st}^{(0)}$. The input of subcritical nuclei is given by Eq. (3.4). Note that for the initial distribution considered one has in this equation $f(g_1)/N_1 \exp(\phi(g_1)/kT) \equiv 1$. In addition, from the definition in Eq. (3.3), one has $dt_{dec} = -dg_1/\dot{g}_1$. Thus the total flux due to preexisting subcritical nuclei and the homogeneous nucleation is given by

$$j^{(0)}[g,t] + \delta j(g,t) = j^{(0)}[g,t] + \int_0^{t_{dec}(g_1^{max})} dt_{dec} \frac{\partial}{\partial t} j^{(0)} \times (g, t+t_{dec}) = j^{(0)}[g, t+t_{dec}(g_1^{max})]. \tag{C3}$$

In the above g_1^{max} has the meaning of the largest size where Eq. (C1) is still applicable. The value g_1^{max} can be estimated as $g_* - \Delta$, so that $t_{dec}(g_1^{max}) \sim \tau \ln(g_*/\Delta)$. Recall that the incubation time of homogeneous nucleation has twice a larger time scale, as one can see from Eq. (3.6). Thus, at $t < \tau \ln(g_*/\Delta)$ when the effect of the overcritical nuclei is important, the flux (C3) is practically zero, while at $t > \tau \ln(g_*/\Delta)$ when the overcritical nuclei do not contribute, it has the steady-state value. Bridging the effects produced by sub- and overcritical nuclei requires a delicate consideration of nuclei in the near-critical region,[27(b)] which is not our purpose at the moment. Anyway, one can see that the steady-state flux persists, due to overcritical nuclei at $t < \tau \ln(g_*/\Delta)$ and due to subcritical nuclei at larger times.

This provides an important independent confirmation of the validity of our solution.

[1] M. Volmer and A. Weber, Z. Phys. Chem. **119**, 227 (1926).
[2] L. Farkas, Z. Phys. Chem. **125**, 236 (1927).
[3] R. Becker and W. Doering, Ann. Phys. **24**, 719 (1935).

25 September 2024 13:41:25

[4] Ya. B. Zeldovich, Acta Physicochim. (USSR) **18**, 1 (1943).
[5] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University, Oxford, 1946).
[6] V. P. Skripov, *Metastable Fluid* (in Russian) (Nauka, Moscow, 1972); V. A. Akulichev, *Cavitation in Cryogenic and Boiling Liquids* (in Russian) (Nauka, Moscow, 1978).
[7] (a) A. J. Leggett, Phys. Rev. Lett. **53**, 1096 (1984); (b) P. Schiffer, M. T. O'Keefe, M. D. Hildreth, H. Fukuyama, and D. D. Osheroff, *ibid.* **69**, 120 (1992).
[8] (a) P. James, Phys. Chem. Glasses **15**, 95 (1974); (b) V. Fokin, A. Kalinina, and V. Filipovich, Fiz. Khim. Stekla **6**, 148 (1980); (c) I. Gutzow, Contemp. Phys. **21**, 121, 243 (1980); (d) J. Deubener, R. Brückner, and M. Sternitzke, J. Non-Cryst. Solids **163**, 1 (1993).
[9] G. F. Neilson and M. C. Weinberg, J. Non-Cryst. Solids **34**, 137 (1979).
[10] V. Shneidman and M. C. Weinberg, Ceram. Trans. **30**, 375 (1993).
[11] D. W. Oxtoby and R. Evans, J. Chem. Phys. **89**, 7521 (1988); C. K. Bagdassarian and D. W. Oxtoby, *ibid.* **100**, 2139 (1994); C. L. Weakliem and H. Reiss, *ibid.* **99**, 5374 (1993).
[12] (a) U. Köster and U. Herold, in *Topics in Applied Physics, Vol. 46, Glassy Metals I*, edited by H.-J. Güntherodt and H. Beck (Springer, New York, 1981), p. 225; (b) K. F. Kelton, J. Non-Cryst. Solids **163**, 283 (1993).
[13] V. M. Fokin, V. N. Filipovich, and A. M. Kalinina, Fis. Khim. Stekla **3**, 129 (1977).
[14] K. Y. Min and W. I. Goldburg, Phys. Rev. Lett. **71**, 569 (1993).
[15] (a) V. A. Shneidman and M. C. Weinberg, J. Chem. Phys. **97**, 3621 (1992); (b) **97**, 3639 (1992).
[16] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[17] V. A. Shneidman and P. Hänggi, Phys. Rev. E **49**, 894 (1994).
[18] V. A. Shneidman, Phys. Lett. **143**, 275 (1990).
[19] (a) V. A. Shneidman, Sov. Phys. Tech. Phys. **32**, 76 (1987); (b) **33**, 1338 (1988).
[20] M. Abramowitz and I. Stegun, *Handbook for Mathematical Functions* (Dover, New York, 1965).
[21] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977); A. Z. Patashinskii and B. I. Shumilo, Sov. Phys. JETP **50**, 712 (1979).
[22] V. A. Shneidman and M. C. Weinberg, J. Chem. Phys. **95**, 9148 (1981).
[23] K. F. Kelton, A. L. Greer, and C. V. Thomson, J. Chem. Phys. **79**, 6261 (1983).
[24] D. R. Uhlman, J. Non-Cryst. Solids **7**, 337 (1992).
[25] See Sec. VII in Ref. 16; N. van Kampen, *Stochastic Processes in Physics and Chemistry*, revised and enlarged edition (Elsevier, Amsterdam, 1993).
[26] A. N. Kolmogorov, Bull. Acad. Sci. U.R.S.S. (Sci. Mater. Natl.) **3**, 355 (1939).
[27] (a) V. A. Shneidman, Physica A **174**, 406 (1991); (b) Phys. Rev. A **44**, 2609 (1991).
[28] This function becomes multiparametric in case two (or more) groups of nuclei are present in the system, each characterized by its own "transition number," Q_1, Q_2,... . Here one can still employ Eq. (6.4) with Q in the normalization factor replaced by $Q_1+Q_2+...$, and the exponent in the square brackets replaced by $Q_1 \exp[-\exp(-\hat{x}^{(1)})] + Q_2 \exp[-\exp(-\hat{x}^{(2)})+\cdots]$. The values $\hat{x}^{(1)}, \hat{x}^{(2)}$, etc. are defined by Eq. (3.8) for each size g_1 present in the system.
[29] P. Hänggi and H. Thomas, Z. Phys. B **22**, 295 (1975).
[30] H. Trinkaus and M. H. Yoo, Philos. Mag. **55**, 269 (1987).
[31] V. A. Shneidman and P. Hänggi, Phys. Rev. E **49**, 641 (1994).

25 September 2024 13:41:25