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Time-dependent effects in nucleation near the critical point

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Application of the critical dynamics to the nucleation process results in a Langevin-type equation for the radius of the nucleus, which is transformed to a Fokker-Planck equation for the distribution function. The time-dependent solution of this equation is shown to be crucially dependent upon the initial conditions. The time lag associated with the establishment of the steady state following a fast quench is exponentially larger than that for a slow quench. Numerical estimates of the time lag are presented.

I. INTRODUCTION

The most familiar examples of metastable states are the supersaturated vapor and the supercooled liquid. Such states are thermodynamically stable against small perturbations. If, however, the "droplet" of the new phase is large enough, it will grow rather than dissipate and will finally bring the entire system into a stable state. An understanding of the kinetics of such a process is very important for many practical applications and, at the same time, is a very interesting task for nonequilibrium thermodynamics.

The traditional phenomenological approach to the decay of metastable states goes back to the classical results of Becker, Döring, Zeldovich, and Frenkel.[1,2] In these theories, the relaxation of a metastable state is described by the distribution function $W(r,t)$ of nuclei of size r at time t. The variation of $W(r,t)$ is related to the flux $J(r,t)$ of nuclei along the size axes. In the appropriate continuity equation,

$$\frac{\partial W(r,t)}{\partial t}=-\frac{\partial J(r,t)}{\partial r}\,, \tag{1.1}$$

the flux $J(r,t)$ can be written as[2]

$$J(r,t)=-FW-D\frac{\partial W}{\partial r}\,. \tag{1.2}$$

The first term in Eq. (1.2) describes the systematic growth (decay) of the nucleus and the second term is responsible for the diffusive growth. The two unknown functions F and D can be related through the "formation energy" ΔG of a nucleus of size r. In fact, the equilibrium distribution function $W_{\text{eq}}(r)$ corresponds to zero flux and, from Eq. (1.2), one obtains

$$W_{\text{eq}}(r)=W_{\text{eq}}(1)\exp\left[-\int_1^r dr'\frac{F(r')}{D(r')}\right]$$

$$=W_{\text{eq}}(1)e^{-\Delta G/kT}\,, \tag{1.3}$$

where $W_{\text{eq}}(1)$ is the number of nuclei of unit size (the unit can be a molecule, a correlation length, etc.).

One usually assumes[2] some model expressions for the two unknown functions $D(r)$ and ΔG [or, alternatively, $F(r)$]. The function $D(r)$ is related to the probability per unit time of a unit nucleus joining a nucleus of size r, and it is usually taken to be proportional to the surface of the nucleus. The formation energy ΔG consists of the volume and surface parts, the competition of which results in the decay of the small nuclei with $r<r_c$, where r_c is the size of the so-called critical nucleus, and the growth of nuclei with $r>r_c$.

As was shown by Langer and Turski[3] and by Patashinsky and Shumilo,[4] near critical points the properties of the metastable state (and thus, of the functions F and D) are completely determined by the critical dynamics. However, in these treatments of the decay of metastable states, only stationary solutions of Eq. (1.1) were considered. In the stationary regime, one finds that the flux J_{st} does not depend upon the size of a nucleus. The lifetime of a metastable state is then defined as J_{st}^{-1}. The major theoretical effort is directed towards the computation of the so-called "preexponential factor" that appears in the expression for J_{st}, and the manner in which the metastable state was reached plays no role in the considerations.

If one considers the time lag associated with the establishment of the steady-state regime following the quench to the metastable state, it is very important to distinguish between "slow" and "fast" quenches. This can be seen from the following argument. The metastable state that appears after a quench is a state of incomplete equilibrium. The short-range degrees of freedom (nuclei with sizes r such that $r<\lambda<r_c$) come to equilibrium immediately and can be described by the Gibbs distribution. The dynamic behavior of the system depends upon the value of the characteristic length λ. In the case of a slow quench ($r_c \gtrsim \lambda \gg 1$), the large nuclei appear immediately after the quench and the stationary regime of nucleation is established after a relatively small time lag. In the case of a fast quench ($1 \lesssim \lambda \ll r_c$), we have a drastically different

situation. The nonstationary contributions to the integrated flux become important and, contrary to what is assumed in traditional treatments of nucleation, they cannot be neglected.

It turns out that, while the characteristic time lag associated with the approach to steady state is $r_c^2/c\Gamma$ for the case of a slow quench, it is

$$\left[\frac{r_c^2}{D_0}\right]^{1/4}\frac{D_0}{c\Gamma}e^{r_c^2/24D_0},$$

i.e., exponentially larger in the case of a fast quench, where kTD_0^{-1} is proportional to the surface tension and $c\Gamma$ is the diffusion coefficient. Only the first time scale has been obtained by previous investigators.[5]

While, strictly speaking, our results apply only in the critical region, we believe that the analysis presented in this paper can be useful in understanding the transient regime of nucleation even away from these points. Note that the application of critical dynamics to the metastability depends only upon the possibility of dividing the dynamical variables into slow and fast ones. Such a partitioning is common to most modern treatments of nonequilibrium states.

In Sec. II, we present the critical-dynamics approach[4] to the problem of metastability and nucleation. The equation of motion for the order parameter is transformed, in the quasistatic approximation, into an equation that describes the motion of the boundary of the nucleus under the influence of systematic and diffusive forces. The transition from a dynamic to a stochastic description is made and a Fokker-Planck equation for the size distribution is derived. In the process, the $F(r)$ and $D(r)$ functions are computed in a straightforward manner. Therefore, the form of the Fokker-Planck equation is uniquely determined by critical dynamics.

In Sec. III, separation of variables is used to reduce the time-dependent Fokker-Planck equation to an eigenvalue problem of the Sturm-Liouville type. The latter equation is then transformed into a Schrödinger equation that must be solved subject to appropriate boundary conditions. The distribution function and the fluxes are expanded in terms of the solutions of the Schrödinger equation. Expressions for the expansion coefficients are then obtained and their dependence upon the initial conditions (slow versus fast quenches) is discussed.

In Sec. IV, the Schrödinger equation is solved in the harmonic approximation and the integrated flux at $r=r_c$ is expanded in terms of the eigenfunctions of the harmonic oscillator. The expansion coefficients are evaluated for the slow- and fast-quench cases, using asymptotic properties of the Hermitian polynomials, and the resulting summations are carried out in the Appendix.

Section V deals with the analysis of the results in the case of fast quenches. We obtain an exponentially large time lag associated with the approach to steady state. Numerical estimates of this time lag are given.

In conclusion, Sec. VI discusses further the appearance of a new time scale for fast quenches and provides a physical interpretation of the time lag in terms of the "preparation" of the steady-state distribution of nuclei, which for fast quenches is very different from the initial distribution. Finally, a quantum-mechanical analogy is drawn between the nucleation process following a fast quench and the vibrational predissociation of "long-range" molecules following excitation by a laser pulse.

II. A CRITICAL-DYNAMICS APPROACH TO METASTABILITY

The general approach of critical dynamics is well known.[6] Near critical points, one distinguishes between slow and fast degrees of freedom. The former determine the critical dynamics and the latter play the role of a thermal bath. Their influence is taken into account by including random forces in the equations of motion for slow variables, such as the hydrodynamic modes and the order parameters considered here. Thus, dynamic variables and fluctuations appear in the same equations as systematic and random forces, respectively.

The situation described is, in fact, the same when a system undergoes a transition from a stable to a metastable state. The small-scale degrees of freedom come to essentially immediate equilibrium and are described by the Gibbs distribution for a given configuration of large-scale degrees of freedom. The latter relax toward the stable state via the formation of nuclei of the new stable phase and their kinetics is determined by their critical dynamics. Therefore, no additional assumptions need be made concerning the form of the functions D and F (or D and ΔG).

Consider the simplest case of a system having only one hydrodynamic mode: the scalar-field order parameter $\phi(r,t)$. The effective free-energy functional can be written in the familiar Landau-Ginsburg form:

$$\mathscr{H}\{\phi\}=\int d^3r\left[\frac{c}{2}\,|\vec{\nabla}\phi|^2+U(\phi)\right]. \tag{2.1}$$

The equation of motion of the order parameter is[6]

$$\frac{\partial\phi}{\partial t}=\hat{\Gamma}\left[-\frac{\delta\mathscr{H}}{\delta\phi}+f_r(r,t)\right], \tag{2.2}$$

where the transport coefficient operator $\hat{\Gamma}$ is given by Γ and $\Gamma_c\nabla^2$ for a nonconserved and a conserved field, respectively.[7] The Gaussian random force $f_r(r,t)$ in Eq. (2.2) simulates a thermal ensemble.

Note that, by using the continuous approximation for the free-energy functional in Eq. (2.1), we have assumed implicitly that some coarse graining (averaging over very short-scale degrees of freedom) has been performed. An additional coarse graining has to be carried out in order to pass from a dynamical to a statistical description of the phase separation process. This will be discussed later in this section.

The evolution of a nucleus of a new phase is described by the quasistationary solution $\phi(r,t)$ of Eq. (2.2), where $\phi(r,t)$ is almost everywhere close to the values ϕ_1 and ϕ_2 in the two coexisting phases, except at the boundary of the nucleus. Therefore, the gradient term in Eq. (2.1) is of crucial importance while the explicit form of $U(\phi)$ plays no role in our treatment.

A typical approach to the solution of Eq. (2.2) is the following. Consider a spherical nucleus with its center at the origin. Nuclei of a size smaller (larger) than the critical one decay (grow) in time while, for the critical nucleus, $\partial\phi/\partial t=0$. In the absence of a random force, the critical nucleus is described by the following equation:

$$c\frac{d^2\phi}{dr^2}+\frac{c(n-1)}{r_c}\frac{d\phi}{dr}+U'(\phi)=0\ , \tag{2.3}$$

where n is the dimensionality of space. For $n=1$, and assuming a typical form of $U(\phi)$, Eq. (2.3) can be solved exactly [$\phi=\tanh(r-r_c)$ for $U(\phi)=-\frac{1}{2}a\phi^2+\frac{1}{4}b\phi^4$].

Consider now the time-dependent solution of Eq. (2.2) which, for a nonconserved order parameter, can be rewritten in the form

$$\frac{\partial\phi}{\partial t}=-\Gamma\left[c\frac{\partial^2\phi}{\partial r^2}+\frac{c(n-1)}{r_c}\frac{\partial\phi}{\partial r}+U'(\phi)\right.$$
$$\left.+c(n-1)\left[\frac{1}{r}-\frac{1}{r_c}\right]\frac{\partial\phi}{\partial r}+f_r\right]\ . \tag{2.4}$$

For a conserved order parameter, an additional operator (∇^2) will act on the right-hand side of Eq. (2.4).

The order parameter depends upon time only through the variation of the boundary of the nucleus, i.e., $\partial\phi/\partial t\simeq(\partial\phi/\partial r)(dr/dt)$. Substituting the latter expression into Eq. (2.4) and taking into account the fact that, for the quasistatic solutions considered here, the sum of the first three terms in Eq. (2.4) is approximately zero [according to Eq. (2.3)], one can rewrite Eq. (2.4) as[8]

$$\frac{dr}{dt}=-\Gamma\left[c(n-1)\left[\frac{1}{r}-\frac{1}{r_c}\right]+X\right]\ , \tag{2.5}$$

where $X=(\partial\phi/\partial r)^{-1}f_r$ and, for the Gaussian random force f_r with a mean deviation of $2kT\Gamma$, the time-correlation function for $X(t)$ is equal to

$$\langle X(r,t)X(r,t')\rangle=2kT\Gamma\left[\int\left[\frac{\partial\phi}{\partial r}\right]^2 d^3r\right]^{-1}\delta(t-t')\ . \tag{2.6}$$

In Eq. (2.6) we consider only the X part of the random force f_r, which determines the change of the size of a nucleus. Equation (2.6) can be rewritten using the well-known formula for surface energy,[9]

$$S\sigma=\frac{n-1}{2}c\int(\nabla\phi)^2d^3r\ ,$$

where $S(r)$ is the surface area of a nucleus and σ is the effective surface tension.[10] Then,

$$\langle X(r,t)X(r,t')\rangle=\frac{2D_0c\Gamma}{r^2}\delta(t-t'),\ D_0=\frac{n-1}{2}\frac{kT}{4\pi\sigma}\ . \tag{2.7}$$

The first term in Eq. (2.5) determines the systematic force driving the decay (growth) of the nuclei of a size smaller (larger) than a critical one. This force tends to conserve the uniformity of a system and by itself cannot induce a transition to a new phase. Such a transition can be induced by the second term in Eq. (2.5), i.e., the random force describing the flucutations.[11] The two forces in Eq. (2.5) determine the exact form of the two functions $D(r)$ and $F(r)$ in Eq. (1.2).

The problem of the statistical description of metastable states has received widespread attention (see, for example, the review article[12]). Strictly speaking, statistical mechanics deal with stable states only. In order to describe the metastable states, an additional coarse graining of the free-energy functional, Eq. (2.1), has to be performed. According to Ref. 12, the appropriate cutoff for dealing with the dynamics of phase separation is of the order of the correlation length ξ. Such a choice means that we restrict our consideration to the region on the phase diagram near the coexistence curve (shaded region in Fig. 1) where the critical nucleus r_c, which is of infinite size on this curve, is much larger than the correlation length ξ, $r_c\gg\xi$. Therefore, the correlation length will be considered as the minimal length in the following analysis.

Using the well-known methods of probability theory,[13] one can pass to the statistical description of systems governed by Eqs. (2.5) and (2.7). We introduce the transition probability as follows:

$$P(r,r_0;t,0)=\langle\delta[r-r(t)]\rangle,\ \ r_0\equiv r(0) \tag{2.8}$$

where the averaging is performed over the realizations of the random force X. The size distribution of the nuclei at time t is given by

$$W(r,t)=\int P(r,r_0;t,0)W_{\text{init}}(r_0,0)dr_0\ , \tag{2.9}$$

where $W_{\text{init}}(r_0,0)$ is the initial distribution.

One can now construct the Fokker-Planck equation[13] corresponding to the Langevin equation (2.5) and obtain

$$\frac{\partial W}{\partial t}=-\frac{\partial}{\partial r}\left[-FW-D\frac{\partial W}{\partial r}\right]\ , \tag{2.10}$$

where, according to Eq. (2.5), for the three-dimensional case we have

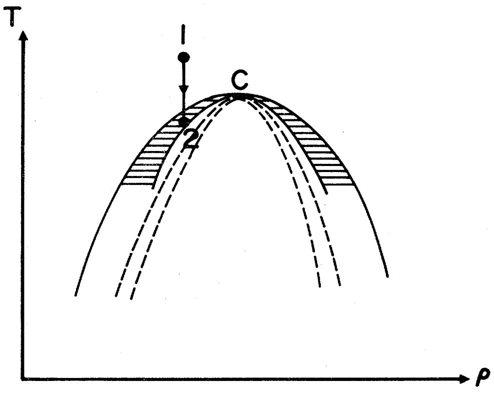

FIG. 1. Typical (T,ρ) phase diagram close to the critical point c. Coexistence curve is given by the solid line. Two dotted lines bound the cloud-point region. System is quenched from the single-phase region (point 1) to the shaded region (point 2).

$$F(r)=2c\Gamma\left[\frac{1}{r}-\frac{1}{r_c}\right] \tag{2.11}$$

and

$$D(r)=c\Gamma\frac{D_0}{r^2},\ D_0\equiv\frac{kT}{4\pi\sigma}\ . \tag{2.12}$$

The equilibrium distribution is obtained by substituting Eqs. (2.11) and (2.12) into Eq. (1.3):

$$W_{\mathrm{eq}}(r)=W_{\mathrm{eq}}(\xi)\exp\left[-\frac{r^2}{D_0}\left[1-\frac{2}{3}\frac{r}{r_c}\right]\right]\ . \tag{2.13}$$

The functions $F(r)$ and $D(r)$ can be found in an analogous way for the case of a conserved order parameter[4]:

$$F(r)=\frac{2c\Gamma r_c}{r}\left[\frac{1}{r}-\frac{1}{r_c}\right] \tag{2.14}$$

and

$$D(r)=\frac{c\Gamma D_0 r_c}{r^3}\ . \tag{2.15}$$

As we have shown in this section, near critical points there is no need for any special assumptions concerning the form of the functions $D(r)$ and $F(r)$; both are determined by the universally accepted critical dynamics.

III. TIME-DEPENDENT PROBLEM

In this paper we consider only the first stage of the nucleation process, before the appearance of a macroscopic amount of the new phase.[14] In this regime, $F(r)$ (or ΔG) and the boundary conditions do not depend explicitly upon time.

We will solve Eqs. (1.1) and (1.2) with $D(r)$ and $F(r)$ given by Eqs. (2.11) and (2.12). In addition to the equilibrium solution Eq. (2.13), one can easily find the steady-state solution of Eq. (1.1), which corresponds to the constant stationary current (1.2), J_{st}, namely,

$$W_{\mathrm{st}}(r)=W_{\mathrm{eq}}(r)\left[1-J_{\mathrm{st}}\int_{\xi}^{r}\frac{dr'}{D(r')W_{\mathrm{eq}}(r')}\right]\ , \tag{3.1}$$

where

$$J_{\mathrm{st}}^{-1}=\int_{\xi}^{\infty}\frac{dr'}{D(r')W_{\mathrm{eq}}(r')} \tag{3.2}$$

and ξ is the correlation length.

The function $W_{\mathrm{eq}}^{-1}(r)$ has a sharp maximum at r_c, which reflects the existence of a barrier to nucleation. Therefore, the integrals Eqs. (3.1) and (3.2) can be evaluated easily by the method of the steepest descent. Performing the integration in Eq. (3.2) and using Eqs. (2.11) and (2.12), one obtains

$$J_{\mathrm{st}}=\left[\frac{D_0}{\pi}\right]^{1/2}\frac{c\Gamma}{r_c^2}W_{\mathrm{eq}}(r_c)\ . \tag{3.3}$$

Application of steepest-descent arguments to Eq. (3.1) results in

$$\frac{W_{\mathrm{st}}(r)}{W_{\mathrm{eq}}(r)}\approx\begin{cases}1, & r<r_c-\delta\\ 0, & r>r_c+\delta\end{cases} \tag{3.4}$$

with a narrow transition region of width $2\delta \ll r_c$ centered at r_c.

In order to find the general time-dependent solution of Eq. (1.1), we separate variables and write

$$W(r,t)=W_{\mathrm{st}}+\sum_n A_n X_n(r)e^{-\lambda_n t}\ . \tag{3.5}$$

Using Eqs. (1.1) and (1.2) we obtain the Sturm-Liouville equation:

$$\frac{d}{dr}\left[F(r)X_n(r)+D(r)\frac{dX_n(r)}{dr}\right]=-\lambda_n X_n(r)\ , \tag{3.6}$$

where the eigenvalues λ_n are determined by the boundary conditions. The coefficients A_n are found from the initial conditions.

In addition to the analysis of the distribution function, it is interesting to consider the nonstationary behavior of the flux $J(r,t)$. This flux can be partitioned into stationary and nonstationary parts,

$$J(r,t)=J_{\mathrm{st}}+\sum_n A_n J_n(r)e^{-\lambda_n t}\ , \tag{3.7}$$

where, using Eqs. (1.2) and (1.3),

$$J_n(r)=-D(r)W_{\mathrm{eq}}(r)\frac{\partial}{\partial r}\left[\frac{X_n(r)}{W_{\mathrm{eq}}(r)}\right]\ . \tag{3.8}$$

Another important quantity is the integrated flux (at r_c) $N(t)$, defined as $N(t)\equiv\int_0^t J(r_c,t')dt'$,

$$N(t)=J_{\mathrm{st}}t+\sum_n A_n\lambda_n^{-1}J_n(r_c)(1-e^{-\lambda_n t})\ . \tag{3.9}$$

Now, let us proceed with the boundary conditions. The appropriate boundary conditions are

$$W(\xi,t)=W_{\mathrm{eq}}(\xi) \tag{3.10}$$

and

$$W(\infty,t)=0\ , \tag{3.11}$$

i.e., the number of correlation-sized nuclei ($r=\xi$) is equal to their number in equilibrium and no large nuclei ($r\to\infty$) are present.

The nonhomogeneous boundary condition (3.10) is time independent. Thus, it must be satisfied by the stationary solution of Eq. (3.6), i.e., by the term in Eq. (3.5) corresponding to the eigenvalue $\lambda=0$:

$$X_{\lambda=0}(\xi)=W_{\mathrm{eq}}(\xi)\ . \tag{3.12}$$

All other nonstationary solutions satisfy homogeneous boundary conditions at $r=\xi$, namely,

$$X_n(\xi)=0\ . \tag{3.13}$$

According to Eq. (3.11) all solutions satisfy homogeneous boundary conditions at infinity, i.e., for all n

$$X_n(\infty)=0\ . \tag{3.14}$$

Before setting up the initial conditions, we transform Eq. (3.6) into a Schrödinger equation to which well-known approximation methods can be applied. First, we define the function

$$U_n(r)=X_n(r)/W_{\text{eq}}(r)\ , \tag{3.15}$$

which satisfies the equation

$$\frac{d}{dr}\left[D(r)W_{\text{eq}}(r)\frac{dU_n(r)}{dr}\right]=-\lambda_n W_{\text{eq}}(r)U_n(r)\ . \tag{3.16}$$

We introduce a new dimensionless variable

$$z=r^2/2D_0\ , \tag{3.17}$$

with D_0 defined in Eq. (2.12).

Finally, defining a new function $\psi(z)$ by

$$X_n(r)=\left[\frac{r}{D_0}\right]^{1/2} W_{\text{eq}}^{1/2}(r)\psi_n(z(r))\ , \tag{3.18}$$

and using Eq. (2.13) for the equilibrium distribution function, we arrive at the Schrödinger equation:

$$-\frac{d^2\psi_n(z)}{dz^2}+[V(z)-E_n]\psi_n(z)=0\ , \tag{3.19}$$

where the "energy" of the nth eigenstate is

$$E_n=\frac{D_0}{c\Gamma}\lambda_n\ . \tag{3.20}$$

The potential $V(z)$ has the form

$$V(z)=-\frac{5}{16z^2}+\frac{1}{2z}+\left[1-\left[\frac{z}{z_c}\right]^{1/2}\right]^2\ , \tag{3.21}$$

with

$$z_c=\frac{r_c^2}{2D_0}\ . \tag{3.22}$$

The boundary conditions, Eqs. (3.13) and (3.14), are

$$\psi_n(z_0)=\psi_n(\infty)=0\ , \tag{3.23}$$

where

$$z_0=\frac{\xi^2}{2D_0}\ . \tag{3.24}$$

Notice that only dimensionless variables (z,E_n) appear in the Schrödinger equation.

After solving the Schrödinger equation, we use Eqs. (3.18) and (3.5) to express the time-dependent distribution function $W(r,t)$ in terms of the eigenfunctions $\psi_n(r)$:

$$W(r,t)=W_{\text{st}}(r)+\left[\frac{r}{D_0}\right]^{1/2} W_{\text{eq}}^{1/2}(r)\times\sum_n A_n\psi_n(z(r))e^{-\lambda_n t}\ . \tag{3.25}$$

The nonstationary contribution to the flux, Eq. (3.7), is found by substituting Eq. (3.18) into Eq. (3.8):

$$J_n(r)=-D(r)W_{\text{eq}}(r)\times\frac{\partial}{\partial r}\left[\left[\frac{r}{D_0}\right]^{1/2} W_{\text{eq}}^{-1/2}(r)\psi_n(z(r))\right]\ . \tag{3.26}$$

The A_n coefficients are determined from the initial conditions, which play an important role in our considerations since it turns out that the temporal behavior of the distribution function $W(r,t)$ and the integrated flux depends crucially upon the nature of the quench (slow or fast).

Immediately following the quench, the system is in a state of incomplete equilibrium characterized by a length scale λ such that an equilibrium distribution (at the new temperature) has been attained only for nuclei of size $r<\lambda$. Correspondingly, for the so-called fast quenches $\lambda\to\xi$, and for slow quenches $\lambda\to r_c$. Therefore, the appropriate initial condition is

$$W(r,0)=W_{\text{eq}}(r)\Theta(\lambda-r)\ , \tag{3.27}$$

where $\Theta(\lambda-r)$ is the unit step function [$\Theta(x)=1$ for $x>0$ and $\Theta(x)=0$ for $x<0$]. Substitution of Eq. (3.27) into Eq. (3.25) leads to

$$\sum_n A_n\psi_n(z(r))=-\left[\frac{D_0}{r}\right]^{1/2} W_{\text{eq}}^{1/2}(r)\times\left[\frac{W_{\text{st}}(r)}{W_{\text{eq}}(r)}-\Theta(\lambda-r)\right]\ . \tag{3.28}$$

Assuming that the $\psi_n(z)$ eigenfunctions are orthogonal

$$\int_{z_0}^{\infty}\psi_n(z)\psi_m(z)dz=\delta_{m,n}\ , \tag{3.29}$$

one obtains for the coefficients A_n

$$A_n=-\int_{z_0}^{\infty}dz\left[\frac{D_0}{r(z)}\right]^{1/2} W_{\text{eq}}^{1/2}(r(z))\psi_n(z)\times\left[\frac{W_{\text{st}}(r(z))}{W_{\text{eq}}(r(z))}-\Theta(\lambda-r(z))\right]\ , \tag{3.30}$$

where, as before, the variables r and z are connected by Eq. (3.17).

Brief reflection on the properties, Eq. (3.4), of the steady-state distribution leads to the final expression

$$A_n=-\int_{z_i}^{z_c+\delta}dz\left[\frac{D_0}{r(z)}\right]^{1/2} W_{\text{eq}}^{1/2}(r(z))\psi_n(z)\ , \tag{3.31}$$

where the lower cutoff is determined by the initial conditions

$$z_i=\frac{\lambda^2}{2D_0}\ . \tag{3.32}$$

Returning now to the Schrödinger equation (3.19), notice that the potential $V(z)$ reaches its minimum at $z\simeq z_c$ (up to corrections of order $1/z_c\ll 1$) and at the minimum $V(z_c)\simeq(1/2z_c)$. Clearly, this is the lower bound to the spectrum of eigenvalues, i.e.,

$$E_n>\frac{1}{2z_c}\ . \tag{3.33}$$

As one can see from Fig. 2, the potential $V(z)$ is almost parabolic close to its minimum, suggesting the use of the eigenvalues E_n and the eigenfunctions $\psi_n(z)$ of the harmonic oscillator. The solutions are oscillatory in the domain bounded by the potential and are exponentially decaying outside this domain. Thus, we will replace the boundary conditions $\psi_n(z_0)=0$ by $\psi_n(-\infty)=0$, approximate the exact potential by that of the linear oscillator, and obtain the harmonic-oscillator spectrum and eigenfunctions. After the eigenfunctions $\psi_n(z)$ are found the expansion coefficients A_n will be found using Eq. (3.31).

IV. SOLUTION OF THE SCHRÖDINGER EQUATION

Turning now to the solution of the Schrödinger equation (3.19) and expanding the potential (3.21) about its minimum, we obtain in the harmonic approximation

$$V_{\mathrm{osc}}(z)=\frac{1}{2z_c}+\frac{1}{4}\left[1-\frac{z}{z_c}\right]^2 . \tag{4.1}$$

The well-known solution for eigenvalues and eigenfunctions is given by[15]

$$E_n=(n+1)/z_c \tag{4.2}$$

and

$$\psi_n(r)=c_n e^{-\beta^2/2}H_n(\beta) , \tag{4.3}$$

where $H_n(\beta)$ are the nth-order Hermite polynomials with

$$\beta=(2z_c)^{-1/2}(z-z_c) . \tag{4.4}$$

The normalization coefficients c_n are given by

$$c_n=(2\pi z_c)^{-1/4}(2^n n!)^{-1/2} . \tag{4.5}$$

Substitution of Eq. (4.3) into Eq. (3.31) yields

$$A_n=-\left[\frac{D_0}{2}\right]^{1/4} W_{\mathrm{eq}}^{1/2}(\xi)c_n I_n , \tag{4.6}$$

where I_n is the following integral:

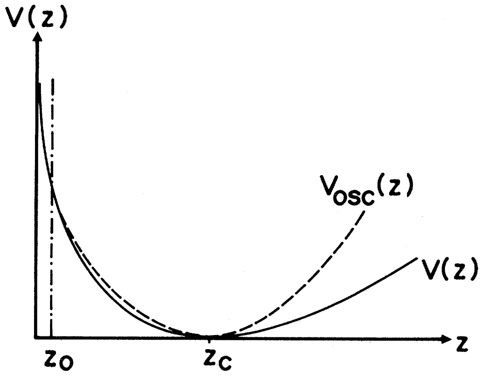

FIG. 2. Characteristic plot of the exact potential $V(z)$ (solid line) and the appropriate harmonic-oscillator potential $V_{\mathrm{osc}}(z)$. Left-hand boundary condition is given at the dotted line ($z=z_0$).

$$I_n=\int_{z_i}^{z_c+\delta} dz\, z^{-1/4}e^{f(z)}H_n(\beta(z)) . \tag{4.7}$$

The function $f(z)$ has the form

$$f(z)=-z\left[1-\frac{2}{3}\left[\frac{z}{z_c}\right]^{1/2}\right]-\frac{z_c}{4}\left[1-\frac{z}{z_c}\right]^2 . \tag{4.8}$$

Using the eigenfunctions (4.3) in Eq. (3.26), the nth-state contribution to the nonstationary flux at r_c can be written in the form

$$\begin{aligned} J_n(r_c)={}&-2^{-9/4}D_0^{-3/4}z_c^{-5/4}c\Gamma W_{\mathrm{eq}}^{1/2}(r_c)c_n\\ &\times[H_n(0)+2^{5/2}z_c^{1/2}nH_{n-1}(0)] . \end{aligned} \tag{4.9}$$

Now, using the expression for the stationary flux, Eq. (3.3), and the eigenvalues λ_n,

$$\lambda_n=\frac{c\Gamma}{D_0 z_c}(n+1) , \tag{4.10}$$

we obtain the integrated flux

$$\begin{aligned} N(t)=J_{\mathrm{st}}\Bigg[t+\tfrac{1}{4}z_c^{1/4}\frac{D_0}{c\Gamma}e^{z_c/3} &\times\sum_{n=0}^{\infty}\frac{1}{(n+1)!}2^{-n}I_n\\ &\times[H_n(0)+2^{5/2}z_c^{1/2}nH_{n-1}(0)]\\ &\times(1-e^{-(c\Gamma t/D_0 z_c)(n+1)})\Bigg] . \end{aligned} \tag{4.11}$$

The initial conditions (slow versus fast quenches) enter through the I_n integral. We notice that the integrand in Eq. (4.7) is a monotonically decreasing function of z. Thus, the main contribution to the integrand comes from its lower limit, i.e., from z_i; and since z_i is inversely proportional to the speed of the quench, we expect larger contributions to I_n in the case of fast quenches. Let us proceed now to analyze the stationary flux for both slow and fast quenches.

A. Slow quenches, $z_i \to z_c$

In this case, the contribution to the integral, Eq. (4.7), comes from a narrow interval z_c-z_i. Expanding $f(z)$, Eq. (4.8), about z_c we obtain

$$f(z)\simeq-\frac{z_c}{3}+\frac{z_c}{4!}\frac{(z_c-z)^3}{z_c^3} ; \tag{4.12}$$

that is, the exponential in Eq. (4.7) varies very slowly close to z_c. Therefore, we can approximate the integral by taking the product of the integrand (at z_c) and the interval z_c-z_i. Using the properties of the Hermite polynomials,[16]

$$H_n(0)=\begin{cases}(-1)^{n/2}2^{m/2}(n-1)!!, & n=\text{even} \qquad (4.13)\\ 0, \quad n=\text{odd} & \qquad\qquad (4.14)\end{cases}$$

we obtain

$$I_n \simeq \begin{cases} z_c^{3/4}\left[1-\dfrac{z_i}{z_c}\right] e^{-z_c/3}(-2)^{n/2}[(n-1)!!], & n=\text{even} \qquad (4.15) \\ 0, & n=\text{odd} \; . \qquad (4.16) \end{cases}$$

Substitution into Eq. (4.11) yields

$$N(t)=J_{\text{st}}\left[t-\frac{1}{8}\frac{r_c^2}{c\Gamma}\left[1-\frac{\lambda^2}{r_c^2}\right] \times \sum_{\substack{n=0 \\ n=\text{even}}}^{\infty} \frac{[(n-1)!!]^2}{(n+1)!}\left(1-e^{(-2c\Gamma t/r_c^2)(n+1)}\right)\right] . \tag{4.17}$$

The summation is carried out in the Appendix. The resulting integrated flux is obtained by combining Eqs. (A3) and (A4):

$$N(t)=J_{\text{st}}\left[t-\frac{1}{8}\left[\frac{\pi}{2}\right]^{1/2}\frac{r_c^2}{c\Gamma}\left[1-\frac{\lambda^2}{r_c^2}\right] \times \operatorname{erf}\left[\left[\frac{2c\Gamma t}{r_c^2}\right]^{1/2}\right]\right] . \tag{4.18}$$

Notice that the integrand flux vanishes for very slow quenches, $\lambda \simeq r_c$.

B. Fast quenches, $z_i \to z_0$

Since the integrand in Eq. (4.7) is decreasing monotonically with z, most of the contribution comes from $z \to z_i$ and we can use as asymptotic expansion of the Hermite polynomials for large values of their argument[16]

$$H_n(\beta) \simeq (2\beta)^n , \tag{4.19}$$

where, since $z_i \ll z_c$,

$$\beta=\left[\frac{1}{2z_c}\right]^{1/2}(z-z_c) \simeq -\left[\frac{z_c}{2}\right]^{1/2} . \tag{4.20}$$

Similarly, neglecting terms of order $(z/z_c)^{3/2}$, we can approximate the exponent in the integrand of Eq. (4.7) by

$$e^{f(z)} \simeq e^{-z/2-z_c/4} , \tag{4.21}$$

leading to the integral

$$I_n \simeq (-1)^n (2z_c)^{n/2} e^{-z_c/4} \int_{z_i}^{z_c} dz\, z^{-1/4} e^{-z/2} . \tag{4.22}$$

The remaining integral can be evaluated,[17] giving

$$I_n \simeq 2^{3/4}\Gamma(\tfrac{3}{4})(-1)^n (2z_c)^{n/2} e^{-z_c/4} , \tag{4.23}$$

where the gamma function $\Gamma(\frac{3}{4})$ has been obtained by neglecting terms of order $e^{-z_c/2}$.

Substituting I_n, Eq. (4.23), into Eq. (4.11) for the integrated flux gives, after some rearrangements,

$$N(t)=J_{\text{st}}\left[t+\frac{\Gamma(\frac{3}{4})}{8}\frac{r_c^2}{c\Gamma}\left[\frac{4D_0}{r_c^2}\right]^{3/4} e^{z_c/12}\sum_{n=0}^{\infty}\frac{\left[-\left[\dfrac{z_c}{2}\right]^{1/2}\right]^n}{(n+1)!}[H_n(0)+2^{5/2}z_c^{1/2}nH_{n-1}(0)]\left(1-e^{-(2c\Gamma t/r_c^2)(n+1)}\right)\right] . \tag{4.24}$$

The n summation is performed in the Appendix. Using Eq. (A10), we obtain

$$N(t)=J_{\text{st}}\left[t-\Gamma(\tfrac{3}{4})\left[\frac{4r_c^2}{D_0}\right]^{1/4}\frac{D_0}{c\Gamma}e^{r_c^2/24D_0} \times \left\{\exp\left[-\frac{r_c^2}{4D_0}e^{-4c\Gamma t/r_c^2}\right]-\exp\left[-\frac{r_c^2}{4D_0}\right] -\frac{1}{4}\left[\frac{\pi D_0}{r_c^2}\right]^{1/2}\left[\operatorname{erf}\left[\left[\frac{r_c^2}{4D_0}\right]^{1/2}\right]-\operatorname{erf}\left[\left[\frac{r_c^2}{4D_0}\right]^{1/2}e^{-2c\Gamma t/r_c^2}\right]\right]\right\}\right] . \tag{4.25}$$

Comparing the slow- [Eq. (4.18)] and fast- [Eq. (4.25)] quench results, we see that the time lag associated with slow quenches is negligible with respect to that for fast quenches. This result has a simple physical meaning. Following the slow quench, the distribution of nuclei with radii $r<\lambda$ is very close to equilibrium and the approach to steady state is incomplete only in a narrow region, $\lambda<r<r_c$ ($\lambda \to r_c$). Therefore, in Sec. V, we will focus on the analysis of the fast-quench results.

V. TIME LAGS FOR FAST QUENCHES

We proceed with the analysis of the integrated flux, Eq. (4.25). It is convenient to rewrite this equation using the two dimensionless parameters

$$\mu=\frac{r_c^2}{2D_0} \quad\text{and}\quad \nu=2\Gamma(\tfrac{3}{4})\mu^{-3/4}e^{\mu/6}\;, \tag{5.1}$$

and the characteristic time

$$\tau=\frac{r_c^2}{4c\Gamma}\;. \tag{5.2}$$

We obtain

$$N(t)=J_{\text{st}}\left[t-\nu\tau\left[e^{-\mu e^{-t/\tau}}-e^{-\mu}-\frac{1}{4\mu^{1/2}}\int_{\mu^{1/2}e^{-t/2\tau}}^{\mu^{1/2}}e^{-x^2}dx\right]\right]\;, \tag{5.3}$$

where the term in the square brackets gives the contribution of the nonstationary flux. This term vanishes at $t=0$ and is negligible for $t>\nu\tau$. Thus, $\nu\tau$ is the time lag associated with the approach to steady state.

Expanding the nonstationary term in Eq. (5.3) in the two limiting cases $t\ll\tau$ and $t\gg\tau$, we obtain

$$N(t)\simeq\begin{cases}J_{\text{st}}(t-\nu\tau e^{-\mu}), & t\ll\tau & (5.4)\\ J_{\text{st}}(t-\nu\tau), & t\gg\tau\;. & (5.5)\end{cases}$$

As we can see from Eqs. (5.4) and (5.5) and Fig. 3, the integrated flux is almost everywhere linear in time, except for a narrow region close to $t=\tau$. Notice that the nonmonotonic behavior of the flux at short times $[t/\tau\sim O(1)]$ can be neglected since, as will be shown below, ν is exponentially larger than unity. Thus, the nonmonotonic region shrinks to a point on the diagram if Fig. 3 is drawn to scale.

The negative value of the integrated flux in Fig. 3, for $t<\nu\tau$, is closely connected with the time-lag phenomenon for nuclei of critical size. However, from mass-conservation considerations, it follows that the integral of the nonstationary flux, over nuclei of all sizes, must vanish. Thus, the nonstationary flux must be positive for nuclei of some sizes other than critical. This phenomenon has been studied by Abraham.[18]

The physically important feature appearing in Fig. 3 is the magnitude of the time lag $\nu\tau$. Let us estimate this time lag for some typical conditions in the shaded region of Fig. 1. Taking the surface tension $\sigma\simeq10^{-2}$ erg/cm^2 and $kT\simeq4\times10^{-14}$ erg (room temperature) and using Eq. (2.12), we obtain (in cm^2)

$$D_0\simeq3\times10^{-13}\;. \tag{5.6}$$

For a quench depth corresponding to a critical radius $r_c\simeq10^{-5}$ cm, using Eq. (5.1) we obtain

$$\mu\simeq150 \quad\text{and}\quad \nu\simeq4\times10^{6}\;. \tag{5.7}$$

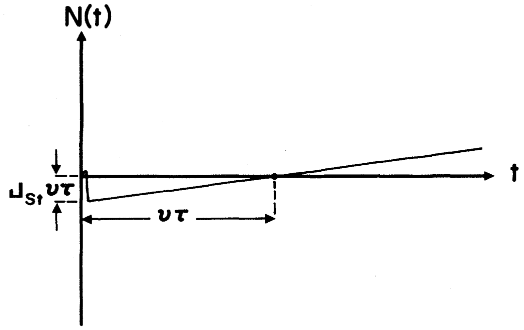

FIG. 3. Plot of the integrated flux $N(t)$ vs time. Time lag is indicated by $\nu\tau$. Nonmonotonic region at small t is blown out of scale.

Since $c\Gamma$ is at a distance of the order of the diffusion coefficient away from the critical point, we take $c\Gamma\simeq10^{-5}$ cm^2/sec and we use Eq. (5.2) to obtain (in seconds)

$$\tau\simeq10^{-5}\;, \tag{5.8}$$

and so the estimated time lag is (in seconds)

$$\nu\tau\simeq40\;. \tag{5.9}$$

As is well known in considerations of nucleation, time estimates are extremely sensitive to the parameters used. The most important parameter is μ, which, according to Eqs. (5.1) and (2.12), is proportional to $r_c^2\sigma/kT$ or, close to the critical point, r_c^2/ξ^2. The time lag depends exponentially upon this parameter and, therefore, physically reasonable time lags can be obtained only for comparatively small values of $(r_c/\xi)^2$; i.e., in the vicinity of the critical point but, at the same time, not too close to the coexistence curve.

VI. CONCLUSIONS

Although direct measurements of the flux $J(r,t)$ and the integrated flux $N(r,t)$ are prohibitively difficult under usual experimental conditions, indirect information about these quantities may be obtained experimentally. Most treatments of nucleation focus on the stationary relaxation regime. In this case, the decay time of the metastable state is J_{st}^{-1} and the integrated flux of nuclei along the size axis grows linearly in time. It is clear, however, that some time is necessary for the establishment of this stationary regime. All previous investigators[5] have estimated this time lag as proportional to $r_c^2/c\Gamma$ (in our notation).

Our treatment of nucleation in the critical region shows that it is essential to distinguish between cases of slow and fast quenches. While, for slow quenches our result, Eq. (4.18), is similar to that of previous treatments, we have obtained a strikingly different result for fast quenches.

In the case of fast quenches, the nonstationary part of the integrated flux, Eq. (4.25), is proportional to an exponentially large factor $\exp(r_c^2/24D_0)$. Accordingly, the time lag acquires a factor of

$$(D_0/r_c^2)^{3/4}e^{r_c^2/24D_0}$$

compared to the case of slow quenches. This new time scale may play an important role in the experimentally observed "slowing down" of the transition from metastable to stable states.

The drastic increase in the time lag has a simple physical interpretation. In the case of a fast quench, the cutoff factor λ in Eq. (3.27) is close to the correlation length ξ; i.e., only relatively small nuclei in equilibrium immediately following the quench. Therefore, it takes a long time for the nonstationary flux to prepare a steady-state distribution of nuclei of sizes from λ to r_c, and only after this time does the flux start to move in the direction of large-sized nuclei.

Following the Landauer-Swanson-Langer analogy[19,20] between the fluctuational decay of a metastable state and the quantum-mechanical tunneling through a potential barrier, we notice that the predicted kinetic effects associated with fast quenches have their counterparts in the predissociation of long-range diatomic molecules.[21] The latter phenomenon occurs when a molecule is excited to a manifold of high-vibrational states that are very close to the barrier to dissociation. Such states are characterized by large distances between the turning points for classical motion and, correspondingly, very long vibrational periods. If a localized combination of such states close to the inner turning point could be prepared by, say, Franck-Condon absorption of pulsed radiation from the ground state, a significant "population" would have to be transferred to the vicinity of the outer turning point prior to the establishment of the steady-state decay through the barrier. This would involve many vibrational periods and result in a considerable time lag in the dissociation process.

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APPENDIX

In order to perform the summation in Eq. (4.17) for the case of slow quenches, we introduce the following approximations.

(a) Use the Wallis formula[17]:

$$\frac{(n-1)!!}{n!!} \simeq \left[\frac{2}{\pi n}\right]^{1/2} . \tag{A1}$$

(b) Replace the sum by an integral:

$$\sum_{n=\text{even}}^{\infty} \frac{[(n-1)!!]^2}{(n+1)!} \left[1-e^{-(c\Gamma t/D_0 z_c)(n+1)}\right] \simeq \pi^{-1/2} \int_0^\infty dx[(2x+1)x^{1/2}]^{-1} \times (1-e^{-(c\Gamma t/D_0 z_c)(2x+1)}) . \tag{A2}$$

The first integral is easily computed[16]:

$$\int_0^\infty dx[(2x+1)x^{1/2}]^{-1} = \frac{\pi}{2^{1/2}} . \tag{A3}$$

The second integral can be represented in terms of the error function, i.e.,[16]

$$\int_0^\infty dx[(2x+1)x^{1/2}]^{-1} e^{-(c\Gamma t/D_0 z_c)(2x+1)} = \frac{\pi}{2^{1/2}} \left[1-\operatorname{erf}\left[\left[\frac{c\Gamma t}{D_0 z_c}\right]^{1/2}\right]\right] . \tag{A4}$$

In the case of fast quenches, we have to compute the sum in Eq. (4.24). We introduce a generating function $f(x;t,\alpha)$,

$$f(x;t,\alpha) = \sum_{n=0}^{\infty} \frac{1}{n+\alpha} \frac{t^n}{n!} H_n(0) e^{x(n+\alpha)} . \tag{A5}$$

The four sums in Eq. (4.24) can be represented in the form $f(0;t,\alpha)$. Taking the derivative of f and performing the resulting summation, we obtain

$$\frac{\partial f(x;t,\alpha)}{\partial x} = e^{\alpha x} \sum_{n=0}^{\infty} \frac{(te^x)^n}{n!} H_n(0) = e^{\alpha x} e^{-t^2 e^{2x}} . \tag{A6}$$

Integration of Eq. (A6) and taking the limit $x \to 0$ yields

$$f(0;t,\alpha) = \alpha^{-1} \int_0^1 dy\, e^{-t^2 y^{2/\alpha}} . \tag{A7}$$

In our case [Eq. (4.24)], we have $\alpha = 1$ and 2. For $\alpha = 1$, we obtain

$$f(0;t,\alpha) = \frac{\pi^{1/2}}{2|t|} \operatorname{erf}(|t|) , \tag{A8}$$

and for $\alpha = 2$ we obtain

$$f(0;t,\alpha) = \frac{1}{2t^2}(1-e^{-t^2}) . \tag{A9}$$

After some simple algebra, we arrive at the final result:

$$\sum_{n=0}^{\infty} \frac{[(-z_c/2)^{1/2}]^n}{(n+1)!} [H_n(0) + 2^{5/2} z_c^{1/2} n H_{n-1}(0)](1-e^{-(c\Gamma t/D_0 z_c)(n+1)}) = \left[\frac{\pi}{2z_c}\right]^{1/2} \left[\operatorname{erf}\left[\left[\frac{z_c}{2}\right]^{1/2}\right] - \operatorname{erf}\left[\left[\frac{z_c}{2}\right]^{1/2} e^{-(c\Gamma t/D_0 z_c)}\right]\right] + 4(e^{-z_c/2} - e^{-(z_c/2)} e^{-(2c\Gamma t/D_0 z_c)}) . \tag{A10}$$

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[1] *Nucleation,* edited by A. C. Zettlemoyer (Dekker, New York, 1969).

[2] K. Binder and D. Stauffer, Adv. Phys. 25, 343 (1976).

[3] J. S. Langer and L. A. Turski, Phys. Rev. A 8, 3230 (1973).

[4] A. Z. Patashinskii and B. I. Shumilo, Zh. Exp. Teor. Fiz. 77, 1417 (1979) [Sov. Phys.—JETP 50(5), 712 (1979)].

[5] R. F. Probstein, J. Chem. Phys. 19, 619 (1951); A. Kantorovitz, *ibid.* 19, 1097 (1951); H. Wakeshima, *ibid.* 22, 1614 (1954); F. C. Collins, Z. Electrochem. 59, 404 (1955); D. Kashchiev, Surf. Sci. 14, 209 (1969); J. Feder, K. G. Russell, J. Lothe, and G. M. Pound, Adv. Phys. 15, 117 (1966).

[6] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. 49, 435 (1977).

[7] In the kinetic Ising model, the conserved and nonconserved order parameters correspond to the dynamics events of the exchange of two neighboring spins and the flopping of a spin, respectively.

[8] The transition from Eq. (2.2) to Eq. (2.5) involves the kind of approximations that are usually made in considerations of quasistatic solutions of nonlinear equations for the so-called solitons, kinks, domain walls, etc.

[9] S. Fisk and B. Widom, J. Chem. Phys. 50, 3219 (1969).

[10] In our case, the nuclei are considered to be large with respect to the correlation length, and we expect no problems with the applicability of the macroscopic concept of surface tension.

[11] Equation (2.5) describes the spherical-symmetric nuclei. It has been shown in Ref. 4 that nonspherical harmonics will decay rapidly in time; i.e., the nuclei become spherical, thus assuming the most energetically favorable configuration for the given amount of a new phase.

[12] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebowitz (Academic, New York, 1983), Vol. VIII, p. 269.

[13] W. Feller, *An Introduction to Probability Theory and Its Application* (Wiley, New York, 1957).

[14] This is no longer the case in the second growth stage, during which the explicit time dependence of $F(r)$ and of the boundary conditions must be taken into account. This stage is considered by J. S. Langer and A. J. Schwartz, Phys. Rev. A 21, 948 (1980).

[15] L. I. Schiff, *Quantum Mechanics,* 3rd ed. (McGraw-Hill, New York 1955).

[16] I. S. Gradstein and I, M. Ryshik, *Table of Integrals, Series and Products* (Academic, New York, 1965).

[17] *Handbook of Mathematical Functions,* edited by M. Abramowitz and L. A. Stegun, National Bureau of Standards Applied Mathematics Series (U.S. GPO, Washington, D.C., 1970).

[18] F. Abraham, J. Chem. Phys. 51, 1632 (1969).

[19] R. Landauer and J. A. Swanson, Phys. Rev. 121, 1668 (1961).

[20] J. S. Langer, Ann. Phys. 54, 258 (1969).

[21] W. C. Stwalley, Contemp. Phys. 19, 65 (1978).