

## Nucleation and growth with periodic modulation: Asymptotic versus exact results

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(Received 5 August 1993)

We consider the nucleation and growth of cavities in a metastable viscous liquid with a periodically modulated pressure. Growth is described from the continuity equation with a source of supercritical nuclei. The solution is matched in an asymptotically smooth manner with the solution of the time-dependent Fokker-Planck equation describing nucleation. It is shown that as a function of the driving frequency the time-dependent flux of nuclei undergoes a characteristic transition. The transition marks the abrupt breakaway from the adiabatic regime. An exactly solvable model of nucleation and growth is introduced which confirms the asymptotic analysis.

PACS number(s): 64.60.Qb

### I. INTRODUCTION

Noisy nonlinear systems which are being perturbed periodically have recently been in the limelight of both theoretical and experimental studies [1]. Usually, the focus has mainly been on bistable and multistable systems. However, equally important effects can be expected for nucleating systems possessing only one metastable well. In clear contrast to bistable systems, nucleation is characterized by the fact that particles can proceed to infinity. Naturally, the growth to large sizes assumes large time scales. This means that even for arbitrary slow modulation of the barrier there will always exist sizes where at least the effects of retardation will become crucial.

In experimental studies of nucleation and related phase-transformation processes modulation effects can be induced by ultrasonic waves in a metastable liquid [2], can result due to a modulated microwave field affecting condensation of an electron-hole liquid [3], or are being induced by sound waves which periodically change the temperature of a binary mixture [4]. A single or double quench, which by now has become almost a standard tool in various studies of nucleation [5], can also be considered as a corresponding limit of the driving process if the time after the switch on is smaller than the period of modulation.

The main purpose of this work is the determination of the flux of growing particles and their distribution over sizes under periodic modulation of the parameters describing nucleation and growth. In Secs. II–IV we present the asymptotic analysis of the problem with the large parameters being the nucleation barrier and the size of the particles.

Another objective of this work is the exactly solvable “imitation” of the modulated nucleation-growth problem. This is presented in Sec. V. It is known that for an analytic form of the barrier exact consideration is possible only in the parabolic case corresponding to the time-dependent Ornstein-Uhlenbeck equation [6]. The main difficulty here is that any attempt to construct a boundary which would prevent the size of particles from

becoming negative ruins the exact solvability [7]. Instead, we introduce a permanent source of particles of the smallest size, making the formulation of the problem somewhat similar to a scattering problem. Remarkably enough, in the physically related region of large sizes this turns out to be an almost precise reproduction of the nucleation situation. This allows us to verify and to refine the asymptotic analysis. In addition, we expect that the proposed model may be of independent interest as exact results with nontrivial time dependence are in short supply in description of phase transitions and related processes [8].

As a particular physical example we shall consider cavitation in a viscous fluid, first discussed in the nucleation context in Ref. [9], and more recently in Ref. [10]. Compared to other models which are often employed in the description of nucleation, the cavitation model turns out to be the closest one to the exactly solvable situation (see Sec. V). We expect, however, that the main results will hold (or require only minor modifications) for other models too. This is further addressed in more detail in Sec. VI.

### II. THE GROWTH MODEL AND BASIC ASSUMPTIONS

Consider a liquid under a negative pressure  $P(t)$ . The temperature  $T$  is assumed to be sufficiently low so that the equilibrium vapor pressure is negligibly small compared to  $|P|$ . In this case a “particle” of a new phase is an empty bubble (cavity) of radius  $x$ . The negative pressure tends to expand the cavity, while the surface tension  $\sigma$  forces it to shrink. Neglecting inertial effects, which we estimate later, the work produced by the difference of these two forces equals the dissipation of energy due to viscosity,  $\eta$ . This gives [9]

$$\dot{x} = [x - x_*(t)]/\tau. \quad (1)$$

Here  $x_*(t) = 2\sigma/|P|$  is the critical radius and  $\tau = 4\eta/|P|$  is the “relaxation time.” We consider a small sinusoidal modulation of pressure around its average value  $\bar{P} < 0$ . As mentioned in the Introduction, the latter can be pro-

duced by ultrasonic waves. In this case one has

$$x_*(t) = \bar{x}_* \{1 - \varphi(t)\}, \quad \varphi(t) = A \sin(\omega t + \Phi_0) < 1, \quad (2)$$

with  $\bar{x}_* = 2\sigma/|\bar{P}|$ . Throughout this work, unless mentioned otherwise, we restrict the modulating frequencies to a regime  $\omega\tau \ll 1$ . This does not mean, however, that the time-dependent effects considered are weak, as the system turns out to be extremely sensitive to the values of the time derivative of the critical size,  $\dot{x}_*(t)$ . On the other hand, the possible effects of the time dependence of  $\tau$  in Equation (1) can be shown to be minor, and in what follows we shall treat it as a constant.

Now suppose that particles are produced with intensity  $I(t)$  ("nucleation rate") by a source of nuclei at some *supercritical* size  $x_0$ . We assume that the source is switched on at  $t=0$ , i.e.,  $I(t < 0) \equiv 0$ . An explicit expression for  $I(t)$  will be derived in Sec. IV after considering nucleation. For the purposes of matching of the solution of Eq. (1) with the nucleation solution, it is reasonable to select the value of  $x_0$  as close to  $x_*$  as possible. There are, however, two restrictions: First, fluctuational corrections to the deterministic growth rate (1) should still be negligible. We discuss this in more detail after incorporating fluctuations in the nucleation picture. Second, the initial growth rate should be much larger than  $\dot{x}_*$ , so that the nucleated particle is not consumed by the critical size. This implies  $x_0 - x_* \gg |\dot{x}_*|\tau$ . In Sec. IV we show that both restrictions lead to a *microscopic* length scale which separates  $x_0$  and  $x_*$  and which does not enter the deterministic growth equation (1). Thus on certain stages of the derivation of the growth solution we will be able to consider the limit  $x_0 \rightarrow x_*$ .

Equation (1) can be integrated explicitly, giving

$$x(t) = x_0 \exp \left[ \frac{(t-t_0)}{\tau} \right] - \frac{\int_{t_0}^t x_*(t') \exp\{(t-t')/\tau\} dt'}{\tau}. \quad (3)$$

Here  $t_0$ , obeying  $0 < t_0 < t$ , is the time of nucleation of the particle, so that  $x(t=t_0) = x_0$ . Equation (3) relates three quantities  $x$ ,  $t$ , and  $t_0$ . In principle, any pair of them can be chosen as independent variables. We choose for such a pair  $x$  and  $t$ , so that Eq. (3) is an equation for the nucleation time  $t_0(x, t)$ . Due to the assumed condition  $I(t_0 < 0) = 0$ , a negative value of  $t_0$  for a given pair of  $x, t$  means that at time  $t$  there will still be no particles with size  $x$  or larger.

Due to the assumed condition  $\omega\tau \ll 1$ , at large times  $t - t_0 \gg \tau$  the main input to the integral in Eq. (3) is dominated by the lower limit of integration, so that

$$x(t) \approx [x_0 - x_*(t_0)] \exp\{(t-t_0)/\tau\}. \quad (3')$$

Note that the mentioned restriction  $x_0 - x_* \gg \tau|\dot{x}_*|$  allows us to neglect the higher-order terms in the expansion of (3). Once, however, Eq. (3) is obtained, one can, at least formally, discuss the limit  $x_0 \rightarrow x_*$ . In this limit  $t_0(x, t)$  exhibits a singularity—an important feature which crucially determines the method of matching with

the nucleation solution (Sec. IV).

The distribution of nuclei over sizes,  $f(x, t)$ , in the growth region satisfies the continuity equation  $\partial f / \partial t = -\partial j_{\text{dr}} / \partial x$  with  $j_{\text{dr}} = \dot{x}f$  being the deterministic (drift) flux. At  $x = x_0$  the flux  $j_{\text{dr}}(x, t)$  coincides with the nucleation rate  $I(t)$ . This serves as the boundary condition for the continuity equation. Integration of this equation along the growth trajectory  $x = x(t)$  gives

$$j_{\text{dr}}(x, t) = I(t_0) \exp \left\{ - \int_{t_0}^t dt' \frac{\partial \ln \dot{x}}{\partial t'} \Big|_{x=x(t')} \right\}. \quad (4)$$

From Eq. (3') one can see that the integral in Eq. (4) converges as  $t \rightarrow \infty$ . Thus, with the integrand being proportional to  $\omega\tau$ , this integral remains small at all times. Hence, Eq. (4) can be replaced by the simpler relation

$$j_{\text{dr}}(x, t) \approx I(t_0(x, t)), \quad (5)$$

which resembles the standard relation for time-independent growth.

Equation (5) determines the flux  $j(x, t)$  via determination of the initial time  $t_0$  from Eq. (3'). Due to the mentioned singularity of  $t_0$ , one still has to ensure that the expression  $I(t_0)$ , with  $I(t)$  determined by the nucleation equation, remains nonsingular as  $x_0 \rightarrow x_*$ .

### III. NUCLEATION

In the above description of deterministic growth we neglected the diffusion component of the flux  $-D\partial f / \partial x$  with  $D$  being the diffusion coefficient. This component, however, becomes crucial at small sizes where it accounts for nucleation, i.e., the "uphill" motion of particles at  $x < x_*$ . In this case one has to consider the general Fokker-Planck equation [9]

$$\frac{\partial f}{\partial t} = -\frac{\partial j}{\partial x}, \quad j = -D\frac{\partial f}{\partial x} + \dot{x}f. \quad (6)$$

Here  $\dot{x}$  is the abbreviated notation for the deterministic growth rate given by Eq. (1), although in the present section we will not use its specific form but only the fact that  $\dot{x}$  changes its sign at the critical size. The inverse of the relaxation time,  $\tau^{-1}$ , should thus be understood as  $\partial \dot{x} / \partial x$  at  $x = x_*$ . The value of  $f(x=0)$ , the distribution at the smallest sizes, is assumed to be known in nucleation theory and can be considered as the left-hand boundary condition. The right-hand boundary condition can be written as  $j(x, t) \rightarrow j_{\text{dr}}(x, t)$ , approaching the deterministic growth of nucleated particles. The values of  $x$  at which this boundary condition should be considered can have arbitrary large values. However, it is absolutely impractical to extend Eq. (6) into the region of large sizes where the incomparably simpler continuity equation can be applied. Thus we shall restrict the region of overcritical sizes by the condition  $x - x_* \ll x_*$ , which turns out to be sufficient for matching with the growth solution obtained in Sec. II.

The diffusion coefficient of Eq. (6), being both size and time dependent, can be obtained from the Einstein relation  $\dot{x} = -(D/kT)\partial W / \partial x$ . Here  $W$  is the minimal work required to create a cavity of a given size under the

current pressure  $P(t) < 0$ , i.e.,

$$W(x;t) = 4\pi x^2 \sigma + (4\pi/3)x^3 P(t). \quad (7)$$

The value of the nucleation barrier  $W_*(t) = (4\pi/3)x_*^2 \sigma$  is assumed to be always larger than the thermal energy  $kT$ . Formally, an equilibrium distribution  $N(x;t) = f(x=0,t) \exp\{-W/kT\}$  which corresponds to zero values of the flux in Eq. (6) can be introduced. This distribution, however, does not satisfy the right-hand boundary conditions and will be used only for auxiliary purposes.

For a time-independent potential the steady-state solution of Eq. (6) corresponds to a size-independent adiabatic flux  $j(x,t) \equiv j_{\text{ad}}$  (see Ref. [9]) with

$$j_{\text{ad}} = \frac{\Delta}{2\tau\sqrt{\pi}} f(x=0) \exp\left\{-\frac{W_*}{kT}\right\},$$

$$\Delta^{-2} = -\frac{1}{2kT} \frac{\partial^2 W}{\partial x^2} \Big|_{x=x_*}. \quad (8)$$

The quantity  $\Delta$  related to the curvature of the barrier near its top naturally arises in the Kramers-type barrier crossing problems. It also determines the region around the critical size where fluctuational corrections to the deterministic growth Eq. (1) are important.

One may expect that for sufficiently slow, adiabatic processes the flux will be almost the same as given by Eq. (8) with the parameters in this equation having their current time-dependent values. Here, however, one recovers an essential drawback of the steady-state solution. The flux (8) is size independent and one cannot expect that it can be matched with the size-dependent flux given by Eq. (5) which exhibits a singularity. Thus one has to take into account the explicit time dependence of the nucleation process.

We shall treat Eq. (6) asymptotically in the spirit of matched asymptotic expansions [11], although the fact that it is a *partial* differential equation adds, of course, additional complications. The small parameter is  $\epsilon = \Delta/x_* \sim (W_*/kT)^{-1/2}$ .

By switching to the reduced variable  $y = x/x_*$  and function  $v(y,t) = f(x,t)/N(x;t)$  one can cast Eq. (6) in the form

$$\tau \frac{\partial v}{\partial t} = \frac{1}{2} \epsilon^2 \frac{\partial}{\partial y} \frac{D}{D_*} \frac{\partial v}{\partial y} + \tau \dot{y} \frac{\partial v}{\partial y} - n v y^3 + O(n\epsilon^2). \quad (9)$$

Here  $D_* \equiv D(y=1)$ ,  $\dot{y} \equiv \dot{x}/x_*$  and we introduced a dimensionless parameter  $n$  to characterize the rate of the barrier change, i.e.,

$$n = -\tau \frac{\partial W_*}{\partial t} \frac{1}{kT} \approx n_{\text{max}} \cos(\omega t + \Phi_0), \quad (10)$$

with

$$n_{\text{max}} = 2A\omega\tau\bar{W}_*/kT, \quad \bar{W}_* = (4\pi/3)\bar{x}_*^2\sigma. \quad (11)$$

Note that despite the assumed condition  $\omega\tau \ll 1$ , the value of  $n_{\text{max}}$  is not necessarily small as it contains a large factor  $\bar{W}_*/kT$ . We, nevertheless, assume that  $n_{\text{max}}$  has moderate (nonasymptotic) values so that the term  $O(n\epsilon^2)$

in Eq. (9) which contains only first-order derivatives in  $y$  [12] can be neglected. The boundary conditions for Eq. (9) have the form  $v(0,t) = 1$ , and  $\partial \ln v / \partial y \rightarrow -2(y-1)/\epsilon^2$  for  $y-1 \gg \epsilon$ . The left-hand boundary condition is completely time independent, and for the situation considered with  $\omega\tau \ll 1$ , the right-hand boundary condition depends on time very weakly. The latter is also true for the coefficients of Eq. (9). Thus it may seem reasonable to neglect the time derivative in this equation once it is applied only for moderate sizes  $y \lesssim 1$ . In this case the process can be described as a "quasi-steady-state" process with deviation from the true steady state determined by the parameter  $n$  [12]. It turns out, however, that neglecting the time derivative may fail for sufficiently large negative values of  $n$  which are inevitably encountered for  $n_{\text{max}} > 1$ . To account for such situations a more general treatment is required.

Consider the switch on of the process at  $t=0$ . The coefficients of Eq. (9) at that instant have well-defined values. Moreover, these values will not change noticeably during time intervals which are small compared to the modulation period. On the other hand, due to the assumed condition  $\omega\tau \ll 1$  such intervals can still be large compared to  $\tau$ . For such coefficients one can perform the Laplace transformation of Eq. (9) with respect to time:

$$\frac{1}{2} \epsilon^2 \frac{d}{dy} \frac{D}{D_*} \frac{dV}{dy} + \tau \dot{y} \frac{dV}{dy} = (m + n y^3) V, \quad (12)$$

with  $V(y,p)$  being the Laplace transform of  $v(y,t)$ , and  $m \equiv p\tau$ . The above equation has a boundary layer near  $y=1$  where the deterministic growth rate  $\dot{y}$  changes its sign. Being an *ordinary* differential equation, it can be solved by standard methods [12]. The left-hand boundary condition is now given by  $V(0,p) = 1/p$ , so that the outer solution at  $0 \leq y < 1$  takes the form

$$V^{\text{out}}(y,p) = \frac{1}{p} \exp\left[\int_0^y \frac{dy(m + n y^3)}{\tau \dot{y}}\right]$$

$$\xrightarrow{y \rightarrow 1} \frac{1}{p} (1-y)^{m+n} \exp(mC' + nC), \quad (13)$$

with

$$C = \int_0^1 du \left[ \frac{y^3}{\tau \dot{y}} - \frac{1}{y-1} \right], \quad C' = \int_0^1 dy \left[ \frac{1}{\tau \dot{y}} - \frac{1}{y-1} \right]. \quad (14)$$

Note that from the definition of  $\tau$  one has  $\tau \dot{y} \rightarrow y-1$ , as  $y \rightarrow 1$ , so that the integrals in Eq. (14) converge.

In the direct vicinity of  $y=1$  we switch to the inner variable  $z = (y-1)/\epsilon$ . In the leading order in  $\epsilon$  one thus obtains from Eq. (12) a standard equation for repeated error functions defined by  $i^{m+n} \text{erfc}(z)$  (see Ref. [13(a)]). Thus the inner solution is given by

$$V^{\text{in}}(z,p) = \frac{1}{2m} \tau \epsilon^{m+n} e^{mC' + nC} e^{z^2}$$

$$\times \Gamma(m+n+1) i^{m+n} \text{erfc}(z), \quad (15)$$

where the proportionality coefficient is obtained through

matching of asymptotes of the inner and outer solutions [12]. To derive the nucleation rate one needs the flux. From its definition in Eq. (6) one has in the inner region  $j^{\text{in}}(z, t) = -j_{\text{ad}}(t)\sqrt{\pi}e^{z^2}\partial v/\partial z$ . On the other hand, from the definition of  $n$  in Eq. (10) one has for the time intervals considered  $j_{\text{ad}}(t) \approx j_{\text{ad}}(0)\exp(nt/\tau)$ . This shifts the Laplace index  $m$  by the value  $n$ . Thus one obtains for the Laplace transform of the flux  $J$

$$\begin{aligned} J^{\text{in}}(z, p) &= -j_{\text{ad}}(0)\sqrt{\pi}e^{z^2}\frac{\partial}{\partial z}V^{\text{in}}(z, p - n/\tau) \\ &= j_{\text{ad}}(0)\frac{\tau\sqrt{\pi}}{2(m-n)}\epsilon^m e^{mC' + n(C-C')}e^{z^2} \\ &\quad \times \Gamma(m+1)i^{m-1}\text{erfc}(z). \end{aligned}$$

Further, we need the asymptote of this expression at large  $z$  which after inversion can be matched with the equations describing the growth (Sec. IV). Using the expansion of the repeated error function [13(a)] one obtains

$$\begin{aligned} J^{\text{in}}(z \gg 1, p) &= j_{\text{ad}}(0)\frac{\tau}{m-n}\Gamma(m+1) \\ &\quad \times \exp\{n(C-C') - mt_i(z)\}. \end{aligned} \quad (16)$$

Here  $t_i(z)$  denotes the ‘‘incubation time’’ [12]

$$t_i(z) = \tau \left\{ \ln \frac{2z}{\epsilon} - C' \right\}, \quad (17)$$

which has the meaning of the time when the unmodulated flux ( $n \equiv 0$ ) acquires  $1/e$  of its steady-state value.

In derivation of Eq. (16) we used asymptotic methods which implied finite values of  $p$ . This restricts the region of validity of this equation to the finite part of the complex  $p$  plane. If, however, one is not concerned with an asymptotically short time interval after the switch on, one can invert Eq. (16) considering the residues solely at finite values of  $p$ . This leads to

$$\begin{aligned} j(x, t) &= j_{\text{ad}}(t - t_i(x)) \\ &\quad \times \Gamma \left[ n(0) + 1, \exp \left[ -\frac{t - t_i(x)}{\tau} \right] \right] \\ &\quad \times \exp\{n(0)(C - C')\}, \end{aligned} \quad (18)$$

with  $\Gamma(a, x)$  being the incomplete ‘‘gamma’’ function [13]. The above expression is valid during a time interval  $\tau \lesssim t \ll \omega^{-1}$ . Note that the values of  $n(0)$  can be replaced by  $n(t)$ , because during such time intervals this value does not change noticeably. The particular form of Eq. (18) crucially depends on the fact that we started from the instant of the switch on—there are no particles at  $t < 0$ . On the other hand, one may suspect that at relatively large times  $t - t_i(x) \gg \tau$  the system ‘‘forgets’’ the initial distribution. Thus the large time asymptote of Eq. (18) with  $n(t)$  substituted instead of  $n(0)$  can be used to evaluate the flux  $j(x, t)$  at arbitrary times. Depending on the current value of  $n(t)$  two situations can arise, i.e.,

$$j(x, t) = j_{\text{ad}}(t - t_i(x))\Gamma(n+1)\exp[(C - C')n], \quad n > -1, \quad (19)$$

$$j(x, t) \sim \exp \left\{ -\frac{t - t_i(x)}{\tau} \right\}, \quad n < -1. \quad (20)$$

The former corresponds to the quasi-steady-state regime of Refs. [10,12]; the latter describes a qualitatively new regime of exponential decay. The reason for this decay is that the flux cannot drop off more rapidly than  $\exp(-t/\tau)$  and it stops tracing the adiabatic flux as soon as the latter requires faster changes. We also note here that the asymptotic dependencies (19) and (20) can be extracted directly from consideration of the right-hand singularity of the Laplace transform (16) avoiding its inversion.

#### IV. MATCHING OF THE NUCLEATION AND GROWTH SOLUTIONS: RESULTS AND DISCUSSION

As discussed in Sec. II, the initial size  $x_0$  from which one starts the deterministic growth of nucleated particles should be large enough to (a) neglect fluctuations and (b) ensure that the initial growth rate is much larger than  $|\dot{x}_*|$ . The former requirement leads to  $x_0 - x_* \gg \Delta$ . The latter, (b), is satisfied for a much weaker condition  $x_0 - x_* \gg |n|\epsilon\Delta$ . This follows from the relation between  $x_*$  and  $W_*$  and the definition of  $n$ . If, on the other hand, this initial size  $x_0$  is still sufficiently close to the critical size  $x_*$ , i.e.,  $x_0 - x_* \ll x_*$ , one can apply the nucleation solution derived in the preceding section. In the region  $\Delta \ll x_0 - x_* \ll x_*$  the value of the flux  $j(x, t)$  in Eqs. (19), (20) with  $x = x_0$  and  $t = t_0$  can be associated with the nucleation rate  $I(t_0)$  in Eq. (5). Due to the mentioned restriction on  $x_0$  the time interval  $t_i(x_0)$  is small compared to the modulation period. Thus, the values of  $n$  in Eqs. (19), (20) can be evaluated at  $t_0 - t_i(x_0)$ , which is at the same instant at which one evaluates the adiabatic flux. This makes the result a function of a unique combination of  $t$  and  $x$  given by the above difference  $t_0 - t_i(x_0)$ . Note that the latter is *nonsingular* with respect to  $x_0$ , as the singularities encountered in expressions for  $t_0$  [Eq. (4)] and  $t_i(x_0)$  [Eq. (17)] compensate each other. The final result for the flux of particles at any size in the growth region takes the form

$$j_{\text{dr}}(x, t) = j_{\text{ad}}(\tilde{t}_0)\Gamma[n(\tilde{t}_0) + 1], \quad n(\tilde{t}_0) > -1, \quad (21)$$

$$j_{\text{dr}}(x, t) \sim \exp(-\tilde{t}_0/\tau), \quad n(\tilde{t}_0) < -1. \quad (22)$$

Here

$$\tilde{t}_0(t, x) = t - \tau \ln \left[ 2 \left( \frac{x_*}{\Delta} \right)^2 \right] - \tau \ln \left[ \frac{x}{x_*} \right] + C \quad (23)$$

can be treated as the (nonsingular) time of nucleation of a particle which grows to size  $x$  at the time  $t$ . The constant  $C$  defined by Eq. (14) equals  $\frac{11}{6}$ . Note that for sufficiently small frequencies the values of  $n < -1$  will not be encountered at all, so that the flux at any instant is deter-

mined by Eq. (21). We call this the “quasiadiabatic” regime: Except for the factor given by the  $\Gamma$  function the flux follows the periodic modulation of the barrier although with a time shift,  $t - \tilde{t}_0$ . The shift can be arbitrarily large for large  $x$ . For larger frequencies leading to  $n_{\max} > 1$ , the system switches to exponential decay during a part of the period. Formally, the inapplicability of the quasiadiabatic description at this stage is indicated by the singularity of the  $\Gamma$  function in Eq. (21). A detailed discussion and illustration of such “nonanalytic” effects will be given in the next section. At present we note that the flux consists of asymmetric peaks which are nonuniformly distributed along the size axis, each peak moving with its own rate  $\dot{x}$  (of course, these peaks are periodic in time). The maxima of all the peaks (except, possibly, the first one) are given by  $j_{\text{ad}}^{\max}$ , which corresponds to the minimal value of the nucleation barrier. The number of particles per modulation period will be evaluated in Sec. V. For amplitudes which are larger than  $(W_*/kT)^{-1}$  the peaks are very well separated from each other. Otherwise, they overlap, forming in the limit  $A \rightarrow 0$  a size-independent constant given by Eq. (8) with a cutoff (“front”) at some value  $x_{\max}(t)$  which is the root of the equation  $\tilde{t}_0(t, x) = 0$ . The shape of this front was described previously [12] and in the limit  $n \rightarrow 0$  it also follows from the more general expression for the first peak which we derive below.

The first peak is of special interest as it provides the earliest indication of the decay of the metastable state and which can be the only peak that can be observed in the system for very small  $\omega$ . In the same manner as we derived Eqs. (21), (22) from Eqs. (19), (20) one can derive the flux from the more detailed expression given by Eq. (18), obtaining

$$j_{\text{dr}}(x, t) = j_{\text{ad}}(\tilde{t}_0) \Gamma[n(0) + 1, e^{-\tilde{t}_0(x, t)/\tau}], \quad (24)$$

with  $n(0) = n_{\max} \cos \Phi_0$ . If one starts with  $n(0) \geq 0$ , the first peak will have the same height as the other ones, otherwise it will be smaller. Note that for sufficiently small times, or large sizes, the values of  $\tilde{t}_0(t, x)$  are negative. No particles were nucleated at negative times, which is signified by the asymptotically small values of the incomplete  $\Gamma$  function in Eq. (24). The condition  $\tilde{t}_0(t, x) = 0$  determines the position of the front part of the first peak,  $x_{\max}(t)$ , while Eq. (24) determines the shape of this front.

We now consider the distribution of particles over sizes given in the growth region by  $f(x, t) = j_{\text{dr}}(x, t) / \dot{x}$ . As seen from Eqs. (21) and (23), in the quasiadiabatic regime the distribution is a *monotonously* decaying function of  $x$  for any permissible driving amplitude. This is a direct consequence of the specific growth rate (1), and we shall discuss alternative possibilities which lead to a nonmonotonous distribution with “humps” later. The distribution which corresponds to the exponential decay turns out to be *size independent* for large  $x$ , as seen from Eqs. (22) and (23). In Fig. 1 we qualitatively verify the above conclusions by plotting the distribution from an exactly solvable model which we describe in the next section. Actually, this model leads to a different constant  $C$  in Eq. (23),

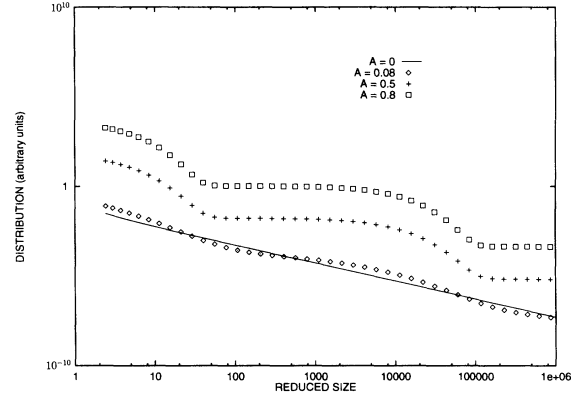


FIG. 1. Distribution of growing particles over reduced sizes,  $x/\bar{x}_*$  for different driving amplitudes. An exact solution of Sec. V was used with the following parameters:  $\bar{W}_*/kT = 10$ ,  $\omega\tau = 0.8$ ,  $t/\tau = 20$ ,  $\Phi_0 = 0$ .

but at the moment we use the exact results only for illustration, postponing the more detailed comparison until Sec. V. For small modulations ( $A = 0.08$  in Fig. 1) the distribution is slightly modulated around its steady-state value  $\sim 1/(x - \bar{x}_*)$ . It, however, still remains a monotonous function of size. With increasing amplitude the distribution becomes larger as more particles are produced during the part of the period with the smallest barrier. One also clearly detects regions with practically constant distribution, which corresponds to exponential decay.

When considering the principal possibility of experimental observation of the distribution of this kind, note that the span of sizes which corresponds to one period of modulation is given by  $\exp(2\pi/\omega\tau)$ . Even keeping in mind the large difference between the size of the critical bubble (of the order of nanometers in homogeneous nucleation) and the size of the bubbles which are usually observed, one has to admit that for small values of  $\omega\tau$  only particles produced within one modulation period can be observed simultaneously. This conclusion is due to the exponentially fast growth predicted by Eq. (1). To assess limitation of this growth law recall that in Eq. (1) we neglect the inertia of the liquid. Estimations can be made from the fact that the kinetic energy of an incompressible liquid around a growing cavity is given by  $4\pi x^3 \rho \dot{x}^2$  [14] with  $\rho$  being the density of the liquid. Neglecting viscosity and surface tension effects for sufficiently large sizes, this energy is due to the work of the negative external pressure  $P$ . This gives  $\dot{x}^{\text{inert}} \sim (-P/\rho)^{1/2}$ . The crossover from viscous growth described by Eq. (1) to growth limited by inertia takes place at  $x \sim \bar{x} = \eta(-P\rho)^{-1/2}$ . Being, unlike Eq. (1), size independent, the inertia-limited growth brings the problem much closer to typical models of nucleation discussed, e.g., in connection with condensation of vapor or in materials science [15]. The above results for the drift flux to a large extent will hold with  $\tilde{t}_0(x, t)$  in Eq. (23) replaced by  $\tilde{t}_0(x, t) - \tau x / \bar{x}$ . The distribution, however, will qualitatively change. The steady-state distribution in this case is constant for large  $x$ , and upon modulation it will be a *periodic* function of size.

**V. EXACTLY SOLVABLE MODEL OF NUCLEATION AND GROWTH**

Let us assume that instead of (7) the barrier is a parabolic function, i.e.,

$$W(x;t) = W_*(t) - kT \{ [x - x_*(t)] / \Delta \}^2, \tag{25}$$

with  $W_*(t)/kT = [x_*(t)/\Delta]^2$ , which implies  $W(0;t) \equiv 0$ . For simplicity,  $\Delta$  will be treated as a constant. A time dependence for  $\Delta$  can be easily incorporated in the exact expression for the Green's function [6] discussed below, although the resulting effects are minor compared to those arising from the time dependencies of  $W_*(t)$  and  $x_*(t)$ , respectively. If one further assumes that  $D(x) = \text{const} = \Delta^2/2\tau$ , one obtains, via the Einstein relation, the correct growth rate (1), so that the model is still rather realistic. Equation (6) now takes the following form:

$$\frac{\partial f}{\partial t} = - \frac{\partial}{\partial x} \frac{x - x_*}{\tau} f + D \frac{\partial^2 f}{\partial x^2}. \tag{26}$$

Further, we extend the region of sizes to  $-\infty$  and introduce a source of unit intensity at  $x=0$  (see Fig. 2). This source is switched on at  $t=0$ . The overwhelming majority of the inserted particles will go to  $-\infty$ , but an ex-

ponentially small fraction of them—via thermal activation—will cross the barrier and grow to large sizes. To treat this problem asymptotically, one should notice that a distribution  $f(x,t) \approx -1/x$  is established at  $x \leq 0$ . The limiting value  $f(x=0,t) = \tau/x_*$  can be employed in Eq. (8), as well as in all other asymptotic results presented above. Minor differences are that for the parabolic barrier the cubic term in Eq. (9) is now replaced by a linear term. This leads to a corresponding modification of Eq. (14), giving  $C=1$ . The constant  $C'$  remains zero. Note that the distribution at  $x=0$  is unaffected (asymptotically) by the nucleation process in complete analogy with the conventional nucleation problem where  $f(x=0)$  is assumed to be determined solely by the concentration of monomers [16].

We now note that the stated problem can be solved *exactly*. The Fokker-Planck Eq. (26) is the well-known Ornstein-Uhlenbeck equation for a time-dependent unstable overdamped oscillator. For the Green's function we use Eq. (4.3) in Ref. [6]. This allows us to obtain the distribution  $f(x,t)$ . The drift flux  $\dot{x}f(x,t)$  can be compared with the asymptotic results of Sec. IV. Employing this mentioned Green's function we end up obtaining the main result of this section,

$$j_{\text{dr}}(x,t) = \frac{x - x_*}{\Delta \sqrt{\pi}} \int_{\exp(-t/\tau)}^1 \frac{du}{\sqrt{1-u^2}} \exp \left\{ - \frac{[(x - \bar{x}_*)u + \bar{x}_* - \bar{x}_* \mu(u,t)]^2}{\Delta^2(1-u^2)} \right\}, \tag{27}$$

with

$$\begin{aligned} \mu(u,t) &= \frac{1}{\tau} u e^{t/\tau} \int_{t+\tau \ln u}^t dt' \varphi(t') e^{-t'/\tau} \\ &= \frac{A}{\sqrt{(\omega\tau)^2 + 1}} \\ &\times \{ \sin[\omega(t + \tau \ln u) + \Phi] - u \sin[\omega t + \Phi] \}, \end{aligned}$$

and  $\Phi = \arctan(\omega\tau) + \Phi_0$ .

To understand the analytical structure of the above result, we note that Eq. (25) depends on three large param-

eters:  $t/\tau$ ,  $(x - x_*)/\Delta$ ,  $x_*/\Delta$ . For the case that the first one is also large compared to the logarithms of the two others, a periodic regime is established. By switching to a new variable of integration  $y = \ln[2u(x - x_*)x_*/\Delta^2]$  and neglecting the asymptotically small terms, one can cast Eq. (27) into the form

$$j_{\text{dr}} = \frac{\Delta}{2x_* \sqrt{\pi}} e^{-\bar{W}_*/kT} \int_{-\infty}^{\infty} dy e^{F(y)}, \tag{28}$$

with

$$\begin{aligned} F(y) &= y - e^y + \frac{2AW_*}{kT\sqrt{1+(\omega\tau)^2}} \\ &\times \sin\{\omega[\tau(y-1) + \tilde{t}_0] + \Phi\}. \end{aligned} \tag{29}$$

Equations (28) and (29)—which do not include the assumption  $\omega\tau \ll 1$ —thereby generalize the analysis of Secs. II–IV. In the Appendix we show that for small values of  $\omega\tau$  these equations predict the same type of transition from quasiadiabatic regime to exponential decay, which is expected from the asymptotic study.

The time-averaged flux  $\bar{j}_{\text{dr}}$  is easily found from the above expression as  $(\Delta/2x_*\sqrt{\pi}) \exp(-\bar{W}_*/kT) I_0(2A^{\text{eff}}W_*/kT)$  with  $A^{\text{eff}} = A/\sqrt{(\omega\tau)^2 + 1}$ . Here  $I_0$  is the modified Bessel function [13(b)] and we did not include the asymptotically small terms which arise from the time dependence of  $x_*$  in the prefactor of Eq. (26). The limiting behavior of  $\bar{j}_{\text{dr}}$  is readily obtained. For  $A \rightarrow 0$  (or  $\omega\tau \rightarrow \infty$ ) it is the standard flux (8) over the

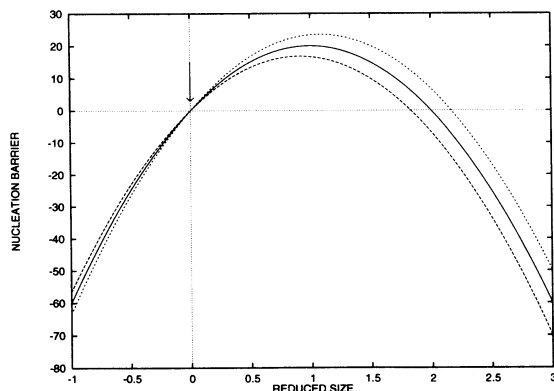


FIG. 2. The modulated nucleation barrier  $W(x;t)/kT$  with a source of particles at  $x=0$ .

average (unmodulated) barrier. In the opposite limit of large arguments of the Bessel function the average flux is given by  $j_{\text{ad}}^{\text{max}} / \sqrt{4\pi A^{\text{eff}} \bar{W}_* / kT}$  where  $j_{\text{ad}}^{\text{max}}$  is to be determined for the *effective* driving amplitude  $A^{\text{eff}}$ . For  $\omega\tau \ll 1$  which was assumed in the asymptotic analysis of previous sections, this average flux can also be obtained by the steepest-descent integration of the adiabatic expression. This implies that in the case of strong modulation practically all particles are nucleated during the fraction of the period when the barrier is the smallest so that the flux is close to its maximum value.

A comparison between the exact result in Eq. (27), and the asymptotic Eqs. (21) and (22) with the constant  $C$  adjusted for the parabolic barrier, is depicted in Figs. 3 and 4. In Fig. 3 we varied the modulating frequency  $\omega$ , obtaining different values of  $n_{\text{max}}$ , see Eq. (11). Other parameters were held constant at the following values:  $\bar{W}_* / kT \equiv (\bar{x}_* / \Delta)^2 = 20$ ,  $A = 0.5$ ,  $(x - \bar{x}_*) / \Delta = 11$ ,  $\Phi_0 = 0$ . With  $n_{\text{max}} < 1$  the two lower curves in Fig. 3 depict very high accuracy of the asymptotic evaluation of the phase shift, as well as the correctness of the potentially singular  $\Gamma$ -function factor. The discontinuity of the latter for  $n_{\text{max}} > 1$ , induced by higher frequencies  $kT / \bar{W}_* < \omega\tau \ll 1$ , corresponds to an extreme deviation from the quasiadiabatic regime as is exhibited in the upper curve. From the foregoing analysis one expects here a transition to exponential decay which is clearly shown in Fig. 4. In this figure are depicted the nonreduced values of the flux, as well as its adiabatic values, for a modulation process with  $n_{\text{max}} > 1$ . In accordance with the analytical prediction, the decrement of the exponential decay is given by  $-1/\tau$ , which is *independent* of the driving parameters. Note the strong asymmetry of the flux with respect to time despite the fact that the modulation process itself is symmetric. This is explained as follows: during the “uprising” phase of modulation ( $n > 0$ ) the flux follows the quasiadiabatic values rather closely—the factor  $\Gamma(n+1)$  is nonsingular. On the other hand, during the “downfall” phase of modulation ( $n < 0$ ) the flux stops tracing the modulation as soon as  $n$

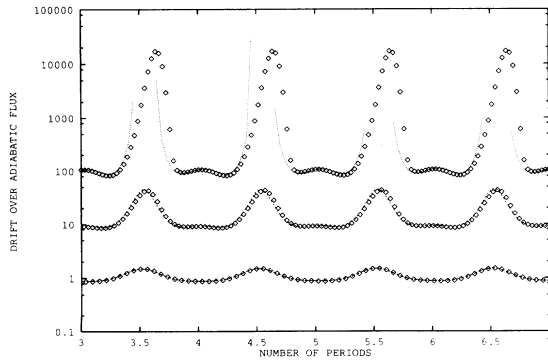


FIG. 3. Deviation from the adiabatic regime for different values of  $n_{\text{max}}$ . Diamonds—exact results from Eq. (27) for  $10^k j_{\text{dr}}(x, t) / j_{\text{ad}}(\bar{t}_0)$  (factor  $10^k$  is introduced for clarity of the figure). Dotted—asymptotic result (the  $\Gamma$ -function expression) from Eq. (21). From top to bottom:  $n_{\text{max}} = 1.2$  ( $k=2$ );  $n_{\text{max}} = 0.8$  ( $k=1$ );  $n_{\text{max}} = 0.4$  ( $k=0$ ).

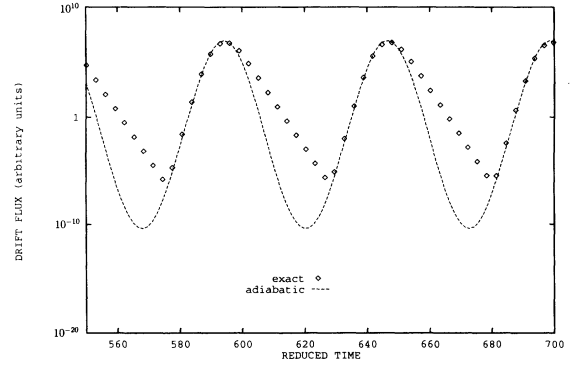


FIG. 4. Transition to exponential decay,  $n_{\text{max}} = 2.4$  ( $\omega\tau = 0.012$ ); other parameters as in Fig. 3. Time is reduced by  $\tau$ . The adiabatic flux is evaluated at the shifted time  $\bar{t}_0$ .

becomes smaller than  $-1$ , which implies a loss of symmetry.

## VI. OTHER GROWTH MODELS AND OTHER TYPES OF MODULATION

The exponentially fast growth predicted by Eq. (1) is possible only for cavities whose growth is not limited by mass exchange with the surrounding and by neglecting inertial effects. Otherwise, as mentioned in Sec. IV, typical models exhibit a power-law growth of large particles. Unfortunately, an exactly solvable imitation of nucleation in such models is impossible in a general case. Nevertheless, in the direct vicinity of the critical size *any* model is described by an equation in the form of (1). Hence the *asymptotic* technique of matching of the nucleation and growth solutions which is performed just in this region and which allows us to get rid of all the singularities will remain essentially the same. Thus we expect that the main conclusion of transition to a “nonanalytic” regime at  $n_{\text{max}} > 1$  will hold for such cases as well, as this conclusion was based on the asymptotic analysis and did not rely on a particular growth model. The exactly solvable model with the specific growth rate (1) was used only to confirm the asymptotic results. The main effect of a nonexponential growth results in a different phase shift. As shown in Sec. IV, the logarithmic dependence on size in Eq. (23) is replaced by some power law, making the effects of retardation much stronger.

In a realistic situation the modulation of the barrier is not necessarily sinusoidal. In this respect we note that most of the results presented above, except for Eqs. (5) and (29), did not specifically rely on the sinusoidal form of  $\varphi(t)$ ; thus a generalization for other time dependencies is straightforward.

## VII. CONCLUSION

In the present work we considered nucleation and growth of cavities under time-dependent modulation of

the external pressure. The growth of the new phase beyond some initial supercritical size  $x_0$  has been described within a deterministic time-dependent growth model. In addition we also incorporate fluctuations when the size becomes smaller than  $x_0$ . The matching procedure, however, is asymptotically smooth, so that our solution given by Eqs. (21) and (22) is explicitly independent of  $x_0$ .

For small frequencies of the modulation,  $\omega\tau \ll kT/\bar{W}_*$ , the flux of growing particles follows the external modulation rather closely, apart from a typical shift in time. Upon increasing the modulating frequency we find an abrupt transition from the adiabaticlike behavior to an exponential decay. The latter persists for a part of the modulation period after which the system switches to the quasiadiabatic regime.

In addition, we considered an exactly solvable model in terms of a time-dependent inverted parabolic barrier. This model—much to our own surprise—describes the realistic physical situation rather accurately. We also like to emphasize that this exactly solvable model can be extended to multidimensional cases, e.g., to a situation of nucleation for which viscous and inertial effects are to be accounted for simultaneously.

#### ACKNOWLEDGMENTS

This work has been supported by the Alexander von Humboldt Foundation (V.S.) and by the Volkswagen Stiftung (P.H.).

#### APPENDIX: QUASIADIABATIC AND DECAY REGIMES FROM THE EXACT EXPRESSION

It is instructive to understand how Eq. (28) can predict two essentially different regimes, namely, the quasiadiabatic regime and the exponential decay. A straightforward, though rather tedious analysis of the function  $F(y)$  for  $\omega\tau \ll 1$  shows that there are two possible locations of its highest maximum for  $n_{\max} > 1$  depending on the current value of time. There is always a maximum at large negative values of  $y$  and, for  $n(\tilde{t}_0) > -1$ , there is also a maximum near  $y=0$ . The latter corresponds to the quasiadiabatic regime described by Eq. (21) [17], while the former means the exponential decay which gets restarted with every period. It makes sense to discuss only the largest input, so that the system “prefers” the regime with the largest flux. The latter conclusion is an important addition to the previous asymptotic analysis and it is clearly illustrated by Fig. 4.

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- [16] The proposed model with a source instead of a boundary can also rather realistically account for different mechanisms of injection of microbubbles which are discussed to explain the reduced stability of a metastable liquid compared to theoretical predictions [2]. In this case the smallest size should be replaced by the size of the injected bubbles, but otherwise the treatment remains unchanged.
- [17] Note that the integral in Eq. (26) cannot be evaluated by the steepest descent method as  $F(y)$  decays slowly for  $y \rightarrow -\infty$ .