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Transient kinetics of nucleation

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Analytical solutions for the time-dependent cluster concentrations and nucleation rate in homogeneous nucleation are obtained by the singular perturbation approach. The effect of cluster scavenging by free molecule particles on the kinetics of nucleation is also investigated through analogous analytical solutions in this case. Apparent conflicting suggestions in the literature concerning the time lag of nucleation are resolved.

I. INTRODUCTION

When the saturation ratio of a vapor is suddenly increased to a value at which homogeneous nucleation occurs, a transient period exists during which the cluster concentrations increase to their eventual steady-state values, and the nucleation rate, defined as the flux of clusters past the critical size, also increases to its steady-state value corresponding to the new vapor saturation ratio. In an effort to understand the general character of nucleation phenomena and the observations in nucleation experiments that utilize sudden changes in saturation ratio, such as expansion cloud chambers, expansion nozzles, and free-molecular expansion methods,[1] the duration of the transient period in nucleation is of interest.

Under actual nucleation conditions preexisting particles are frequently present that act as scavengers for the vapor molecules and clusters, thereby depressing the rate of new particle formation by nucleation below that in their absence. One needs also to understand the effect of preexisting particles on the transient nucleation kinetics; that is, for example, is the characteristic time required to establish a steady-state nucleation rate increased or decreased in the presence of preexisting particles over that in their absence? Such open systems occur in many different situations, such as nucleation in the presence of cluster scavenging by a preexisting aerosol,[2,3] of cluster diffusion loss to the walls in a cloud chamber,[4] and of a strong diffusion (or drift) loss of nuclei on the boundaries of a crystal in the case of an electron-hole liquid formation by nucleation.[5]

Previous studies of transient nucleation kinetics have been reviewed by several authors.[6-8] Those studies are either restricted to special numerical solutions[6,9,10] or are based on inappropriate approximations.[11,12] Kashchiev's solution of the classic kinetic equation of nucleation had generally been considered to be the most accurate and had been widely used,[7,8] although his choice of the eigenfunction cutoff was shown to lead to incorrect results.[6] Recent work by Trinkaus and Yoo,[12] which employed a Green's-function approach, confirmed the analysis of Kashchiev's work by Binder and Stauffer.[6] The earlier studies tend to predict a characteristic lag time to attain a steady state of order $10^{-5}-10^{-6}$ s for liquid systems, although Gitterman and co-workers[13-18] have suggested that the time lag can reach dozens of seconds. They have attributed the overlooking of this time-lag effect in the previous studies to the approximations used in those studies, including the quadratic approximation for the energy barrier and the method of the steepest descent used in evaluating the integrals involved.

In using those "diffusion" approximations the time lag obtained does not include the time needed for the subcritical clusters to reach steady state. Instead, the time lag obtained is only the time required for a cluster to diffuse across the energy barrier.

The present work is an attempt to solve the time-lag problem in nucleation. With the aid of singular pertubation theory,[2,19] an analytical time-dependent solution is presented for the cluster size distribution for realistic boundary and initial conditions. We obtain the characteristic time scales for establishing the steady-state cluster size distribution, the nucleation rate, and the total particle formation without incorrect approximation other than associated with the matched asymptotic expansion. Our solutions are free of the problem of the incorrect boundary conditions associated with several previous studies.

We also solve the time-dependent kinetic equation of nucleation in the presence of cluster scavenging by free molecule particles. Thus we provide a quantitative answer to the time-lag question in an open system in which the characteristic lifetimes of clusters also play a critical role in the kinetics of nucleation.

II. BASIC EQUATIONS

The equation governing the continuous cluster size distribution $f(g,t)$ in a supersaturated vapor is[6,20]

$$\frac{\partial f(g,t)}{\partial t} = -\frac{\partial J(g,t)}{\partial g}, \tag{1}$$

where $J(g,t)$ is the cluster flux defined in the continuous cluster size (g) space

$$J(g,t)=-\beta(g,t)n(g,t)\frac{\partial}{\partial g}\frac{f(g,t)}{n(g,t)}\ , \tag{2}$$

and $\beta(g,t)$ is the rate of collision between monomers at concentration $f(1,t)$ and a g-mer

$$\beta(g,t)=f(1,t)s_1g^{2/3}(kT/2\pi m_1)^{1/2}\ . \tag{3}$$

The equilibrium cluster size distribution corresponding to a monomer concentration $n(1,t)$ is

$$n(g,t)=n(1,t)\exp[-W(g,t)/kT]\ , \tag{4}$$

with s_1 and m_1 the surface area and mass of the monomer, respectively. The critical size

$$g_*=\left[\frac{2\theta}{3\ln S}\right]^3 \tag{5}$$

is the size of cluster corresponding to the maximum free energy of cluster formation

$$W(g,t)=-gkT\ln S+s_1g^{2/3}\sigma\ , \tag{6}$$

where $\theta=s_1\sigma/kT$, the saturation ratio $S(t)=n(1,t)/n_{\mathrm{eq}}(1)$, and $n_{\mathrm{eq}}(1)$ is the saturation monomer concentration.

About g_* a critical region exists in which the difference between $W(g)$ and $W(g_*)$ is smaller than kT, i.e.,

$$|W(g)-W(g_*)|\le kT\ , \tag{7}$$

the width of which is given by[20]

$$\delta=\left[-\frac{1}{2kT}\frac{\partial^2W}{\partial g^2}\right]^{-1/2}\Bigg|_{g=g_*}\ , \tag{8}$$

which is related to the Zeldovich factor Z by

$$\delta=\frac{1}{\sqrt{\pi}Z}=3g_*^{2/3}\theta^{-1/2}\ . \tag{9}$$

Solutions of Eq. (1) for the dynamic cluster size distribution must be subject to appropriate boundary and initial conditions. The boundary conditions can be specified at both ends of the cluster size distribution. At $g=1$, the monomer number concentration can be assumed to be the same as the value used to define the equilibrium distribution

$$\frac{f(g,t)}{n(g)}=1,\quad g\to 1\ . \tag{10}$$

While for large g, the boundary condition can be established by noting that above the critical region the function $n(g)$ defined by Eq. (4) increases without limit, whereas the true cluster size distribution $f(g,t)$ remains finite. Thus

$$\frac{f(g,t)}{n(g)}=0,\quad g\to\infty\ . \tag{11}$$

We wish to study the transient nucleation kinetics that occur when the saturation ratio S is raised at $t=0$ to a specified value. Since the equilibrium cluster concentrations for $g\ge 2$ are much smaller than that of the monomer, it is reasonable to take the initial condition as

$$f(g,0)=n(1)\delta(g-1)\ , \tag{12}$$

where $\delta(g-1)$ is the Dirac delta function.

III. TRANSIENT KINETICS OF NUCLEATION — THE SINGULAR PERTURBATION APPROACH

As in the steady-state case, the normalized cluster size distribution $f(g,t)/n(g)$ exhibits a boundary layer structure about the critical-sized cluster g_*.[2] The small parameter, denoted as ϵ, which multiplies the term containing the highest derivative in the equation governing the cluster distribution, is related to the width of the critical region δ. A singular perturbation approach[2,19] can be used to obtain the transient cluster size distribution, transient nucleation rate, and transient total number of particles nucleated.

We define the independent variable $y(x,t)=f(g,t)/n(g)$ and the normalized cluster size $x=g/g_*$, and transform Eq. (1) into

$$\frac{x^{-2/3}\delta^2}{\beta(g_*)}\frac{\partial y(x,t)}{\partial t}=\left[\frac{\delta}{g_*}\right]^2\frac{\partial^2y(x,t)}{\partial x^2}+\left[\frac{2}{3x}\left[\frac{\delta}{g_*}\right]^2+6(1-x^{-1/3})\right]\times\frac{\partial y(x,t)}{\partial x}\ , \tag{13}$$

in which Eqs. (2), (4), (6), and (9) have been used and $\beta(g_*)$ is $\beta(g,t)$ evaluated by Eq. (3) at $g=g_*$ and $f(1,t)=n(1)$. Letting $\delta/g_*\equiv\epsilon$, Eq. (13) becomes

$$\epsilon^2\frac{\partial^2y(x,t)}{\partial x^2}+\left[\frac{2}{3x}\epsilon^2+6(1-x^{-1/3})\right]\frac{\partial y(x,t)}{\partial x}-\frac{x^{-2/3}\delta^2}{\beta(g_*)}\frac{\partial y(x,t)}{\partial t}=0 \tag{14}$$

The condition $\epsilon\ll 1$ holds as long as $\ln S\ll\frac{2}{9}\theta^{3/2}$, which is the case in nearly all practical situations.

After a Laplace transformation, Eq. (14) becomes

$$\epsilon^2\frac{\partial^2y(x,s)}{\partial x^2}+\left[\frac{2}{3x}\epsilon^2+6(1-x^{-1/3})\right]\frac{\partial y(x,s)}{\partial x}=\frac{x^{-2/3}\delta^2}{\beta(g_*)}[y(x,s)s-y(x,0)]\ , \tag{15}$$

where

$$y(x,s)=\int_0^\infty y(x,t)e^{-st}dt\ . \tag{16}$$

Equation (15) together with the boundary conditions

$$y(1/g_*,s)=\frac{1}{s},\quad y(\infty,s)=0\ , \tag{17}$$

can now be solved by the method of singular perturbation. Since the dominant term of $\partial y(x,s)/\partial x$ changes sign at $x=1$ in the interval $[1/g_*,\infty]$, we expect a boundary layer (transition layer) at $x=1$ as noted above. Thus there are two outer solutions: a $y_{\mathrm{out}}^{l}(x,s)$ that satisfies the left boundary condition at $x=1/g_*$ and a $y^r_{\rm out}(r,s)$ that satisfies the right boundary condition at $x\rightarrow\infty$. The outer solution is expected to be valid far from the critical region (inner region) around $x=1$.

The outer solution must satisfy the boundary condition $y^1_{\rm out}(1/g_*,s)=1$ and $y^r_{\rm out}(\infty,s)=0$. To the leading order in ϵ (the first-order correction vanishes), the outer solutions to Eq. (15) that satisfy the boundary conditions are

$$y^l_{\rm out}(x,s)=\frac{1}{s}\left[\frac{1-x^{1/3}}{1-g_*^{-1/3}}\right]^{s\tau}\exp[s\tau(x^{1/3}-g_*^{-1/3})] \tag{18}$$

and

$$y^r_{\rm out}(x,s)=0\ , \tag{19}$$

where $\tau=\delta^2/2\beta(g_*)$. Since the growth of the clusters near g_* can be viewed as a diffusion process, the time necessary to pass through the critical region is the order of τ, with $\beta(g_*)$ playing the role of an equivalent diffusion coefficient. τ is of the order of 10^{-6} s for liquid systems.

As expected, the outer solutions are not valid near $x=1$, so a transition layer about $x=1$ exists. Since the thickness of this boundary layer is ϵ, we introduce the inner variables $X=(x-1)/\epsilon^{\lambda}(\lambda>0)$ and $Y_{\rm in}(X,s)\equiv y_{\rm in}(x,s)$. In terms of these variables, Eq. (15) becomes

$$\frac{\epsilon^{2-\lambda}}{3}\frac{\partial Y_{\rm in}(X,s)}{\partial X}+\frac{1}{2}\epsilon^{2(1-\lambda)}(1+\epsilon^{\lambda}X)\frac{\partial^2 Y_{\rm in}(X,s)}{\partial X^2}$$
$$+3\epsilon^{-\lambda}(1+\epsilon^{\lambda}X)[1-(1+\epsilon^{\lambda}X)^{-1/3}]\frac{\partial Y_{\rm in}(X,s)}{\partial X}$$
$$=\frac{\delta^2}{2\beta(g_*)}(1+\epsilon^{\lambda}X)^{-1/3}sY_{\rm in}(X,s)\ . \tag{20}$$

As $\epsilon\rightarrow 0$ with X being fixed, the distinguished limit of Eq. (20) corresponds to $\lambda=1$. The boundary condition $y(\infty,s)=0$ translates into

$$Y_0(\infty,s)=0,\quad Y_n(\infty,s)=0,\quad n\geq 1\ . \tag{21}$$

The leading-order inner solution of Eq. (20) that satisfies the boundary conditions is

$$Y_{\rm in}(X,s)=\tfrac{1}{2}A(s)i^{s\tau}{\rm erfc}(X)+\tfrac{1}{2}B(s)i^{s\tau}{\rm erfc}(-X)\ , \tag{22}$$

where $i^{s\tau}{\rm erfc}(X)$ is a repeated error function. The constants $A(s)$ and $B(s)$ have to be determined by asymptotically matching the outer and inner solutions. The match consists of requiring that at the intermediate limits $[x\rightarrow 1-, X\rightarrow -\infty; x\rightarrow 1+, X\rightarrow +\infty]$ the inner and outer solutions agree. The leading-order match gives

$$A(s)=\frac{1}{s}(1-g_*^{-1/3})^{-s\tau}\left[\frac{\epsilon}{3}\right]^{s\tau}$$
$$\times e^{(1-g_*^{-1/3})s\tau}\Gamma(s\tau+1),\quad B(s)=0\ . \tag{23}$$

A. Transient cluster size distribution

To determine the nucleation rate we are most interested in the cluster size distribution near the critical size which is given by the inner solution

$$y_{\rm in}(x,s)=\frac{1}{2s}(1-g_*^{-1/3})^{-s\tau}\left[\frac{\epsilon}{3}\right]^{s\tau}e^{(1-g_*^{-1/3})s\tau}$$
$$\times\Gamma(s\tau+1)i^{s\tau}{\rm erfc}\left[\frac{x-1}{\epsilon}\right]\ . \tag{24}$$

After an inverse Laplace transformation, we have

$$y_{\rm in}(g,t)=\frac{1}{2}{\rm erfc}\left[\frac{g-g_*}{\delta}+\exp\left[-\frac{t-\lambda\tau}{\tau}\right]\right]\ , \tag{25}$$

where $\lambda=g_*^{-1/3}-1+\ln[3(1-g_*^{-1/3})/\epsilon]$.

The transient cluster size distribution far from the critical region is given by the outer solutions which are the inverse Laplace transformations of Eqs. (18) and (19),

$$y^l_{\rm out}(g,t)=\Theta(t-\mu(g)\tau) \tag{26}$$

and

$$y^r_{\rm out}(g,t)=0\ , \tag{27}$$

where $\mu(g)=(g_*^{-1/3}-x^{1/3}-\ln[(1-x^{1/3})/(1-g_*^{-1/3})]$ and Θ is the unit step function: $\Theta(z)=1$ for $z>0$, $\Theta=\frac{1}{2}$ for $z=0$, and $\Theta=0$ for $z<0$.

According to Eq. (26), the subcritical clusters approach a steady state one by one with a time lag $\mu(g)\tau$. As shown in Fig. 1, the coefficient $\mu(g)$ of the characteristic time $\mu(g)\tau$ for subcritical clusters to attain steady state is not overly sensitive to the value of the critical cluster size g_*. On the other hand, $\mu(g)$ increases as g increases, in-

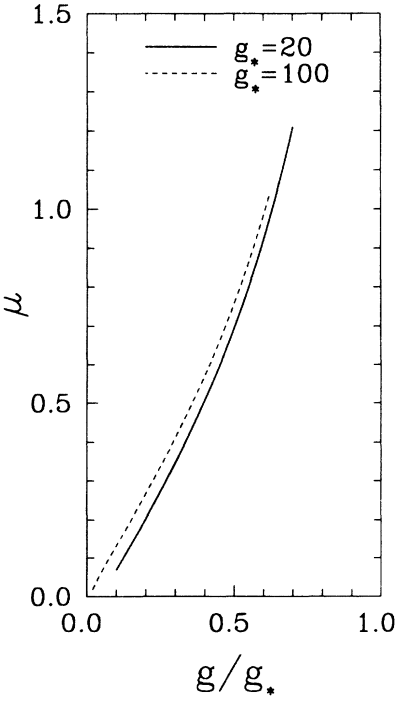

FIG. 1. Coefficient $\mu(g)$ in the effective time lag $\mu(g)\tau$ associated with the subcritical cluster size distribution as a function of the normalized cluster size g/g_*.

dicating that the subcritical clusters attain steady state, also equilibrium, one by one from the smaller clusters to the larger ones, such that the rapid establishment of steady state for the smaller clusters from the monomer is followed by a lengthening period for each g-mer as the size increases. In overcoming the larger Gibbs energy barrier to form a larger cluster the time needed in establishing a steady-state cluster distribution at larger size is longer than that for the smaller clusters.

The cluster size distribution beyond the critical region $y_{\rm out}^r$ vanishes as indicated by Eq. (27). This is also true in the stationary case as required by the boundary condition Eq. (16).[2]

The characteristic parameter in the transient behavior of the clusters in the critical region λ is a function of g_* and θ. For $\theta=10$, the value of λ is about 0.34 for $g_*=30$ and 0.45 for $g_*=100$. For $\theta=5$, its value is about 0.3 for $g_*=30$ and 0.40 for $g_*=100$. According to Eq. (25), the cluster size distribution in the critical region becomes essentially steady state (about 95% of its steady-state value) for $t>(1.5+\lambda)\tau$ (about 3τ), i.e.,

$$f(g)=\tfrac{1}{2}n(g)\operatorname{erfc}\left[\frac{g-g_*}{\delta}\right], \tag{28}$$

which agrees with the classical steady-state case.[18]

We can estimate the ratio between the characteristic time needed for the establishment of a steady-time subcritical cluster distribution $\mu(1-\epsilon)\tau$ and that required to form a steady-state cluster flux in the critical region $(\lambda+1.5)\tau$. For $g_*=30$ and $\theta=10$, this ratio is about 0.45. Thus about one-third of the time needed to establish full steady-state cluster distribution is spent in forming a steady-state subcritical cluster size distribution. For $g_*=100$ and $\theta=10$ this ratio of characteristic times increases to about 0.53. As g_* increases, more time is spent on establishing a steady-state cluster size distribution outside the critical region. This ratio decreases with decrease in θ; for $\theta=5$, this ratio is about 0.37 for $g_*=30$ and 0.47 for $g_*=100$. It is clear that in calculating the time needed to reach a steady-state cluster size distribution the time needed to reach steady state below the critical region cannot be neglected. This aspect thus has been neglected implicitly or explicitly in most previous analyatic studies.[6,11]

B. Transient nucleation rate

The transient cluster flux at any size g is given by

$$\begin{aligned} J(g,t)&=-\beta(g)n(g)\frac{\partial}{\partial g}\left[\frac{f(g,t)}{n(g)}\right]\\ &=Z(g_*)\beta(g)n(g)\exp\\ &\quad\times\left\{-\left[\frac{g-g_*}{\delta}+\exp\left[-\frac{t-\lambda\tau}{\tau}\right]\right]^2\right\}, \end{aligned} \tag{29}$$

and the transient nucleation rate at $g=g_*$ is

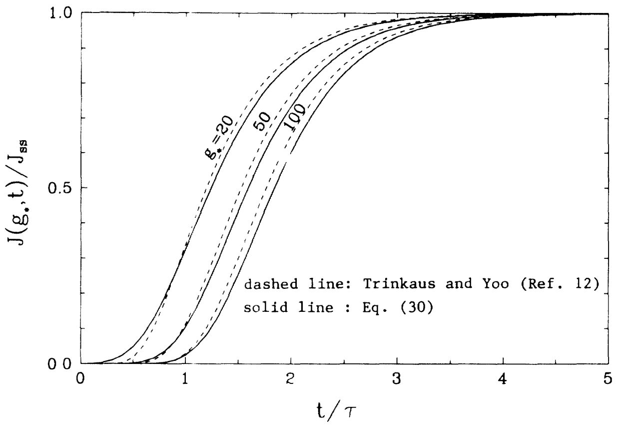

FIG. 2. Normalized transient nucleation rate $J(g_*,t)/J_{\rm ss}$ as a function of the normalized time t/τ.

$$\begin{aligned} J(g_*,t)&=-\beta(g_*)n(g_*)\frac{\partial}{\partial g}\left[\frac{f(g,t)}{n(g)}\right]\Bigg|_{g=g_*}\\ &=J_{\rm ss}\exp\left\{-\left[\exp\left[-2\frac{t-\lambda\tau}{\tau}\right]\right]\right\}, \end{aligned} \tag{30}$$

where $J_{\rm ss}$ is the steady-state homogeneous nucleation rate

$$J_{\rm ss}=Z(g_*)\beta(g_*)n(g_*)\ , \tag{31}$$

and $Z(g_*)$ is Zeldovich factor. In the limit as $t\rightarrow\infty$, we have from Eq. (30) that $J(g_*,t)=J_{\rm ss}$.

It is noted that the new derived formula for the transient nucleation rate, Eq. (30), is functionally different from the previous ones which have usually been expressed[7] in the form of $J=J_{\rm ss}[1-\exp(-t/t_c)]$, where t_c is the characteristic time of relaxation of the nucleation process to a steady state. Different authors have obtained different expressions for t_c, but of the order of τ.

In Fig. 2, we show the nucleation rate as a function of t/τ for different values of g_* based on Eq. (30) and that obtained by Trinkaus and Yoo.[12] The two results are numerically consistent with each other. As shown in Fig. 2, the time lag associated with the nucleation rate is about 4τ.

C. Time-dependent number density of critical clusters nucleated

The number density of critical clusters formed in the system following the increase in saturation ratio at $t=0$ is the integrated flux $N(g_*,t)=\int_0^t J(g_*,t')dt'$. The dimensionless total number is

$$\frac{N(g_*,t)}{J_{\rm ss}\tau}=\frac{1}{2}\int_{ae^{-bt}}^{a}\frac{dx}{xe^x}=\tfrac{1}{2}[E_1(ae^{-bt})-E_1(a)]\ , \tag{32}$$

where $a=e^{2\lambda}=[3(1-g_*^{-1/3})/\epsilon]^2e^{2(g_*^{-1/3}-1)}$ and $b=2/\tau$, and E_1 is the exponential integral.

As $t/\tau\rightarrow\infty$, we have $ae^{-bt}\rightarrow 0$, and $E_1(ae^{-bt})=-\gamma-\ln a+bt+O(ae^{-bt})$, thus

$$\frac{N(g_*,t)}{J_{\rm ss}\tau}=-\frac{1}{2}[E_1(a)+\gamma_e+\ln a]+\frac{t}{\tau}\ , \tag{33}$$

where $\gamma_e = 0.5772$ is Euler's constant.

Equation (33) thus indicates that at large times, $N(g_*,t)$ increase linearly with time t as expected. The beginning of the steady-state regime can be determined experimentally by the time at which the increase of $N(g_*,t)$ becomes linear with time. The time lag (τ_e) defined in such a way is given by

$$\tau_e = \tfrac{1}{2}[E_1(a) + \gamma_e + \ln a]\tau \ . \tag{34}$$

The time dependence of $N(g_*,t)$ is shown in Fig. 3 for $g_* = 30$ and $g_* = 100$. The effective time lag associated with the approach of $N(g_*,t)$ to steady state is about 3τ which, as expected, is the same order of the time lag associated with the nucleation rate. This result is in contrast with that obtained by Gitterman and his associates.[13–18] They have suggested the time lag associated with $N(g_*,t)$ can reach dozens of seconds even for liquid systems for "fast" quench cases. For a fast quench the initial condition is given by Eq. (12). It is this fast quench case that is the one considered in the present work. They have attributed the overlooking of this effective long-time lag in the previous studies to the approximations used in those studies, including the neglect of the time required to reach the steady-state cluster distribution below the critical region, the quadratic approximation for the energy barrier, and the method of steepest descent used in evaluating the integrals involved. Since the present approach is free of those approximations, and we do not find any anomalous increase in the time lag associated with $N(g_*,t)$, we conclude that the increase in the time lag found by Gitterman and co-workers must arise from one of two sources. Either it is a phenomenon related to nucleation near the critical point of phase transition, since they used critical dynamics to determine the physical parameters in the kinetic equation of nucleation, or the error was introduced by the approximation of shifting the real boundary conditions to an unphysical domain in solving the associated eigenvalue problem. However, there is no experimental evidence as reviewed in Ref. 20 to support the first possibility.

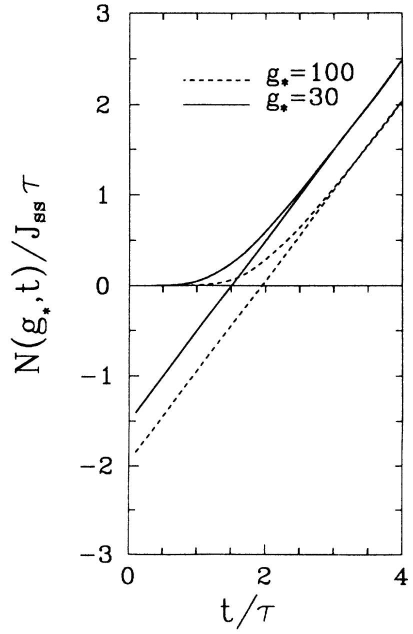

FIG. 3. Normalized number density of critical clusters formed $N(g_*,t)/J_{ss}\tau$ as a function of the normalized time t/τ.

In solving for the time-dependent cluster size distribution, the problem was condensed by Gitterman and coworkers into solving the appropriate Schrödinger equation by approximating the potential as a harmonic oscillator and shifting the boundary from the lowest end of the size distribution to $-\infty$. The potential with this equation could be approximated by the harmonic oscillator only near the critical cluster size, which is equivalent to the quadratic approximation for the Gibbs energy barrier. The second assumption in shifting the boundary condition from $g = 1$ to the region $g < 0$ is similar to that of Trinkaus and Yoo[12] in using a Green's-function approach. A consequence of this approximation is that the solution does not satisfy the physical boundary condition. This approximation, however, may not cause serious error since the transient nucleation rate obtained by Trinkaus and Yoo[12] shows a similar behavior with ours as shown in Fig. 2.

IV. TRANSIENT KINETICS OF NUCLEATION IN THE PRESENCE OF CLUSTER SCAVENGING

Let us consider a supersaturated vapor system with preexisting free-molecule particles of sizes larger than that of the critical cluster corresponding to the existing supersaturation in the system. The equation governing the continuous cluster size distribution is given by[2]

$$\frac{\partial f(g,t)}{\partial t} = -\frac{\partial J(g,t)}{\partial g} - \gamma g^{-7/6}\beta(g,t) f(g,t) \ , \tag{35}$$

where γ is a dimensionless surface area concentration parameter defined by

$$\gamma = \frac{A}{s_1 f(1,t)} \ , \tag{36}$$

with s_1 the surface area of the monomer and A the surface area density of preexisting particles.

The boundary and initial conditions to Eq. (36) are given by Eqs. (10)–(12). As in the absence of cluster scavenging, we can solve for the time dependent $f(g,t)$ by the singular perturbation approach.

To the leading order in ϵ (the first-order correction vanishes), the outer solutions to these equations that satisfy the boundary conditions are

$$y^l_{\text{out}}(x,s) = \frac{1}{s}\left[\frac{1-x^{1/3}}{1-g_*^{-1/3}}\right]^{s\tau} \exp[s\tau(x^{1/3} - g_*^{-1/3})] \times \left[\frac{1-x^{1/6}}{1+x^{1/6}}\right]^{m} \eta^{-m} \tag{37}$$

and

$$y^r_{\text{out}}(x,s) = 0 \ , \tag{38}$$

where m is given by

$$m = \tfrac{1}{2}\gamma\delta^2 g_*^{-7/6} = \tfrac{9}{2}\gamma\theta^{-1} g_*^{1/6} \ ,$$

and $\eta=(1-g_*^{-1/6})/(1+g_*^{-1/6})$. As expected, the outer solutions are not valid near $x=1$, so a transition layer at $x=1$ exists. Since the thickness of this boundary layer is ϵ, we introduce the inner variables $X=(x-1)/\epsilon$ and $Y_{\text{in}}(X,s)\equiv y_{\text{in}}(x,s)$. Using a similar method to obtaining the outer solutions we obtain the following leading-order inner solution:

$$Y_{\text{in}}(X,s)=\frac{1}{2s}\exp(-\lambda s\tau)\alpha^m\Gamma(m+s\tau+1)\times i^{s\tau+m}\text{erfc}(X)\ , \tag{39}$$

where $\alpha=\epsilon/12\eta$. In the limit of $m=0$, Eqs. (37) and (39) reduce to Eqs. (18) and (24).

A. Transient cluster size distribution

The cluster size distribution near the critical size is given by the inner solution

$$y_{\text{in}}(x,s)=\frac{1}{2s}\exp(-\lambda s\tau)\alpha^m\Gamma(m+s\tau+1)\times i^{s\tau+m}\text{erfc}\left(\frac{x-1}{\epsilon}\right) . \tag{40}$$

After an inverse Laplace transformation, we have

$$y_{\text{in}}(g,t)=\frac{1}{2}\alpha^m\Gamma(m+1)i^m\text{erfc}\left(\frac{g-g_*}{\delta}\right)-\frac{1}{\sqrt{\pi}}\int_X^{X+\exp(-t/\tau+\lambda)}\alpha^m(w-X)^m e^{-w^2}dw\ . \tag{41}$$

In the limit of $m\rightarrow 0$, Eq. (41) reduces to

$$\begin{aligned}y_{\text{in}}(g,t)&=\frac{1}{2}\text{erfc}\left(\frac{g-g_*}{\delta}\right)-\frac{1}{\sqrt{\pi}}\int_X^{X+\exp(-t/\tau+\lambda)}e^{-w^2}dw\\&=\frac{1}{2}\text{erfc}\left[\frac{g-g_*}{\delta}+\exp\left(-\frac{t-\lambda\tau}{\tau}\right)\right]\ ,\end{aligned} \tag{42}$$

which is the transient cluster size distribution in the absence of cluster scavenging, Eq. (25).

The subcritical transient cluster size distribution far from the critical region is given by the outer solutions which are the inverse Laplace transformations of Eqs. (37) and (38), respectively,

$$y_{\text{out}}^l(g,t)=\Theta(t-\mu(g)\tau)\left(\frac{1-x^{1/6}}{1+x^{1/6}}\right)^m\eta^{-m}\ , \tag{43}$$

which reduces to Eq. (26) for $m=0$ and

$$y_{\text{out}}^r(g,t)=0\ . \tag{44}$$

In the subcritical region, by comparison with Eq. (26), we note that the presence of cluster scavenging does not change the time $\mu\tau$ needed to reach the steady state. The steady-state number density of subcritical clusters is the same as the equilibrium one corresponding to the Gibbs energy potential in the absence of cluster scavenging,[2] while in the presence of cluster scavenging the steady-state number density of subcritical clusters is smaller than the equilibrium one. The presence of cluster scavenging does not change the time needed for the subcritical clusters to reach steady state indicating the time for the establishment of a dynamic balance between the cluster scavenging process and the cluster flux across the g space is always the same regardless of the values of m. A consequence of this is the cluster flux becomes g dependent.

B. Transient nucleation rate

The transient cluster flux as defined by Eq. (2) in the critical region can be obtained from Eq. (41),

$$J(g,t)=\beta(g)n(g)Z(g)\times\left[\frac{1}{2}\alpha^m\sqrt{\pi}\Gamma(m+1)i^{m-1}\text{erfc}\left(\frac{g-g_*}{\delta}\right)-\int_X^{X+\exp(-t/\tau+\lambda)}2\alpha^m(w-X)^{m+1}\times e^{-w^2}dw\right]\ , \tag{45}$$

and the cluster flux in the subcritical region is obtained from Eq. (42),

$$J(g,t)=\beta(g)n(g)\Theta(t-\beta\tau)\left(\frac{1-x^{1/6}}{1+x^{1/6}}\right)^{m-1}\times\frac{m\eta^{-m}x^{-5/6}}{3g_*(1+x^{1/6})^2}\ . \tag{46}$$

The nucleation rate defined as the cluster flux at g_* is given by

$$J(g_*,t)=J_{\text{ss}}\left[\sqrt{\pi}\left(\frac{\alpha}{2}\right)^m\frac{\Gamma(m+1)}{\Gamma(m/2+1/2)}-\int_0^{\exp(-t/\tau+\lambda)}2\alpha^m w^{m+1}e^{-w^2}dw\right]\ . \tag{47}$$

In the absence of preexisting particles, that is, as $m\rightarrow 0$, we have from Eq. (25), or Eq. (46), $J(g_*,t)=J_{\text{ss}}\exp(-\{\exp[-2(t-\lambda\tau)/\tau]\})$, which is the same result as that obtained in the case without cluster scavenging, Eq. (30).

In the limit of large times, we recover the steady-state nucleation rate in the presence of cluster scavenging,[2]

$$J_{sm}=J_{\text{ss}}\eta^{-m}\sqrt{\pi}\left(\frac{\epsilon}{24}\right)^m\frac{\Gamma(m+1)}{\Gamma(m/2+1/2)}\ . \tag{48}$$

It is known previously[2] and from Eq. (46) that the nucleation rate in the presence of cluster scavenging can be reduced significantly from that in its absence depending on the surface area density present in the system.

The normalized nucleation rate $J(g_*,t)/J_{sm}$ as a function of t/τ based on Eq. (46) is shown in Fig. 4 for different values of m. We note that the presence of cluster scavenging shortens the time lag needed for the nucleation rate to approach the steady state. For $m=0$ we

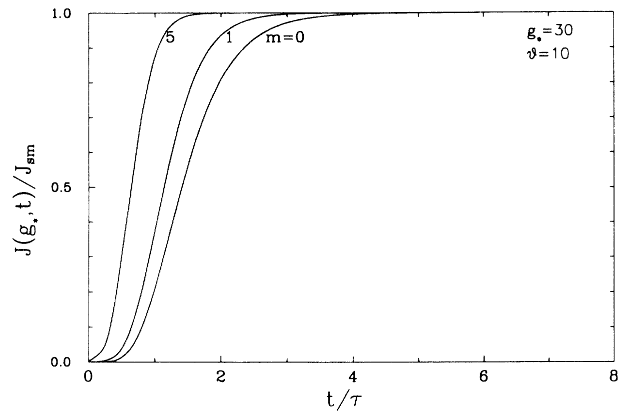

FIG. 4. Normalized nucleation rate $J(g_*,t)/J_{sm}$ as a function of normalized time t/τ for different values of m.

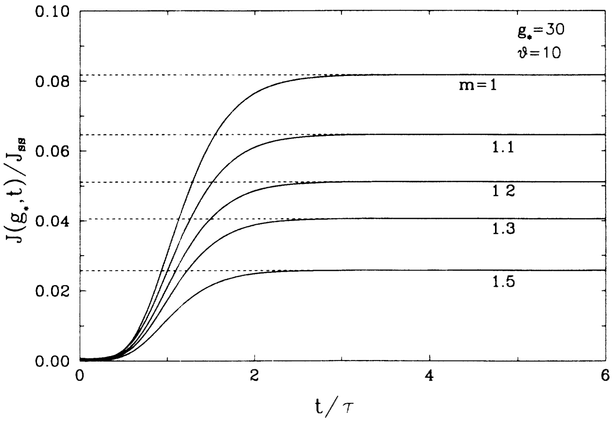

FIG. 5. Normalized nucleation rate $J(g_*,t)/J_{ss}$ as a function of normalized time t/τ for different values of m.

have the case of transient nucleation in the absence of cluster scavenging. Thus the suggestion that the time lag should be very long for an open system[5] is shown to be not correct. At a higher surface area density of cluster scavengers (larger m) present the nucleation rate reaches the steady state faster than at the lower surface area density.

This behavior can be understood by analogy to two chemical reaction systems: $A \rightleftharpoons B$ and $A \rightleftharpoons B \rightarrow C$. In the first system the concentration of B reaches a steady state in a time scale $\tau_1 = 1/k_{-1}$, and $\tau_2 = 1/(k_{-1}+k_2)$ is required for B to reach steady state in the second system. Here k_{-1} and k_2 are the rate constants of the reactions of B and A and of B and C, respectively. $\tau_1 > \tau_2$ as a result of the additional removal path for B in the second system. By analogy, the nucleation time lag in the presence of cluster scavenging is shorter than that in its absence. As k_2 increases τ_2 decreases, and the time lag in the case of higher surface area concentration of preexisting particles is shorter than that at lower concentrations.

Figure 5 shows $J(g_*,t)/J_{ss}$. For a suppressed nucleation rate, the time for the appearance of nuclei in a unit volume becomes very long. For example, for $J(g_*,t)/J_{ss} = 0.04$ in the case presented in Fig. 5 for $m = 1.3$, the time for a given concentration of critical sized clusters to appear in a unit volume in the case of cluster scavenging is about 25 times longer than in absence.

C. Time-dependent number concentration

The time-dependent number density of critical cluster nucleation in the system with cluster scavenging is given by

$$N(g_*,t) = J_{sm}t - J_{ss}\int_0^t \int_0^{\exp(-t'/\tau+\lambda)} 2\alpha^m w^{m+1} \times e^{-w^2} dw\, dt' \ . \tag{49}$$

Thus the effective time lag that can be verified experimentally is

$$\tau_{em} = \int_0^t \int_0^{\exp(-t'/\tau+\lambda)} 2\alpha^m w^{m+1} e^{-w^2} dw\, dt' \ , \tag{50}$$

which becomes equal to τ_e given by Eq. (34) in the limit of $m = 0$.

V. CONCLUSIONS

In this work we have investigated the transient nature of nucleation by examining the time dependence of the cluster size distribution, the nucleation rate, and the time-dependent number density of critical sized clusters formed. The approach used is based on a singular perturbation method in which approximations made previously, such as, the quadratic approximation for the nucleation barrier, and the steepest descent method to evaluate the integrals involved are avoided.

We have also investigated the transient kinetics of nucleation in the presence of cluster scavenging by free-molecule particles by solving the kinetic equation of nucleation. It is shown that the presence of cluster scavenging shortens the total time lag, which decreases with increasing surface area density of cluster scavengers.

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