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Kinetics of nucleation controlled formation and condensational growth of disperse particles

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The kinetics of nucleation controlled formation and condensational growth of disperse particles is considered under the assumptions that: (i) only a small amount of condensable substance nucleates and forms the particles that grow by condensing the rest of the substance. (ii) The condensation efficiency is a power function of the particle mass. A nontrivial perturbation theory with respect to the smallness parameter $\mu=$ (the mass of nucleated matter)/(the total mass of condensable matter) is developed allowing one to describe the source-enhanced and free (no source) condensation processes in terms of universal functions: the particle-mass spectrum and the concentration of condensable matter. The theory relies upon a scaling transformation that removes at all the smallness parameter from the evolution equations (if the nucleation rate is a power function of the concentration of condensable matter) or leaves it in the expression for the nucleation rate where this parameter defines only a concentration scale of the nucleation process (for the nucleation rates of general form). The theory is illustrated by the exact analytical solutions of the nucleation-condensation kinetic equations for three practically important cases: (i) gas-to-particle conversion in the free-molecular regime, (ii) formation and diffusion controlled condensational growth of islands on surfaces, and (iii) formation and diffusion controlled growth of disperse particles in the continuum regime. The analytical expressions for the mass spectra of growing particles are found in the case of free condensing particles. The final mass spectra in free condensing systems display rather unusual behavior: they are either singular at small particle masses or not, depending on the value of the power exponent in the mass dependence of the condensation rate.

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I. INTRODUCTION

A new phase formation in the first-order phase transitions often goes through a disperse phase state, i.e., the new phase appears as disperse particles suspended in a carrier medium. The processes responsible for the disperse particle formation are: (i) the formation of stable embrii by nucleation, (ii) their growth by condensation and (iii) the coagulation aging of thus formed disperse system.

The formation of a disperse phase by spontaneous nucleation plays an extremely important role in numerous atmospheric and technological processes. Very diverse manifestations of this process like the formation of aerosol in atmospheric conditions [1–4] or well-managed technological processes of nanomaterial production via aerosol or hydrosol states [5,6] prevent us from describing this process uniquely: the complexity of general models makes their predictions unreliable and difficult for use.

However, not only practical needs impell one to study the kinetics of disperse phase formation. This process is also of great theoretical interest, for the universality specific to phase transitions reveals here itself in full scale.

This paper returns the reader to a simple model of the particle formation growth already studied by us [7–10] in this very context. The model considers the particle formation by nucleation and their subsequent condensational growth in a spacially uniform gas-vapor mixture (for definiteness gas-to-particle conversion will examplify our further consideration). The simple power dependence of the condensational efficiency $\alpha(g)$ on the particle mass is assumed to be

$$\alpha(g)=\alpha g^{\gamma},$$

where g is the number of molecules in the particle, and α and γ are constants. In Ref. [7] it was shown that at $\gamma=n/(n+1)$, with n being an integer, the condensation stage can be described in terms of $n+1$ moments of the particle-mass distribution and that all kinetic curves are the universal functions of specially defined universal variable playing the role of time. The question then immediately comes up: does this universality hold sometime else? Here we give a positive answer to this question and propose a renormalization procedure valid in a general case.

Later, in Ref. [9] we showed, that if the nucleation converts a small amount of condensable vapor to disperse particles then the coagulation process is well separated in time from the condensation stage and occurs much later. We thus postpone the consideration of this very important period of the development of disperse systems for a future publication.

This paper focuses on the nucleation-condensation process. After formulating the basic equations in Sec. II we consider the source-enhanced condensation where a constant in time source supplies the disperse system with the fresh portions of condensable substance. Although this process has been studied in Refs. [7–10] it is pertinent to show how to relax the restrictions related to the application of the moment method [11,12]. Sec. III demonstrates that the universal description proposed in [7] is applicable for the powerlike dependencies of more general form than $g^{n/(n+1)}$. This result is extended in Section IV to the free condensing systems (no source) that are not less important than the source-enhanced ones. We show that for the barrierless nucleation (the nucleation rate is a quadratic function of the concentration of condensable matter) the particle-mass spectra can be found analytically, and we use this fact in Sec. V for considering the nucleation-condensation process in three practically important cases:

(1) The free-molecular formation and growth of aerosol particles ($\gamma = 2/3$) often met in nanoparticle technologies. Although the moment consideration is effective in this case, we use a more general approach.

(2) The diffusion controlled condensational growth of island films [13,14] ($\gamma = 1/2$),

(3) The diffusion controlled particle growth [15,16] ($\gamma = 1/3$). The solution of the kinetic equations cannot be found by the moment method in this case. But a little bit more complicated general consideration allows for expressing the final particle-mass spectrum in terms of a contour integral that is then reduced to an ordinary one.

Section VI discusses the differences in the behavior of source-enhanced and free condensing systems. In the source-enhanced systems the evolution of the particle-mass spectrum never ceases. Its right wing moves to the right (toward bigger masses) and a powerlike singularity forms simultaneously at the left wing (small masses). In free systems there exist limiting (final) mass spectra that form at $t \to \infty$. These spectra are either singular at small g at $\gamma > 1/2$ or remain finite otherwise ($\gamma \leqslant 1/2$).

II. BASIC EQUATIONS

We consider a spacially uniform disperse system and assume that:

(1) There is a constant in time source of a condensable vapor (source-enhanced condensation) or the condensable vapor presents initially at a given concentration (no source, free condensation).

(2) The particles are produced from the vapor phase by nucleation. The nucleation rate is low compared to the source productivity. It means that nucleation converts only a small part of the vapor mass to disperse particles.

(3) The newly born particles then grow by condensation, i.e., the condensable molecules join to the particle by one [the process $(g) + (1) \to (g+1)$]. The efficiency of the growth process (condensation) is a power function of the particle mass with the power exponent $0 \leqslant \gamma < 1$.

The vapor concentration $C(t)$ changes with time because of the simultaneous action of three factors:

(i) the source that adds the condensable molecules with the rate I.

(ii) the nucleation that consumes g monomers to form an embryo of the mass g, and

(iii) the condensation of vapor molecules onto the particles formed by nucleation.

Hence, the equation for $C(t)$ is formulated as follows:

$$\frac{dC}{dt} = I - \int_0^\infty g J(g,t)\,dg - \alpha C \int_0^\infty g^\gamma N(g,t)\,dg. \tag{1}$$

Here I is the productivity of the external source of condensable vapor, $J(g,t)$ is the nucleation rate depending on the vapor concentration, and the last term describes the vapor condensation on the newly born particles whose mass spectrum is $N(g,t)$ ($N(g,t)dg$ is the number concentration of particles within the mass interval $[g, g+dg]$). The particle masses are measured in the units of vapor molecule mass, i.e., g is simply the number of vapor molecules in a particle.

The continuity equation

$$\frac{\partial N}{\partial t} + \frac{\partial}{\partial g}\dot{g} N = J(g,t) \tag{2}$$

describes the time evolution of the particle-mass spectrum $N(g,t)$. The rate $\dot{g}$ of the condensational growth of a g-mer is assumed to be

$$\dot{g} = \alpha(g) C = C \alpha g^\gamma, \tag{3}$$

where $0 \leqslant \gamma < 1$ and α is a condensation coefficient whose value depends on the details of the condensation process. For example [1], $\gamma = 2/3$ and $\alpha = \pi r_0^2 v_T$ for the condensational growth of aerosol particles in the free molecular regime (r_0 is the vapor molecule radius and v_T is its thermal velocity).

The nucleation rate $J(g,t)$ appearing on the right-hand sides (rhs) of Eqs (1) and (2) has the form

$$J(C) = A C_c^2 j(C/C_c)\,\delta(g-G) = J_G(C)\,\delta(g-G), \tag{4}$$

where C_c is a characteristic concentration scale (it can be, let us say, the saturating concentration), G is the critical embryo mass, A is a dimensionality carrier, and $\delta(x)$ is Dirac's delta function.

The concrete examples considered in this paper use the expression for the rate of barrierless nucleation:

$$J_2 = J = AC^2, \tag{5}$$

which describes the nucleation via stable dimers. In this case $A =$ cross section of the dimer formation times the thermal velocity of vapor molecules. The use of Eq. (6) simplifies very much the consideration retaining the main features of the nucleation-condensation process.

We assume also that only a small part of vapor converts to disperse particles by nucleation, i.e.,

$$\lim_{T \to \infty} \frac{1}{M(T)} \int_0^T G J_G\,dt \ll 1, \tag{6}$$

with $M(t)$ being the total particle mass concentration.

Equations (1) and (2) are to be subject to the initial conditions that are specified by the situation under consideration.

III. SOURCE-ENHANCED CONDENSATION

At nonzero I it is reasonable to use the system of units $\alpha = I = 1$, i.e., all concentrations are measured in the units of $\sqrt{I/\alpha}$ and time in $1/\sqrt{I\alpha}$.

In these nondimensional variables Eqs (1) and (2) take the form

$$\frac{dC}{dt}=1-\mu jG-C\int g^{\gamma}N(g,t)dg, \tag{7}$$

$$\frac{\partial N(g,t)}{\partial t}+C\frac{\partial}{\partial g}g^{\gamma}N(g,t)=\mu j\,\delta(g-G), \tag{8}$$

where $\mu=AC_c^2/I$ is the smallness parameter for the source-enhanced nucleation-condensation process. The term $\propto\mu$ on the rhs of Eq. (7) can be ignored ($\mu\ll 1$) in contrast to the similar term on the rhs of Eq. (8), because this very term is responsible for the production of new particles.

Equations (7) and (8) are subject to zero initial conditions:

$$N(g,0)=0,\quad C(0)=0. \tag{9}$$

Now it becomes clear, that there is no way to develop a straightforward perturbation theory with respect to the smallness parameter μ, because the zero approximation gives the trivial result: the linear growth of $C(t)$ and no new particles. The fact that some nontrivial steps are in order was noticed in [7], where a version of the perturbation theory was proposed for the set of equations describing the time evolution of the moments of the particle mass distribution. Here we extend this approach to the general case.

Let us rescale the variables and unknown functions:

$$g=g_0y,\quad t=t_0\theta,\quad C=C_0c,\quad N=N_0n. \tag{10}$$

We choose the scales t_0, g_0, N_0, C_0 from the condition that Eqs (7) and (8) do not change on rescaling. It is possible to do putting four conditions on four scales t_0, g_0, N_0, C_0:

$$\frac{C_0}{t_0}=1,\quad C_0g_0^{\gamma+1}N_0=1,$$

$$\frac{N_0}{t_0}=C_0,\quad g_0^{\gamma-1}N_0=\frac{\mu}{g_0}. \tag{11}$$

The scales are now readily defined

$$C_0=t_0=\mu^{-(1-\gamma)/(4-2\gamma)},\quad g_0=\mu^{-1/(2-\gamma)},$$

$$N_0=\mu^{(3+\gamma)/(4-2\gamma)}. \tag{12}$$

Rescaled equations take the form:

$$\frac{dc}{d\theta}=1-\phi_{\gamma}c, \tag{13}$$

$$\frac{\partial n}{\partial\theta}+c\frac{\partial}{\partial y}y^{\gamma}n=j\left(\frac{c}{c_c}\right)\delta(y), \tag{14}$$

where $c_c=C_c/C_0$. The terms containing the positive powers of μ were ignored in deriving Eqs (13) and (14). The moments $\phi_{\gamma}(\theta)$ are introduced by the equation

$$\phi_{\gamma}(\theta)=\int_0^{\infty}y^{\gamma}n(y,\theta)dy. \tag{15}$$

Continuity equation (14) can be solved independently of Eq. (13). To this end we replace the rhs of this equation by the boundary condition

$$\lim_{y\to 0}y^{\gamma}n(y,\theta)=j(c/c_c). \tag{16}$$

Hence, we must solve the homogeneous equation

$$\frac{\partial n}{\partial\theta}+c\frac{\partial}{\partial y}y^{\gamma}n=0 \tag{17}$$

with the boundary condition given by Eq. (16).

Now let us introduce a new variable

$$\tau=\int_0^{\theta}c(\theta')d\theta' \tag{18}$$

that reduces Eq. (17) to the partial linear first-order differential equation whose solution is readily found by standard methods. The result is

$$n(y,\tau)=\frac{1}{y^{\gamma}}\frac{j(x)}{c(x)}\Theta(x). \tag{19}$$

Here

$$x=\tau-(1-\gamma)^{-1}y^{1-\gamma}, \tag{20}$$

$j(x)=j(c(x)/c_c)$, and $\Theta(x)$ is the Heaviside step function. The spectrum is thus stretched from $y=0$ to $y=y_{max}$, where

$$y_{max}=[(1-\gamma)\tau]^{1/(1-\gamma)}. \tag{21}$$

Let us return now to Eq. (13) for c. Simply replacing the variable $\zeta=\tau-(1-\gamma)^{-1}y^{1-\gamma}$ in the integral on the rhs of Eq. (13) leads to the closed equation for c (see also [8])

$$c\frac{dc}{d\tau}=1-(1-\gamma)^{\gamma/(1-\gamma)}c\int_0^{\tau}(\tau-\zeta)^{\gamma/(1-\gamma)}\frac{j(\zeta)}{c(\zeta)}d\zeta, \tag{22}$$

and a useful formula for the moments,

$$\phi_{\sigma}(\tau)=\int_0^{\infty}y^{\sigma}n(y,\tau)dy$$

$$=(1-\gamma)^{\sigma/(1-\gamma)}\int_0^{\tau}(\tau-\zeta)^{\sigma/(1-\gamma)}\frac{j(\zeta)}{c(\zeta)}d\zeta. \tag{23}$$

This formula gives especially simple results at $\sigma=n(1-\gamma)$ (n is a non-negative integer). In particular, for the total particle number concentration we have

$$\phi_0(\tau)=\int_0^{\tau}\frac{j(\zeta)}{c(\zeta)}d\zeta. \tag{24}$$

Now it is seen why $\gamma=n/(n+1)$ simplifies the consideration of the condensation process: at such γ the power of $\tau-\zeta$ on the rhs of Eq. (22) is integer, and this equation can be either reduced to an ordinary differential equation of the order of

$n+1$ for $c(\tau)$ or to a set of equations for the moments. There are other dependencies of the condensational efficiency $\alpha(g)$ allowing for reducing the continuity equation to a finite set of the first-order ordinary differential equations for generalized moments [10].

The formula allowing one to find $\theta(\tau)$ once $c(\tau)$ has been found from Eq. (13), is readily derived by using Eq. (18) in the differential form $d_\theta \tau = c$. The latter immediately gives

$$\theta(\tau) = \int_0^\tau \frac{d\zeta}{c(\zeta)}. \tag{25}$$

IV. FREE CONDENSATION

The above theory is readily extended to the case of free condensation (there is no source, but the initial vapor concentration is not zero). The initial conditions are now

$$N(g,0)=0, \quad C(0)=C_i. \tag{26}$$

The system of units used in this case is $\alpha = C_i = 1$, i.e., the concentrations $C(t)$ and $N(g,t)$ are measured in the units of C_i and time in $1/\alpha C_i$. Equations (7) and (8) change very slightly,

$$\frac{dC}{dt} = -C\int_0^\infty g^\gamma N(g,t)\,dg, \tag{27}$$

$$\frac{\partial N(g,t)}{\partial t} + C\frac{\partial}{\partial g} g^\gamma N(g,t) = \mu j(C/C_c)\,\delta(g-G). \tag{28}$$

Here $\mu = AC_c^2/\alpha C_i^2$ is the smallness parameter.

Let us now rescale the variables and unknown functions,

$$g = g_0 y, \quad t = t_0\theta, \quad N = N_0 n. \tag{29}$$

In contrast to the source-enhanced case the monomer concentration is not renormalized.

Let us again choose the scales from the condition that Eqs (27) and (28) do not change on rescaling. These conditions are

$$g_0^{\gamma+1} N_0 t_0 = 1, \quad g_0^{\gamma-1} t_0 = 1, \quad \mu = g_0^\gamma N_0. \tag{30}$$

Equations (30) express the scales in terms of μ as follows:

$$t_0 = \mu^{-(1-\gamma)/(2-\gamma)}, \quad g_0 = \mu^{-1/(2-\gamma)}, \quad N_0 = \mu^{2/(2-\gamma)}. \tag{31}$$

Now the set of Eqs (27) and (28) is replaced with

$$\frac{dC}{d\theta} = -C\int_0^\infty n(y,\theta) y^\gamma dy, \tag{32}$$

$$\frac{\partial n}{\partial \theta} + C\frac{\partial y^\gamma n}{\partial y} = 0. \tag{33}$$

The latter equation is subject to the boundary condition

$$\lim_{y\to 0} y^\gamma n = \frac{j(C/C_c)}{C}. \tag{34}$$

Following the route of the preceding section one finds the equation for $C(\tau)$ in the form

$$\frac{dC}{d\tau} = -(1-\gamma)^{\gamma/(1-\gamma)}\int_0^\tau (\tau-\xi)^{\gamma/(1-\gamma)}\frac{j(C(\xi)/C_c)}{C(\xi)}\,d\xi. \tag{35}$$

This equation can be solved analytically for the barrierless nucleation. The substitution $j = C^2$ [see Eq. (5)] to the integrand of Eq. (35) linearizes this equation. Taking then the Laplace transform and using the convolution theorem yield

$$C(p) = \frac{p^{1/(1-\gamma)}}{p^{(2-\gamma)/(1-\gamma)} + (1-\gamma)^{\gamma/(1-\gamma)}\Gamma[1/(1-\gamma)]}, \tag{36}$$

where $\Gamma(x)$ is the Euler gamma function and $C(p) = \int_0^\infty C(\tau)e^{-p\tau}d\tau$ is the Laplace transform of $C(\tau)$.

Equations (19)–(21) and (23)–(25) hold for free condensation.

V. EXACTLY SOLUBLE MODELS

Below we analyze the cases

(i) $\gamma = 2/3$ (kinetically controlled growth of aerosol particles [12]),

(ii) $\gamma = 1/2$ (diffusion controlled growth of islands on flat surfaces [13,14]), and

(iii) $\gamma = 1/3$ (diffusion controlled growth of spherical particles [1,15,16]).

These cases are sufficiently simple and of great practical importance. They present rare examples where the practical importance and the possibility of exact analysis are compatible.

A. The case $\gamma = 2/3$

Equation (36) gives for $\gamma = 2/3$

$$C(p) = \frac{p^3}{p^4 + 2/9}. \tag{37}$$

The singularities of the Laplace image $C(p)$ are simple poles located at $p_k = (2/9)^{1/4}\exp[i(2k+1)\pi/4]$, $k = 0,1,2,3$. Standard methods restore $C(\tau)$. The result is

$$C(\tau) = \cosh(p_0\tau)\cos(p_0\tau), \tag{38}$$

where $p_0 = (18)^{-1/4}$. The variable τ changes from 0 to $\tau_\infty = \pi/(2p_0) \approx 3.235$ [the first root of the equation $C(\tau) = 0$]. The point τ_∞ corresponds to $t = \infty$ where the monomer concentration is entirely depleted.

The particle mass distribution found from Eq. (19) is

$$n(y,\tau) = y^{-2/3}C(\tau - 3y^{1/3})\Theta(\tau - 3y^{1/3}). \tag{39}$$

The moments of the order of 0, 1/3, and 2/3 are also readily found from Eqs (23) and (24). Elementary integrations give

$$\phi_0=\frac{1}{2p_0}[\cosh(p_0\tau)\sin(p_0\tau)+\sinh(p_0\tau)\cos(p_0\tau)], \tag{40}$$

$$\phi_{1/3}=\frac{1}{6p_0^2}[\sinh(p_0\tau)\sin(p_0\tau)], \tag{41}$$

$$\phi_{2/3}=\frac{1}{18p_0^3}[\cosh(p_0\tau)\sin(p_0\tau)-\sinh(p_0\tau)\cos(p_0\tau)]. \tag{42}$$

The moments of the final ($t=\infty$ or $\tau=\tau_\infty$) particle-mass distribution are

$$\phi_0(\tau_\infty)=\frac{1}{2p_0}\cosh\left(\frac{\pi}{2}\right)=2.584,$$

$$\phi_{1/3}(\tau_\infty)=\frac{1}{6p_0^2}\sinh\left(\frac{\pi}{2}\right)=1.627,$$

$$\phi_{2/3}(\tau_\infty)=\frac{1}{18p_0^3}\cosh\left(\frac{\pi}{2}\right)=1.218. \tag{43}$$

Of central interest is the final spectrum. On substituting $\tau=\tau_\infty$ to the rhs of Eq. (39) yields

$$n(y,\infty)=y^{-2/3}\cosh\left(\frac{\pi}{2}-3p_0y^{1/3}\right)\times\sin(3p_0y^{1/3})\Theta\left(\frac{\pi}{2}-3p_0y^{1/3}\right). \tag{44}$$

It is not very difficult to check that the spectrum is correctly normalized

$$M(\infty)=\int_0^{y_{max}}yn(y,\infty)dy=1, \tag{45}$$

i.e., all vapor has condensed on the dispersed particles. Here $y_{max}=(\pi/6p_0)^3$. This restriction comes from Θ function on the rhs of Eq. (44).

B. The case $\gamma=1/2$

At $\gamma=1/2$ Eq. (36) gives

$$C(p)=\frac{p^2}{p^3+1/2}. \tag{46}$$

Again, the singularities of $C(p)$ are the simple poles at $p_k=2^{-1/3}\exp(ik\pi/3)$, $k=1,2,3$. The Laplace inversion of Eq. (46) is restored by standard methods. The result is

$$C(\tau)=\tfrac{1}{3}[e^{-2a\tau}+2e^{a\tau}\cos(a\sqrt{3}\tau)], \tag{47}$$

where $a=2^{-4/3}$. The first zero of $C(\tau)$ defines $\tau_\infty=2.330\,63$.

The moments can be also restored. Rather simple but tedious integrations give

$$\phi_{1/2}(\tau)=\frac{1}{3\times2^{1/3}}\{e^{-2a\tau}-e^{a\tau}[\cos(a\sqrt{3}\tau)-\sqrt{3}\,\sin(a\sqrt{3}\tau)]\}, \tag{48}$$

$$\phi_0(\tau)=\frac{2^{1/3}}{3}\{-e^{-2a\tau}+e^{a\tau}[\cos(a\sqrt{3}\tau)+\sqrt{3}\,\sin(a\sqrt{3}\tau)]\}. \tag{49}$$

The final values of the moments are

$$\phi_{1/2}(\tau_\infty)=1.217,\quad \phi_0(\tau_\infty)=1.734, \tag{50}$$

and the final spectrum of particles has the form

$$N_\infty(g)=\frac{1}{\sqrt{y}}C(\tau_\infty-2\sqrt{y})\Theta(\tau_\infty-2\sqrt{y}), \tag{51}$$

where $C(\tau)$ is given by Eq. (47).

C. The case $\gamma=1/3$

As was shown in [7], the above examples can be reduced to the solution of a set of ordinary differential equations. This trick does not work at $\gamma=1/3$, and all the difficulties inherent to the general case come up in full.

The Laplace image $C(p)$ of $C(\tau)$ is readily found from Eq. (36)

$$C(p)=\frac{p^{3/2}}{p^{5/2}+\sqrt{\pi/6}}. \tag{52}$$

The function $C(\tau)$ is now expressed in terms of a contour integral as

$$C(\tau)=\frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty}\frac{p^{3/2}}{p^{5/2}+\pi/\sqrt{6}}e^{p\tau}dp. \tag{53}$$

The integration contour passes on the right of all singularities of the integrand. The latter has the branch point at $p=0$ and two simple poles at $p_{1,2}=(\pi/6)^{1/5}\exp(\pm i\pi/5)$ on the sheet of the complex plane p $(-\pi<\arg p<\pi)$ (see Fig. 1). We cut the complex plane p along the negative part of the real axis $\mathrm{Re}(p)<0$, $\mathrm{Im}(p)=0$ and deform the integration contour as shown in Fig. 1. So the integral on the rhs of Eq. (53) becomes the sum of two terms

$$C(\tau)=F_1(\tau)+F_2(\tau), \tag{54}$$

where F_1 and F_2 are the contributions from the cut and the poles, respectively. They are

$$F_1(\tau)=\frac{1}{\sqrt{6\pi}}\int_0^\infty\frac{p^{3/2}e^{-p\tau}dp}{p^5+\pi/6}, \tag{55}$$

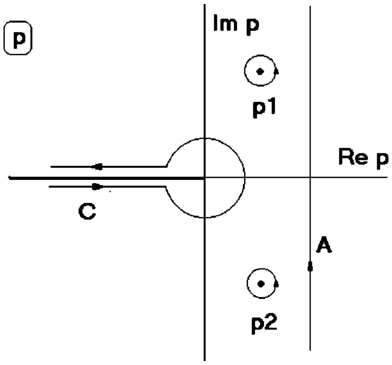

FIG. 1. The integration contour *A* in Eq. (51) is transformed to the contour *C* going along the cut in the complex plane *p* and two contours circumventing the poles of the intergrand on the rhs of Eq. (51) located at the first sheet of *p*-plane $[-\pi/2<\arg(p)<\pi/2]$.

$$F_2(\tau)=\tfrac{4}{5}e^{a\tau}\cos(b\tau), \tag{56}$$

where $a=(\pi/6)^{1/5}\cos(2\pi/5)$ and $b=(\pi/6)^{1/5}\sin(2\pi/5)$. The values of τ_∞ and $\phi_0(\tau_\infty)$ found numerically are $\tau_\infty=1.918$ and $\phi_0(\tau_\infty)=1.346$.

VI. RESULTS AND DISCUSSION

The theory developed above allows for the universal description of the kinetics of nucleation-condensation process in source-enhanced and free systems. This means that the governing equation (and thus the kinetic curves) do not contain any free parameters at all. Strictly speaking, this statement is valid only for the powerlike dependencies of nucleation rate on the concentration of condensable vapor. For arbitrary nucleation rates the nondimensional group c_c appears in Eq. (14). Still the perturbation theory with respect to the smallness parameter μ can be developed similarly to the case of powerlike nucleation rates [7], and the losses of universality are not huge: the scale C_0 renormalizing the characteristic concentration contains the governing parameter μ to low powers 1/8, 1/6, and 1/5 for $\gamma=2/3$, 1/2, and 1/3, respectively, for source-enhanced condensation. In the case of free condensation this scale defines the initial supersaturation $c_\mathrm{c}=C_\mathrm{c}/C_i$.

There are some qualitative differences in the kinetics of particle formation and growth in source-enhanced and free condensing systems. The integral $\tau_\infty\propto\int_0^\infty C(t)dt$ converges for sourceless systems and diverges in source-enhanced ones. The dependencies of nondimensional concentrations on τ are demonstrated in Figs. 2(a) and 2(b). Figure 2(a) shows that they are not drastically different for free systems in the three considered cases $\gamma=1/3$, 1/2, 2/3. The difference in the behavior of free [curve 1 of Fig. 2(b)] and source enhanced [curve 2 of Fig. 2(b)] systems is clearly seen. The free condensation ceases at $\tau=\tau_\infty$ whereas the source-enhanced condensation is endless in τ representation.

The final mass spectra in free systems are shown in Fig. 3(a) for $\gamma=2/3$, 1/2, and 1/3 (curves 1–3, respectively). The curves are normalized to unity [see Eq. (43)] and presented in the coordinates $C, x=y/y_{max}=g/g_{max}$ [see Eq. (21)]. There is a clear difference in their behavior. At $\gamma=2/3$ the final mass spectrum has the singularity at small masses: $C(g)\propto g^{-1/3}$ [curve 1 in Fig. 3(a)]. The spectrum is finite at small masses at $\gamma=1/2$ (curve 2), and it goes to 0 at $\gamma=1/3$ (curve 3). This is a reflection of the phase transition at $\gamma=1/2$ discussed in [8].

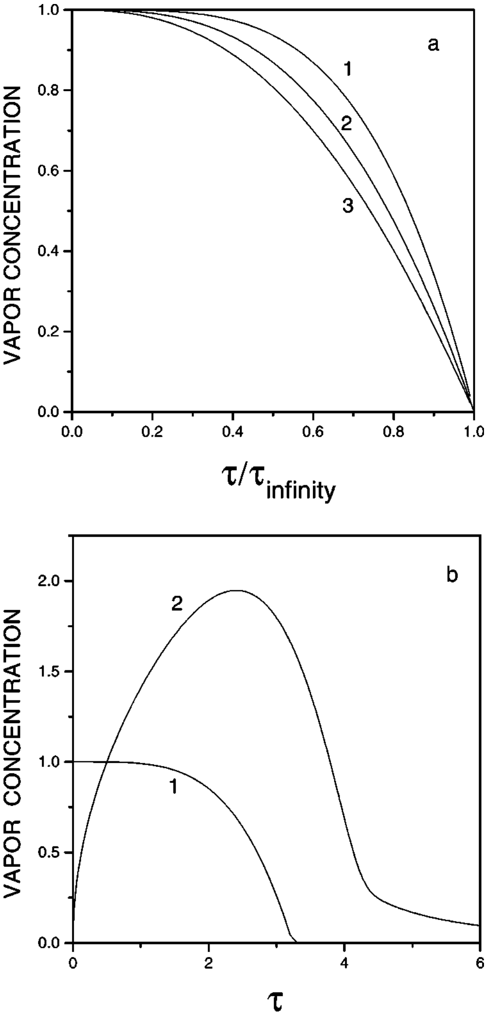

FIG. 2. (a) The nondimensional concentration of condensable vapor in the case of free condensation as the functions of ratio τ/τ_0 playing the role of time. The vapor is seen to deplete entirely during a finite interval of τ. The curves 1–3 correspond to $\gamma=2/3$, 1/2, 2/3, respectively. (b) In contrast to free condensation the same process in the presence of a source of vapor never ends (curve 2, $\gamma=2/3$). Curve 1 for free condensation ($\gamma=2/3$) is shown for comparison. The nondimensional variable τ is introduced by Eq. (18).

The difference in the spectral behavior of the final spectra at small masses is related to the fact that the function $C[\tau_\infty]=0$. On expanding $C(\tau)$ in the Taylor series in the vicinity of $\tau=\tau_0$ yield

$$n(y)\approx C'(\tau_0)(\gamma-1)y^{1-2\gamma}\propto g^{1-2\gamma}. \tag{57}$$

Equation (57) accounts for the origination of the phase transition at $\gamma=1/2$.

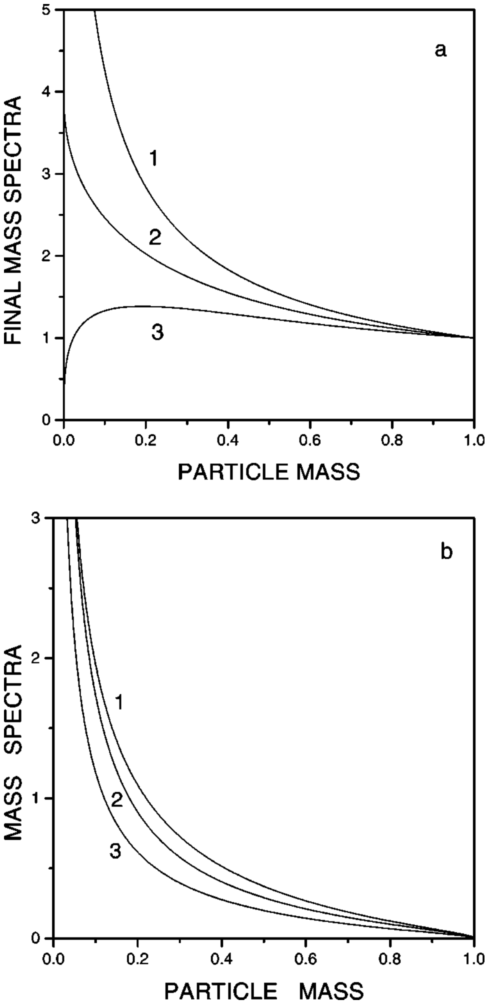

FIG. 3. (a) The nondimensional mass spectra are shown as the functions of particle mass (in the units of maximally reachable mass $x=y/y_{max}=g/g_{max}$ [see Eqs (19)–(21)]). The spectrum at $\gamma=2/3$ (curve 1) has a singularity at small masses. At $\gamma=1/2$ (curve 2) the spectrum remains finite at small masses, and at $\gamma=1/3$ the spectrum goes to 0 (curve 3). (b) The nondimensional mass spectrum at $\gamma=2/3$ for the source-enhanced condensation. Curves 1–3 correspond to $\tau=1$, 3, 5, respectively. The maximal mass in this case is $y_{max}=(\tau/3)^3$ [see Eq (21)].

Even more remarkable is the fact that all the mass spectra are singular at $\tau<\tau_\infty$. The explanation is simple: the factor $C(\tau-(1-\gamma)y^{1-\gamma})$ remains finite at $y=0$, and nothing cancels the singularity coming from the factor $y^{-\gamma}$ in Eq. (19). For this very reason the spectra in source-enhanced systems are always singular: $\tau_\infty=\infty$ in this case, and respectively, the function $c(\tau)>0$. These spectra are shown in Fig. 3(b) in the coordinates $c, x=y/y_{max}$ for $\gamma=2/3$ and $\tau=1$, 3, 5 (curves 1–3 respectively). Here $y_{max}=(2\tau/3)^3$ [see Eqs (19)–(21)].

The value $g_0=\mu^{-1/(2-\gamma)}$ defines the characteristic scale of the particle mass spectra. Hence, the average mass of the particles and the width of the mass distribution are of the same order, which means that the latter is not described by a narrow curve, i.e., the particles formed in the nucleation controlled condensation process are polydisperse.

VII. CONCLUSION

We considered the kinetics of nucleation controlled formation and condensational growth of particles in disperse systems. The disperse particles were assumed to be born from a volatile vapor in a nucleation process and then to grow by its condensation.

The main results of this paper can be summarized as follows:

(1) The process of particle formation growth was shown to be governed by one small parameter: the ratio of vapor mass converted to newly born particles to the total vapor mass spent in particle formation. However, a direct application of the perturbation theory with respect to this parameter was not possible, and only the rescalings Eqs (10) and (11) for source-enhanced systems, and Eqs (29) and (30) for free systems saved the situation and made it possible to resolve the problem. In contrast to Ref. [7] the renormalization procedure was applied to the full equations describing the time evolution of the particle-mass spectra in disperse systems rather than to the equations for the moments. It was shown that the final equations either contain no smallness parameter at all (when the nucleation rate is a power function of the vapor concentration) or this parameter appears in the expression for nondimensional nucleation rate and defines the length of the nucleation period. Of course, the results of Ref. [7] are readily obtained from the present consideration.

(2) We showed that for the barrierless nucleation (the nucleation rate is a quadratic function of the concentration of condensable matter) the particle mass spectra can be found analytically, and we used this fact for considering the free nucleation-condensation process in three practically important systems:

(i) The free molecular formation and growth of aerosol particles (the mean free path of condensable molecules much exceeds the particle size) often met in nanoparticle technologies ($\gamma=2/3$).

(ii) Diffusion controlled condensational growth of island films ($\gamma=1/2$).

(iii) Diffusion controlled particle growth ($\gamma=1/3$).

We found the differences in the behavior of the source-enhanced and free condensing systems. In the source-enhanced systems the evolution of the particle mass spectrum never ceases. Its right wing moves right (toward bigger masses) and a powerlike singularity forms simultaneously at the left wing (small masses). In the free systems there exist limiting (final) mass spectra that form at $t\to\infty$. These spectra are either singular at small g at $\gamma>1/2$ or remain finite otherwise ($\gamma\leqslant 1/2$).

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