

## Source-enhanced condensation in monocomponent disperse systems

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Homogeneous condensation in the presence of a spatially uniform source producing a condensible monocomponent substance is considered within the model assuming the condensation growth to follow the scheme  $(g) + (1) \rightarrow (g + 1)$ , with  $g$  being the number of monomers (molecules of the condensing substance) in the growing particle. The mass spectrum is expressed in terms of the function describing time evolution of the monomer concentration. In contrast to the case of free condensation (no external source) the mass spectrum is a smooth function of the particle mass with the frontal peak moving with time to the right along the mass axis. The particle number concentration is shown to either grow unlimitedly with increasing time or remain finite, depending on how fast the condensation coefficients  $\alpha_g$  describing the rates for monomer accretion grow with the particle mass  $g$ . For power dependencies  $\alpha_g \propto g^\lambda$ , the condensation regime changes at  $\lambda = \frac{1}{2}$ . The analogy of this phenomenon with the second order phase transitions is marked. Numerical calculations for powerlike  $\alpha_g$  at  $\lambda = 0, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$ , and 1 illustrate the characteristic features of the mass spectra in source-enhanced condensing systems. The cases  $\lambda = 0$  and  $\lambda = 1$  are treated analytically.

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### I. INTRODUCTION

Although the investigation of the formation and growth of disperse particles by condensation had started rather long ago [1–5], a few works considered the condensation processes in the presence of a permanently acting source of fresh molecules of condensing substance (see, however, [6], and references therein). Meanwhile, the situations where newly formed molecules of a condensing substance appear during the course of the condensation process are not as rare. It is enough to mention the condensation of sulphuric acid molecules on water droplets and other aerosol particles [7–9], formation of aerosols from low volatile vapors [8–10], condensational growth of suspensions in liquids [11], and voids and bubbles in solids [12].

In this paper, we study the following process: a spatially uniform source whose productivity  $I(t)$  is known as a function of time  $t$  provides the system with the molecules of a condensing substance. These molecules may then be involved in the growth process in three ways:

(1) Upon collision, two vapor molecules form a stable dimer which then serves as a condensation nucleus, i.e., it is able to grow by joining other monomeric molecules to form  $g$ -mers (nonbarrier nucleation).

(2) The molecules start to nucleate. The nucleation process produces overcritical disperse particles that serve as condensation nuclei. Their production rate is connected with the function  $I(t)$  and the rates of elementary

processes for a monomer to escape from or condense onto the  $g$ -mer surface.

(3) The molecules resulting from the source condense on preexisting particles (heterogeneous condensation).

In what follows, we consider only the nonbarrier nucleation leaving the other two cases for future work. Starting with the set of equations describing the kinetics of the condensation process in the presence of the external source, we will show that the mass spectrum of forming disperse particles can be expressed in terms of the function describing the time dependence of the monomer concentration. This function is derivable from an ordinary nonlinear integro-differential equation. The solution of the equation is found for two exactly soluble models and three realistic cases corresponding to surface or diffusion controlled growth of disperse particles. Respective growth laws are summarized in Ref. [6] where the growth rates are shown to be power functions of the growing particle mass.

The main result of our present consideration is the recognition of the fact that the mass spectrum of condensing particles can be expressed in terms of the function describing time evolution of the monomer concentration. In contrast to the case of free condensation (no external source) the mass spectrum is a smooth function of the particle mass with the frontal peak moving with time to the right along the mass axis. The particle number concentration is shown either to grow unlimitedly with increasing time or remain finite depending on how fast the condensation coefficients  $\alpha_g$  describing the rate for monomer accretion grow with the particle mass  $g$ . For power laws  $\alpha_g \propto g^\lambda$  the critical exponent is  $\lambda = \frac{1}{2}$ . The analogy of this phenomenon with the second order phase transition is emphasized.

The remainder of this paper is divided as follows. Sec-

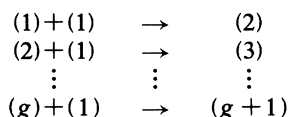
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tion II gives a general statement of the problem and formulation of basic equations for the case of nonbarrier nucleation. The third section contains a formal solution of the set of equation for the condensation process. We are able to express the mass spectrum in terms of the function describing the time dependence of the monomer concentration and a Green's function that can be found from a set of linear ordinary differential equations. Two exactly solvable models are introduced and analyzed in Sec. IV. The condensation coefficients in these models are either independent of the growing particle mass or depend linearly on the latter. Exact Green's functions are found and rather simple differential equations are formulated governing the time evolution of the monomer concentration. The exact results prompt a suitable approximation allowing the general case to be solved in a more or less closed form. The idea is that the respective Green's functions are very narrow peaks as functions of time which allows one to reduce the particle mass distribution to a combination of the monomer concentration as a function of time and some simple functions of the condensation coefficients and time. An asymptotic analysis of these simplified equations is then performed and the laws of decreasing the monomer concentration with time are found analytically for the condensation coefficients increasing as a power of growing particle mass. All this is done in Sec. V. The results are summarized and discussed in Sec. VI. The paper concludes with several remarks on possible applications and the extension of the theory of source enhanced condensation (Sec. VII).

## II. BASIC EQUATIONS

We begin by considering the situation when the carrier medium contains a spatially uniform source of condensing molecules (monomers in what follows). We assume the following:

(1) The monomers are able to form stable dimers, growing them by joining monomers along the scheme



(2) The rate  $\alpha_g$  (condensation coefficients) of joining a monomer to a  $g$ -mer is a known function of the mass  $g$  of growing particle. Everywhere below  $\alpha_g$  is assumed to be a power function of the particle mass  $g$ ,

$$\alpha_g = \alpha g^\lambda \quad (1)$$

with  $0 \leq \lambda \leq 1$ . The justification of this choice can be found in Ref. [6] where a wide number of growth processes in disperse systems are shown to be described by power functions with  $\lambda = \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, 1$ .

(3) The source productivity  $I(t)$  is a known function of time  $t$ . Here we consider the sources independent of time.

Let  $c_1(t), c_2(t), \dots, c_g(t)$  be the concentrations of  $1, 2, \dots, g$ -mers (mass spectrum). The set of equations describing its time evolution is of the form

$$\frac{dc_1}{dt} = I - c_1 \sum_{g=1}^{\infty} \alpha_g c_g, \quad (2)$$

$$\frac{dc_2}{dt} = \frac{1}{2} \alpha_1 c_1^2 - \alpha_2 c_1 c_2, \quad (3)$$

⋮

$$\frac{dc_g}{dt} = \alpha_{g-1} c_1 c_{g-1} - \alpha_g c_1 c_g. \quad (4)$$

These equations have quite a transparent physical meaning. The change in the concentration of  $g$ -mers results from two processes:  $(g-1)+(1) \rightarrow (g)$  and  $(g)+(1) \rightarrow (g+1)$  [the first and second terms on the right-hand side (rhs) of Eq. (4), respectively]. The first process adds  $g$ -mers into the system while the second one leads to their losses which stipulates the opposite signs of these terms.

The first two equations of this set are of a different structure. Equation (3) contains  $\frac{1}{2}$  before the first term on its rhs that reflects the identity of two colliding monomers. The right-hand side of Eq. (2) describes the monomer production [the term  $I(t)$ ] and the sink due to monomer capture by *all* forming particles.

This set of equations should be supplemented with the initial conditions. We assume now that no disperse particles existed until  $t=0$  which means that

$$c_g(0) = 0. \quad (5)$$

Let us write down two useful consequences of the above equations. On summing all Eqs. (3) and (4) over  $g$  within the interval  $[2, \infty)$  gives an equation for the number concentration  $N$  of aerosol particles,

$$\frac{dN}{dt} = \frac{1}{2} \alpha_1 c_1^2 \quad (6)$$

with  $N = \sum_{g=2}^{\infty} c_g$ . The summation in  $N$  begins with  $g=2$ , since the monomeric molecules are not attributed to the disperse phase.

The second consequence reflects the conservation of the total mass concentration  $M(t) = \sum_{g=2}^{\infty} g c_g(t)$ . Multiplying both sides of the set of Eqs. (3) and (4) by  $g$  and summing again over all  $g \geq 2$  yield  $\dot{M} = I - \dot{c}_1$  or

$$M = It - c_1. \quad (7)$$

The set of Eqs. (2)–(4) is invariant under the scaling transformation

$$c \rightarrow \frac{c}{c_0}, \quad t \rightarrow \frac{t}{t_0}, \quad I \rightarrow \frac{I}{I_0}, \quad \alpha \rightarrow \frac{\alpha}{\alpha_0} \quad (8)$$

once the subsidiary restrictions

$$\alpha_0 c_0 t_0 = 1, \quad \frac{I_0 t_0}{c_0} = 1 \quad (9)$$

are imposed on the characteristic scales of the transformation. These restrictions define the characteristic scales of time and concentrations in terms of the scales of the condensation coefficient and the source intensity ( $\alpha_0$  and  $I_0$ , respectively),

$$t_0 = \frac{1}{\sqrt{I_0 \alpha_0}}, \quad c_0 = \sqrt{I_0 / \alpha_0}. \quad (10)$$

In particular, the latter equations will allow us to put  $I = 1$  and  $\alpha_1 = 1$  in Eqs. (2)–(4) under certain conditions.

### III. A FORMAL SOLUTION

The strategy for solving the infinite set of nonlinear coupled differential Eqs. (2)–(4) includes the following six steps:

(1) Equations (3) and (4) are treated independently of Eq. (2), the concentration  $c_1$  being considered as a *given* function of time.

(2) The new variable (see also Refs. [4,6])

$$\tau = \int_0^t c_1(t') dt' \quad (11)$$

is introduced instead of  $t$ . This step casts Eqs. (3) and (4) into an infinite set of *uncoupled linear* ordinary differential equations affording the truncation at any  $g$  not affecting the remaining equations containing the concentrations with higher numbers.

(3) The Laplace transform with respect to  $\tau$  reduces these equations to a set of recurrence relations allowing the Laplace transform of any concentration  $C_g(p)$  to be expressed in terms of  $C_1(p)$ .

(4) On inverting  $C_g(p)$  one finds the  $\tau$  dependence of  $c_g$ , which is then used to close Eq. (2) for  $c_1(\tau)$ . The ordinary integro-differential equation thus obtained is available for further numerical and asymptotic analysis.

(5) The mass spectrum  $\{c_g(\tau)\}$  is finally expressed in terms of  $c_1(\tau)$  and the Green's function obeys the same set of equations as  $c_g(\tau)$  but with a  $\delta$ -function nonuniformity.

(6) There are no problems when returning from  $\tau$  to  $t$  once  $c_1(\tau)$  is found,

$$t(\tau) = \int_0^\tau \frac{d\tau'}{c_1(\tau')}. \quad (12)$$

Let us start to fulfill this program. The first step has been done [see Eq. (11)]. Now Eqs. (3) and (4) take the form

$$\frac{dc_2}{d\tau} = \frac{1}{2}\alpha_1 c_1 - \alpha_2 c_2. \quad (13)$$

This equation contains the nonuniformity  $c_1(\tau)$  which at this stage is considered a known function of the new variable  $\tau$ . Other equations of this set are homogeneous,

$$\frac{dc_g}{d\tau} = \alpha_{g-1} c_{g-1} - \alpha_g c_g. \quad (14)$$

Let us apply the Laplace transform to Eqs. (3) and (4). Recalling zero initial conditions (5) one finds

$$(p + \alpha_2)C_2 = \frac{1}{2}\alpha_1 C_1, \quad (15)$$

⋮

$$(p + \alpha_g)C_g = \alpha_{g-1} C_{g-1}, \quad (16)$$

where

$$C_g(p) = \int_0^\infty c_g(\tau) e^{-p\tau} d\tau. \quad (17)$$

The solution of the above set of linear algebraic equations is readily found,

$$C_g(p) = G_g(p) C_1(p), \quad (18)$$

where

$$G_g(p) = \frac{\alpha_1 \alpha_2 \dots \alpha_{g-1}}{2(p + \alpha_2)(p + \alpha_3) \dots (p + \alpha_g)}. \quad (19)$$

The inversion of Eq. (18) gives

$$c_g(\tau) = \int_0^\tau \mathcal{G}_g(\tau - \tau') c_1(\tau') d\tau', \quad (20)$$

where  $\mathcal{G}_g(t)$  is the inversion of  $G(p)$  and plays the role of the Green's function for the set of Eqs. (3) and (4). It obeys the same equations as  $c_g(\tau)$  with the only difference being that  $c_1(\tau)$  in Eq. (13) is replaced by the Dirac  $\delta$  function  $\delta(\tau)$ . The explicit equation for  $\mathcal{G}_g(\tau)$  can also be written down,

$$\mathcal{G}_g(\tau) = \frac{1}{2} \sum_{s=2}^g e^{-\alpha_s \tau} \prod_{r=2}^g \frac{\alpha_{r-1}}{\alpha_r - \alpha_s}. \quad (21)$$

Here the prime over  $\prod$  indicates that the multiplier with  $s = r$  is omitted.

Equation (20) allows one to close Eq. (2),

$$c_1 \frac{dc_1}{d\tau} = I - \alpha_1 c_1^2 - c_1 \int_0^\tau R(\tau - \tau') c_1(\tau') d\tau'. \quad (22)$$

Here

$$R(\tau) = \sum_{g=2}^\infty \alpha_g \mathcal{G}_g(\tau). \quad (23)$$

### IV. EXACTLY SOLUBLE MODELS

In this section, we consider two exactly soluble models with specially chosen condensation rates  $\alpha_g$ , (1) the condensation rate  $\alpha_g = \alpha$  is independent of the growing particle mass  $g$  and (2) the condensation rate  $\alpha_g = \alpha g$  grows linearly with the mass of the condensing particle. In what follows, we put  $\alpha = 1$  and  $I = 1$  (see the explanations at the end of Sec. II). Although both these models do not allow completely analytical results, they are of great importance and use because they demonstrate explicitly the structure of the solution. In addition, the second model describes the condensation growth of fractal clusters in the free molecular regime, so it is not so unrealistic [13]. Let us begin with the first case.

#### A. The model $\alpha = 1$

As follows from Eq. (19) the Laplace transform of the Green's function  $G_g(p)$  is

$$G_g(p) = \frac{1}{2(p+1)^{g-1}}. \quad (24)$$

The inversion of Eq. (24) yields

$$\mathcal{G}_g(\tau) = \frac{\tau^{g-2}}{2(g-2)!} e^{-\tau}. \quad (25)$$

On substituting this into Eqs. (23) and (22) gives

$$c_1 \frac{dc_1}{d\tau} = 1 - c_1^2 - \frac{1}{2} c_1 \int_0^\tau c_1(\tau') d\tau'. \quad (26)$$

Exact mass spectrum now can be found with the aid of Eqs. (20) and (25),

$$c_g(\tau) = \frac{1}{2(g-2)!} e^{-\tau} \int_0^\tau (\tau-\tau')^{g-2} e^{\tau'} c_1(\tau') d\tau'. \quad (27)$$

Further analytical results are impossible to get.

### B. The model $\alpha_g = g$

The model  $\alpha_g = g$  allows more analytical results. In this case;

$$G(p) = \frac{(g-1)!}{2(p+2)(p+3)\cdots(p+g)}. \quad (28)$$

The inversion made with the aid of Eq. (21) gives so-called Yule-Furry distribution (see Ref. [14]),

$$\mathcal{G}_g(\tau) = \frac{1}{2}(g-1)e^{-2\tau}(1-e^{-\tau})^{g-2}. \quad (29)$$

This result is used to restore the function  $R(\tau)$  [see Eq. (23)];

$$R(\tau) = e^\tau \quad (30)$$

and one can then write down Eq. (22) in the explicit form

$$c_1 \frac{dc_1}{d\tau} = 1 - c_1^2 - c_1 \int_0^\tau e^{\tau-\tau'} c_1(\tau') d\tau'. \quad (31)$$

In this model, it is easy to find the dependence of  $c_1$  on  $t$ . Indeed, using the conservation of the total mass [Eq. (7)], Eq. (2) may be rewritten as

$$\frac{dc_1}{dt} = 1 - c_1 t. \quad (32)$$

Its solution is

$$c_1(t) = \exp\left[-\frac{t^2}{2}\right] \int_0^t \exp\left[\frac{s^2}{2}\right] ds. \quad (33)$$

The dependence of  $\tau$  on  $t$  is also readily restored,

$$\tau(t) = \int_0^t dr \int_0^r ds \exp\left[-\frac{r^2}{2} + \frac{s^2}{2}\right]. \quad (34)$$

The integral on the rhs of this equation can be cast as follows (see the Appendix):

$$\tau(t) = 2 \int_0^1 \frac{dx}{x} \exp\left[-\frac{t^2 x^2}{2}\right] \sinh\left[\frac{t^2}{2}(x-x^2)\right]. \quad (35)$$

Although the source permanently produces fresh monomeric molecules, the particle number concentration remains finite at  $t \rightarrow \infty$ . As follows from Eq. (6):

$$N(\infty) = \frac{1}{2} \int_0^\infty c_1^2(t) dt = \frac{\pi\sqrt{\pi}}{4}. \quad (36)$$

The integral  $\int_0^\infty c_1^2(t) dt$  with  $c_1(t)$  given by Eq. (33) is calculated in the appendix.

## V. ASYMPTOTIC ANALYSIS

Although the preceding section gives the exact solution of the problem reducing it to the solution of the ordinary nonlinear integro-differential equation (22) with the kernel  $R$  containing the Green's functions  $\mathcal{G}_g$ , a further analysis is almost impossible (except some exactly soluble cases considered above) without the simplifications arising in the asymptotic limit  $g, \tau \gg 1$ . Actually this very limit is of practical interest in the theory of condensation.

We begin this section by analyzing the asymptotic behavior of the Green's function  $\mathcal{G}$ , then consider the time asymptotics of the monomer concentration and complete with the relations allowing us to link the particle mass spectra with  $c_1(\tau)$ .

### A. Asymptotics of the Green's function

Our objective now is to find the Green's function  $\mathcal{G}_g(\tau)$  at large  $g$  and  $\tau$ . To this end let us rewrite Eq. (19) as follows:

$$G_g(p) = \frac{\alpha_1}{2\alpha_g} \exp\left[-\sum_{s=2}^g \ln(1+p/\alpha_s)\right]. \quad (37)$$

The next step is the expansion of the logarithm in the power series with respect to  $p$ ,

$$G_g(p) = \frac{\alpha_1}{2\alpha_g} \exp\left[-p \sum_{s=2}^g \alpha_s^{-1} + \frac{p^2}{2} \sum_{s=2}^g \alpha_s^{-2} - \frac{p^3}{3} \sum_{s=2}^g \alpha_s^{-3} \cdots\right]. \quad (38)$$

Our idea now is to put the upper summation limits  $g = \infty$  in Eq. (38) where it is possible.

At  $\frac{1}{2} < \lambda \leq 1$  only the first sum in Eq. (38) diverges and the function  $G$  is the product of two multipliers the second of which is  $g$  independent,

$$G_g(p) = \frac{\alpha_1}{2\alpha_g} e^{-p\tau_g} Q_2(p). \quad (39)$$

Here

$$\tau_g = \sum_{s=2}^g \alpha_s^{-1}, \quad (40)$$

and the function  $Q_2$  is defined as (arbitrary  $n$ )

$$Q_n(p) = \exp\left[\sum_{k=n}^{\infty} \frac{(-p)^k}{k} \sum_{s=2}^{\infty} \alpha_s^{-k}\right]. \quad (41)$$

Equation (38) is then readily inverted by using the convolution theorem,

$$\mathcal{G}_g(\tau) = \frac{\alpha_1}{2\alpha_g} q_2(\tau - \tau_g) \theta(\tau_g - \tau), \quad (42)$$

where  $q_2(\tau)$  is the Laplace inversion of  $Q_2(p)$  and  $\theta(x)$  is the Heaviside step function,  $\theta(x) = 1$  at  $x > 0$  and 0 otherwise.

Since the function  $q_2(\tau)$  has a peaklike structure, the function  $\mathcal{G}_g(\tau)$  is the peak moving to the right. The

width of this peak is of the order of unity.

If  $\frac{1}{2} \geq \lambda > \frac{1}{3}$ , the second sum on the rhs of Eq. (38) diverges,

$$G_g(p) = \frac{\alpha_1}{2\alpha_g} \exp \left[ -p \sum_{s=2}^g \alpha_s^{-1} + \frac{p^2}{2} \sum_{s=2}^g \alpha_s^{-2} \right] Q_3(p). \quad (43)$$

Now we can neglect the  $p$  dependence of  $Q_3$  and the Green's function  $\mathcal{G}_g(\tau)$  is thus simply the Gaussian

$$\mathcal{G}_g(\tau) \approx \frac{\alpha_1}{2\alpha_g} \sqrt{1/2\pi\Gamma_g^2} \exp \left[ -\frac{(\tau - \tau_g)^2}{2\Gamma_g^2} \right] \quad (44)$$

with

$$\Gamma_g = \sqrt{\sum_{s=2}^g \alpha_s^{-2}}. \quad (45)$$

The Laplace inversion of the divergent part is the Gaussian curve with the width

$$\Gamma_g = \sqrt{\sum_{s=2}^g \alpha_s^{-2}} \alpha_g^{(1-2\lambda)/2} \quad (46)$$

at  $\lambda \neq \frac{1}{2}$  and

$$\Gamma_g \propto \sqrt{\ln g} \quad (47)$$

at  $\lambda = \frac{1}{2}$ . The maximum of the curve is located at

$$\tau_{\max} = \tau_g \propto g^{1-\lambda}. \quad (48)$$

The ratio of the width to the maximum position drops as

$$\frac{\Gamma_g}{\tau_g} \propto \frac{1}{\sqrt{g}} \quad (49)$$

(or  $\sqrt{\ln g/g}$  at  $g = \frac{1}{2}$ ).

At  $\lambda \leq \frac{1}{3}$  the third sum in the expansion (47) begins to diverge. The respective term contributes

$$\frac{p^3}{3} \sum_{s=2}^g s^{-3\lambda} \propto p^3 g^{1-3\lambda}. \quad (50)$$

At small  $p \propto 1/\Gamma_g$  this essentially determines the asymptotic behavior of the Green's function  $\mathcal{G}_g(\tau)$  at large  $\tau$  and the contribution of the third and higher terms should be ignored. The function  $\mathcal{G}_g(\tau)$  thus preserves the Gaussian form [Eq. (44)] for all  $\lambda \leq \frac{1}{2}$ .

Now we are ready to return to  $c_1(\tau)$  and then to the mass spectrum. To this end we must find the function  $R(\tau)$  [see Eq. (23)]. We start by replacing the sum on the rhs of Eq. (23) with the integral. The next simplification concerns the function  $\mathcal{G}_g(\tau)$  which has the peaklike structure with the width of the peak much smaller than its position. Since  $\alpha_g$  is a smooth function of  $g$  (powerlike in our case) the function  $\mathcal{G}$  can be replaced by the  $\delta$  function,

$$\mathcal{G}_g(\tau) \approx \frac{\alpha_1}{2\alpha_g} \delta(\tau - \tau_g). \quad (51)$$

This gives

$$R(\tau) = \sum_g \alpha_g \mathcal{G}_g(\tau) \approx \frac{1}{2} \alpha_1 \alpha(\tau). \quad (52)$$

Here we introduced the function  $\alpha(\tau) = \alpha_{g(\tau)}$  where the function  $g(\tau)$  is defined from the equality

$$\tau = \int_2^{g(\tau)} \frac{ds}{\alpha_s} \quad (53)$$

and we have replaced the sum in Eq. (40) by an integral.

Combining Eqs. (22) and (52) gives the closed equation for  $c_1(\tau)$ ,

$$c_1 \frac{dc_1}{d\tau} = I - \alpha_1 c_1^2 - \frac{1}{2} \alpha_1 c_1 \int_0^\tau \alpha(\tau - \tau') c_1(\tau') d\tau'. \quad (54)$$

This equation had been derived earlier in a different way [6].

It is pertinent to mention here that the approximations leading to Eq. (54) reproduce exact results [Eqs. (26) and (31)] when applied to the exact models considered above.

### B. Asymptotics of monomer concentration

In this section, we will analyze the asymptotic behavior at  $g, t \gg 1$  of the monomer concentration  $c_1(t)$  and the mass spectrum  $\{c_g(t)\}$ .

Let us begin by considering the asymptotics of  $c_1(t)$ . In order to do this we again adopt the assumption (1) on the power growth of the condensation rate and put  $\alpha_1 = 1$  and  $I = 1$ . Next, we neglect the left side of Eq. (54) and the term quadratic in  $c_1$ . Both these terms go to zero faster than the two remaining ones, so we have

$$1 = \frac{1}{2} c_1(\tau) \int_0^\tau \alpha(\tau - \tau') c_1(\tau') d\tau'. \quad (55)$$

Equations (1) and (53) give at large  $t$ ,

$$\alpha(\tau) = [(1 - \lambda)\tau]^{\lambda/(1-\lambda)}. \quad (56)$$

Assuming also that  $c_1(\tau)$  drops as a power of  $\tau$

$$c_1(\tau) \approx C\tau^{-\gamma}, \quad (57)$$

one finds from Eq. (55),

$$\gamma = \frac{1}{2(1-\lambda)}, \quad (58)$$

and

$$C^{-2} = \frac{1}{2} (1-\lambda)^{\lambda/(1-\lambda)} B \left[ \frac{1}{1-\lambda}, \frac{1-2\lambda}{2(1-\lambda)} \right], \quad (59)$$

where  $B(x, y)$  is the Euler  $\beta$  function. This solution is valid at  $\lambda < \frac{1}{2}$ . At larger  $\lambda$  the integral in Eq. (55) diverges and the analysis becomes more complicated.

At  $\lambda > \frac{1}{2}$  there is only one way to move ahead. Integrating by parts the rhs of Eq. (55) gives

$$\int_0^\tau (\tau - \tau')^{\lambda/(1-\lambda)} c_1(\tau') d\tau' = \tau^{\lambda/(1-\lambda)} \int_0^\infty c_1(\tau') d\tau' + \frac{\lambda}{(1-\lambda)} \int_0^\tau (\tau - \tau')^{(2\lambda-1)/(1-\lambda)} d\tau' \int_{\tau'}^\infty c_1(\tau'') d\tau'' . \quad (60)$$

Here we assumed that the integral  $\int_0^\infty c_1(\tau) d\tau$  converges. It is not so at  $\lambda \leq \frac{1}{2}$  and the above transformation is impossible. The next essential point is that the concentration  $c_1(\tau)$  in Eq. (60) is *exact* [the solution of the full Eq. (54)], which removes the problem of convergence of the integral at the lower limit.

Now we can again start the procedure of balancing the powers in the asymptotically valid Eq. (55). In doing so we neglect the second term on rhs of Eq. (55), which is small compared to the first one. The asymptotic  $\tau$  dependence of  $c_1$  then becomes:

$$c_1(\tau) \approx \mathcal{A} \tau^{-\lambda/(1-\lambda)} \propto \tau^{-\lambda/(1-\lambda)} \quad (61)$$

where

$$\mathcal{A}^{-1} = \frac{1}{2} (1-\lambda)^{\lambda/(1-\lambda)} \int_0^\infty c_1(\tau) d\tau . \quad (62)$$

This equation justifies all the above assumptions, (1) the integral  $\int_0^\infty c_1(\tau) d\tau$  converges at  $\lambda > 1/2$ , (2) the contribution of the second term on the rhs of Eq. (60) is small as  $\tau^{-(2\lambda-1)/(1-\lambda)}$  at large  $\tau$ .

The case  $\lambda = \frac{1}{2}$  needs special consideration, for the integral  $\int_0^\infty c_1(\tau) d\tau$  diverges at the lower limit and the trick leading to Eq. (60) does not work. The asymptotic solution can be found only with a logarithmic accuracy ( $\ln \tau \gg \ln \ln \tau$ )

$$c_1(\tau) \approx \frac{\sqrt{2}}{\tau \sqrt{\ln \tau}} \propto \frac{1}{\tau \sqrt{\ln \tau}} . \quad (63)$$

The transition from  $\tau$  to  $t$  is done with the aid of Eqs. (12), (57), (61), and (63). The results are summarized in Table I, giving the asymptotic dependency of monomer and particle number concentrations on  $\tau$  and  $t$ . The coefficients entering these expressions are shown in Fig. 1(a)–1(c) as functions of  $\lambda$ .

### C. Asymptotics of the mass spectra

In studying the asymptotics of the mass spectra we again should consider separately two cases, (i)  $\lambda > \frac{1}{2}$  and (ii)  $\lambda \leq \frac{1}{2}$ .

(i) At  $1 > \lambda > \frac{1}{2}$ , Eqs. (20) and (42) give

TABLE I. Asymptotic time behavior of monomer and particle number concentrations ( $t, \tau \gg 1$ ).

	$0 \leq \lambda < \frac{1}{2}$	$\lambda = \frac{1}{2}$	$\frac{1}{2} < \lambda < 1$	$\lambda = 1$
$c_1(\tau)$	$\tau^{-1/[2(1-\lambda)]}$	$1/\tau \sqrt{\ln \tau}$	$\tau^{-\lambda/(1-\lambda)}$	$e^{-\tau}$
$c_1(t)$	$t^{-1/(3-2\lambda)}$	$1/\sqrt{t \sqrt{\ln t}}$	$t^{-\lambda}$	$t^{-1}$
$N(t)$	$t^{(1-2\lambda)/(3-2\lambda)}$	$\sqrt{\ln t}$	$N_\infty(\lambda)$	$(\pi \sqrt{\pi})/4$

$$c_g(\tau) \approx \frac{\alpha_1}{2\alpha_g} \int_0^\tau q_2(\tau - \tau_g - \tau') c_1(\tau') d\tau' \approx \frac{\alpha_1}{2\alpha_g} c_1(\tau - \tau_g) . \quad (64)$$

Here we have used the fact that  $c_1(\tau)$  is mainly a smooth powerlike function whereas the function  $q_2(\tau)$  is a narrow peak (its width is of the order of unity). This approximation does not reproduce correctly the form of the frontal peak ( $\tau - \tau_g \propto 1$ ) which, however, is so narrow that it can be approximated by any suitable peaklike function [let us say  $c_1(\tau)$ , as was already done in Eq. (64)].

The situation is different at  $\lambda = 1$ . As it follows from Eq. (31),  $c_1(\tau)$  decreases exponentially with  $\tau$  which means that the above approximation [Eq. (64)] does not hold. Fortunately, an exact analysis is possible in this case.

At large  $g, t$  the function  $\mathcal{G}_g(\tau)$  takes the form

$$\mathcal{G}_g(\tau) \approx \frac{1}{2g} x^2 e^{-x} , \quad (65)$$

where  $x = g e^{-\tau}$ .

The mass spectrum is given by Eqs. (20) and (65),

$$c_g(\tau) \approx \frac{1}{2g} x^2 \int_0^\tau e^{2\tau'} e^{-x e^{\tau'}} c_1(\tau') d\tau' . \quad (66)$$

The integral on the rhs of Eq. (66) converges rapidly, thus allowing the replacement of the upper limit by infinity. The final result looks like following:

$$c_g(\tau) = \frac{1}{2g} x^2 \int_0^\infty e^{2\tau'} e^{-x e^{\tau'}} c_1(\tau') d\tau' = \frac{1}{2g} U(x) . \quad (67)$$

Together with Eqs. (11) and (33), Eq. (67) gives the full solution of the problem on the asymptotic mass spectrum which evolves in this case simply by changing its scale [the variable  $\tau$  appears in the combination  $x = g/g_0(\tau)$ , where  $g_0(\tau) = e^\tau$ ].

(ii) At  $\lambda \leq \frac{1}{2}$  we use the fact that  $\Gamma_g \gg 1$ , which allows the replacement the function  $c_1(\tau)$  by its asymptotic expression Eq. (57). Together with Eq. (44) one finds after minute transformations,

$$c_g(\tau) = \frac{\alpha_1 C}{2\alpha_g \Gamma_g^\gamma} \Psi_\gamma(\xi) , \quad (68)$$

with

$$\Psi_\gamma(\xi) = \frac{1}{\sqrt{2\pi}} \int_0^\infty \exp \left[ -\frac{(\xi - \eta)^2}{2} \right] \frac{d\eta}{\eta^\gamma} . \quad (69)$$

Here

$$\xi = (\tau_g - \tau) / \Gamma_g . \quad (70)$$

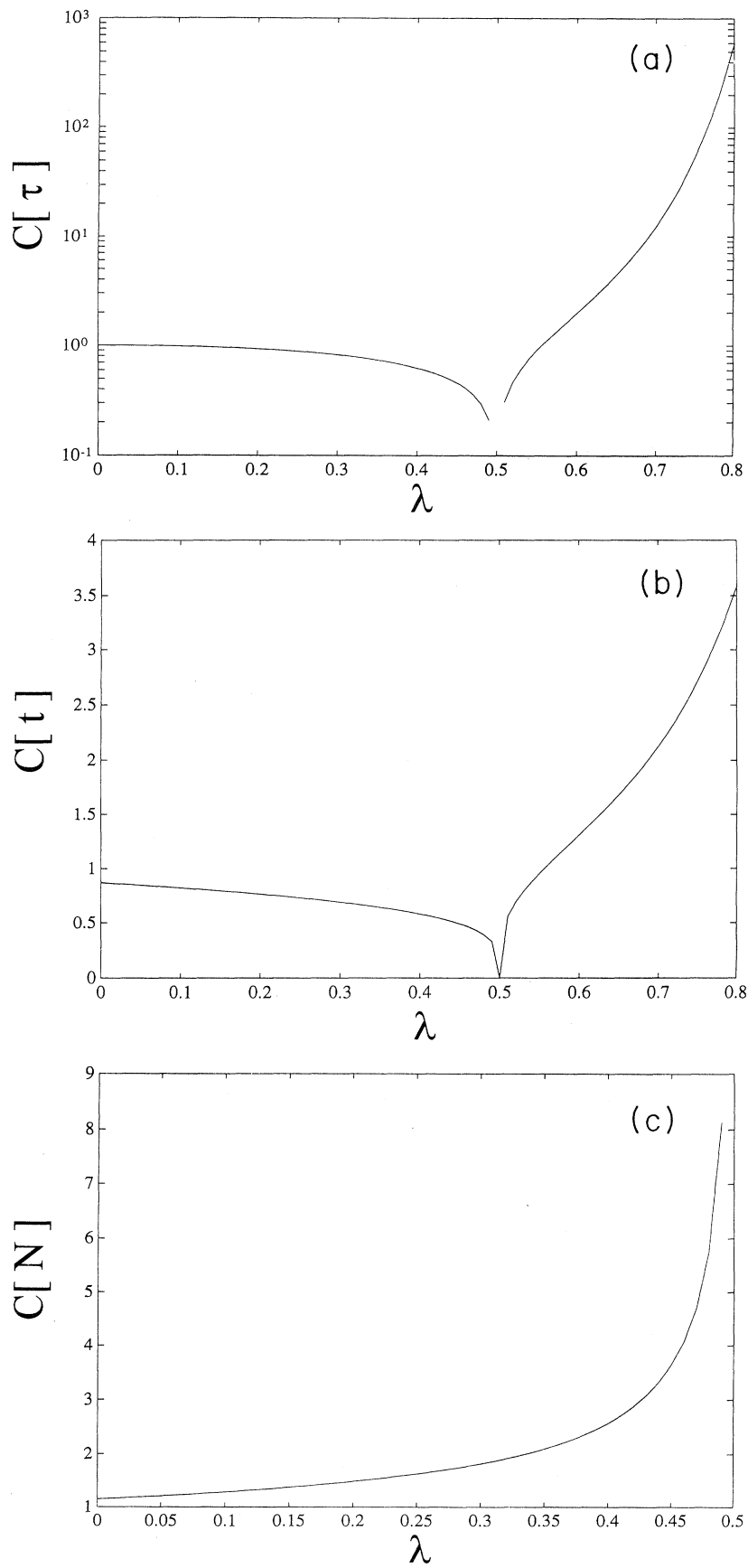


FIG. 1. The dependence of coefficients at power asymptotics given in Table I is shown as the function of  $\lambda$ , (a)  $c_1 \approx C[\tau]\tau^{-\gamma}$ , (b)  $c_1 \approx C[t]t^{-\gamma_1}$ , and (c)  $N \approx C[N]t^\gamma$ .

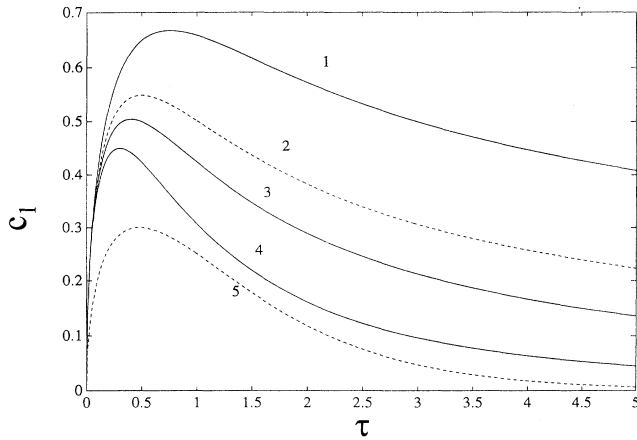


FIG. 2. The dependence of the monomer concentration on  $\tau$  for five types of condensation coefficients: (1)  $\alpha_g=1$ , (2)  $\alpha_g=g^{1/3}$ , (3)  $\alpha_g=g^{1/2}$ , (4)  $\alpha_g=g^{2/3}$ , and (5)  $\alpha_g=g$ .

In deriving Eq. (59) we replaced the upper limit in the integral of Eq. (69) ( $\tau/\Gamma_g \rightarrow \infty$ ).

At  $\lambda=\frac{1}{2}$ , the above transformations are divergent at  $\eta=0$ . The spectrum can be found within the logarithmic accuracy,

$$c_g(\tau) \approx \frac{\alpha_1}{\sqrt{\pi\alpha_g\Gamma_g}} \int_0^\infty \exp\left[-\frac{(\xi-\eta)^2}{2}\right] \times (\eta-\xi) \sqrt{\ln(1+\eta\Gamma_g)} d\eta. \quad (71)$$

## VI. RESULTS AND DISCUSSION

The main attention above concentrated on the asymptotic behavior of mass spectra which is of major interest in the theory of condensation and, on the other hand, rather tedious for a numerical analysis. The initial stages of condensation being of less theoretical and practical interest may be more or less easily treated both analytically and numerically.

The crucial step that allowed us to divide the whole problem into two independent parts, (i) to find  $c_1(\tau)$  and  $\tau(t)$  ( $c_1$  problem) and (ii) to find the mass spectrum ( $c_g$  problem) was the introduction of the new variable  $\tau$  that, in addition, reduced the infinite set of nonlinear equations (2)–(4) to the linear ones [Eqs. (13) and (14)].

### A. Monomeric concentration: $c_1$ problem

Figures 2–5 show all the attributes of the solution to the  $c_1$  problem.

(1) The dependence of  $c_1$  on  $\tau$  is shown in Fig. 2 for five different types of the condensation coefficients: (i)  $\alpha_g=1$ , (ii)  $\alpha_g=g^{1/3}$ , (iii)  $\alpha_g=g^{1/2}$ , (iv)  $\alpha_g=g^{2/3}$ , and (v)  $\alpha_g=g$ . All the curves begin with a sharp increase at small  $\tau$  ( $\propto\sqrt{\tau}$ ), then on reaching their maxima they approach the asymptotic regimes (see Table I). The asymptotic tails are typically negative powers of  $\tau$  [Eqs. (57), (58),

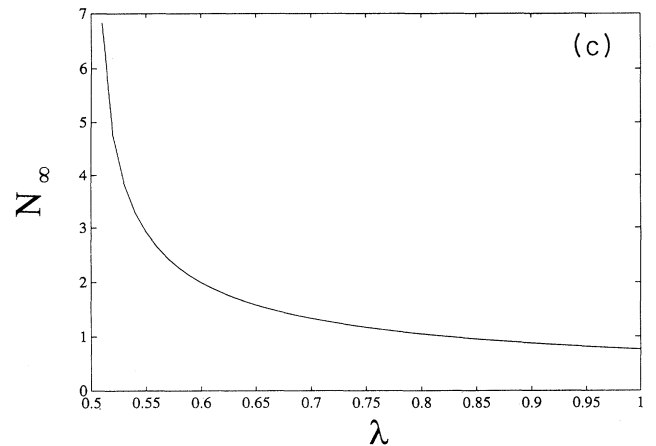
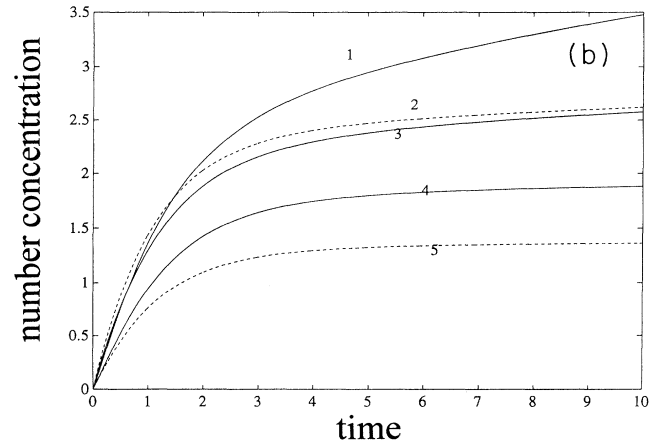
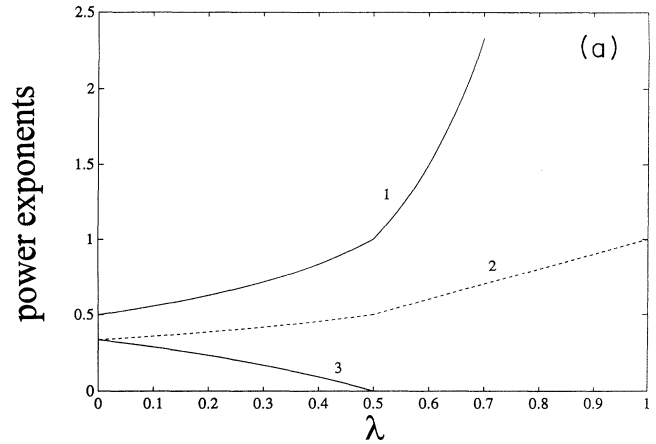


FIG. 3. The phase transition in condensing systems. The behavior of source-enhanced condensing systems changes at  $\lambda=\frac{1}{2}$ : (a) the power exponents in  $\tau$  and  $t$  dependencies of  $c_1$  and  $n$  [ $\gamma$ ,  $\gamma_1$ , and  $\nu$ , respectively (curves 1–3)] have discontinuities in their first derivatives, (b) the number concentration grows unlimitedly with time at  $\lambda \leq \frac{1}{2}$  (curves 1–3) and remains finite in increasing time at  $\lambda > \frac{1}{2}$  (curves 4 and 5) and (c) the dependence  $N_\infty$  on  $\lambda$ .



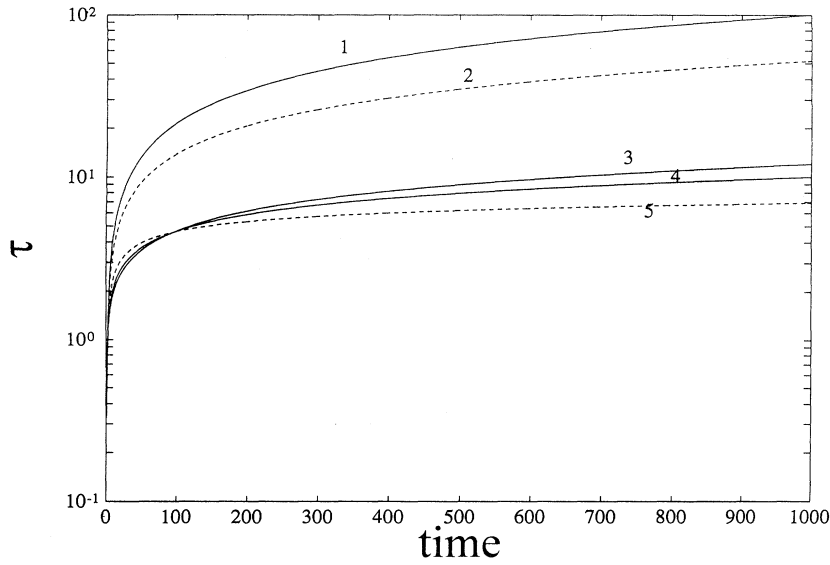


FIG. 4. The dependence of  $\tau$  on time for five values of  $\lambda=0, \frac{1}{3}, \frac{1}{2}, \frac{2}{3},$  and 1 (curves 1–5, respectively).

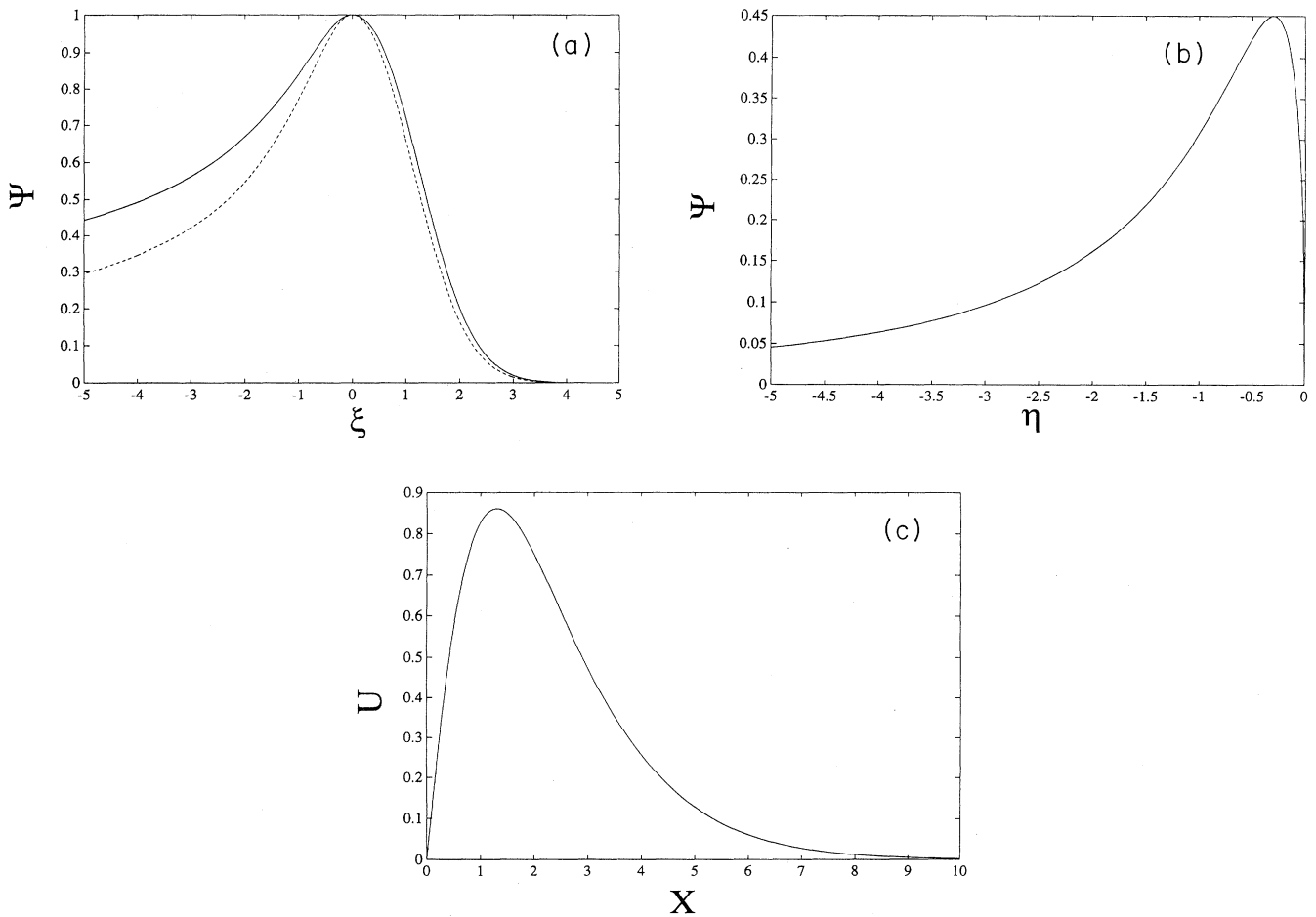


FIG. 5. The mass spectra in source-enhanced condensing systems: (a)  $\lambda=0$  (solid curve),  $\lambda=\frac{1}{3}$  (dash curve). The functions  $\Psi_\nu(\xi)$  describe the shape of the peak [see Eqs. (69) and (70)]. They are seen to differ from zero even at  $\tau_g > \tau$ . (b) The function  $\Phi(\eta)=(2\alpha_g/\alpha_1)c_1(\eta)$ , where  $\eta=\tau_g-\tau$  characterizes the shape of the peak at  $\lambda > \frac{1}{2}$  (here  $\lambda=\frac{1}{3}$ ). (c) The case  $\lambda=1$ . The function  $U(x)$  giving the form of the asymptotic mass spectrum [Eq. (67)] depends on the scaled variable  $x=ge^{-\tau}$ .

and (61)]. The exponent of the asymptotic decrease depends on  $\lambda$  and changes from  $\gamma = \frac{1}{2}(1-\lambda)$  at  $\lambda \leq \frac{1}{2}$  [Eq. (58)] to  $\gamma = \lambda/(1-\lambda)$  at  $\lambda > \frac{1}{2}$ . The function  $\gamma(\lambda)$  is continuous at  $\lambda = \frac{1}{2}$  while its first derivative has a discontinuity (a kind of phase transition). Figure 3 illustrates this phase transition by showing the dependence of  $\gamma$  on  $\lambda$  [Fig. 3(a)].

At  $\lambda = 1$  the asymptotic decrease becomes exponential.

(2) Figure 3(b) portrays the time dependence of the particle number concentration. The phase transition at  $\lambda = \frac{1}{2}$  reveals now more expressively: at  $\lambda > \frac{1}{2}$  the number concentrations become finite at  $\tau \rightarrow \infty$  which means that the degree of vapor-to-particle conversion is *finite* despite the fact that the source produces new portions of condensing vapor. The vapor excess is, however, consumed so fast that no new particles have time to form. At  $\lambda \leq \frac{1}{2}$ , the number concentration grows unlimitedly with time. The dependence of  $N(\tau = \infty)$  on  $\lambda$  is shown in Fig. 3(c).

(3) The dependences of  $\tau$  on  $t$  for the above-mentioned five models are displayed in Fig. 4. These functions serve as the transition from  $\tau$  to the real time scale. In particular, this transition allows one to find the asymptotic time behavior of  $c_1(t)$  and  $N(t)$ . The results are given in Table I.

### B. Mass spectra: $c_g$ problem

In Sec. V, we showed that in source-enhanced condensing systems the mass spectra are rather smooth curves. Typically, these spectra look like waves with clearly expressed frontal peaks moving to the right along the mass axis (Fig. 5). There exist two types of such mass spectra:

(1) If the condensation rate grows slower than  $\sqrt{g}$ . The shape of the peak in the mass spectra is described mainly by the universal function  $\Psi_\gamma(\eta)$  where  $\eta = (\tau_g - \tau)/\Gamma_g$  [Eqs. (69) and (70)]. The spectra are seen to be rather smooth [Fig. 5(a)] and have tails at negative  $\eta$ . The peak position defined by the equation  $\tau_g = \tau$  moves along the  $g$  axis to the right with increasing time (and, therefore,  $\tau$  see Fig. 4).

(2) At  $\lambda = \frac{1}{2}$  the function  $\Psi_\gamma$  loses its universality and becomes independent on the width  $\Gamma_g$  [Eq. (71)]. This dependence, however, is very weak.

(3) The situation changes when the condensation rate  $\alpha_g$  grows with  $g$  sufficiently fast (faster than  $g^{1/2}$ ). Then a smooth polydisperse mass spectrum [Eq. (64)] forms,

$$c_g(\tau) \approx \frac{\alpha_1}{2\alpha_g} c_1(\tau - \tau_g).$$

The time evolution of such spectrum [the models (iv)] is shown in Fig. 5(b). The peak now is sharper and has no tail at  $\tau_g > \tau$ .

(4) At  $\lambda = 1$  the spectrum evolves by changing its scale [Eq. (67), Fig. 5(c)].

## VII. CONCLUDING REMARKS

We considered in detail the particle formation by condensation in the presence of a spatially uniform and constant in time external source producing the molecules of a

condensing vapor. We showed that for physically realistic and for model condensation rates (typically growing with the particle mass as its power) the mass spectra of forming particles are described by rather smooth functions linearly linked with the time dependence of the monomer concentration. This result reduces the rather complicated problem of solving an infinite set of nonlinear differential equations to the integration of a single ordinary integro-differential equation. This procedure is readily solvable even on a moderately powerful PC.

The most important physical consequence of the above theory is the existence of two types of the mass spectra behavior. When the condensation rate  $\alpha_g$  does not grow very quickly with the particle mass (slower than  $\sqrt{g}$ ), the mass spectrum has at its front a peak not so clearly expressed (better to say, a nonintegrable peak) which moves to the right along the mass axis. The number concentration of the aerosol particles reveals unlimited growth with time.

At stronger dependencies of  $\alpha_g$  on  $g$  the maximum becomes integrable and sometimes can be replaced with a  $\delta$  function. The most remarkable fact in this case is the finiteness of the degree of gas-to-particle conversion: the number concentration of the aerosol particles formed by the condensation process remains finite despite the fact that the source is producing new and new portions of the condensing matter.

In both the above cases the mass spectrum has the frontal maximum (integrable or nonintegrable) and a long power tail [see Fig. 4 and Eq. (61)]. The monomer concentration decreases with time despite the presence of the source. This is not a surprising fact, for the vapor consumption grows with increasing particle size and the source has no time to produce enough vapor molecules to support the monomer concentration at a given level.

Primarily, this work was strongly motivated with a necessity to create a sufficiently simple approach that would allow attacks on much more complicated and more realistic situations including binary mixtures (see [15]), nucleation stages, and the presence of condensation nuclei. Our theory also has its ramifications for certain polymerization processes. Actually, similar systems have been treated in polymerization kinetics [16–18], but typically without a source term (see e.g., [18]). We believe that the simplifications made above are, in a sense, the maximum admissible in allowing one to solve these problems.

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## APPENDIX

Here we show how to transform Eq. (34) into Eq. (35). The replacement of variables

$$r - s = x, \quad r + s = y$$

leads to the final result through the following chain of equalities:

$$\int_0^t dr \int_0^r ds \exp[-\frac{1}{2}(r^2-s^2)] = \frac{1}{2} \int_0^t dx \int_x^{2t-x} dy \exp\left[-\frac{xy}{2}\right] = 2 \int_0^t \frac{dx}{x} e^{-tx/2} \sinh[\frac{1}{2}(tx-x^2)].$$

Next, we calculate the integral entering Eq. (36)

$$\begin{aligned} \mathcal{J} &= \int_0^\infty c_1^2(t) dt \\ &= \int_0^\infty e^{-t^2} dt \int_0^t e^{\tau_1^2/2} d\tau_1 \int_0^t e^{\tau_2^2/2} d\tau_2 \\ &= 2 \int_0^\infty e^{-t^2} dt \int_0^t e^{\tau_1^2/2} d\tau_1 \int_0^{\tau_1} e^{\tau_2^2/2} d\tau_2. \end{aligned}$$

We introduce new variables,

$$t - \tau_1 = \xi, \quad t - \tau_2 = \eta, \quad \tau_1 + \tau_2 = \theta$$

or, resolving these equalities with respect to  $\xi, \eta, \theta$ ,

$$t = \frac{\xi + \eta + \theta}{2}, \quad \tau_1 = \frac{\eta + \theta - \xi}{2}, \quad \tau_2 = \frac{\xi + \theta - \eta}{2}.$$

The Jacobian of this transformation is  $J=2$ . The integral  $\mathcal{J}$  now takes the form,

$$\mathcal{J} = \int_0^\infty d\xi \int_\xi^\infty d\eta e^{-\xi\eta} \int_{\eta-\xi}^\infty d\theta \exp\left[-\frac{\theta(\xi+\eta)}{2}\right].$$

The restrictions imposed on the intervals of variation of the variables  $\xi, \eta$ , and  $\theta$  follow immediately from the set of inequalities:  $0 < \tau_2 < \tau_1 < t$ .

The integration over  $\theta$  is readily performed giving

$$\mathcal{J} = \int_0^\infty d\xi \int_\xi^\infty d\eta \frac{2}{\xi+\eta} \exp\left[-\frac{\eta^2 - \xi^2 + 2\xi\eta}{2}\right].$$

Introducing the variable  $s = \eta/\xi$  yields

$$\mathcal{J} = 2 \int_0^\infty d\xi \int_1^\infty \frac{ds}{s+1} \exp\left[-\frac{\xi^2}{2}(s^2+2s-1)\right].$$

The integration over  $\xi$  reduces this integral to the standard one,

$$\begin{aligned} \mathcal{J} &= \sqrt{2\pi} \int_1^\infty \frac{ds}{(s+1)\sqrt{s^2+2s-1}} \\ &= 2\sqrt{\pi} \arctan(\sqrt{2}-1) = \frac{\pi\sqrt{\pi}}{4}. \end{aligned}$$

Perhaps it will be useful for further studies to mention that the functions  $c_1(\tau)$  for the two models considered in Sec. IV obey the following ordinary differential equations of the second order:

$$\ddot{c}_1 + \dot{c}_1 \left[1 + \frac{1}{c_1^2}\right] + \frac{1}{2}c_1 = 0$$

for the model  $\alpha_g = 1$  and

$$\ddot{c}_1 + \frac{\dot{c}_1}{c_1^2} + \frac{1}{c_1} = 0$$

for the model  $\alpha_g = g$ . The solution of the latter equation is given by Eqs. (33) and (34).

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