

## Nucleation burst in a coagulating system

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(Received 30 March 2000)

The source-enhanced formation and growth of disperse particles is considered assuming the particles born by nucleation grow then by coagulation and condensation of a low volatile vapor onto their surfaces. After formulating the basic equations governing the particle-formation-growth process a realistic process is considered: nucleation-coagulation growth of aerosol particles in a free molecular regime. The kinetics of this process is studied under the assumption that the particle mass spectrum has a log-normal form whose parameters are expressed in terms of three moments of particle mass distribution: particle number concentration, and the moments of the orders  $1/3$  and  $2/3$ . These three moments together with condensable vapor concentration are shown to meet a set of four first-order nonlinear differential equations that contain a small parameter: relative vapor concentration spent to the disperse particle production. This parameter, however, does not permit a direct application of the perturbation theory: only after two consequent rescalings it becomes possible to remove the small parameter and describe the particle-formation-growth process in terms of universal functions, depending on a specially defined nondimensional group playing the role of time. It is shown that the particle-formation-growth process can be naturally separated into two stages: (i) formation by nucleation and condensational growth of particles, and (ii) growth of formed particles by coagulation and condensation. Each stage is described by its own set of universal functions which are found from the solution of respective differential equations. The asymptotic stage of the process is shown to be described by a self-preserving distribution depending only on two moments: particle number concentration and the moment of particle-mass distribution of the order of  $2/3$ .

PACS number(s): 68.10.Jy, 05.70.-a, 64.60.Qb

### I. INTRODUCTION

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, such as the formation of aerosol in random atmospheric conditions [1–4] or well managed technological processes of nanomaterial production via an aerosol state [5], prevent us from describing this process uniquely: general models taking into account everything are too difficult even for very powerful modern computers. So in attempting to treat gas-to-particle conversion the models sacrificing some details are in order.

This paper reports on a simple model of the particle-formation-growth process which takes into account nucleation, condensational growth, and coagulation. The particles are assumed to form in a free molecular regime (the particle sizes are much smaller than the mean free path of carrier gas molecules) which defines the size dependence of the rates of particle growth due to coagulation and condensation. We consider the free molecular regime not only because of its practical importance. The simple and specific dependence of the condensational efficiency on the particle mass [ $\alpha(g) = \alpha g^{2/3}$ , where  $g$  is the number of molecules in the particle and  $\alpha$  is the condensation efficiency] allows for restricting the whole consideration by three moments of the particle mass distribution, which meet the set of four first-order differential equations together with the vapor concentration [6–8]. Some complications appear if the process involves other moments. In this case the assumption on a log-normal

shape of the particle-mass distribution function saves the simplicity of the scheme.

We assume next that there is a spacially uniform source of condensable vapor of productivity  $I$ , and only a small part of it is spent in the formation of particles by nucleation. Of course, newly born particles grow after the nucleation burst by condensing the nonvolatile vapor onto their surfaces, and change their total number concentration by coagulation.

Hence, there appear four well distinguishable periods in developing the aerodisperse system: (i) the prenucleation period during which no particles are formed yet, and the vapor concentration grows linearly with time; (ii) a very short nucleation burst producing particles which then grow by condensing the vapor molecules; (iii) the period of condensational growth when the newly born particles deplete the vapor and thus cease nucleation; (iv) coagulation aging when the particles begin to coalesce, with their number concentration dropping down and the total surface area growing up. The rate of vapor consumption for gas-to-particle conversion is normally much slower than that for vapor condensation on newly born particles, and the vapor molecules prefer to deposit onto the particle surfaces rather than to form new particles. Coagulation, in turn, requires the collisions between newly born particles and is much slower than condensation, for the latter is related to the interaction between particles and condensable vapor whose concentration is normally much higher than that of newly born particles. The whole process is thus regulated by one smallness parameter (nondimensional)  $\mu$  equal to the ratio of the vapor consumption rate for the formation (or nucleation) of newly born particles to the total vapor production rate by the source. The ratios of

the characteristic times can be expressed in terms of this parameter.

Although we consider here the barrierless nucleation (the nucleation rate  $J$  is proportional to the squared vapor concentration  $C$ ), the results can be easily extended to any arbitrary dependence of the nucleation rate on the vapor supersaturation. This is absolutely clear because the time of the nucleation burst is much shorter than other characteristic time scales. On the other hand, the barrierless nucleation is very often met in the processes of formation of nanomaterials and functionally is rather simple to operate with. So we assume  $J = AC^2$ .

Our model uses the moment method that is very well suited for considering the particle-formation-growth process in the free molecular regime. The papers [7,8] discuss the application of this method to the condensational growth processes in the free molecular regime and show that three moments of particle-size distribution and the concentration of condensable vapor can be expressed in terms of universal functions, with all details of the process being hidden in the scales of the time and concentration axes.

This work extends this approach by including the coagulation process into consideration. We show that there are two different scales of time, the shorter of which defines the dynamics of the nucleation-condensation stage while the longer one scales coagulation aging. It is found that each stage is described by a set of four universal functions that meet four (different for each stage) first-order differential equations, the right-hand sides of which contain coagulation integrals. These integrals are evaluated and expressed in terms of the parameters of log-normal particle-mass distribution. In contrast to commonly accepted approaches the latter includes particle number concentration and two moments of the order of  $1/3$  and  $2/3$ . This step allows one to formulate the close set of equations for these three values and the vapor concentration. This set contains the smallness parameter  $\mu$  which can be expressed in terms of  $A$  and  $\alpha$  as  $\mu = A/\alpha$ . This parameter is not treatable by a straightforward application of the perturbation theory, for setting  $\mu = 0$  removes the particle formation by nucleation. However, two rather nontrivial rescalings allow for the separation of the nucleation-condensation and coagulation-condensation stages of the particle-formation-growth process and the formulation of two closed sets of equations containing no smallness parameter at all.

It is shown that the time for the condensation-nucleation stage is longer than the characteristic condensation time  $1/\sqrt{I\alpha}$  by the factor  $\mu^{-1/8}$ . The particle number concentration contains the smallness parameter to the power  $5/8$ :  $\phi_0 \propto \mu^{5/8}\sqrt{I/\alpha}$ .

The coagulation stage is longer than the condensation stage by  $\mu^{-3/16}$ . The asymptotic analysis shows that the moments and particle number concentration are the power functions of time:  $\phi_{1/3} \propto t^{-3/5}$ ,  $\phi_{2/3} \propto t^{1/5}$ , and  $\phi_0 \propto t^{-7/5}$ . These values of exponents correspond to the predictions of the self-preservation theory for source-enhanced coagulation in the free molecular regime. Numerical analysis confirms these power laws and gives the values of the constants before the powers. Above asymptotic dependencies correspond to the constant width of the log-normal function ( $s = 0.692$  for the source-enhanced growth process).

## II. BASIC EQUATIONS

We consider a spacially uniform disperse system and assume the following.

(i) There is a source of condensable vapor of the productivity  $I$ .

(ii) Newly born particles are produced from the vapor by nucleation and can coagulate and grow by condensation. The particle production rate by nucleation is low compared to the source productivity.

(iii) All growth processes go in the free molecular regime.

According to the above assumptions the evolution equations look as follows. The rate of change with time in the monomeric concentration  $C(t)$  is

$$\frac{dC}{dt} = I - \int gJ(g)dg - \alpha C\phi_{2/3}, \quad (1)$$

where  $I(t)$  is the productivity of the external source of vapor,  $\alpha = \pi a^2 v_m$  is the condensation coefficient,  $a$  is the particle radius, and  $v_m = \sqrt{8kT/\pi m}$  is the molecular thermal velocity ( $m$  is molecular mass,  $T$  is temperature). The moments of particle-mass distribution  $\phi_\sigma$  are defined as follows:

$$\phi_\sigma(t) = \int g^\sigma N(g,t)dg, \quad (2)$$

where  $N(g,t)$  is the particle-mass spectrum,  $g$  is the number of monomers in the particle, and  $\alpha(g) = \alpha g^{2/3}$  is the condensation efficiency.

The first term on the right-hand side (rhs) of Eq. (1) gives the increase in the monomer concentration due to an action of the source, the second describes the nucleation losses, and the last one is responsible for depleting the condensable vapor due to its condensation onto the surfaces of newly born (by nucleation) particles. The continuity equation

$$\frac{\partial N}{\partial t} + \alpha C \frac{\partial}{\partial g} g^{2/3} N = J(g,t) \quad (3)$$

describes the time evolution of particle-mass spectrum. The source term can be written down in the form

$$J = J_{coag}(g,t) + J_{nucl}(g,t), \quad (4)$$

where

$$J_{coag} = \frac{1}{2} \int_0^g K(g-l,l)N(g-l,t)N(l,t)dl - N(g,t) \int_0^\infty K(g,l)N(l,t)dl \quad (5)$$

is the contribution to mass spectrum changes due to coagulation,  $K(g,l)$  is the coagulation kernel: In the free molecular regime it has the form (see, e.g., [1])

$$K(g,l) = \alpha(g^{1/3} + l^{1/3})^2 \sqrt{\frac{1}{g} + \frac{1}{l}}. \quad (6)$$

Nucleation is assumed to produce the particles of a critical mass  $G(C)$ . The rate of nucleation is chosen in the form

$$J_{nuc}(g,t) = J_G(C) \delta(g - G). \tag{7}$$

Here  $\delta(x)$  is Dirac's delta function and  $G$  stands for the critical mass of particles produced by nucleation. In what follows we assume that

$$J_G(C) = AC_0^2 j(C/C_0), \tag{8}$$

where  $A$  is a constant (with respect to  $C$ ) and  $C_0$  is a characteristic concentration at which nucleation becomes noticeable.

Equations (1) and (3) are subject to zero initial conditions

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

The continuity equation (3) can be cast into the equations for the moments of mass distributions  $\phi_\gamma = \int N(g,t) g^\gamma dg$  on multiplying it by  $g^\gamma$ , integrating over  $g$ , and using the equality:

$$\int_0^\infty g^\gamma [\partial_t N(g,t) + \alpha \partial_g g^{2/3} N(g,t)] dg = d_t \phi_\gamma - \gamma \phi_{\gamma-1/3}. \tag{10}$$

In what follows we use the system of units  $\alpha = I = 1$ , i.e., all concentrations are measured in the units of  $\sqrt{I/\alpha}$  and time in  $1/\sqrt{I\alpha}$ .

The basic equations then acquire the form

$$d_t C = 1 - G \mu j(C) - C \phi_{2/3}, \tag{11}$$

$$d_t \phi_{2/3} = G^{2/3} \mu j(C) + \frac{2}{3} C \phi_{1/3} - K_{2/3}, \tag{12}$$

$$d_t \phi_{1/3} = G^{1/3} \mu j(C) + \frac{1}{3} C \phi_0 - K_{1/3}, \tag{13}$$

$$d_t \phi_0 = \mu j(C) - K_0. \tag{14}$$

Here  $\mu = AC_0^2/I \ll 1$  is the smallness parameter. For barrierless nucleation  $C_0 \propto \sqrt{I/\alpha}$  and  $\mu \propto A/\alpha$ . The reasons why  $\mu$  is small were discussed in [8]. The coagulation terms  $K_\gamma$  are specified as follows:

$$K_\gamma = \frac{1}{2} \int K(g,l) [(g+l)^\gamma - g^\gamma - l^\gamma] N(g) N(l) dg dl. \tag{15}$$

The initial conditions to these equations follow from Eq. (9):

$$\phi_\alpha(0) = 0, \quad C(0) = 0. \tag{16}$$

### III. LOG-NORMAL APPROXIMATION

The details of the particle-mass distribution can be now excluded from the consideration at the cost of only one and quite reasonable approximation: the mass spectrum of the nucleation mode is assumed to be log normal,

$$N(g,t) dg = \phi_0(t) F(g/g_0|s) \frac{dg}{g}, \tag{17}$$

where the function

$$F(x|s) = \frac{1}{\sqrt{2\pi s}} \exp\left(-\frac{1}{2s} \ln^2 x\right) \tag{18}$$

is normalized to 1.

Let us express the parameters  $s$  and  $g_0$  of the log-normal mass distribution in terms of  $\phi_0, \phi_{1/3}, \phi_{2/3}$ . According to the Appendix [Eq. (A3)],

$$\phi_{1/3} = \phi_0 g_0^{1/3} e^{s/18}, \quad \phi_{2/3} = \phi_0 g_0^{2/3} e^{2s/9}, \tag{19}$$

and

$$e^{s/9} = \phi_{2/3} \phi_0 / \phi_{1/3}^2, \tag{20}$$

$$g_0^{2/3} = \phi_{1/3}^4 / (\phi_{2/3} \phi_0^3). \tag{21}$$

In what follows we widely use the identity (A6) from the Appendix:

$$\begin{aligned} \int_0^\infty x^\sigma f\left(\frac{y}{x}\right) F(x|s) F(y|s) \frac{dx}{x} \frac{dy}{y} \\ = \exp\left(\frac{s\sigma^2}{4}\right) \int_0^\infty \xi^{-\sigma/2} F(\xi|2s) f(\xi) \frac{d\xi}{\xi}. \end{aligned} \tag{22}$$

For an arbitrary homogeneous coagulation kernel  $K_\lambda(x,y)$ , with  $\lambda$  being the homogeneity exponent, one has (see the Appendix)

$$\begin{aligned} (KNN)_{\lambda,\gamma} &= \frac{1}{2} \int K_\lambda(g,l) [(g+l)^\gamma - g^\gamma - l^\gamma] N(g) N(l) dg dl \\ &= \frac{1}{2} g_0^{\lambda+\gamma} \phi_0^2 \exp\left(\frac{s}{4}(\lambda+\gamma)^2\right) f_{\lambda,\gamma}(s), \end{aligned} \tag{23}$$

where

$$\begin{aligned} f_{\lambda,\gamma}(s) &= \int_0^\infty \xi^{-(\lambda+\gamma)/2} [(\xi+1)^\gamma - \xi^\gamma - 1] \\ &\quad \times K_\lambda(1,\xi) F(\xi|2s) \frac{d\xi}{\xi}. \end{aligned} \tag{24}$$

Now

$$K_0 = \frac{1}{2} g_0^{1/6} \phi_0^2 e^{s/144} f_0(s), \tag{25}$$

$$K_{1/3} = \frac{1}{2} g_0^{1/2} \phi_0^2 e^{s/16} f_{1/3}(s), \tag{26}$$

$$K_{2/3} = \frac{1}{2} g_0^{5/6} \phi_0^2 e^{25s/144} f_{2/3}(s). \tag{27}$$

For the kernel given by Eq. (6) the functions  $f$  are

$$f_0(s) = \int_0^\infty \xi^{1/12} (1 + \xi^{-1/3})^2 \sqrt{1+x} F(\xi|2s) \frac{d\xi}{\xi}, \tag{28}$$

$$\begin{aligned} f_{1/3}(s) &= \int_0^\infty \xi^{-1/12} [\xi^{1/3} + 1 - (\xi+1)^{1/3}] \\ &\quad \times (1 + \xi^{-1/3})^2 \sqrt{1+\xi} F(\xi|2s) \frac{d\xi}{\xi}, \end{aligned} \tag{29}$$

$$f_{2/3}(s) = \int_0^\infty \xi^{-1/4} [\xi^{2/3} + 1 - (\xi + 1)^{2/3}] \times (1 + \xi^{-1/3})^2 \sqrt{1 + \xi} F(\xi | 2s) \frac{d\xi}{\xi}. \quad (30)$$

Finally one has

$$K_0 = -\frac{1}{2} \phi_{1/3}^{7/8} \phi_{2/3}^{-3/16} \phi_0^{21/16} f_0, \quad (31)$$

$$K_{1/3} = -\frac{1}{2} \phi_{1/3}^{15/8} \phi_{2/3}^{-3/16} \phi_0^{5/16} f_{1/3}, \quad (32)$$

$$K_{2/3} = -\frac{1}{2} \phi_{1/3}^{15/8} \phi_{2/3}^{5/16} \phi_0^{-3/16} f_{2/3}. \quad (33)$$

#### IV. RESCALING

It is seen that the smallness parameter  $\mu$  cannot so easily be removed from the set of Eqs. (11)–(14). No new particles can form while  $\mu=0$ . The situation can be improved and the perturbation theory restored after an analysis in the spirit of the renormalization group. This was already done by us in Ref. [7] for powerlike dependencies of the nucleation rate on the vapor concentration.

Let us rescale the unknown functions and time,

$$t = \eta^{-1} \xi, \quad C = \eta^{-1} x, \quad \phi_{2/3} = \eta y, \\ \phi_{1/3} = \eta^3 z, \quad \phi_0 = \eta^5 u. \quad (34)$$

The next step is the choice of the parameter  $\eta$  of the transformation. It is fixed by the condition  $\eta^6 = \mu$  which removes the multiplier  $\mu$  from the first term on the rhs of Eq. (14). In three other equations (11), (12), and (13) the positive powers of  $\mu$  still accompany the nucleation terms (the first terms on their right-hand sides).

After the renormalization one has

$$d_\xi x = 1 - G \mu j(x) - xy, \quad (35)$$

$$d_\xi y = G^{2/3} \mu^{2/3} j(x) + \frac{2}{3} xz - \frac{1}{2} \mu^{1/2} z^{15/8} y^{5/16} u^{-3/16} f_{2/3}, \quad (36)$$

$$d_\xi z = G^{1/3} \mu^{1/3} j(x) + \frac{1}{3} xu - \frac{1}{2} \mu^{1/2} z^{15/8} y^{-3/16} u^{5/16} f_{1/3}, \quad (37)$$

$$d_\xi u = j(x) - \frac{1}{2} \mu^{1/2} z^{7/8} y^{-3/16} u^{21/16} f_0. \quad (38)$$

It is important to notice that the renormalization [Eq. (34)] leaves  $s$  unchanged.

#### V. HIERARCHY OF TIME SCALES

Coagulation terms in Eqs. (35)–(38) are seen to be proportional to a positive power of the small parameter  $\mu$ . If we simply put  $\mu=0$  in these equations we lose coagulation and leave only the stage of formation and condensational growth. Let us do this, and in the zeroth order in  $\mu$  we can consider nucleation condensation alone. This statement, however, holds while the particle distribution moments are of the order of unity. At larger times they are expected to grow (except for the total particle number, the moment  $u$  in our list of dimensionless and renormalized moments). Their growth

compensates for the smallness of  $\mu$  at sufficiently large times, and then we must take the coagulation process into consideration.

Nothing like this happens to the first terms on the rhs of Eqs. (35)–(38) responsible for the particle formation. These terms never contribute much because the particle number concentration of the nucleation mode does not grow with time, and no factors can come up canceling the smallness of  $\mu$ . This fact just means that the two stages of particle aging (condensation and coagulation) proceed during very different time scales. The coagulation process begins to develop much later than the nucleation burst and can thus be considered separately. Our idea is to demonstrate that the asymptotic stage of the coagulation processes can also be described in terms of universal functions.

In order to consider the coagulation on an equal foot with the condensational growth we notice that if we rescale similarly all the moments and  $\xi$  as

$$y = \mu^{-1/4} y_1, \quad z = \mu^{-1/4} z_1, \\ u = \mu^{-1/4} u_1, \quad \xi = \mu^{-1/4} \xi_1, \quad (39)$$

then the smallness parameter  $\mu^{1/2}$  disappears in the coagulation terms in Eqs. (36)–(38). Rescaling  $x = \mu^{1/4} x_1$  leaves Eqs. (36), (37), and (38) unchanged while the left-hand side (lhs) of Eq. (35) acquires the small multiplier:  $(d/d\xi)x = \mu^{1/2} (d/d\xi_1)x_1$ . We set this multiplier equal to 0, and retain only the rhs of this equation which now reads as  $x_1 = 1/y_1$ . Next, all terms containing the particle production can be replaced by proper initial conditions. Then three other equations (36), (37), and (38) are rewritten as

$$\frac{dy_1}{d\xi_1} = \frac{2z_1}{3y_1} - \frac{1}{2} z_1^{15/8} y_1^{5/16} u_1^{-3/16} f_{2/3}, \quad (40)$$

$$\frac{dz_1}{d\xi_1} = \frac{u_1}{3y_1} - \frac{1}{2} z_1^{15/8} y_1^{-3/16} u_1^{5/16} f_{1/3}, \quad (41)$$

$$\frac{du_1}{d\xi_1} = -\frac{1}{2} z_1^{7/8} y_1^{-3/16} u_1^{21/16} f_0. \quad (42)$$

The initial conditions to these equations are convenient to have in the form

$$y_1(0) = (2\mu)^{2/3} u_1(0), \quad z_1(0) = (2\mu)^{1/3} u_1(0), \\ u_1(0) = \mu^{1/4} u_\infty, \quad (43)$$

where  $u_0 = \int_0^\infty j(\xi) d\xi$  and  $\epsilon \rightarrow 0$ . We did not put  $\epsilon=0$  in order to retain the initial value of  $s(0)=0$ . This simplifies performing the numerical calculations.

#### VI. RESULTS AND DISCUSSION

In what follows we assume the simplest possible dependence of the nucleation rate on the condensable vapor concentration:

$$J = A C^2. \quad (44)$$



This dependence corresponds to barrierless nucleation, i.e., dimers are considered to be stable. The constant  $A$  is normally very small, for it contains the average number of carrier gas molecules in the interaction volume,  $nV_m$ . Here  $n$  is the number concentration of the carrier gas and  $V_m \propto a_m^3$ . This factor appears because the dimerization (the reaction  $A + A \rightarrow A_2$ ) does not go without a third body. Usually a molecule of the carrier gas plays this role (see [8]).

The characteristic concentration in this case is  $C_0 = \sqrt{J/\alpha}$ , and the parameter  $\mu = A/\alpha \propto (nV_m) \approx 10^{-4}$  is independent of the source productivity  $I$ . The exact numerical value of this parameter is not very important because it defines only the scales of the time-concentration axes. The functions describing the particle growth kinetics are universal.

### A. Nucleation-condensation stage

Setting  $\mu = 0$  in the set (35)–(38) gives the equations describing the nucleation-condensation stage,

$$d_\xi x = 1 - xy, \quad (45)$$

$$d_\xi y = \frac{2}{3}xz, \quad (46)$$

$$d_\xi z = \frac{1}{3}xu, \quad (47)$$

$$d_\xi u = j(x), \quad (48)$$

where  $j(x) = x^2$ . These equations were solved for zero initial conditions. The results are shown in Figs. 1(a)–1(c). The vapor concentration drops down on passing the maximum [Fig. 1(a)] while the moments  $y$  and  $z$  always grow [Fig. 1(b)]. The particle number concentration saturates at  $\xi \approx 2$  and reaches the value  $u_\infty = 6.58$ . At large  $\xi$  the moments grow as

$$y \approx u_\infty^{1/3} \xi^{2/3}, \quad z \approx u_\infty^{2/3} \xi^{1/3}. \quad (49)$$

The shapes of these curves depend on the functional form of the nucleation rate  $j(x)$ .

The particle-mass distribution of the condensing particles cannot be described in terms of log-normal distribution [8]. Still this distribution is a narrow function. The attempt to approximate it by a log-normal function is shown in Fig. 1(c). One sees that the width which, according to Eq. (49), should go to 0 at  $\xi \rightarrow \infty$  remains appreciable even at  $\xi = 10$ . At  $\xi = 1000$ ,  $s(1000) = 0.137$ . This very slow drop is a manifestation of the fact that the log-normal approximation is not very good for describing the condensation stage. On the other hand, it is not a great loss, because no assumptions are required for the description of the nucleation-condensation stage in terms of the moments of mass distribution [7,8].

### B. Coagulation stage

Equations (40), (41), and (42) with the initial conditions (43) were solved numerically. Approximations for the functions  $f_\gamma(s)$  used in the numerical calculations are

$$f_0(s) = 4\sqrt{2}e^{0.185s}, \quad f_{1/3}(s) = 4\sqrt{2}(2 - 2^{1/3})e^{0.11s}$$

$$f_{2/3}(s) = 4\sqrt{2}(2 - 2^{2/3})e^{0.063s}. \quad (50)$$

The results are presented in Figs. 2(a)–2(d). It should be emphasized that the shape of all curves in these figures is entirely independent of the functional form of the nucleation rate and includes only the final result of nucleation: the total particle number concentration. The parameter  $\mu$  entering the initial condition Eq. (43) defines the length of the transient period during which the asymptotic mass distribution is settled.

The power asymptotic dependencies of  $y$ ,  $z$  and  $u$  can be found analytically. Substituting  $y_1(\xi_1) = Y\xi_1^a$ ,  $z_1(\xi_1) = Z\xi_1^b$ , and  $u(\xi_1) = U\xi_1^c$  into Eqs. (40), (41), and (42) gives

$$y_1 = 0.682\xi_1^{1/5}, \quad z_1 = 0.5\xi_1^{-3/5}, \quad u_1 = 0.394\xi_1^{-7/5}. \quad (51)$$

Figures 2(a)–2(c) demonstrate how these dependencies are reached. It is seen that the numerically calculated dependencies of the moments are well reproduced by the asymptotic dependencies Eqs. (51). Figure 2(d) shows the time dependence of the width of the mass distribution. It grows from zero to the value  $s = 0.692$  at  $t \rightarrow \infty$ . The saturation is not reached fast: during 10–20 units of nondimensional time for  $\mu = 10^{-4}$ . This period slowly grows as  $\mu^{-1/4}$  in decreasing  $\mu$ .

The asymptotic mass distribution thus depends only on two parameters: number concentration and  $\phi_{2/3}$ . The value of  $\phi_{1/3}$  is readily found from Eq. (22).

## VII. CONCLUSION

We considered the source-enhanced particle formation and growth process. The dispersed particles were assumed to be born from a low volatile vapor in a nucleation process and then grow by condensing it onto their surfaces. Additional growth due to particle coagulation was also taken into account. Although the vapor source was assumed to be constant, the time evolution of the whole system never led to a steady-state picture. The vapor concentration and the concentration of newly born particles dropped with time after a short splash (nucleation burst).

The process of particle formation and growth is governed by one small parameter: the ratio of vapor mass converted to newly born particles to the source productivity. However, a direct application of the perturbation theory was not possible, and only two subsequent rescalings saved the situation and made resolving the problem possible. It occurred that the particle-formation–aging problem goes into two stages, the first of which was comparatively short and included only nucleation formation of the particles and their condensational growth. This stage had been considered in [7]. The coagulation aging (the second stage) occurs very slow and is therefore insensitive to the nucleation mechanism.

The result of the nucleation stage important for the coagulation aging is just the total particle number concentration of particles produced by the nucleation stage rather than its

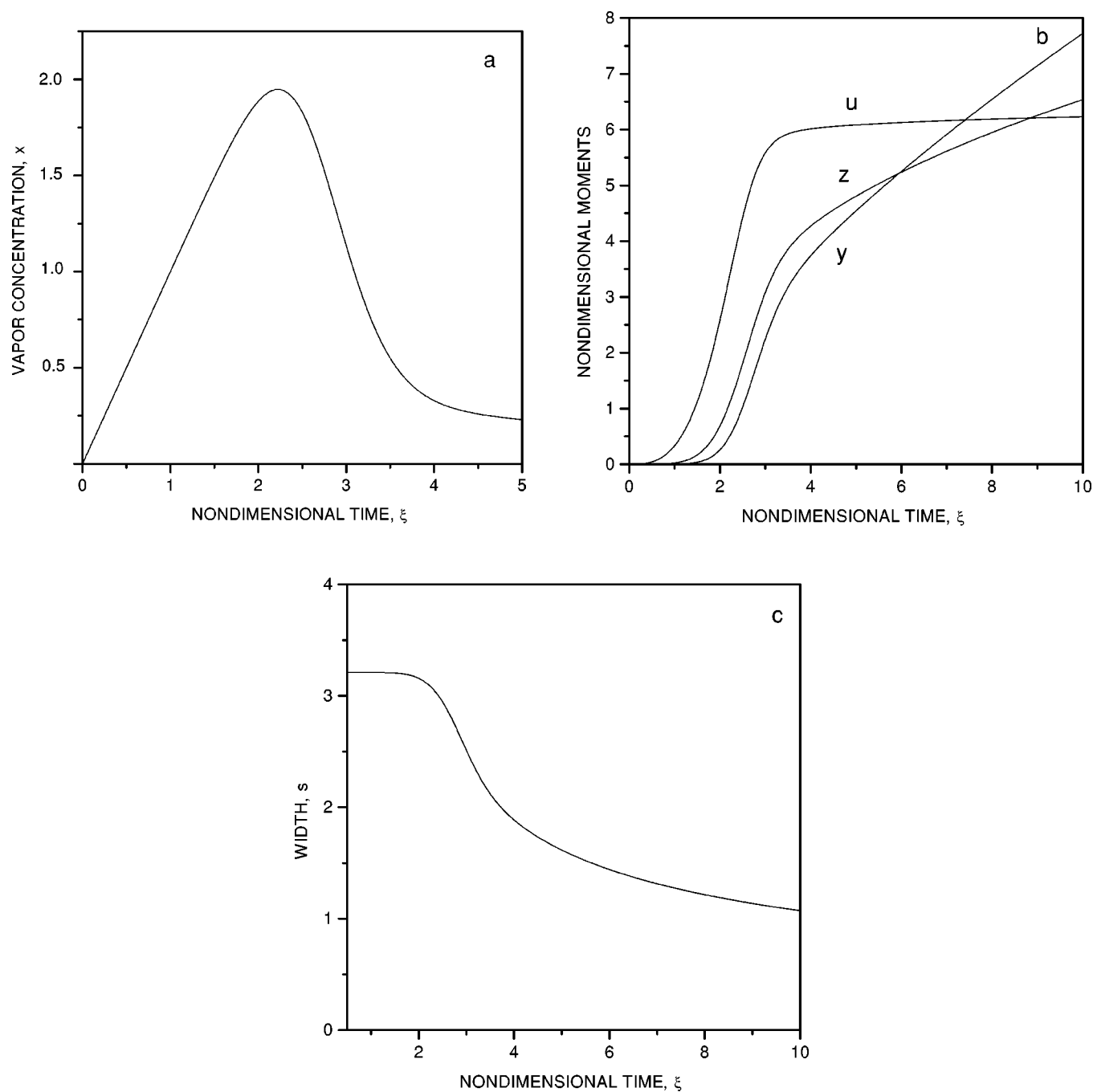


FIG. 1. Kinetics of the nucleation-condensation stage. Shown are (a) the universal function  $x$  describing the time dependence of vapor concentration, (b) universal functions describing the time dependence of particle number concentration (curve  $u$ ), the moment of the order of  $1/3$  (curve  $z$ ), and the moment of the order of  $2/3$  (curve  $y$ ). Assuming that the particle-mass distribution at this stage can be described by a log-normal function the width  $s$  was calculated (c). This value drops with time unexpectedly slow.

detailed kinetics. The remarkable feature of the coagulation stage is a kind of self-preservation: the asymptotic mass spectrum depends only on two parameters rather than three. In principle, the self-preservation is not a rare feature of coagulating systems with homogeneous coagulation kernels [9–14], but external sources and simultaneous condensational growth usually prevent the universal asymptotics of particle-mass distributions in such systems [1,2].

In addition the above consideration gives the following.

(i) A simple computational scheme allowing one to find the parameters of the particle-mass distribution in such a

complicated process like the formation of particles by nucleation accompanied by condensational growth and coagulation.

(ii) A recipe for universalizing the description of the particle-formation-growth kinetics. The parameters of the particle-mass distribution are shown to be universal functions of nondimensional time. The details of the process like the source productivity, nucleation rate constant, and condensational efficiency define only time-concentration scales. The shape of the asymptotic particle-mass distribution is defined by two parameters: the particle number con-

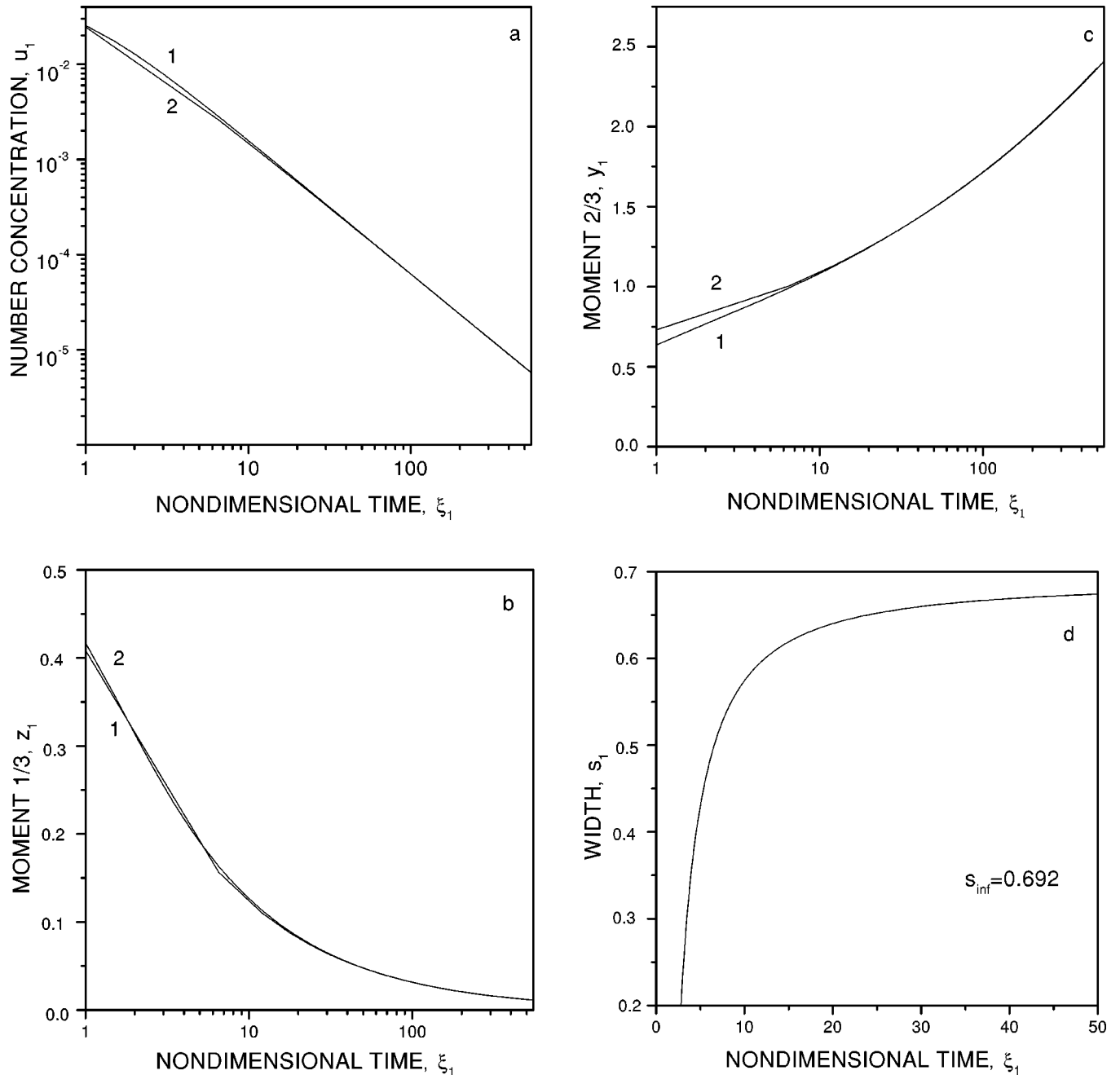


FIG. 2. Kinetics of the coagulation stage. The time dependence of the number concentration (a) and moments of particle-size distribution [(b) and (c)] and the width (d). Numerically found functions  $y$ ,  $z$ , and  $u$  are seen to be well approximated by their asymptotic dependencies. The width  $s$  saturates rather fast: after five units of dimensionless time.

centration and the moment  $\phi_{2/3}$  which defines the average particle mass. This fact means that a kind of self-preservation works at large times. The power exponents in Eq. (49) correspond to the self-preservation in source-enhanced coagulating systems.

Although we considered here a particular problem of aerosol particle formation and growth the strategy proposed above can be applied for solving other similar problems.

#### ACKNOWLEDGMENTS

One of us (A.L.) acknowledges Grant No. 521-98 of ISTD and ESF for financial support.

#### APPENDIX: SOME INTEGRALS WITH LOG-NORMAL DISTRIBUTION

Here the identity (A6) is derived and used for performing necessary integrations that help to reduce Eq. (31) to Eqs. (34)–(36).

Let  $F(s|x)$  be the log-normal distribution,

$$F(x|s) = \frac{1}{\sqrt{2\pi s}} \exp\left(-\frac{1}{2s} \ln^2 x\right). \quad (\text{A1})$$

The integral

$$\langle x^\sigma, f \rangle = \int_0^\infty x^\sigma f\left(\frac{y}{x}\right) F(x|s_1) F(y|s_2) \frac{dx}{x} \frac{dy}{y} \quad (\text{A2})$$

is calculated below for an arbitrary function  $f$ . At  $f=1$  the result is known

$$\langle x^\sigma, 1 \rangle = \exp\left(\frac{\sigma^2 s_1}{2}\right). \quad (\text{A3})$$

Let us introduce  $s_{12} = s_1 s_2 / (s_1 + s_2)$ . Then the identity whose validity is readily checked

$$F(x|s_1) F(x\xi|s_2) = F(x\xi^{s_{12}/s_2}|s_{12}) F(\xi|s_1 + s_2) \quad (\text{A4})$$

helps in transforming Eq. (A2),

$$\begin{aligned} \langle x^\sigma, f \rangle &= \int x^\sigma f(\xi) F(x|s_1) F(x\xi|s_2) \frac{d\xi}{\xi} \frac{dx}{x} \\ &= e^{\sigma^2 s_{12}/2} \int x^\sigma F(x\xi^{s_{12}/s_2}|s_{12}) \\ &\quad \times F(\xi|s_1 + s_2) f(\xi) \frac{d\xi}{\xi} \frac{dx}{x}. \end{aligned} \quad (\text{A5})$$

On integrating over  $x$  ends the calculation up,

$$\langle x^\sigma, f \rangle = \exp\left(\frac{s_{12}\sigma^2}{2}\right) \int_0^\infty \xi^{-\sigma s_{12}/s_2} F(\xi|s_1 + s_2) f(\xi) d\xi. \quad (\text{A6})$$

Let the mass distribution have the form (17) and the coagulation kernel be the homogeneous function of its arguments:  $K(ax, ay) = a^\lambda K(x, y)$ . Then, using the identity (A6) yields:

$$K_0 = \int K(x, y) N(x, t) N(y, t) dx dy = \phi_0^2 g_0^\lambda \langle x^\lambda, \mathcal{K} \rangle, \quad (\text{A7})$$

where  $\mathcal{K}(\xi) = K(1, \xi)$  and

$$\begin{aligned} K_2 &= \int xy K(x, y) N(x, t) N(y, t) dx dy \\ &= \phi_0^{-\lambda} g_0^{2+\lambda} \langle x^{2+\lambda}, \mathcal{K}_1 \rangle = \phi_0^{-\lambda} g_0^{2+\lambda} \langle x^\lambda, \mathcal{K} \rangle, \end{aligned} \quad (\text{A8})$$

where  $\mathcal{K}_1(\xi) = \xi K(1, \xi)$ . It is remarkable that both the values  $K_0$  and  $K_2$  are expressed in terms of one and the same integral  $\langle x^\lambda, \mathcal{K} \rangle$ .

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