

A Mathematical Investigation of the Evaporation– Condensation Process with the Lifshitz–Slyozov Theory

Evgeny N. Bodunov⁺, Mario N. Berberan-Santos[^], Lionello Pogliani^{*}

⁺*Department of Physics, Petersburg State Transport University, St. Petersburg 190031, Russia,
evgeny.bodunov@inbox.ru*

[^]*Centro de Química-Física Molecular and Institute of Nanoscience and Nanotechnology, Instituto
Superior Técnico, Universidade Técnica de Lisboa, 1049-001 Lisboa, Portugal
berberan@ist.utl.pt*

^{*}*Dipartimento di Chimica, Università della Calabria, via P. Bucci, 14/C, Rende CS I-87036, Italy,
lionp@unical.it*

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Abstract

The condensation-evaporation process has been analyzed in detail from the point of view of droplet dynamics, i.e., shape of the distribution function, number of droplets, their size and their evolution with time. The theoretical study of the process is centered on the Lifshitz-Slyozov (LS) equations that are here generalized to take into account such characteristics as the precipitation, the volume distribution of the droplets, the time dependences of the droplet number and the average droplet volume. It has been shown, among other things that after a rather short time, the distribution function, in a small volume domain, can be approximated by a series. It has also been shown that the inverse number of droplets, the average droplet volume, and the dimensionless supersaturation (dimensionless critical radius) become linear functions of time in agreement with the LS asymptotic solution. Over the entire volume domain, the distribution function approaches the asymptotic solution only at large times.

Introduction

In our previous studies [1-5] we examined many problems related with the pressure and the behavior of perfect, van der Waals and real gases either at the macroscopic and/or microscopic level. Throughout the present study we will examine the dynamics and the droplet formation during a condensation-evaporation process. This study has a bearing not only for the understanding of the specific phase transition but also for the understanding of the same concept of phase transition, seen as a general nucleation process. It should be borne in mind that the concept of phase transition has not only to do with the behavior of fluids but also with weather dynamics, with materials and lately also with the origin-of-life problem from a primordial soup [6].

The spinodal* phase demixing of binary fluid mixtures occurs in three stages: (i) an early stage where loose aggregates are spontaneously formed, (ii) an intermediate stage where the equilibrium concentrations in both the majority and minority phases are reached, and (iii) a final stage where aggregates grow by coarsening, to reduce their interfacial energy due to the minor surface/volume ratio [7-9]. While the early stage is well understood, the intermediate stage is still very controversial. The late stage mechanism depends both on the system components and composition [10]. For solutions with near-symmetrical compositions, an interconnected bicontinuous pattern is developed, while in very asymmetric systems polydisperse droplets coexist with a very dilute solution. The coarsening in bicontinuous pattern systems is driven by hydrodynamic effects [11, 12], while in asymmetric solutions it occurs either by the evaporation-condensation mechanism of Lifshitz-Slyozov-Wagner (LSW) [13-15] or by the diffusion-reaction mechanism of Binder-Saufer (BS) [16, 17].

In the BS mechanism droplets travel by Brownian motion through the majority phase and coagulate when they meet. Contrarily, in the LSW mechanism, the translation motion of the droplets is negligible and larger droplets grow at the expense of the nearby smaller ones: individual molecules leave small droplets, migrate through the majority phase by diffusion, and condensate into larger droplets. This results from the decrease of the chemical potential with droplet size increase, a phenomenon due to the surface tension. None of the BS and LSW mechanisms consider the particle-particle interactions and are restricted to systems with low volume fraction of the minority phase [18-20]. The BS mechanism dominates when encounters between droplets are frequent. This depends on both the number density of droplets and the viscosity of the medium. For this reason the coarsening in dilute viscous systems (metal alloys and polymer blends) occurs with the LSW mechanism, while in dilute solutions the BS mechanism takes over. Both mechanisms predict a linear increase of the average volume of droplets with time, and its slope depends on the volume fraction of the minority phase in the BS but not in the LSW mechanism [20]. The coarsening is responsible for the increase in droplets volume, reducing their number without changing the majority phase composition.

The equations describing the coarsening with the BS and LSW mechanisms have obtained autonomous mathematical importance [21-23]. As many authors [13, 15] believed that only one asymptotic solution to the LS equations (independent on initial volume distribution function of droplets) exists, mathematical investigation of the generalized LS equations for the search of new possible solutions were started [22, 23]. In this paper, we show that LS

asymptotic solution is not unique and there are other solutions that depend on the initial conditions. Our conclusions are based not on mathematical methods (theorems and lemmas), but on the understanding of the physics of evaporation-condensation process that is described by the LS equations.

When droplets larger than a critical volume are formed, precipitation occurs [24-25]. Notice that precipitation is important in vapors and liquids and is absent in solid solutions (metal alloys) where grains of new phase grow.

Precipitation and its effect on volume distribution function of droplets within the framework of the BS theory were investigated [26] in connection with the late stage phase demixing of a very dilute toluene solution of a poly(ethylene oxide) chain labeled at one end with pyrene. In this work, we concentrate our attention on the evaporation-condensation LSW mechanism. Here the Lifshitz-Slyozov (LS) equations [13, 15] are generalized to take into account precipitation, volume distribution function of droplets, time dependences of droplet number and average droplet volume are investigated. Considerations done in this paper have also some bearing on the problem of quantum dots [27].

Basic Equations

Let the equilibrium concentration C_R at the boundary of a droplet be related to the droplet radius R by the well known Gibbs-Thomson equation [13, 15],

$$C_R = C_\infty + \frac{\alpha}{R} \tag{1}$$

C_∞ is the concentration of the saturated solution, $C_\infty = C_{R=\infty}$, $\alpha = 2\sigma C_\infty V_0/kT$ [m^{-2}], σ is the inter-phase surface tension [Nm^{-1}], and V_0 is atomic volume of the solute. Thus, the equilibrium concentration of solute near small droplets is larger than the equilibrium concentration near large droplets.

If we ignore the interaction between droplets (droplet sizes R are small compared with the mean distance between them), the diffusion current of solute across the droplet boundary is given by the following Fick's first law, J [$\text{m}^{-2}\text{s}^{-1}$], where D_0 is the diffusion coefficient [m^2s^{-1}], and C is the population density, i.e., number of particles per volume [m^{-3}],

$$J_R = -D_0 \left. \frac{\partial C}{\partial r} \right|_{r=R} \tag{2}$$

The change of volume of the droplet is determined by the flow of solute atoms,

$$\frac{d}{dt} \left(\frac{4}{3} \pi R^3 \right) = -4\pi R^2 V_0 J_R = 4\pi R^2 V_0 D_0 \left. \frac{\partial C}{\partial r} \right|_{r=R} \quad (3)$$

Introduction of the effective diffusion coefficient, $D = V_0 D_0$ [$\text{m}^5 \text{s}^{-1}$], allows to obtain the change of the droplet radius with time,

$$\frac{dR}{dt} = D \left. \frac{\partial C}{\partial r} \right|_{r=R} \quad (4)$$

To obtain $\partial C / \partial r$ the diffusion equation (5, where, $\nabla^2 = \partial^2 / \partial x^2 + \partial^2 / \partial y^2 + \partial^2 / \partial z^2$) must be solved with the boundary conditions (6),

$$\frac{dC}{dt} = D_0 \nabla^2 C \quad (5)$$

$$C|_{r=R} = C_R, \quad C|_{r=\infty} = \bar{C} \quad (6)$$

Here, $\bar{C} = \bar{C}(t)$ is the average concentration in solution. At small droplet growing speed, or under the condition of small initial supersaturation, $\bar{C}_0 - C_\infty = \Delta_0 \ll 1$, $\bar{C}_0 = \bar{C}(t=0)$, it is enough to solve the stationary diffusion equation, $dC/dt = 0$, to obtain the flow J_R , and the result is,

$$C = \bar{C} - \frac{R(\bar{C} - C_\infty) - \alpha}{r}, \quad \left. \frac{\partial C}{\partial r} \right|_{r=R} = \frac{1}{R} \left(\Delta - \frac{\alpha}{R} \right) \quad (7)$$

Here, $\Delta = \Delta(t) = \bar{C} - C_\infty$ is the supersaturation at a given time. Finally, for the speed of a growing droplet we have,

$$\frac{dR}{dt} = \frac{D}{R} \left(\Delta - \frac{\alpha}{R} \right) \quad (8)$$

Equation (8) is valid if the characteristic time scale of the supersaturation change is much larger than the time of establishing stationary current J_R at the droplet surface. This means

that Eq (1) supposes the existence of local thermodynamic equilibrium near the droplet surface.

Eq. (8) implies that a critical radius R_c ($R_c = \alpha/\Delta$) exists. If the radius of a droplet becomes $R = R_c$ than the droplet is in equilibrium with the solution. If $R > R_c$, the droplet is growing, and if $R < R_c$, the droplet is vanishing, while at the initial time, the critical radius is given by, $R_c(t = 0) = R_{c0} = \alpha/\Delta_0$.

Let us work from now on with dimensionless variables, i.e., dimensionless radius $\rho = R/R_c$, dimensionless volume $v = \rho^3$, dimensionless time $t' = t\alpha D/R_{c0}^3$, and dimensionless supersaturation (dimensionless critical radius) $x(t) = \Delta_0/\Delta(t) = R_c(t)/R_{c0}$. In this way Eq (8) can be rewritten as

$$\frac{dv}{dt} = 3 \left(\frac{v^{1/3}(t)}{x(t)} - 1 \right) \quad (9)$$

From now on we will omit the prime on t , i.e., this omission will be maintained throughout the remaining paper. Let function $f(v,t)$ be the volume distribution function so that the number of droplets in the unit volume, $n(t)$, is given by,

$$n(t) = \int_0^{\infty} f(v,t) dv \quad (10)$$

This function f obeys the following equation of continuity,

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial v} \left(f \frac{dv}{dt} \right) = 0 \quad (11)$$

By the law of matter conservation we have,

$$\Delta_0 + q_0 = Q_0 = \Delta(t) + q(t) \quad (12)$$

Where Q_0 is the total initial supersaturation taking into account that at time $t = 0$, some amount of solute, q_0 , was present in the droplets (q_0 has a meaning of a number of solute

atoms initially in the droplets per unit volume); $q(t)$ is the number of solute atoms in the droplets per unit volume given by,

$$q(t) = \frac{1}{V_0} \frac{4\pi}{3} R_{c0}^3 \int_0^\infty v f(v, t) dv \quad (13)$$

Taking into account that $x(t) = \Delta_0/\Delta(t) = R_c(t)/R_{c0}$, then Eq (12) can be rewritten as,

$$1 = \frac{\Delta_0}{Q_0} \frac{1}{x(t)} + k \int_0^\infty v f(v, t) dv \quad (14)$$

Here, $k = \frac{4}{3} \pi R_{c0}^3 V_0^{-1} Q_0^{-1}$. Equations (9), (11), and (14) together with the corresponding initial condition [$t = 0, f(v, 0)$] allow to obtain the distribution function f .

Lifshitz-Slyozov Asymptotic Solution

Lifshitz and Slezov [13, 15] obtained an asymptotic solution for Eqs (9), (11), and (14), which is independent on the initial conditions [i.e., on the shape of the distribution function at time $t = 0, f(v, 0)$],

$$f(v, t) = n(t) \frac{9}{4t} p\left(\frac{9v}{4t}\right) \quad (15)$$

Function $p(z)$, which is here estimated at $z = 9v/(4t)$, obeys the normalization condition,

$\int_0^\infty p(z) dz = 1$, and has the analytic form, shown in Fig. 1,

$$p(z) = \begin{cases} \frac{3^3 e}{2^{5/3}} \frac{1}{(z^{1/3} + 3)^{7/3} (3/2 - z^{1/3})^{1/3}} \exp\left(-\frac{3/2}{3/2 - z^{1/3}}\right), & z \leq \frac{27}{8}, \\ 0, & z > \frac{27}{8}, \end{cases} \quad (16)$$

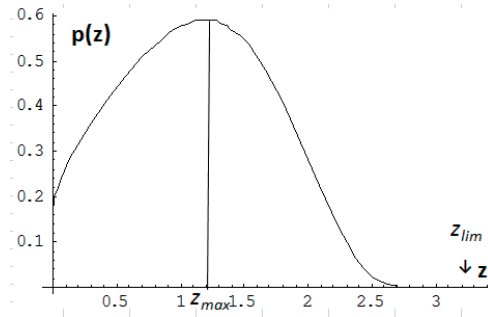


Fig. 1. Plot of the function $p(z)$ [Figs. 1-7 have been obtained with Mathematica[®]]

From Eqs (15) and (16) it follows that: (i) $f(v,t) > 0$ at $v = 0$, (ii) there is a $z_{lim} = 27/8$ where $f(v,t) = 0$ if $v > v_{lim} = 3t/2$, and (iii) there is a $z_{max} = 27/(16\sqrt{2})$ where the distribution function $f(v,t)$ has a maximum value at $v = v_{max} = 3t/(4\sqrt{2})$. Notice that v_{max} grows more slowly than v_{lim} and from this follows that the distribution function becomes broader in time. The asymptotic character of the function $p(z)$ at $z \ll 1$ is,

$$p(z) = \frac{4}{27} \left(1 + z^{1/3} + z^{2/3} + \frac{19}{27}z + \frac{4}{9}z^{4/3} + \frac{28}{135}z^{5/3} + \frac{62}{1215}z^2 + \dots \right) \quad (17)$$

Integrating Eq (11) over the dimensionless volume v taking into account Eqs (9) and (10), we obtain,

$$\frac{dn(t)}{dt} = -3 \left(\frac{v^{1/3}}{x(t)} - 1 \right) f(v,t) \Bigg|_{v=0}^{v=\infty} = -3f(0,t) \quad (18)$$

This means that at small times, when $f(0,t) = 0$ (due to the initial conditions), the number of droplets in solution is constant ($n(t) = \text{const}$), while the sizes of the droplets is changing: small droplets [with $\rho < x(t)$] decrease their size and large droplets [with $\rho > x(t)$] increase their size. The number of the droplets begins to decrease only when the inequality $f(0,t) > 0$ is fulfilled. At long times Eqs (15) and (16) are valid, then together with Eqs (16) and (17), we obtain,

$$\frac{dn(t)}{dt} = -3 \frac{9}{4t} n(t) \frac{4}{27} = -\frac{1}{t} n(t) \quad (19)$$

The solution to this equation is,

$$n(t) = \frac{n_0 t_0}{t} \quad (20)$$

Here, n_0 is the number of droplets in the unit volume at time t_0 . Cited authors [13, 15] have also obtained,

$$x^3(t) = \frac{4}{9} t \quad (21)$$

Now, using Eqs (15) and (16), it is possible to obtain, $\bar{z}^{1/3} = 1$ and $\bar{z} = 1.1296$. Thus, the average droplet radius and the average droplet volume, $\bar{\rho}$ and \bar{v} , are,

$$\bar{\rho} = x(t) = \sqrt[3]{\frac{4}{9} t^{1/3}}, \quad \bar{v} = \bar{\rho}^3 \approx 0.502t \quad (22)$$

Authors [13, 15] believe that the obtained results are independent on the initial conditions if the initial distribution function has a finite width and is continuous (not a sum of δ -function). Other authors [22, 23] questioned this statement and found some new solutions that contradict it. We begin our investigation of the basic equations with the distribution function that equals a sum of δ -function, because it will help us to understand the behavior of the distribution function from a physical point of view.

Note that the modified distribution function (15) and (16) is often used as distribution function of quantum dots [27-29]. Let us introduce the relative radius of the droplets (quantum dots) $u = \rho / \bar{\rho}$ and take into account, according to the definition of z and Eq (22), the droplet volume $v = \rho^3$, $dv = 3\rho^2 d\rho$, and $z^{1/3} = u$. If $\bar{\rho}$ is the average radius of the droplets

(quantum dots), the normalized distribution function of the droplets (quantum dots) over their radius, $N(u)$, $\int_0^\infty N(u)d\rho = 1$, can be obtained from Eqs (15) and (16) [28, 29],

$$N(u) = 3u^2 \frac{f(v,t)}{n(t)} = \frac{3^4 e u^2}{2^{5/3} \rho} \frac{1}{(u+3)^{7/3} (3/2-u)^{11/3}} \exp\left(-\frac{3/2}{3/2-u}\right), u \leq 3/2,$$

$$N(u) = 0, u > 3/2.$$

Solution of the basic equations with monodisperse distribution of droplets

In the case of initial monodisperse distribution of droplets, this distribution, according to the basic equations and to the physics of the process, continues to be monodisperse at any time. Let at time $t = 0$ be $f(v,0) = n_0\delta(v-v_0)$, i.e., the initial droplet volume is $v(t = 0) = v_0$. For longer times according to the basic equations and the physics of the process under investigation, $f(v, t)$ continues to be a δ -function and the number of droplets is constant, i.e., $f(v, t) = n_0\delta(v-v(t))$ where $v(t)$ senses the droplet volume, $v(t) = \rho^3(t)$, and obeys Eq. (9). At this condition, the basic Eq. (14) becomes

$$1 = \frac{a}{x(t)} + bv(t) \tag{23}$$

Where, $a = \Delta_0/Q_0$, and $b = n_0k$. Note, that if the initial size v_0 of the droplet is larger than the critical size, the droplets grows, $v^{1/3}(t) > x(t)$, until the establishment of equilibrium conditions, when the droplet stops growing. Thus, the physical process foretells that at some $t \rightarrow \infty$, $dv/dt = 0$ and from Eq. (9) we obtain, $v(\infty) = x^3(\infty)$ (Fig. 2).

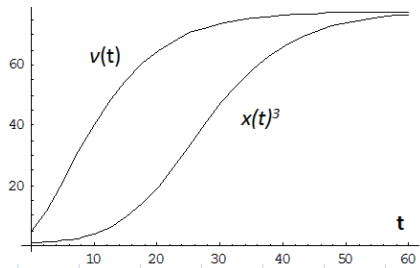


Fig. 2. The $v(t)$ (higher curve) and $x(t)^3$ (lower curve) functions at: $b = 0.01$, and $v_0 = 5$

At time $t = 0$, $x(0) = 1$, $v(0) = v_0$, and from Eq. (23) we have that, $1 = a + bv_0$, i.e., $a = 1 - bv_0$.

From Eq. (23), we get, $\frac{1}{x(t)} = \frac{1 - bv(t)}{a} = \frac{1 - bv(t)}{1 - bv_0}$. Inserting this equation into Eq (9), we

obtain,

$$\frac{dv}{dt} = 3 \left(v^{1/3} \frac{1 - bv}{1 - bv_0} - 1 \right) \tag{24}$$

Equation (24) can be solved with Mathematica[®]. For growing droplets ($v_0 > 1$), the concentration of the solution and $\Delta(t)$ decrease, therefore $x(t) = \Delta_0/\Delta(t)$ increase. At $t \rightarrow \infty$, the process of droplet growing stops, $dv/dt = 0$, and in accordance with Eq. (9), $v(\infty) = x^3(\infty)$ (see Fig. 2). For dissolving droplets ($v_0 < 1$), instead, the concentration of the solution and $\Delta(t)$ increase, therefore $x(t) = \Delta_0/\Delta(t)$ decreases. At some later moment t , all droplets dissolve, $v(t) = 0$, and from Eq. (23), we obtain $x(t) = a = 1 - bv_0$. Fig. 3 illustrates this behavior.

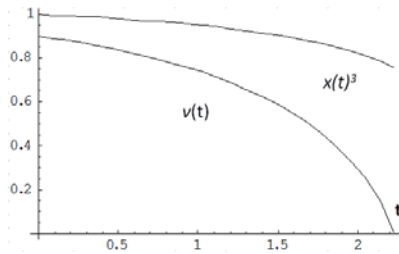


Fig. 3. The $v(t)$ (lower curve) and $x(t)^3$ (upper curve) functions at: $b = 0.1$, and $v_0 = 0.9$

The distribution function of the droplets is the sum of two δ -functions

According to the basic LS equation (9, 11, and 14) for this case, if the initial distribution function is a sum of two δ -functions it continues to be a sum of two δ -functions with the same coefficients (the numbers of droplets of two different volumes are constant) at later times. Let $f(v, t) = n_0 \{ \delta(v - v_1(t)) + \delta(v - v_2(t)) \}$. For simplicity, we suppose that the numbers of the droplets of different size are equal to n_0 . Their initial volumes are $v_1(0) = v_{10}$ and $v_2(0) = v_{20}$. With this condition, the basic equations (9) and (14) become,

$$\frac{dv_1}{dt} = 3 \left(\frac{v_1^{1/3}(t)}{x(t)} - 1 \right) \quad (25)$$

$$\frac{dv_2}{dt} = 3 \left(\frac{v_2^{1/3}(t)}{x(t)} - 1 \right) \quad (26)$$

$$1 = \frac{a}{x(t)} + b(v_1(t) + v_2(t)) \quad (27)$$

Parameters a and b have the same meaning as before. At time $t = 0$, $x(0) = 1$, $v_1(0) = v_{10}$, and $v_2(0) = v_{20}$, and from Eq. (27) we have $1 = a + b(v_{10} + v_{20})$. Thus $a = 1 - b(v_{10} + v_{20})$ and from

Eq (23) we get, $\frac{1}{x(t)} = \frac{1 - b(v_1(t) + v_2(t))}{a} = \frac{1 - b(v_1(t) + v_2(t))}{1 - b(v_{10} + v_{20})}$. Inserting this equation into

Eq (25) and (26), we obtain,

$$\frac{dv_1}{dt} = 3 \left(v_1^{1/3} \frac{1 - b(v_1 + v_2)}{1 - b(v_{10} + v_{20})} - 1 \right) \quad (28)$$

$$\frac{dv_2}{dt} = 3 \left(v_2^{1/3} \frac{1 - b(v_1 + v_2)}{1 - b(v_{10} + v_{20})} - 1 \right) \quad (29)$$

Eqs (28) and (29) can be solved with Mathematica[‡]. Let us inspect the different situations.

i. The initial radius of the droplets is smaller than the critical radius ($v_{10} = 0.9$, $v_{20} = 0.8$) and their number is small ($b = 0.01$). In this case, the droplets dissolve, the concentration of the solution increases, therefore $x(t)$ decreases quite slowly (Fig. 4).

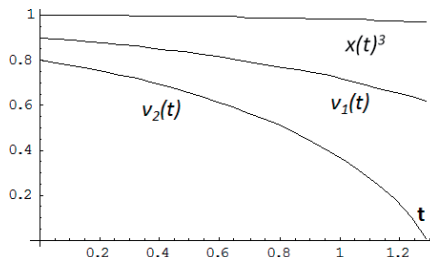


Fig. 4. The $v_1(t)$ (middle) $v_2(t)$ (bottom), and $x(t)^3$ functions at: $v_{10} = 0.9$, $v_{20} = 0.8$, and $b = 0.01$.

ii. The initial radius of the droplets is smaller than the critical radius ($v_{10} = 0.9$, $v_{20} = 0.8$), and their number is large ($b = 0.1$). In this case the droplets start dissolving and the concentration of solution increases, and therefore $x(t)$ decreases. Later on, when radius of the first droplets

become larger than the critical radius, the first droplets start increasing, but the next ones decrease and, at the end, they dissolve completely (Fig. 5).

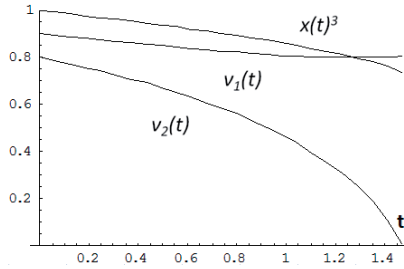


Fig. 5. The $v_1(t)$ (middle), $v_2(t)$ (bottom), and $x(t)^3$ functions at: $v_{10} = 0.9$, $v_{20} = 0.8$, and $b = 0.1$.

iii. The initial radius of the first droplets is larger than the critical radius ($v_{10} = 5$), the initial radius of the following droplets is equal to the critical radius ($v_{20} = 1$), and their number is small ($b = 0.01$). In this case, the first droplets grow while the next ones dissolve. The concentration of the solution decreases slowly, therefore $x(t)$ increases quite slowly (Fig. 6).

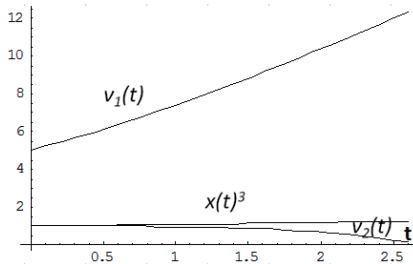


Fig. 6. The $v_1(t)$ (top), $v_2(t)$, and $x(t)^3$ (middle) functions at: $v_{10} = 5$, $v_{20} = 1$, and $b = 0.01$.

iv. The initial radius of the droplets are larger than the critical radius ($v_{10} = 5$, $v_{20} = 3.5$) and their number is small ($b = 0.01$). In this case the droplets start increasing and the concentration of the solution decreases, therefore $x(t)$ increases. Later on, when the radius of the next droplets become smaller than the critical radius, the droplets continue to increase, but then they begin to dissolve, till when they dissolve completely. During this interval of time, the concentration of the solution can even increase and therefore $x(t)$ decreases (Fig. 7).

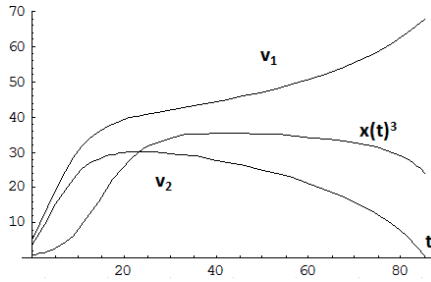


Fig. 7. The $v_1(t)$ (top), $v_2(t)$ (bottom), and $x(t)^3$ functions at: $v_{10} = 5$, $v_{20} = 3.5$, and $b = 0.01$.

The obtained solutions allow explaining the qualitative behavior of the distribution function $f(v,t)$ and the concentration of the droplets $n(t)$. For example, let $f(v,t)$ be a sum of a large number of δ -functions at the initial time, $t = 0$. In this case, during the evaporation-condensation, the process (for $t \rightarrow \infty$) admits only two results,

- i. All droplets dissolve if their initial radius is smaller than the critical radius and their concentrations are small.
- ii. At the end of the process, only the largest droplets continue to exist in solution. Their number will be equal to the initial number. Their volume and the concentration of the solution are, in this case, described by Fig. 2, after that all smaller droplets have disappeared.

These conclusions allow explaining the behavior of the volume distribution function of the droplets if the initial distribution function is continuous. Let the initial distribution function be the sum of a (any) continuous function (located in the low volume domain) and the δ -function $n_0\delta(v-v_0)$ (located in the large volume domain, $v_0 > 1$). Then the distribution function will approach a δ -function $n_0\delta(v-v(t))$ at $t \rightarrow \infty$ (see section 4).

Let the distribution function have a form of a rung from the high side of the volumes, i.e., $f(v,0) > 0$ if $v < v_{lim}$; $f(v,0) = 0$ if $v > v_{lim}$, and $\left. \frac{df(v,0)}{dt} \right|_{v=v_{lim}} \propto \delta(v - v_{lim})$. Then the distribution

function preserves this characteristic property at any time.

The distribution function is a continuous broad function.

Five situations due to various initial conditions of the distribution function will be considered.

- i. The initial distribution function $f(v,0) \neq 0$ for $v < 1$ is,

$$f(v,0) = \begin{cases} 0, & v < 0.2, \\ n_0 750(0.01 - (v - 0.3)^2), & 0.2 \leq v \leq 0.4, \\ 0, & v > 0.4 \end{cases}$$

See Fig. 8, curve 1, where $f(v,0) \neq 0$ for $0.2 < v < 0.4$. Here, the droplets have a radius smaller than the critical radius and should dissolve. In this case at the starting time, when there are no droplets with almost zero volumes, i.e., $f(0,t) = 0$, the radius and the volume, v , of the droplets decrease and the distribution function $f(v,t)$ displaces to the left (Fig. 8, curves 1 - 5), but the number of the droplets remains constant [$n(t) = n_0$, Fig. 9, curve 2]. As time goes by the inequality $f(0,t) > 0$ begins to be fulfilled (Fig. 8, curves 6 - 8), the droplets start to disappear and their number decreases (Fig. 9, curve 2). While the droplets dissolve, the concentration of the solution increases and approaches a constant value, as a result $x(t)$ decreases and approaches $a = A_0/Q_0 [x^3 \rightarrow a^3]$ (Eq 14, Fig. 9, curve 1).

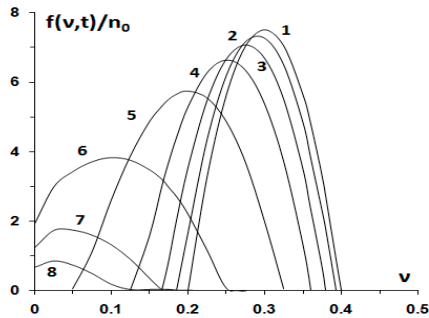


Fig. 8. The behavior of $f(v,t)$ at: $a = A_0/Q_0 = 0.8$. $t = 0$ (1), 0.01 (2), 0.025 (3), 0.05 (4), 0.1 (5), 0.2 (6), 0.3 (7), and 0.35 (8).

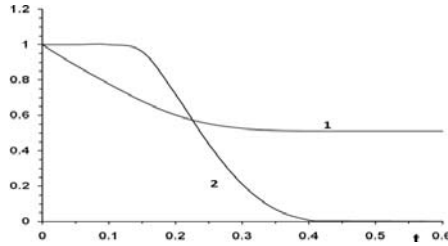


Fig. 9. The behavior of $f(v,t)$ at: $a = \Delta_0/Q_0 = 0.8$. 1: $x^3(t)$; 2: $n(t)/n_0$.

ii. The initial distribution function $f(v,0) \neq 0$ for $v > 1$ is,

$$f(v,0) = \begin{cases} 0, & v < 3, \\ n_0 0.75(1 - (v-4)^2), & 3 \leq v \leq 5, \\ 0, & v > 5 \end{cases}$$

See Fig. 10, curve 1, where $f(v,0) \neq 0$ for $3 < v < 5$. In this case, all the droplets have radius larger than the critical radius and should increase their volumes. For the initial period of time when the equality $f(0,t) = 0$ is valid, the radius and the volumes v of the droplets increase, the distribution function $f(v,t)$ shifts to the right (Fig. 10, curve 2), and the number of the droplets remains constant ($n(t) = n_0$, Fig. 11, curve 2).

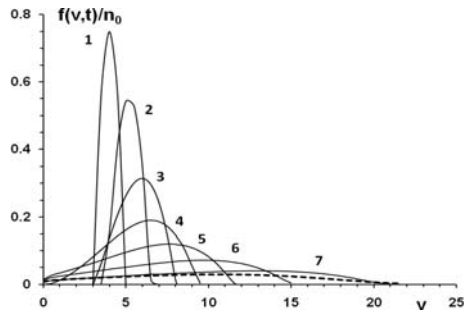


Fig. 10. The behavior of $f(v,t)$ at: $a = 0.5$. $t = 0$ (1), 1 (2), 4 (3), 7 (4), 10 (5), 14 (6), 20 (7). Last curve (- -) is the asymptotic solution.

For the intermediate period of time, when the equality $f(0,t) = 0$ continues to be valid (Fig. 10, curves 2 - 4), droplets with a radius smaller than the critical one start to appear (see Fig.

7), the droplets with radius larger than the critical one continue to grow. As a result, the width of the distribution function increases, but the number of the droplets continues to be constant.

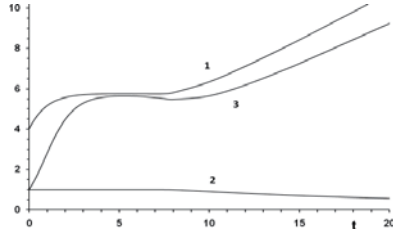


Fig.11. The behavior of $f(v,t)$ at: $a = 0.5$. **1:** $x^3(t)$; **2:** $n(t)/n_0$; **3:** average droplet volume, $\bar{v} = \int_0^\infty v f(v,t) dv / n(t)$.

During the third time period the inequality $f(0,t) > 0$ starts to be fulfilled (Fig. 10, curves 5 - 7), i.e., the smallest droplets arise due to the dissolution of the largest ones and start to disappear, consequently the number of droplet decreases (Fig. 11, curve 2). The dependence of the concentration of the solution on time is not monotonic (Fig. 11, curve 1). It looks like that for longer times the distribution function $f(v,t)$ approaches to the asymptotic LS solution (dotted curve in Fig. 10). For instance, when the distribution function increases with v , like curve 7 in Fig. 10, then it can be approximated with Eq. (15) (dotted curve).

iii. The initial distribution function $f(v,0) \neq 0$ for $v < 1$ is,

$$f(v,0) = \begin{cases} 0, & v < 0.7, \\ n_0 750(0.01 - (v - 0.8)^2), & 0.7 \leq v \leq 0.9, \\ 0, & v > 0.9 \end{cases}$$

See Fig. 12, curve 1, $f(v,0) \neq 0$ for $0.7 < v < 0.9$. In this case, all the droplets have radius smaller than the critical radius and should decrease their volumes. At the initial time, when $f(0,t) = 0$, the radius and the volume v of the droplets decrease, the distribution function $f(v,t)$ displaces to the left (Fig. 12, curve 2 - 4), the number of the droplets is constant [$n(t) = n_0$, Fig. 13, curve 2]. The concentration of the solution increases (due to the dissolution of the droplets), therefore $x(t)$ decreases (Fig. 13, curve 1), and the critical radius decreases.

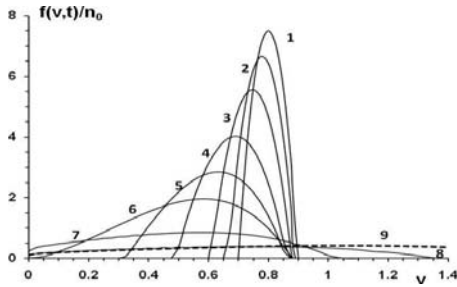


Fig.12. The behavior of $f(v,t)$ at: $a = 0.8$. $t = 0$ (1), 0.1 (2), 0.25 (3), 0.5 (4), 0.75 (5), 1 (6), 1.5 (7), 2 (8). The dotted curve 9 is the LS asymptotic solution.

The critical radius decreases faster than the decreasing of the largest volume of the droplets, and, at a certain moment it becomes smaller than the largest droplet volume. From this moment on, the largest droplets begin to grow; the distribution function becomes broader (Fig. 12, curves 5 - 7). During this period of time the equality $f(0,t) = 0$ is fulfilled, therefore the number of the droplets continues to be constant (Fig. 13, curve 2). During a third time period the inequality $f(0,t) > 0$ starts to be fulfilled (Fig. 12, curves 7 and 8), the smallest droplets start to disappear, and the droplet number start to decrease (Fig. 13, curve 2) with exponential behavior.

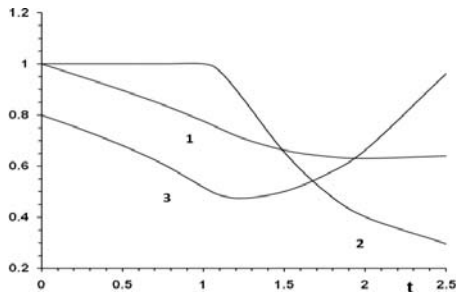


Fig. 13. The behavior of $f(v,t)$ at: $a = 0.8$. 1: $x^3(t)$; 2: $n(t)/n_0$; 3: average droplet volume, $\bar{v} = \int_0^\infty v f(v,t) dv / n(t)$.

The dependence of the concentration of the solution on time is not monotonic (Fig. 13, curve 1). It looks like the one for large times, the distribution function $f(v,t)$ approaches to the

LS asymptotic solution (curve **9** in Fig. 12), i.e., curve **8** (within the domain, where the distribution function grows with v) can be approximated by Eq (15) (dotted curve **9**).

iv. The initial distribution function $f(v,0) \neq 0$ for $v < 4$ is,

$$f(v,0) = \begin{cases} n_0 \frac{3}{32} (4 - (v-2)^2), & 0 \leq v \leq 4, \\ 0, & v > 4 \end{cases}$$

See Fig. 14, curve **1**, $f(v,0) \neq 0$ for $0 < v < 4$. In this case, the distribution function is broad. The largest droplets grow, the distribution function broadens (Figs 14 and 15, for two different sets of t , solid curves **1 - 10**). The smallest droplets disappear, therefore the droplet number decreases from the start (Fig. 16, curve **2**).

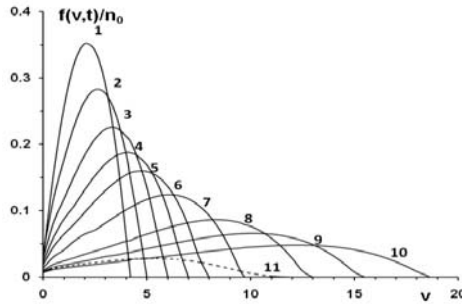


Fig. 14. The behavior of $f(v,t)$ at: $a = 0.8$. $t = 0$ (**1**), 0.1 (**2**), 0.5 (**3**), 1 (**4**), 1.5 (**5**), 2 (**6**), 3 (**7**), 5 (**8**), 7 (**9**), 10 (**10**), the dotted curve **11** is the LS asymptotic solution to the curve **10**.

The dependence of the concentration of the solution with time is monotonic (Fig. 16, curve **1**). It looks like that for larger times the distribution function $f(v,t)$ approaches to the LS asymptotic solution, which gives rise to curve **11** in Fig. 15 (here only odd-numbered curves are given). The solid curve **11** (Fig. 15) can be approximated with Eq. (15), and in this case it gives rise to the dotted curve (near curve **11**) in Fig. 15. For smaller times, such approximation is good only for small droplet volumes (Fig. 14, compare dotted curve **11** and solid curve **10**).

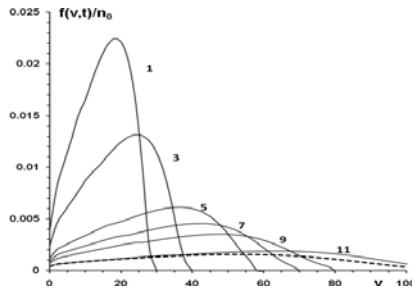


Fig. 15. The behavior of $f(v,t)$ at $a = 0.8$. $t = 20$ (1), 30 (3), 50 (5), 60 (7), 70 (9), 100 (11). The dotted lower curve is the LS asymptotic solution.

Notice that for longer times, $x(t)^3$ and $1/n(t)$ grows linearly with time (Fig. 16, curves 1 and 2) in accordance with the LS solution (Eqs 12 and 13a). The growing velocity of the average droplet volume ($\bar{v} \sim 0.49t$) is larger than the velocity of growing $x(t)^3$ ($x(t)^3 \sim 0.42t$) in accordance with Eqs 21 and 22 where numerical coefficients are 0.502 and 0.444 respectively.

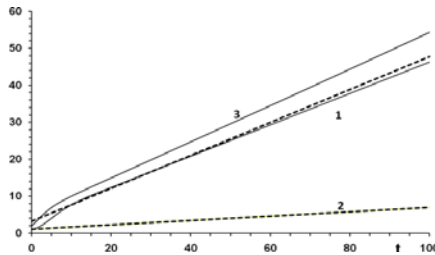


Fig. 16. The behavior of $f(v,t)$ at $a = 0.8$. 1: $x^3(t)$; 2: $n_0/n(t)$; 3: average droplet volume, $\bar{v} = \int_0^\infty v f(v,t) dv / n(t)$. The higher dotted curve obeys the approximation $x^3(t) = (4/9)t$; the lower dotted curve that overlaps curve 2 obeys, instead, the approximation $n_0/n(t) = 1.13 + 0.0587t$.

v. The initial distribution function is wide and has a form of a rectangle,

$$f(v,0) = \begin{cases} 0, & v < 3, \\ 0.5n_0, & 3 \leq v \leq 5, \\ 0, & v > 5. \end{cases}$$

As a matter of fact, $f(v,t)$ is a trapezium with sharp boundaries limited by the precision of numerical calculations (Fig. 17, curve 1).

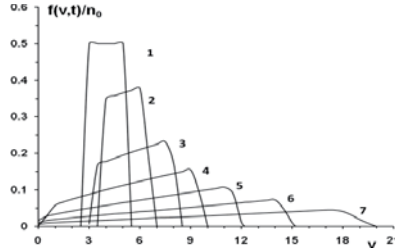


Fig. 17. The behavior of $f(v,t)$ at: $a = 0.5$, $t = 0$ (1), 1 (2), 4 (3), 7 (4), 10 (5), 14 (6), 20 (7).

At the start the distribution function widens, a slope at the top of distribution function appears, sharp boundaries continue to exist (Fig. 17, curves 1 - 3), and the number of the droplets is constant while $f(v=0,t) = 0$ (Fig. 18, curve 2).

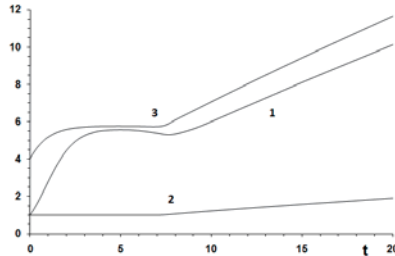


Fig.18. The behavior of $f(v,t)$ at: $a = 0.5$, **1**: $x^3(t)$; **2**: $n_0/n(t)$; **3**: average droplet volume

$$\bar{v} = \int_0^{\infty} v f(v,t) dv / n(t).$$

When the left boundary of the distribution function approaches the vertical axis and the inequality $f(v=0,t) > 0$ begins to hold, the smallest droplets start to disappear, the number of the droplets start to decrease (Fig. 18, curve 2), the right boundary of the distribution function continues to be very sharp and moves to the left (Fig. 17, curves 4 - 7) in agreement with known results [23]. The average droplet volume \bar{v} and $x^3(t)$ grow linearly with time, but with

different speeds (Fig. 18, curves **1** and **3**). Note that in this time domain, the distribution function can be approximated by the series (17) (Fig. 19, dotted curves).

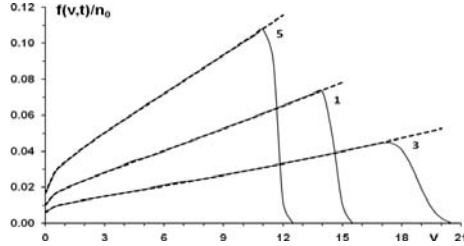


Fig. 19. The behavior of $f(v,t)$ at: $a = 0.5$, $t = 10$ (**5**), 14 (**1**), 20 (**3**). Dotted curves **5**, **1**, and **3** are approximated by the series of eq. (17).

The distribution function under precipitation

Let us suppose that precipitation occurs when the droplet volume becomes larger than a critical volume, v_{pr} . In this case, Eqs (9) and (11) are still valid, and Eq. (10) takes the form

$$n(t) = \int_0^{v_{pr}} f(v,t) dv \quad (30)$$

Now, the number of droplet decreases not only because the smallest droplets dissolves ($f(0,t) > 0$), but also because the droplets with $v > v_{pr}$ start to precipitate, therefore Eq. (19) changes to,

$$\frac{dn(t)}{dt} = -3 \left(\frac{v^{1/3}}{x(t)} - 1 \right) f(v,t) \Big|_{v=0}^{v=v_{pr}} = -3f(0,t) - 3 \left(\frac{v_{pr}^{1/3}}{x(t)} - 1 \right) f(v_{pr},t) \quad (31)$$

The first term in Eq. (31) describes the dissolution of the droplets (see Eq. (19)) while the second term describes the precipitation. Equation (12) should be rewritten as,

$$\Delta_0 + q_0 = Q_0 = \Delta(t) + q(t) + s(t) \quad (32)$$

$s(t)$ is the number of solute atoms per unit volume that precipitated in the droplets. Here, [see Eq. (13)]

$$q(t) = \frac{1}{V_0} \frac{4\pi}{3} R_{c0}^3 \int_0^{v_{pr}} v f(v, t) dv \quad (33)$$

From Eq. (31), it follows that, $\frac{ds}{dt} = 3f(v_{pr}, t) \left(\frac{v_{pr}^{1/3}}{x(t)} - 1 \right) \frac{1}{V_0} \frac{4\pi}{3} R_{c0}^3$. Supposing that there were no droplets with volumes larger than v_{pr} at the initial time $t = 0$, we obtain,

$$s(t) = \frac{1}{V_0} \frac{4\pi}{3} R_{c0}^3 \int_0^t f(v_{pr}, t') \left(\frac{v_{pr}^{1/3}}{x(t')} - 1 \right) dt' \quad (34)$$

Finally, Eq. (14) takes the form

$$1 = \frac{\Delta_0}{Q_0} \frac{1}{x(t)} + k \int_0^{v_{pr}} v f(v, t) dv + \frac{1}{Q_0} s(t) \quad (35)$$

Here, $k = \frac{4}{3} \pi R_{c0}^3 V_0^{-1} Q_0^{-1}$. To obtain the needed dependences, Eqs (9), (11), (30), (34), and (35) must be solved. In the calculations below, we suppose that $v_{pr} = 10$ and the initial distribution function $f(v, 0) \neq 0$ for $v < 4$ (as in the case **iv**) is,

$$f(v, 0) = \begin{cases} n_0 \frac{3}{32} (4 - (v - 2)^2), & 0 \leq v \leq 4, \\ 0, & v > 4 \end{cases}$$

This distribution function is shown in Fig. 20, curve **1**. Solutions of equations (9), (11), (30), (34), and (35) for $t > 0$ are also shown in Fig. 20. For small times, while there are no droplets with volumes larger than v_{pr} , $f(v_{pr}, t) = 0$, curves **1 - 7** (in Fig. 20) repeat curves **1 - 7** in Fig. 14. In this time domain, the behavior of parameters $x^3(t)$, $n_0/n(t)$ and \bar{v} (Fig. 21) are the same as in Fig. 16.

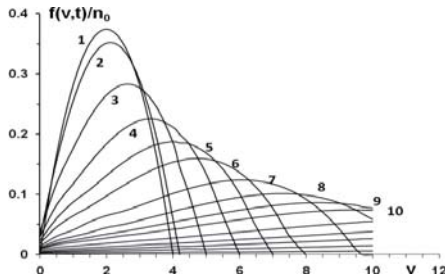


Fig. 20. The behavior of $f(v,t)$ at: $a = \Delta_0/Q_0 = 0.8$. $t = 0$ (1), 0.1 (2), 0.5 (3), 1 (4), 1.5 (5), 2 (6), 3 (7), 4 (8), 5 (9), 6 (10), 8 (11), 10 (12), 12 (13), 15 (14), 20 (15) [curves 11-15 are after curve 10 with decreasing values].

At larger times, when droplets with volumes $v = v_{pr}$ appeared and $f(v_{pr},t) > 0$, precipitation begins (curves 8 - 15). It follows from Eq. (24), that under condition $t \rightarrow 0$, the solution concentration approaches a constant value ($x(t) \rightarrow \text{const}$) as the number of droplets $n(t) \rightarrow 0$ due to precipitation, and therefore $x^3(t) \rightarrow \text{const}$ (Fig. 21, curve 1), the number of droplets (as approximation shows) increases exponentially (curve 2), and the average droplet volume \bar{v} begins to decrease slowly approaching $x^3(t)$ (curve 3).

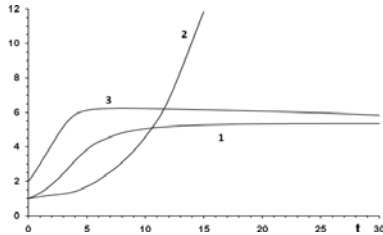


Fig. 21. The behavior of $f(v,t)$ at: $a = 0.8$, 1: $x^3(t)$; 2: $n_0/n(t)$; 3: average droplet volume $\bar{v} = \int_0^\infty v f(v,t) dv / n(t)$.

In this time domain, distribution function is well approximated by the series (17) (Fig. 22, solid and dotted curves 1 - 3). Note that the asymptotic behavior of the distribution function shown in Fig. 22 is similar to the asymptotic behavior obtained for BS mechanism of the coarsening in [26].

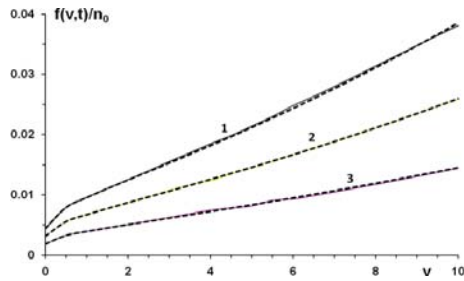


Fig. 22. The behavior of $f(v,t)$ at: $\alpha = 0.8$. $t = 10$ (1), 12 (2), 15 (3). The dotted curves are approximations obtained using the series of eq. (17).

Conclusions

In the following are the Five conclusions that are possible for our system of droplets.

1. The solution of LS basic equations for the initial volume distribution function as a sum of δ -functions allows a qualitative forecasting of the behavior of the distribution function for any initial condition.
2. If the initial distribution function is continue and it is concentrated in a small volume domain (for $v < 1$) and the number of droplets is small, then all droplets dissolve and the distribution function never approached the LS asymptotic solution (as contrasted to statement [13, 15]).
3. After comparatively short time, the distribution function can be approximated (in small volume domain) by the series (17); the inverse number of droplets, the average droplet volume, and $x^3(t)$ become linear functions of time in agreement with the LS asymptotic solution, but over all the volume domain, the distribution function approaches the asymptotic solution only at very large time.
4. If the initial distribution function has a sharp boundary from the side of large volumes (derivative of the distribution function is a δ -function at this boundary), this sharp boundary continues to exist (the derivative continues to be a δ -function) for every time (as contrasted to statement [13, 15] and in agreement with obtained results [23]). Thus, such distribution function never approaches the LS asymptotic solution, but in a small volume domain, this distribution function can be approximated by the series (23).

5. If precipitation is taken into account, the distribution function can be approximated by the series (23) at large times, the number of droplets decreases almost exponentially, and $x^3(t)$ approaches a constant value.

References and Notes

* In thermodynamics, the *spinodal* is the limit of stability of a solution. *Spinodal decomposition* is, instead, a mechanism by which a solution of two or more components can separate into distinct regions (or phases) with distinctly different chemical compositions and physical properties. This mechanism differs from classical nucleation in that phase separation due to spinodal decomposition is much more subtle, and occurs uniformly throughout the material, not just at discrete nucleation sites.

#Mathematica 5.0, Wolfram Research, <http://www.wolfram.com>.

- [1] M. N. Berberan-Santos, E. N. Bodunov, L. Pogliani, On the barometric formula, *Am. J. Phys.* **65** (1997) 404–412.
- [2] M. N. Berberan-Santos, E. N. Bodunov, L. Pogliani, Liquid–vapor equilibrium in a gravitational field, *Am. J. Phys.* **70** (2002) 438–443.
- [3] M. N. Berberan-Santos, E. N. Bodunov, L. Pogliani, Classical and quantum study of the motion of a particle in a gravitational field, *J. Math. Chem.* **37** (2005) 101–115.
- [4] M. N. Berberan-Santos, E. N. Bodunov, L. Pogliani, The Van der Waals equation: Analytical and approximate solutions, *J. Math. Chem.* **43** (2008) 1437–1457.
- [5] M. N. Berberan-Santos, E. N. Bodunov, L. Pogliani, On the barometric formula inside the earth, *J. Math. Chem.* **47** (2010) 990–1004.
- [6] A. S. Kauffman, *The Origins of Order: Self–Organisation and Selection in Evolution*, Oxford Univ. Press, Oxford, 1993.
- [7] J. D. Gunton, M. San Miguel, P. Sahni, *Phase Separation and Critical Phenomena*; Academic Press, London, 1983.
- [8] H. Furukawa, A dynamic scaling assumption for phase separation, *Adv. Phys.* **34** (1985) 703–750.
- [9] T. Hashimoto, *Materials Science and Technology, Vol. 12: Structure and Properties of Polymers* (VCH, Weinheim, 1993); *Phase Transitions* **12** (1988) 47–119.
- [10] H. Tanaka, Critical dynamics and phase-separation kinetics in dynamically asymmetric binary fluids: New dynamics universality class for polymer mixtures or dynamic crossover? *J. Chem. Phys.* **100** (1994) 5323:1–15.
- [11] E. D. Siggia, Late stages of spinodal decomposition in binary mixtures, *Phys. Rev. A* **20** (1979) 595–605.

- [12] H. Tanaka, A new coarsening mechanism of droplet spinodal decomposition, *Phys. Rev.* **E51** (1995) 1313.
- [13] I. M. Lifshitz, V. V. Slyozov, The kinetics of precipitation from supersaturated solid solutions, *J. Phys. Chem. Solids* **19** (1961) 35–50.
- [14] C. Wagner, Theorie der Alterung von Niederschlägen durch Umlösen (Ostwald-Reifung), *Z. Elektrochem.* **65** (1961) 581–591.
- [15] V. V. Slezov, V. V. Sagalovich, Diffusive decomposition of solid solutions, *Sov. Phys. Uspekhi* **30** (1987) 23–45.
- [16] K. Binder, D. Stauffer, Theory for the slowing down of the relaxation and spinodal decomposition of binary mixtures, *Phys. Rev. Lett.* **33** (1974) 1006–1009.
- [17] K. Binder, D. Stauffer, Statistical theory of nucleation, condensation and coagulation, *Adv. Phys.* **25** (1976) 343–396.
- [18] M. San Miguel, M. Grant, J. D. Gunton, Phase separation in two-dimensional binary fluids, *Phys. Rev.* **A31** (1985) 1001–1005.
- [19] H. Tanaka, New coarsening mechanisms for spinodal decomposition having droplet pattern in binary fluid mixture: Collision-induced collisions, *Phys. Rev. Lett.* **72** (1994) 1702–1705.
- [20] H. Tanaka, A new coarsening mechanism of droplet spinodal decomposition, *J. Chem. Phys.* **103** (1995) 2361:1–4.
- [21] J. M. Ball, J. Carr, O. Penrose, The Becker-Döring equations: Basic properties and asymptotic behavior of solutions, *Commun. Math. Phys.* **104** (1986) 657–692.
- [22] B. Niethammer, R. L. Pego, The LSW model for domain coarsening: Asymptotic behavior for conserved total mass, *J. Stat. Phys.* **104** (2001) 1113–1144.
- [23] J. A. Carrillo, T. Goudon, A numerical study on large-time asymptotic of the Lifshitz-Slyozov system, *J. Sci. Comput.* **20** (2004) 69–113.
- [24] J. R. Philip, D. E. Smiles, Macroscopic analysis of the behavior of colloidal suspensions, *Adv. Colloid Interface Sci.* **17** (1982) 83–103.
- [25] R. J. Hunter, *Foundations of Colloid Science*, Oxford Univ. Press, Oxford, 1987.
- [26] S. Picarra, E. J. N. Pereira, E. N. Bodunov, J. M. G. Martinho, Kinetics of coarsening and precipitation of dilute polymer solutions: Fluorescence study of PEO in toluene, *Macromolecules* **35** (2002) 6397–6403.
- [27] E. Bodunov, M. N. Berberan-Santos, L. Pogliani, On the shape of quantum-dot distribution-function on sizes, *Optics Spectroscopy* **111** (2011) 66–70.
- [28] M. Ivanda, K. Babocsi, C. Dem, M. Schmitt, M. Montagna, W. Kiefer, Low-wave-number Raman scattering from CdS_xSe_{1-x} quantum dots embedded in a glass matrix, *Phys. Rev.* **B67** (2003) 235329:1–8.
- [29] M. Yu. Leonov, A. B. Baranov, A. B. Fedorov, Transient interband light absorption by quantum dots: Degenerate pump-probe spectroscopy, *Optics Spectroscopy* **109** (2010) 358–365