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Kinetics of heterogeneous condensation under dynamic conditions

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An analytical kinetic condensation theory for arbitrary power in the law of supercritical growth of embryos is constructed. Exhausting of the heterogeneous centers is taken into account. A system of balance equations is formulated based on a quasistationary approach. Properties of the solution for the essential period of the droplet formation are obtained using an iteration procedure. The universal solution method gives practically precise expressions for all coefficients in the brief description of the evolution process.

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I. INTRODUCTION

Condensation of supersaturated vapor into droplets can be regarded as a model of first-order phase transitions where some alternative methods of description are implemented. We introduce some ideas to describe phase transitions in this situation. Usually some heterogeneous centers become centers of supercritical embryos during condensation, which indicates the occurrence of the process of heterogeneous condensation. Heterogeneous condensation is described by nonlinear equations since droplets consume metastable substances and free heterogeneous centers decrease at the same time.

Kinetic theory of first-order phase transition appears naturally from the classical theory of nucleation, which describes formation of embryos of the new phase. This theory was developed first by Volmer [1], Becker and Doering [2], Zeldovitch [3] and Frenkel [4] and modified later by Lothe and Pound [5], Reiss, Cohen and Katz [6], Reiss [7] and Fisher [8].

Wakeshima [9] started to investigate the kinetic problem of the metastable phase decay. Homogeneous decay of the metastable phase was studied by Kuni, Grinin, and Kabanov [10]. The theory of homogeneous condensation under dynamical conditions was considered in [11,12]. A corresponding iteration procedure for homogeneous condensation was proposed by Kuni [12]. Heterogeneous condensation under dynamic conditions was investigated in [13]. The method of the universal solution was introduced in [14] and was studied in detail in [15,16]. All the theories mentioned above are valid only until the beginning of coalescence (Ostwald ripening). The coalescence process, which is not observed here, was investigated first by Slyozov and Lifshitz [17,18].

The process of phase transition is caused by the variation in time of the external conditions. The most natural external conditions have a rather smooth continuous form—the variation of the external thermodynamic parameters occurs during the whole period of the phase transformation. Such external conditions will be called dynamical. The main goal of the present paper is to give an analytical description of the phase transition under dynamic external conditions. This description will be based on the methods suggested in [19] and is valid when the critical embryo contains a large number of molecules. This means that the capillarity approximation for the free energy can be used.

The following assumptions will be used in this paper:

(i) The system is homogeneous in space (it means that the elementary hydrodynamical element can be considered).

(ii) All heterogeneous centers are of the same nature.

(iii) The total number of the heterogeneous centers in the whole system is fixed.

(iv) The regime of the substance exchange between an embryo and environment is free molecular.

(v) No thermal effects are observed.

We want to mention that the method presented here is rather general and can be applied to some other complicated physical phenomena.

II. EXTERNAL SUPERSATURATION

All values of magnitudes will belong to the unit volume of the considered system in the further considerations. All the energylike values, such as free energy F of the formation of the embryo, will be measured in thermal units $k_b T$, where k_b is the Boltzman constant and T is the temperature of the system. Let us denote the total number of the condensing molecules by n_{tot} and the total number of the heterogeneous centers by η_{tot}. Values of η_{tot} and n_{tot} are certain functions of time, which are supposed to be known. The temperature is defined by the external conditions, so the number of molecules of the saturated vapor is also known at every moment. The approximate but rather precise connection is given by the thermodynamic equation

$$n_{\infty}(T)=n_{\infty}(T_*)\exp\left[\beta\frac{T-T_*}{T_*}\right],\qquad \frac{T}{T_*}\approx\left[\frac{n_{\infty *}}{n_{\infty}}\right]^{1/\beta}, \tag{1}$$

where β is the condensation heat per one molecule and the index $*$ marks the values at some moment t_* of time.

Since approximations like (1) are based on values at a particular time t_*, the choice of t_* leads to an estimated error of the theory. In order to minimize this error the time t_* has to be chosen as the time when the number of already condensated droplets is equal to the number of droplets which will be formed later.

The power of the initial phase metastability can be described by the supersaturation

$$\zeta = \frac{n}{n_\infty} , \tag{2}$$

where n is the number of molecules in the vapor. Let us introduce the magnitude similar to the supersaturation but independent from the vapor consumption. Ideal supersaturation is given by

$$\Phi = \frac{n_{\text{tot}}}{n_\infty} , \tag{3}$$

where n_{tot} is the total number of the molecules of the substance. This value can be considered as the supersaturation which can be attained in the system where no vapor consumption by the droplets occurs. Meanwhile, the value of the supersaturation can be decreased by binding part of molecules with the heterogeneous centers in the process of solvatation. So the value of ideal supersaturation must be substituted by the value of external supersaturation

$$\Omega = \frac{1}{n_\infty} (n_{\text{tot}} - \eta_{\text{tot}} \nu_e |_{\zeta=\Omega}) , \tag{4}$$

where ν_e is the number of molecules in the equilibrium embryo. Equation (4) gives the self-consistent definition of Ω. Due to the weak dependence of ν_e on Ω this equation can be easily solved by standard iterations. The first iteration

$$\Omega = \frac{1}{n_\infty} (n_{\text{tot}} - n_{\text{tot}} \nu_e |_{\zeta=\Phi}) \tag{5}$$

is sufficient for the majority of cases. The behavior of Ω resembles the behavior of Φ. We shall assume that it changes smoothly in time.

III. EQUATIONS OF THE CONDENSATION KINETICS

Let us extract the characteristic of the supercritical embryo which has ν molecules and grows in time with a regular velocity independent from the embryo size. A rather wide class of the supercritical embryo growth laws is covered by the power functions $d\nu/dt \sim \nu^{1-\alpha}\varphi(\zeta(t))$ where φ is a known function. Then the variable

$$\rho = \nu^\alpha \tag{6}$$

grows with the regular velocity independent from the size of the supercritical embryo.

The iterational procedure suggested in [19] provides rather precise results for $\alpha \ll 1$. The procedure suggested here can be applied for arbitrary $\alpha \leq 1$. When $\alpha = 1$ the system of condensation equations can be solved analytically. We assume that $1-\alpha$ is not too small in comparison with unity.

We shall use two assumptions which will be justified later. The first one establishes that the leading role in vapor consumption belongs to the supercritical embryos, i.e., to the droplets. So the characteristic size ρ_1 of the embryos at the middle of the period of essential formation of new droplets (PEFD) strongly exceeds the size ρ_c of the critical embryo:

$$\rho_1 \gg \rho_c . \tag{7}$$

Hence we can consider only regular growth and set the initial size of embryos entering the supercritical region equal to zero. In the regular growth approximation the Volmer-Zeldovitch-Frenkel equation for the distribution function $p(\rho,t)$ is reduced to the equation

$$\frac{\partial}{\partial t} p(\rho,t) = -\frac{\partial}{\partial t} \left[p(\rho,t) \frac{d\rho}{dt} \right] . \tag{8}$$

In the region of the positive arguments the solution has to be multiplied by the characteristic function of the positive half-axis $\Theta\{\Theta(\rho \geq 0) = 1, \Theta(\rho < 0) = 0\}$. As a result, the distribution $p(\rho,t)$ of the droplets over the ρ axis is given by the expression

$$p(\rho,t) = \frac{n_{\infty *} V_*}{n_\infty V} \Theta(z-x) f(x) , \tag{9}$$

where f is some function of the argument

$$x = z - \rho \tag{10}$$

and z is the coordinate on the ρ axis of the droplet which appeared at $t = t_*$. Thus the function z can be obtained as the solution of the equation

$$\frac{dz}{dt} = \frac{d\rho}{dt} \equiv \varphi(\zeta(t)) , \tag{11}$$

$$z|_{t=t_*} = 0 . \tag{12}$$

The form of the function $f(x)$ in (9) is determined from the boundary conditions. This function is called the size spectrum.

The second assumption is necessary to obtain the boundary conditions. We assume that the state of the near-critical embryos during the PEFD is close to the quasistationary one. This distribution is described by the stationary distribution function $f_s(\zeta)\eta/n_\infty$, where explicit dependence on η is extracted. The stationary classical theory gives the following formula for the stationary distribution:

$$f_s \sim \frac{K \exp(-\Delta F)}{\Delta\nu_e \Delta\nu_c \varphi(t)} , \tag{13}$$

where ΔF is the height of the activation free energy, K is the kinetic factor obtained from the gas kinetic theory and Folmer-Frenkel theory, $\Delta\nu_e$ is the normalizing factor of the equilibrium distribution

$$\Delta\nu_e \approx \sum_{\nu=1}^{(\nu_c+\nu_e)/2} \exp[-F(\nu) + F(\nu_e)] , \tag{14}$$

$\Delta\nu_c$ is the half-width of the near-critical region

$$\Delta\nu_c \approx \left|2\Big/\frac{d^2F(\nu)}{d\nu^2}\right|^{1/2} , \tag{15}$$

and ν_c is the number of molecules in the critical embryo.

The second assumption must be valid during the period of the essential formation of droplets. Let t_ζ be the characteristic time of the variation of the stationary state in the near-critical region and let t_s be the time of relaxation to the stationary state in the near-critical region. Then the required assumption can be written as

$$t_\zeta \gg t_s \ . \tag{16}$$

These assumptions will be valid in all situations except the case when almost all heterogeneous centers are exhausted at the end of the essential formation period. In this case the result of the PEFD is obvious: the number of droplets coincides with the total number of the heterogeneous centers, the form of the spectrum is unessential during the period of essential formation, and the spectrum is monodispersive when the supersaturation starts to fall.

We obtain the following expression for the function $f(x)$ using $f_s(\zeta)\eta/n_\infty$ as the boundary condition for the distribution $p(\rho,t)$ when $\rho=0$:

$$f(x)=f_s(\zeta)|_{\zeta=\zeta(x)}\frac{\eta(x)}{n_\infty} \ . \tag{17}$$

In order to determine the form of the functions $\zeta(x)$ and $\eta(x)$ the balance equations must be taken into account:

$$\Omega=\zeta+g \ , \quad g(z)=\frac{n_{\infty *}V_*}{n_\infty V}\int_{-\infty}^{z} dx(z-x)^{1/\alpha}f(x) \ , \tag{18}$$

$$\eta_{\text{tot}}=\eta+N \ , \quad N(z)=\frac{n_{\infty *}V_*}{V}\int_{-\infty}^{z} dx\, f(x) \ . \tag{19}$$

The first equation is the balance equation for the condensing substance. The second is the balance equation for the heterogeneous centers. These balance equations together with explicit expressions (13) and (17) for $f(x)$ form a closed system.

IV. SOME APPROXIMATIONS

Several approximations will be used in order to simplify the balance equations. We introduce parameter Γ:

$$\Gamma=-\Omega_*\frac{d\Delta F(\zeta)}{d\zeta}\Bigg|_{\zeta=\Omega_*} \ . \tag{20}$$

Due to the equation

$$\Gamma=\nu_c(\Omega_*)-\nu_e(\Omega_*) \tag{21}$$

this parameter satisfies the strong inequality

$$\Gamma \gg 1 \ . \tag{22}$$

Due to (22) the following inequality is valid in the neighborhood of Ω_* for the majority of external conditions:

$$\Gamma\left[\frac{d\Omega}{dx}\right]^2 \gg \Omega\frac{d^2\Omega}{dx^2} \ . \tag{23}$$

This inequality describes the class of dynamic external conditions completely. Actually all natural external conditions belong to this class. Inequality (23) allows us to write a linear approximation for $\Omega(x)$ at the essential formation period.

Due to (13) and (17) the function $f(x)$ is a sharp function of the supersaturation ζ and argument x. The exponential dependence in (13) and (17) is much stronger then the power dependence $(z-x)^{1/\alpha}$ and the subintegral functions in (18) and (19) are well localized on the x axis. Thus the PEFD can be extracted on the basis of the behavior of the subintegral function in (18) and (19). The following inequalities are valid during this period:

$$\frac{\Omega-\Omega_*}{\Omega_*}\le\Gamma^{-1} \ , \quad \frac{\zeta-\Omega_*}{\Omega_*}\le\Gamma^{-1} \ . \tag{24}$$

These inequalities will appear in further considerations automatically. Equation (24) leads to

$$V\approx V_* \ , \quad n_\infty \approx n_{\infty *} \tag{25}$$

during the PEFD. Due to (13), (17), and (24), the approximation

$$f(x)=f_s\exp\left[\Gamma\frac{\zeta(x)-\Omega_*}{\Omega_*}\right]\frac{\eta(x)}{n_\infty} \ , \quad f_s\equiv f_s(\Omega_*) \tag{26}$$

is valid during the PEFD. To justify (26) the following estimates have to be taken into account:

$$\frac{d\nu_c}{d\zeta}\sim\frac{d\nu_{c\,\text{hom}}}{d\zeta} \ , \quad \frac{d\nu_c}{d\zeta}-\frac{d\nu_e}{d\zeta}\sim\frac{d\nu_c}{d\zeta} \ , \quad \nu_c-\nu_e\sim\nu_c \ , \tag{27}$$

where $\nu_{c\,\text{hom}}$ is the number of molecules in the critical homogeneous embryo. Then we come to the strong inequality

$$\left|\frac{d\Delta F(\zeta)}{d\zeta}\right|^2 \gg \left|\frac{d^2\Delta F(\zeta)}{d\zeta^2}\right| \ . \tag{28}$$

According to (28) we can linearize ΔF as a function of ζ. We suppose that the sharpest dependence on the supersaturation is given by $\exp(-\Delta F)$. This assumption puts, however, very weak restrictions on $\varphi(t)$. Certainly, it is necessary to check (28) directly for every concrete model of heterogeneous centers.

Another parameter will be defined by the expression

$$c=\frac{\Gamma}{\Omega_*}\frac{d\Omega(x)}{dx}\Bigg|_{x=0} \ . \tag{29}$$

This parameter is important for the linearization of the function $\Omega(x)$ during the PEFD. Linearization leads to the equation

$$\Omega(x)=\Omega_*+\frac{\Omega_* cx}{\Gamma} \ . \tag{30}$$

This linearization is based on the strong inequality

$$\left[\frac{d\Omega}{dx}\right]^2 \gg \delta_1\Omega\frac{d^2\Omega}{dx^2} , \tag{31}$$

where $\delta_1\Omega$ is the variation of Ω during the PEFD. Taking into account (24) we see that Eq. (31) follows from (23). Equation (23) leads to the following form of (18):

$$g(z)=f_s\int_{-\infty}^{z}dx(z-x)^{1/\alpha}\exp\left[cx-\Gamma\frac{g(x)}{\Omega_*}\right]\frac{\eta(x)}{n_{\infty *}} . \tag{32}$$

The balance equation for the heterogeneous center leads to the form

$$f(x)=-\frac{d\eta(x)}{n_{\infty *}dx} . \tag{33}$$

This differential equation can be easily solved:

$$\eta(z)=\eta(-\infty)\exp\left[-f_s\int_{-\infty}^{z}dx\exp\left[cx-\Gamma\frac{g(x)}{\Omega_*}\right]\right] . \tag{34}$$

The argument $-\infty$ marks values of the magnitudes at the very beginning of the PEFD and the argument ∞ corresponds to the end of the PEFD.

The total number of the droplets is introduced by the equality

$$N(x)=\eta(-\infty)-\eta(x) . \tag{35}$$

The following integral representation for $N(z)$ can be derived:

$$N(z)=\int_{-\infty}^{z}f(x)dx\, n_{\infty *} . \tag{36}$$

V. ITERATION PROCEDURE

Some properties of the solution of the system of balance equations ar important to justify further constructions. We are going to determine these properties using an iteration procedure. Let us denote the operator on the right-hand side (rhs) of (32) by $G(g(x),\eta(x))$ and operator on the rhs of (34) by $H(g(x))$. The iterations will be constructed in accordance to the following rule:

$$g_{a(i+1)}=G(g_{a(i)},\eta_{a(i)}) , \quad \eta_{a(i+1)}=H(g_{a(i)}) . \tag{37}$$

If the initial approximation is chosen as $g_{ax(0)}=0,\eta_{a(0)}=\eta(-\infty)$, then the iteration procedure gives upper and lower bounds for the solution. These bounds converge to the exact solution. The main property of the operators g and h is the "monotonous" character of these operators. Namely, if

$$g_p(x)\ge g_q(x)$$

for all values of the arguments then

$$H(g_p(x))\ge H(g_q(x)) \tag{38}$$

for all values of x. If

$$g_p(x)\ge g_q(x) , \quad \eta_q\le\eta_p$$

for all values of the arguments then

$$G(g_p(x),\eta_p(x))\le G(g_q(x),\eta_q(x)) . \tag{39}$$

From (38) and (39) and the obvious inequalities

$$\begin{gathered} g_{a(0)}\le g , \quad g_{a(2)}\ge g_{a(0)}=0 , \\ \eta\le\eta_{a(0)} , \quad \eta_{a(2)}\le\eta_{a(0)}=\eta(-\infty) , \end{gathered} \tag{40}$$

the following chains of inequalities can be constructed:

$$\begin{aligned} &g_{a(0)}\le g_{a(2)}\le \cdots \le g_{a(2i)}\le \cdots \le g \\ &\quad\le \cdots \le g_{a(2i+1)}\le \cdots \le g_{a(3)}\le g_{a(1)} , \end{aligned} \tag{41}$$

$$\begin{aligned} &\eta_{a(0)}\ge \eta_{a(2)}\ge \cdots \ge \eta_{a(2i)}\ge \cdots \ge \eta \\ &\quad\ge \cdots \ge \eta_{a(2i+1)}\ge \cdots \ge \eta_{a(3)}\ge \eta_{a(1)} . \end{aligned} \tag{42}$$

It follows from (41) and (42) that iterations $\{g_{a(2i)}\}$ and $\{\eta_{a(2i+1)}\}$ are growing monotonically, being restricted from below. A similar fact is valid for $\{g_{a(2i+1)}\}$ and $\{\eta_{a(2i)}\}$. So odd iterations and even iterations converge. A solution of the system exists if the limits of the odd and even iterations coincide. The limits of odd and even iterations are solutions of the iterated system (32) and (34). If the initial system has a solution then this solution is a solution of the iterated system also and the limits of the odd and even iterations coincide. We have proved the uniqueness of the solution of the system. The existence of the solution has to be proved also.

New iterations $g_{b(i)}$ (reduced iterations) will be constructed in accordance with the rule

$$g_{b(i+1)}=G(g_{b(i)},H(g_i)) . \tag{43}$$

For the initial approximation we take $g_{b(0)}=0$. These iterations slightly differ from the initial iterations $g_{a(i)}$ and $\eta_{a(i)}$. Iterations $g_{a(2i)}$ and $g_{a(2i+1)}$ estimate iterations $g_{b(i)}$:

$$g_{a(2i+1)}\ge g_{b(2i+1)} , \quad g_{a(2i)}\le g_{b(2i)} . \tag{44}$$

Equation (43) can be rewritten in the form

$$g_{b(i+1)}=\int_{-\infty}^{z}(z-x)^{1/\alpha}L(g_{b(i)}(x))dx , \tag{45}$$

where we have extracted the function

$$L(g_i(z))=f_s\frac{\eta(-\infty)}{n_{\infty *}}\exp\left[\frac{cx-\Gamma g_i(z)}{\Omega_*}\right] \times\exp\left[-f_s\int_{-\infty}^{z}\exp\left[\frac{cx-\Gamma g_i}{\Omega_i}\right]dx\right] . \tag{46}$$

The next iteration (both initial and reduced) is formed on the basis of the previous iteration with an argument less than z. So the second iteration of type "a" gives an estimate from above for the region of the essential values of z, i.e., the estimate from above for the end of the PEFD. These iterations give also approximations for the droplet number and size spectrum:

$$N_{(i)}(z)=\eta(-\infty)-\eta_{(i)}(z) , \tag{47}$$

$$f_{(i)}=-\frac{d\eta_{(i)}}{n_{\infty *}dz} . \tag{48}$$

The second approximation gives

$$f_{a(2)}(x)=\frac{\eta(-\infty)}{n_{\infty *}}f_s\exp\left[cx-hf_s\frac{\exp(cx)}{c}-\frac{1-\exp\left[-hf_s\frac{\exp(cx)}{c}\right]}{h}\right], \tag{49}$$

$$\eta_{a(2)}=\eta(-\infty)\exp\left[-\frac{1-\exp\left[-hf_s\frac{\exp(cz)}{c}\right]}{h}\right], \tag{50}$$

$$N_{a(2)}=\eta(-\infty)\left[1-\exp\left[-\frac{1-\exp\left[-hf_s\frac{\exp(cx)}{c}\right]}{h}\right]\right], \tag{51}$$

where

$$h=\frac{\gamma\left[\frac{1}{\alpha}\right]\Gamma\eta(-\infty)}{\Omega_* n_{\infty *}c^3}\,,\qquad \gamma\left[\frac{1}{\alpha}\right]=\int_0^\infty y^{1/\alpha}\exp(-y)dy\ . \tag{52}$$

The chain of inequalities for $N_{a(i)}$ is valid:

$$N_{a(2)}\le N_{a(4)}\le\cdots\le N_{a(2i)}\le\cdots\le N \le\cdots N_{a(2i+1)}\le\cdots\le N_{a(3)}\le N_{a(1)}\ . \tag{53}$$

It follows from (49) that the upper bound for the PEFD in variable z can be well defined. This bound will be denoted by "b". Analysis of $g(x)$ and $\eta(x)$ asymptoticly leads to the existence of the absolutely unessential region of big negative values of z due to (1) inequalities

$$g(x)\ge 0\ ,\quad \eta(x)\ge\eta_{a(2)}\ ,\quad \frac{d\eta}{dx}\le 0\ ,\quad \frac{dg}{dx}\ge 0\ ;$$

(2) the explicit form of $f(x)$:

$$f(x)=f_s\frac{\eta(-\infty)}{n_{\infty *}}\exp\left[\frac{cx-\Gamma g(x)}{\Omega_*}\right]; \tag{54}$$

and (3) the explicit form of subintegral functions in expressions for g and η.

We shall mark the upper boundary of this region by "$-a$." Substitution of the lower limit of integration by $-a$ is unessential.

Let us consider L as a functional of two arguments

$$L(y)=L\left[y,\psi=f_s\int_{-a}^{z}\exp\left[\frac{cx-\Gamma g}{\Omega_*}\right]\right]. \tag{55}$$

Then

$$L(y_1)-L(y_2)\le\max_{-a\le x\le b}\left|\frac{\partial L}{\partial y}\right|(y_1-y_2) +\max_{-a\le x\le b}\left|\frac{\partial L}{\partial\psi}\right|(\psi_2-\psi_2)\ . \tag{56}$$

Introducing

$$\|y\|=\max_{-a\le x\le b}y\ , \tag{57}$$

we obtain the inequality

$$L(y_1)-L(y_2)\le l_1+l_2\ , \tag{58}$$

where

$$l_1=\max_{-a\le x\le b}\left|\frac{\partial L}{\partial y}\right|\|y_1-y_2\|\ , \tag{59}$$

$$l_2=\max_{-a\le x\le b}\left|\frac{\partial L}{\partial\psi}\right|\|y_1-y_2\| \times\max_{-a\le x\le b}\left|\frac{d\exp\left[cx-\frac{\Gamma g}{\Omega_*}\right]}{dg}\right|f_s(b+a)\ . \tag{60}$$

This inequality can be rewritten as

$$L(y_1)-L(y_2)\le\max_{-a\le x\le b}\left|\frac{\partial L}{\partial y}\right|\omega\ , \tag{61}$$

where

$$\omega=1+(b+a)\max_{-a\le x\le b}\left|\frac{\partial L}{\partial\psi}\right|\frac{n_\infty}{\eta(-\infty)}\|y_1-y_2\|\ . \tag{62}$$

The final estimate is

$$L(y_1)-L(y_2)\le\beta\|y_1-y_2\|\ , \tag{63}$$

where β is a certain constant.

We have the following expression and inequalities for the iterations:

$$g_{b(i+1)}-g_{b(i)}=\int_{-a}^{z}dx(z-x)^{1/\alpha}[L(g_{b(i)})-L(g_{b(i-1)})]\ , \tag{64}$$

$$g_{b(i+1)}-g_{b(i)}\le\int_{-a}^{z}dx(z-x)^{1/\alpha}\|g_{b(i)}-g_{b(i-1)}\|\beta\ , \tag{65}$$

$$g_{b(i+1)}-g_{b(i)}\le(z+a)(a+b)^{1/\alpha}\beta\|g_{b(i)}-g_{b(i-1)}\|\ . \tag{66}$$

Recurrent procedure leads to

$$\|g_{b(i)}-g_{b(i+1)}\| \le \frac{(z+a)^i}{i!}\text{const} . \tag{67}$$

Summation of the rhs of (67) over all i gives the function const $\exp(z+a)$. So this sequence is fundamental. All terms of the rhs of (57) are positive. So the sequence of iterations is a fundamental sequence, and also the sequence of iterations is converging. The limit of iteration defines the solution of the system of balance equations. We have proved the existence of the solution. Odd and even iterations are converging to one and the same limit. The solution of balance equation system is unique.

Inequalities (41) and (42) allow one to estimate the errors of $g_{a(i)}$ and $\eta_{a(i)}$ and due to (44) the error of $g_{b(i)}$. The measure of the sufficient precision has to be defined in accordance with the accuracy of modern experiments. The most important characteristic of the process is the total number of droplets. So we shall measure the accuracy of our theory in the relative error in the total number of droplets:

$$\Delta_i=\frac{\|f_i-f\|_{L_1}}{\|f\|L_1}\equiv\frac{\int_{-\infty}^{\infty} f_i-f\,dx}{\int_{-\infty}^{\infty} f\,dx} . \tag{68}$$

Due to (53) we can obtain the following estimate for the error of the initial iterations:

$$\Delta_{a(2i)}\le\frac{|N_{a(2i+1)}(\infty)-N_{a(2i)}(\infty)|}{N_{a(2i)}(\infty)} . \tag{69}$$

One the basis of (69) we can see that the initial iterations are converging rather fast. The second iteration gives the relative error less than 0.16. It can be shown by comparison of (51) with the expression

$$N_{a(3)}=\eta(-\infty)[1-\exp(-Y/h)] , \tag{70}$$

where

$$Y=\int_{-\infty}^{\infty} d\xi \exp\left[\xi-\tfrac{1}{6}\int_{-\infty}^{\xi}(\xi-\sigma)^{1/\alpha}\exp\left[\sigma-\frac{h+1}{h}\exp(\sigma)\right]d\sigma\right] . \tag{71}$$

Unfortunately, an analytical expression for $g_{a(2)}$ can not be obtained. Hence an analytical expressions for the further iterations can not be presented either. So the real problem is to obtain a more precise approximation.

First of all, we can use the second initial iteration for analytical estimates for the duration of the PEFD in order to justify (24). We require that the relative number of droplets formed outside the PEFD is equal to δ:

$$|N(0)-N(\pm\Delta_{\pm}x)|=|N(0)-N(\pm\infty)|(1-\delta) , \tag{72}$$

where the parameter δ has a rather small value. We denote by $\delta_{\pm}x$ the right and left characteristic sizes of the PEFD in x scale. Then we have for $\delta_{\pm}x$ in the second approximation in iteration procedure a almost precise expressions:

$$\Delta_{\pm}x=\frac{1}{c}\left|\ln\frac{\ln(1+h\ln\lambda_0)}{\ln(1+h\ln\lambda_{\pm})}\right| , \tag{73}$$

where

$$\lambda_0=\frac{1}{2}\left[1+\exp\left[-\frac{1}{h}\right]\right] , \tag{74}$$

$$\lambda_{-}=1-\frac{\delta}{2}\left[1-\exp\left[-\frac{1}{h}\right]\right] , \tag{75}$$

$$\lambda_{+}=\exp\left[-\frac{1}{h}\right]+\frac{\delta}{2}\left[1-\exp\left[-\frac{1}{h}\right]\right] . \tag{76}$$

Thus the value of $\Delta_{\pm}x$ has the power of c^{-1}. Hence $\Delta\Omega$ has the power Ω_*/Γ and the first inequality (24) is justified. The second inequality follows immediately from the first and from (26). During the period of essential formation of the droplets the variations of ζ, Ω, and φ are very small.

Inequalities (7) and (16) can be rewritten as

$$c^{-1}\gg\rho_c , \tag{77}$$

$$t_s\ll c^{-1}\varphi^{-1} . \tag{78}$$

VI. UNIVERSAL SOLUTION

The leading idea for the further consideration is to reduce the description of the process thought the minimal set of variables. Let us extract those characteristics of the spectrum $f(x)$ which are sufficient for the condensation process.

The balance equation for the condensing substance can be presented in the form (18), which is valid not only during the PEFD but also during the whole evolution. So g can be expressed through

$$\mu_i=\int_{-\infty}^{z} x^i f(x)dx . \tag{79}$$

When the essential formation period is over the balance equation for the heterogeneous centers is unessential and the evolution of the system is described only by the balance equation for the substance. The following expression for g is valid due to the rapid vanishing of $f(x)$:

$$g=\frac{n_{\infty *}V_*}{n_{\infty}V}\int_{-\infty}^{\infty} f(x)(z-x)^{1/\alpha}dx . \tag{80}$$

Now the evolution is determined by the constant values of the full momentums of spectrum. Even when the law of droplet growth differs from the free-molecular one the leading term is proportional to the total number of embryos—the zero momentum of the spectrum

$$g(z)\approx\mu_0 z^{1/\alpha}\frac{n_{\infty *}V_*}{n_{\infty}V} . \tag{81}$$

The turning point in our consideration will be the analysis of the velocity of convergence of the iterations $g_{a(i)}$ and $\eta_{a(i)}$. Calculations by (51), (70), and (71) show that the error increases with the growth of the parameter h. Hence the situations $h \ll 1$ are well described. But the situations of the pseudohomogeneous condensation when $h \gg 1$ are described with a certain error. At the same time the final approximations for the internal iterational procedure are obtained directly without taking into account the exhausting of the free heterogeneous centers.

The balance equation for the heterogeneous centers disappears when $\eta \equiv \eta(-\infty)$ and the balance equation for the substance has the form of the homogeneous condensation. Hence it can be reduced to the universal form. This form can be obtained by analytical expression of the solution as a function of the parameter f_s from the situation when t_* is the moment of the supersaturation maximum. We introduce the function

$$\phi = \Gamma \frac{\Omega - \zeta}{\Omega_*} \tag{82}$$

and obtain the universal equation [14–16]

$$\phi(z) + \frac{1}{\alpha} z \int_{-\infty}^{0} (z-x)^{-1+1/\alpha} \exp[-\phi(x)]dx = \int_{-\infty}^{z} (z-x)^{1/\alpha} \exp[-\phi(x)]dx \tag{83}$$

in appropriately normalized variables. It follows from (83) that $\phi(x)$ is a universal function [15]. The approximation of the pseudohomogeneous universal solution is a base for the further iterations.

The change of the variables from x,z to cx,cz and from g,η to $G = \Gamma_g/\Omega_*$, $\Theta = \eta/\eta(-\infty)$ leads to the equations

$$G = A \int_{-\infty}^{z} (z-x)^{1/\alpha} \Theta(x) \exp(x-G)dx \ , \tag{84}$$

$$\Theta = \exp\left[-B \int_{-\infty}^{z} \exp(x-G)dx \right] , \tag{85}$$

where constants A and B are defined by

$$A = \frac{\Gamma f_s \eta(-\infty)}{c^{1+1/\alpha} \Omega_* n_{\infty *}} \ , \quad B = \frac{f_s}{c} \ . \tag{86}$$

Some choice of the basic point in the construction of approximations (linearization of the external supersaturation as a function of x and linearization of the free energy as a function of the supersaturation) is essential only if the exhausting of vapor plays a leading role in the interruption of the embryo formation, i.e., $h \gg 1$. In the alternative situation $h \ll 1$ ("almost total exhausting of the heterogeneous centers") the result of the condensation is obvious—almost all heterogeneous centers are the centers of droplets. So the total number of droplets is equal to the total number of heterogeneous centers and the spectrum has a monodispersious form. If the parameters of the ideal supersaturation are fixed then the relative sizes of region $\Delta_g \Omega$ of Ω_* corresponding to all situations except $h \ll 1$ are rather small:

$$\frac{\Delta_g \Omega}{\Omega_*} \le \frac{\epsilon}{\Gamma} \ , \quad \epsilon \sim 3 \ . \tag{87}$$

The inequalities mentioned above are so strong that linearization remains valid in a region covering $\Delta_g \Omega$. So the choice of an arbitrary point in this interval as the base for the approximations leads to the applicability of linearization in every situation except $h \ll 1$. So the value of Ω at the moment when half of the imaginary droplets are formed can be used as a base point in the case of pseudohomogeneous formation. Then the coefficient

$$A_0 = \frac{1}{\alpha} \int_{-\infty}^{0} (z-x)^{-1+1/\alpha} \exp[-\phi(x)]dx$$

is determined as a constant. For example, $A_0 = 0.136$ in the case $\alpha = \frac{1}{3}$.

As far as the dependence in the evolution process is implemented through $\{\mu_i\}$ and $\int_{-\infty}^{z} \exp[x - G(x)]dx$, an ordinary evolutional (not the net one) calculation is required. Moreover, as far as the position of the base point is not essential we do not need the exact definition of t_* but must keep in mind the values of $\mu_0(\infty)$ and $\mu_0(0)$. Instead of the precise value of the source intensity $(1/\alpha)\int_{-\infty}^{0} (z-x)^{-1+1/\alpha} \exp[-\phi(x)]dx$ we can take some appropriate number ($\sim \frac{1}{5}$ in the case $\alpha = \frac{1}{3}$). The result of calculation gives the total number of droplets. This number ($\sim \frac{1}{5}$ in the case $\alpha = \frac{1}{3}$) is connected with the accuracy of the procedure. It must be chosen to minimize the error introduced by the approximations.

This solution has maximum at some point z_0. The notation that this point must be the real maximum of supersaturation gives the algebraic equation on the parameters of the process similar to [13]. It must be solved by ordinary numerical methods or by the methods proposed in [20].

The concrete value of A_0 with the help of (86) allows one to justify (77) and (78) for all situations except $h \ll 1$. Let us take for t_s the estimate analogous to Zeldovitch's for the homogeneous case [3]:

$$t_s \approx \frac{(\Delta \nu_c)^2}{W^+} \tag{88}$$

where W^+ is the direct flow on the critical embryo which can be estimated as

$$\frac{W^+}{\nu_c^{1-\alpha}} \sim \varphi \ .$$

The height of the activation barrier ΔF can be estimated by $F|_{\nu=\nu_c}$. According to Gibbs equation this value is proportional to the surface square

$$F \sim \rho_c^{(1/\alpha)[(\dim - 1)/\dim]} \tag{89}$$

(dim is the dimension of space). Then we can justify (77) and (78).

In further considerations the initial approximation will be the solution for $h \gg 1$. It will be marked by the subscript ∞. In application of the initial iteration procedure the first and second approximations for η will coincide as far as $g_{a(0)} = g_{a(1)} = g_{\infty}$. It is impossible to obtain an analytical formula for the second approximation for g and for the third approximation for η. So we shall consider reduced iterations only. The first iteration takes into account the exhausting of the heterogeneous centers:

$$G_{(1)}=A_0\int_{-\infty}^{z}dx(z-x)^{1/\alpha}\times\exp\left[-B\int_{-\infty}^{x}d\xi\exp[\xi-G_\infty(\xi)]\right]\times\exp[x-G_\infty(x)]\ , \tag{90}$$

where

$$G_\infty(x)\equiv G(x)|_{\Theta=1}\ .$$

For the normalized total number of droplets an explicit expression can be used:

$$N_{(2)}^{+}(\infty)\sim\int_{-\infty}^{\infty}f(x)dx\sim\int_{-\infty}^{\infty}\exp(x-G_{(1)})dx\ . \tag{91}$$

As far as

$$N_{(1)}^{+}(z)=\int_{-\infty}^{z}d\xi\exp(\xi-G_\infty) \tag{92}$$

is a universal function, we can construct universal expansion at the first step. Decomposition of the exponential gives

$$N_{(2)}^{+}(\infty)=\int_{-\infty}^{\infty}dz\exp[z-A_0Q_0(z)]\prod_{l=1}^{\infty}D_l\ , \tag{93}$$

where

$$D_j=\sum_{l=0}^{\infty}\left[\frac{(-1)^{j+1}B^j}{j!}Q_jA_0\right]^l\frac{1}{l!}\ , \tag{94}$$

$$Q_i=\int_{-\infty}^{z}dx(z-x)^{1/\alpha}\exp[x-G_\infty(x)]N_{(1)}^{i}(x)\ , \tag{95}$$

which leads to the representation

$$N_{(2)}^{+}(\infty)=\sum_i P_iB^i\ , \tag{96}$$

where P_i are some constants. This expression can be linearized as a function of B because the result will be substituted into the exponential formula for the number of the free heterogeneous centers:

$$N_{(2)}^{+}(\infty)=P_0+P_1B\ , \tag{97}$$

where

$$P_0=\int_{-\infty}^{\infty}\exp[x-A_0Q_0]dx\ , \tag{98}$$

$$P_1=\int_{-\infty}^{\infty}\exp[x-A_0Q_0]Q_1dx\ A_0\ . \tag{99}$$

Then the final expression is

$$N_+(\infty)=1-\exp[-B(P_0+P_1B)]\ . \tag{100}$$

In the case $\alpha=\frac{1}{3}$ the relative error of this expression is less than 0.003. The analogous results can be obtained for arbitrary α. It means that further iterations are unessential. The expressions for the other times of the spectrum can be obtained by the same procedure.

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