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Homogeneous Nucleation and Diffusional Growth of a Nanoparticle under Ultraso Irradiation

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A theoretical model is proposed for the homogeneous nucleation and growth of an individual nucleus (nanoparticle) in a liquid-phase medium under ultrasonic excitation. The model combines a thermodynamic approach, which enables calculation of the nucleation work and the critical radius of the nucleus in a non-stationary pressure field, with a kinetic description of diffusion-driven mass transfer and the growth of an individual nanoparticle under acoustic oscillations. The proposed approach establishes a relationship between the intensity of ultrasonic exposure and the characteristics of nanoparticle formation and can also serve as a basis for constructing the statistical size distribution of nanoparticles.

Keywords: homogeneous nucleation, ultrasonic treatment, critical nucleus radius, diffusion growth, acoustic oscillations, nanoparticle, thermodynamic model, kinetic mode.

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1. Introduction

Creation of nanoparticles with pre-defined dimensional and morphological properties is a fundamental task of modern material science and is required in catalysis, medicine and electronics [1,2]. One of the method of controlling processes of nucleation and growth of nanoobjects is to treat liquid-phase media with ultrasonic waves (USW). Here, ultrasonic effect can be implemented in two main modes [1–5]: 1), a cavitation mode that is related to formation and collapse of gas bubbles creating extreme local conditions (temperatures up to 5000 K, pressures up to 1000 atm, cooling rates above 10^9 K/s); 2) a non-cavitation one, at which low-amplitude oscillations cause periodic changes of pressure and supersaturation of a medium without bubbling. The present study investigates impact of low ultrasonic oscillations on homogenous nucleation and growth of the nanoparticles.

Unlike traditional approaches based on using stabilizers or kinetic traps for controlling nanoparticle sizes, the low-amplitude ultrasonic oscillations affect early stages of formation of a new phase by modulating thermodynamic and kinetic parameters of the medium [5–9]. Experimental studies show that ultrasonic treatment can result in formation of monodisperse nanosystems [2,6], but theoretical description of the processes in the non-cavitation mode is still underdeveloped. Treatment of solid amorphous alloys is also accompanied by formation of the nanoparticles, which is related to availability of a free volume [10]. Various studies show [4,9,13] that classical theories of homogenous nucleation [11,12], which are designed for e conditions, are insufficient for correctly describing processes, since they do not take into account fast pressure oscillations that significantly affect the thermodynamic characteristics of the system.

The present study considers formation of the nanoparticle in the liquid-phase medium under impact of ultrasonic oscillations. It proposes a theoretical model of homogenous nucleation and subsequent diffusion growth of a nucleus, which combines the thermodynamic approach and the kinetic approach. The thermodynamic part of the model describes formation of the critical nucleus of the new phase in a nonstationary pressure field. Its base is used to calculate nucleation work and an effective critical radius of the nucleus, which are averaged across an oscillation period. The kinetic part of the model describes diffusion growth of the nucleus in a spherical geometry with a slowly moving boundary. Special attention is paid to a ratio between a nucleation time, a diffusion time and an oscillation period as well as to a condition of stable growth of the nanoparticle in a quickly oscillating acoustic field.

2. Homogenous nucleation of the nanoparticles

Homogenous nucleation is a process of spontaneous formation of new-phase nuclei in a supersaturated medium (it is a liquid-phase medium in our case) without involvement of foreign surfaces or impurity centers [11,12]. The classical theory of nucleation considers this process as a result of competition between a gain in bulk free energy and consumption for forming an interphase boundary. For the spherical nucleus of the radius R, a change of free Gibbs energy is written as

$$\Delta G = \frac{4}{3}\pi R^3 \Delta g + 4\pi R^2 \sigma, \quad (1)$$

where Δg is a change of specific free energy during the phase transition (J/m^3), σ is surface tension at a phase interface. A balance of the contributions in (1) is determined by an energy barrier. At the small radii, the surface contribution prevails and prevents the growth, whereas at the large radii a bulk component is predominant.

Under conditions of ultrasonic effect, the classical theory needs to be modified. The nonstationary acoustic field induces periodic pressure oscillations, thereby resulting in oscillation of the thermodynamic parameters. Taking into account acoustic effect, let us generalize the expression (1) as

$$\Delta G(R, t) = \frac{4}{3}\pi R^3 \Delta g + 4\pi R^2 \sigma + \Delta G_a(R, t), \quad (2)$$

where $\Delta G_a(R, t)$ described the contribution by acoustic pressure. In an approximation of homogeneous pressure in the nucleus volume we have

$$\Delta G_a(R, t) = \frac{4}{3}\pi R^3 \Delta p \sin(\omega t), \quad (3)$$

where Δp is an amplitude of pressure oscillations, ω is an ultrasonic angular frequency. An extremum condition

$$\left(\frac{\partial \Delta G(R, t)}{\partial R}\right)_{R=R_c(t)} = 0$$

taking into account (2) and (3), provides

$$R_c(t) = \frac{2\sigma}{|\Delta g + \Delta p \sin(\omega t)|}, \quad (4)$$

$$\Delta G_c(t) = \frac{16\pi\sigma^3}{3\big(\Delta g + \Delta p \sin(\omega t)\big)^2}. \quad (5)$$

It should be underlined that the expressions (4) and (5) do not determine the critical radius and the nucleation barrier in a classical sense, since they depend on time and pre-define an instantaneous state of the system in the acoustic field. When $|\Delta p| \ll |\Delta g|$, these „instantaneous critical radii“ can be regarded as quasistatic analogs of classical magnitudes. It is true at high USW frequencies, when the system has not enough time to track the fast pressure oscillations and reacts only to their averaged effect. At the low frequencies, nucleation can be described as a quasistatic problem with „instantaneous“ parameters. In the intermediate case, a strict nonstationary analysis based on a Zeldovich equation [14–16] is required with taking into account ultrasonic effect.

It follows from (4) and (5) that the most favorable for nucleation are positive-pressure phases, when denominators in (4) and (5) are the highest ones. Negative pressures (liquid tensioning) that occur in a phase of depressurization of the acoustic wave reduce supersaturation. As a result, the critical radius increases and probability of nucleus formation decreases. However, a physical limit of negative pressure is restricted by a liquid strength limit. Although the written form of (4) and (5) formally allows negative values of pressure, in practice the stable nucleus growth is possible only until reaching this limit.

Now we proceed to calculation of average values of the critical radius and nucleation work. Since effective supersaturation of the medium quickly oscillates in time, let us determine the following critical parameters that are averaged over the period of the acoustic oscillations

$$\langle R_c \rangle = \frac{\int_0^{2\pi/\omega} R_c(t) f(t) dt}{\int_0^{2\pi/\omega} f(t) dt}, \quad (6)$$

$$\langle \Delta G_c \rangle = \frac{\int_0^{2\pi/\omega} \Delta G_c(t) f(t) dt}{\int_0^{2\pi/\omega} f(t) dt}, \quad (7)$$

where upper integration limits correspond to the oscillation period. The function $f(t)$ pre-defines probability of nucleus formation

$$f(t) = \exp\left(-\frac{\Delta G_c(t)}{k_B T}\right) = \exp\left(-\frac{16\pi\sigma^3}{3k_B T\big(\Delta g + \Delta p \sin(\omega t)\big)^2}\right), \quad (8)$$

where k_B is the Boltzmann constant, T is a temperature. Let us note that the distribution (8) is used not as a strictly equilibrium one, but as an instantaneous weight of probability of nucleus formation. This approximation is justified when the pressure oscillation period is significantly less than the time of formation of the critical nucleus so that the system reacts only to an average perturbation. In this case, averagings over the period of the acoustic oscillations correspond to a standard procedure of exclusion of fast variables in statistical physics and kinetics of chemical reactions. Taking into account (8), the integrals in (6) and (7) can be expressed via known elementary functions. We will use numerical methods for their calculation. For convenience of the numerical calculations, the formulas (6) and (7) are transformed into a dimensionless form

$$\frac{\langle R_c \rangle}{R_c} = \int_0^{2\pi} \frac{\exp\left(-\frac{\varepsilon}{(1+\gamma\sin x)^2}\right)}{1+\gamma\sin x} dx \times \left(\int_0^{2\pi} \exp\left(-\frac{\varepsilon}{(1+\gamma\sin x)^2}\right) dx\right)^{-1}, \quad (9)$$

$$\frac{\langle G_c \rangle}{\Delta G_c} = \int_0^{2\pi} \frac{\exp\left(-\frac{\varepsilon}{(1+\gamma\sin x)^2}\right)}{(1+\gamma\sin x)^2} dx \times \left(\int_0^{2\pi} \exp\left(-\frac{\varepsilon}{(1+\gamma\sin x)^2}\right) dx\right)^{-1}, \quad (10)$$

$$\varepsilon = \frac{16\pi\sigma^3}{3k_B T(\Delta g)^2}, \quad \gamma = \frac{\Delta p}{\Delta g},$$

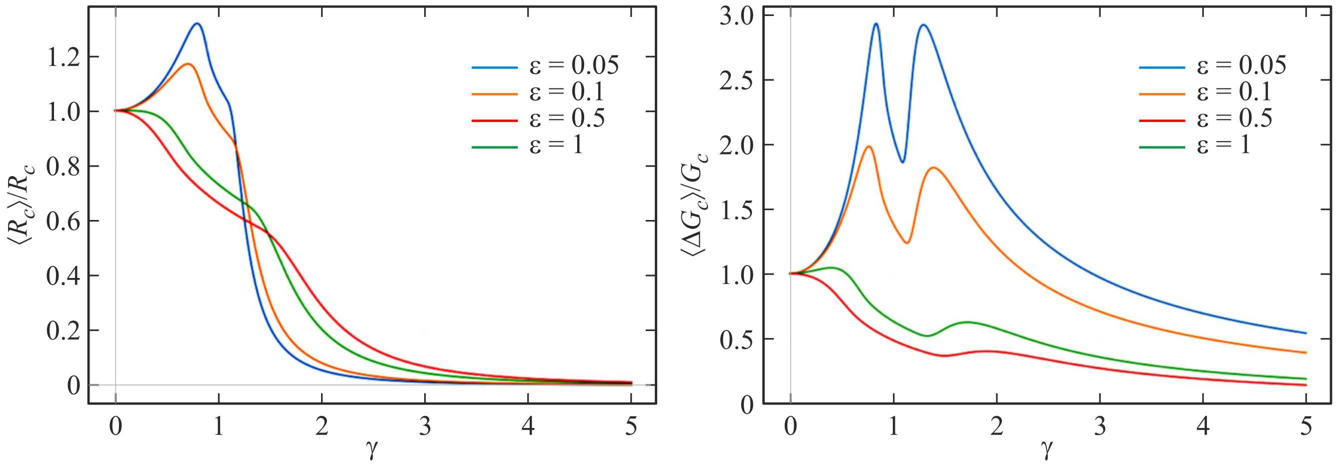

Figure 1. Averaged critical radius and energy of formation of the nucleus as a function of the pressure modulation amplitude at the various values of the parameter ε (a relative height of the nucleation barrier).

where ε and γ pre-define dimensionless values of the energy barrier and amplitudes of ultrasonic oscillations, R_c and ΔG_c are a radius of the critical nucleus and the nucleation barrier when $\Delta p = 0$.

The integrals in (9) and (10) were calculated using a grid integration method (the Gauss-Kronrod quadrature), in which a numerator and denominator were calculated separately and then an average value was determined by division. This procedure provides accurate approximation of the integrals for smooth functions at a quite small step of discretization.

The calculation results are shown in Figure 1. In general, the averaged critical radius decreases with an increase of the amplitude of acoustic pressure, thereby facilitating overcoming of the nucleation barrier. When $\gamma \to 0$, we get asymptotics $\langle R_c\rangle \to 0$. The averaged nucleation work also decreases $\langle G_c\rangle \to 0$, thereby resulting in an increase of probability of formation of new nuclei within reach of the ultrasonic oscillations.

For small values of the dimensionless barrier ε (which corresponds to the high temperatures), thermal energy of the system becomes comparable with the energy nucleation barrier. In these conditions, the surface barrier less limits nucleus formation and a weight function $f(t)$is still close to unity for most oscillation phases. As a result, the pressure oscillations are averaged almost without suppressions, thereby resulting in an increase of the average critical radius as compared to the stationary case. When $\varepsilon \to 0$, exact analytical expressions are obtained from (9) and (10)

$$\frac{\langle R_c\rangle}{R_c} = \frac{1}{\sqrt{1-\gamma^2}} \geq 1, \tag{11}$$

$$\frac{\langle \Delta G_c\rangle}{\Delta G_c} = \frac{1}{\sqrt{(1-\gamma^2)^3}} \geq 1, \tag{12}$$

when $0 \leq \gamma < 1$. At the high values of the dimensionless barrier ε (which corresponds to the low temperatures, high surface tensions or small moving forces of the process), a negative exponent in the weight function becomes higher in modulus. It results in the fact that the weight function sharply suppresses a contribution by the phases of ultrasonic oscillations, in which effective supersaturation is reduced, i.e. when the denominator $(1+\gamma\sin x)^2$ is low. In these conditions, the average nucleation parameters are mainly contributed only by narrow time intervals near the pressure maximums, where the critical radius is the lowest and the energy barrier is substantially reduced. As a result, the averaged values $\langle R_c\rangle$ and $\langle G_c\rangle$ turn out to be less than in the stationary case, which corresponds effective acceleration of nucleation under ultrasonic effect.

Two maximums on the dependence of $\langle \Delta G_c\rangle$ on γ are worth noting. Their presence is explained by specific features of an intergrand (10), which are related to solving the equation $1+\gamma\sin(x) = 0$ within an interval $[0, 2\pi]$. These specific features occur at certain amplitudes of ultrasonic effect, when supersaturation reaches extreme values. This effect is physically interpreted by the fact that in the phase of depressurization the acoustic field reduced supersaturation, increasing the energy nucleation barrier and worsening the nucleus formation conditions. On the contrary, in the phase of compression supersaturation increases, decreasing the barrier. The maximums are noticeable for the small values $\varepsilon \ll 1$, which corresponds to the high temperatures, when the exponential dependence of probability of nucleation becomes less sharp. At the same time, the specific features of a subintegral function are more pronounced due to attenuation of exponential suppression of the contribution by the phases of reduced supersaturation. It is for this reason that the peaks are typical for the integral (10), where sensitivity of activation energy to supersaturation modulation is enhanced by the quadratic dependence.

3. Diffusion growth of the nanoparticles

After the critical nuclei are formed, further evolution of the system is determined by a growth of the nanoparticles due to matter transfer from the environment to their surface. Here, the main mechanism is diffusion of atoms or monomers.

It should be noted that for the standard ultrasound (the frequencies 20−100 kHz) the oscillation period is by several orders less than the typical nucleation time. In this situation, the process of formation and growth of the nuclei can not react to instantaneous pressure fluctuations. Therefore, dynamics of the system is determined by an averaged ultrasonic effect. In other words, in theoretical description, it is required to use an effective barrier that is averaged over the period of the ultrasonic oscillations.

Mathematical simulation of diffusion growth reduces to solving an initial boundary value problem with a movable boundary $R(t)$ (the so-called Stefan problem [17]). In this case, a concentration field and a growth rate are described by the equations:

$$\frac{\partial C(r,t)}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right), \tag{13}$$

$$n_V \frac{dR(t)}{dt} = D\left(\frac{\partial C}{\partial r}\right)_{r=R(t)}, \tag{14}$$

$$C(R,t) = C_0 \exp\left[\frac{V_a}{k_\mathrm{B}T}\left(\frac{2\sigma}{R} + \Delta p \sin(\omega t)\right)\right], \tag{15}$$

$$R(0) = R_c + \Delta R, \quad C(r \to \infty, t) = C_\infty, \tag{16}$$

where $C = C(r,t)$ is a concentration of atoms or monomers (m^{-3}), n_V is an average bulk concentration of the particles in the solid phase (m^{-3}), C_0 is an equilibrium concentration above the flat surface (m^{-3}), V_a is a volume per one atom or monomer ($V_a = V_m/N_A$), D is a diffusion constant, $\Delta R > 0$ is a certain small deviation from the equilibrium radius (fluctuation), which is required for further growth [14], C_∞ is a concentration in the volume of the liquid-phase medium (m^{-3}).

The problem (13)−(16) is extremely complicated for analytical solution and numerical analysis due to presence of the movable boundary and the fast ultrasonic oscillations. In order to exclude their influence, the Gibbs-Thomson formula (15) shall be averaged over the period of these oscillations:

$$\langle C(R)\rangle = \frac{C_0\omega}{2\pi}\exp\left(\frac{2\sigma V_a}{k_\mathrm{B}TR}\right)\int_0^{2\pi/\omega}\exp\left(\frac{V_a\Delta p\sin(\omega t)}{k_\mathrm{B}T}\right)dt$$

$$= C_0^* \exp\left(\frac{2\sigma V_a}{k_\mathrm{B}TR}\right), \tag{17}$$

$$C_0^* = C_0 I_0\left(\frac{V_a\Delta p}{k_\mathrm{B}T}\right), \tag{18}$$

where $I_0(x)$ is a modified first-kind zero-order Bessel function. Since the radius $R(t)$ varies insignificantly for one period of acoustic oscillations, it can be taken from a sign of the averaging integral. Thus, the ultrasound influence is reduced to substituting the initial concentration C_∞ with its effective value C_∞^* in the Gibbs-Thomson formula (15); it physically means that USW effect is equivalent to an increase of the concentration of atoms or monomers in the volume of the medium. Another simplification is application of an approximation of an almost immovable boundary $R \approx \mathrm{const}$. It corresponds to a quasi-steady-state approximation that is true if the growth time is small as compared to the typical diffusion time. In this case, a solution of the equation (13) is written as

$$C(r,t) = C_\infty + \left[\langle C(R)\rangle - C_\infty\right]\frac{R}{r}\,\mathrm{erfc}\left(\frac{r-R}{2\sqrt{Dt}}\right), \tag{19}$$

where $\mathrm{erfc}(x)$ is an additional error function. By substituting (17) and (19) into (14) and calculating a gradient, we obtain a differential equation

$$\frac{dR(t)}{dt} = \frac{D}{n_V}\left[C_\infty - C_0^*\exp\left(\frac{2\sigma V_a}{k_\mathrm{B}TR}\right)\right]\left(\frac{1}{R} + \frac{1}{\sqrt{\pi Dt}}\right). \tag{20}$$

Then we go to dimensionless variables

$$r \to \frac{r}{R_c}, \quad t \to \frac{t}{\tau}, \quad R \to \frac{R}{R_c},$$

where

$$R_c = \frac{2\sigma V_a}{k_\mathrm{B}T\ln(C_\infty/C_0^*)}, \quad \tau = \frac{n_V R_c^2}{DC_0^*}.$$

Finally, we obtain the dimensionless concentration

$$\tilde{C}(r,t) = \frac{C(r,t) - C_\infty}{C_0^* - C_\infty}$$

$$= \frac{1-\beta^{1-1/R}}{1-\beta}\frac{R}{r}\,\mathrm{erfc}\left(\frac{r-R}{2\sqrt{\frac{t}{\alpha\beta}}}\right), \tag{21}$$

as well as the following Cauchy problem

$$\frac{dR(t)}{dt} = \alpha\left(1-\beta^{1-1/R}\right)\left(\frac{1}{R} + \frac{1}{\sqrt{\pi t}}\right), \tag{22}$$

$$R(0) = 1 + \rho, \tag{23}$$

where $\alpha = C_\infty/n_V$, $\beta = C_0^*/C_\infty$ and $\rho = \Delta R/R_c$. The problem (22), (23) is solved by universal growth curves, which can be scaled for any real parameters of the system via respective similarity parameters: the critical-nucleus radius, the diffusion constant and the temperature and the ultrasound amplitude.

Figure 2 shows results of calculation by the formula (21) and numerical solution of the problem (22), (23) when $\alpha = 0.01$ and $\rho = 0.001$. The Runge-Kutta method of the 4−5 order with an adaptive step (RK45) was applied. It is obvious from the formula (18) that the parameter β that is directly related to the effective concentration on the nanoparticle surface C_0^* depends on the amplitude

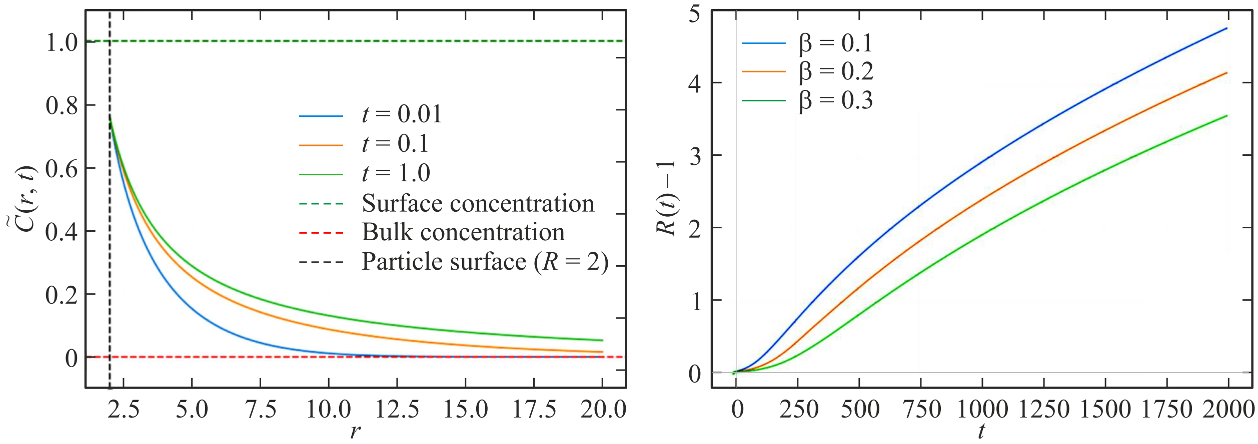

Figure 2. Evolution of concentration profiles and kinetics of the growth of the nanoparticle.

of the ultrasonic oscillations Δp via the modified zero-order Bessel function $I_0(x)$. At the small amplitudes ($\Delta p \ll k_BT/V_a$), the approximation $I_0(x) \approx 1 + x^2/4$ true, thereby resulting in a quadratic dependence $\beta \sim (\Delta p)^2$. At the high amplitudes ($\Delta p \gg k_BT/V_a$), the Bessel function behaves as $I_0(x) \sim \exp(x)/\sqrt{2\pi x}$ and β exponentially increases together with Δp. Consequently, an increase of the amplitude of the ultrasonic oscillations results in a non-linear increase of the nanoparticle radius, which is initially moderated (quadratic) at the small amplitudes and then rapid (exponential) at the high values of Δp.

Finally, we note that the process of the nanoparticle growth turns out to be sensitive to a value of the initial deviation ρ from the equilibrium size $R = 1$. The smaller ρ the longer the step of slow increase, which precedes the active stage of growth.

4. Conclusion

The study has proposed a theoretical model that describes thermodynamics of homogenous nucleation and kinetics of the subsequent diffusion growth of the nanoparticle under the conditions of ultrasonic effect within the single framework. The main conclusion of the study is that the ultrasound not only reduces the thermodynamic barrier of nucleation of the new phase, but decisively affects the subsequent kinetics of the growth, wherein this influence is the most critical exactly at the initial state just after formation of the critical nucleus.

It is shown that the acoustic field leads to modification of the classical parameters of nucleation. The critical radius and the nucleus formation energy were averaged and it made it possible to adequately describe the process of nucleation of the new phase in the nonstationary conditions in terms of physics. It is found that with the increase of the ultrasound amplitude the average critical radius and energy barrier decrease, thereby contributing to activation of the nucleation process in real experiments.

The main result for the initial stage of the growth is that it is found that the ultrasound effect is equivalent to an effective increase of the concentration of atoms or monomers in the volume of the liquid-phase medium, which is described by introducing the parameter C_0^* via the modified Bessel function (the formulas (17), (18)). This effective increase of the concentration is a moving force of the growth. The obtained growth equation (22) was numerically solved to demonstrate that the increase of the ultrasound amplitude caused the non-linear acceleration of the nanoparticle growth — from the quadratic dependence at the small amplitudes to the exponential one at the high ones.

Thus, the proposed approach makes it possible to find a direct quantitative relation between intensity of ultrasound treatment and the characteristics of the nanoparticles being formed. The developed thermodynamic and kinetic models can be a base for predicting results of sonochemical synthesis of the nanomaterials. Their further development is related to taking into account competitive growth and processes of agglomeration under effect of acoustic flows as well as to numerical solution of the problem (13)–(16) without any simplification.

Conflict of interest

The author declares that he has no conflict of interest.

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