

Dispersion reduction in size of new phase inclusions by changing solve supersaturation

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Control operation over a new phase inclusions growth by supersaturation change when it is reducing with time is represented in this work. We have got a solution that defines the low of supersaturation variation with time for maintaining the required law of a new phase growth.

Предложен режим управления ростом выделения новой фазы изменением пересыщенности раствора, при котором дисперсия размеров выделений уменьшается со временем. Получена асимптотическая зависимость, определяющая закон изменения пересыщенности со временем для поддержания требуемого закона роста выделения новой фазы.

New phase growth has already become a canonical section of phase transition physics [1]. In the common sense the main question deals with definition of the law of inclusion growth under certain conditions. The rule is to recognize three stages of growth: stage of generation, independent growth and stage of coalescence [2]. Under modern conditions there is an increasing interest to inclusion growth because of rapid nanotechnology development [3]. The reason for that is connected with requirements in nanoparticles of the certain size [4]. It stands to reason that the inverse problem is in the foreground. The problem should answer the question what conditions are required for the support of a given law of inclusion growth? In the simplest case the conditions mean the solution supersaturation degree. Clearly this problem is very difficult even in the simplify case of inclusion growth in the solution supersaturation. We should pay attention that the condition of independent growth can be put into practice. That is why the work will study the inverse problem in the regime of independent growth of inclusions or the one-particle problem.

The work uses the approach considered in [6] for description of inclusion growth under nonstationary conditions. As it was proved before this approach is also efficient for solution to the inverse problem [7]. Using the results for inclusion growth in nonstationary conditions we have got the solution to the inverse problem [7]. The regime of inclusion growth under which dispersion of the size is reducing with time is proposed in the work. We have also obtained supersaturation change over time, providing the required law of growth. Thus we offer the regime of dispersion reduction according to the size of inclusion during the growth process through changing supersaturation with certain methods.

Let's assume that the law of inclusion growth is realized in accordance with still undefined law of supersaturation change

$$R(t) = \frac{\gamma R_0 + t R_\infty}{\gamma + t}\,. \tag{1}$$

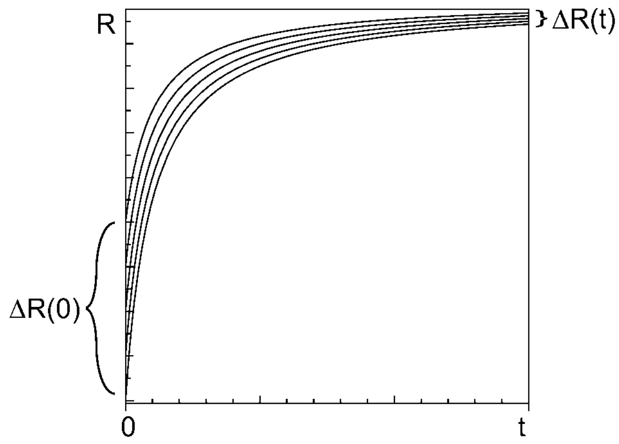

Fig. 1. The changing of initial inclusion size $\Delta R(0)$ with time $\Delta R(t)$ by the law of inclusion growth (1).

In this expression γ is a proper time scale of size change and R_∞ is a size of inclusion required to be obtained in the growth process. On realization of this operation the initial scatter of source dimensions size ΔR_0 is decreasing with time as

$$\Delta R(t) = \Delta R_0 \frac{\gamma}{\gamma + t}\,. \tag{2}$$

In other words size dispersion is decreasing with time inversely proportional to time. In Fig. 1 the mechanism of dispersion decrease under the law of growth is shown (1). For a wide range of technological purposes the size dispersion decrease is quite desirable .In principle from a ratio (2) it is easy to define time for any necessary dispersion level. Thus the problem leads to finding out the conditions of such operation realization. Below we will show how it is necessary to change supersaturation for such operation of growth. For this purpose we use the result of [7] on solution to the inverse problem. According to the work the supersaturation is defined by the expression

$$\Delta(t) = \partial_t^{-\frac{1}{2}} \left\{ \beta(t)\cdot e^{-F(t)} \left(C + \int_0^t \alpha(\tau) e^{F(\tau)} d\tau \right) \right\}. \tag{3}$$

Were $\Delta(t)$ is the supersaturation and functions entering into this expression are defined with the law of inclusions growth. Thus

$$F(t) = \int_0^t \beta(\tau) d\tau$$

$$\beta(t) = \frac{D}{D\cdot z(t) - R(t)^2}$$

$$z(t) = \frac{1}{\sqrt{D}} \left(\partial_t^{-\frac{1}{2}} R(t) \right)$$

$$\alpha(t) = \partial_t \left(\partial_t^{-\frac{1}{2}} - \frac{R(t)}{\sqrt{D}} \right) \frac{R(t)\dot{R}(t)}{D}$$

$$\partial_t^{-\alpha} f(t) = \frac{1}{\Gamma(\alpha)} \int_0^t \frac{f(\tau)}{(t-\tau)^{1-\alpha}} d\tau.$$

Here D is diffusion coefficient. The constant C is also defined by initial conditions or more precisely initial supersaturation $\Delta(0)$. Using these ratios we will define the law of supersaturation changes for realization of the growth regime (1).

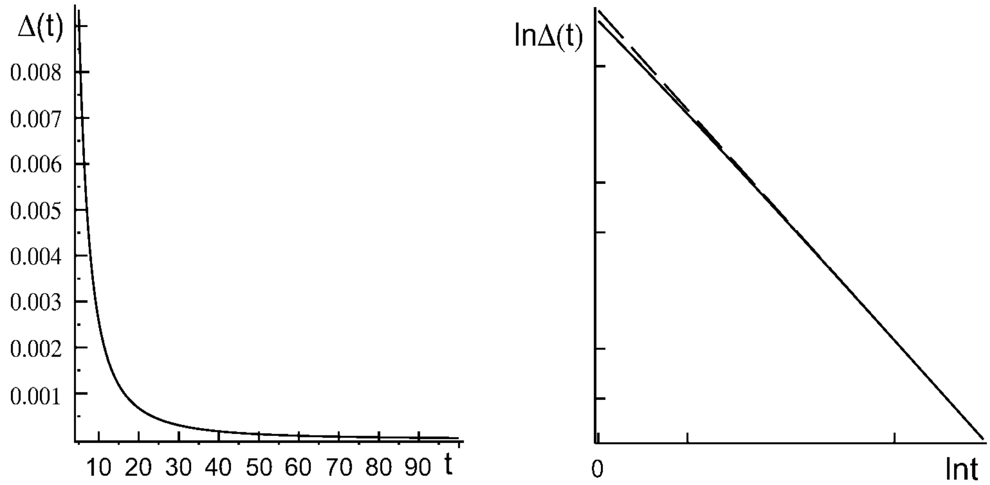

Fig. 2. In the left the obtained function $\Delta(t)$ (D=0,00001,$R_\infty/R_0 = 100$), in the right it is represented in the double logarithm zoom with the line approximation.

First of all we will note that function evolution of $z(t)$ can be calculated in the elementary functions. Thus

$$z(t) = \frac{2}{\sqrt{D\pi}}\left\{R_\infty\sqrt{t} + \gamma(R_0 - R_\infty)\cdot\frac{arc\sinh(\sqrt{t/\gamma})}{\sqrt{t+\gamma}}\right\}$$

and the function $\beta(t)$ is expressed in explicit form. The function evolution $\alpha(t)$ can be also calculated in elementary functions although it has got a rather lengthy form

$$\alpha(t) = \frac{1}{2D}\frac{\partial^2}{\partial t^2}\left[\frac{\gamma\sqrt{t}}{\sqrt{\pi}(t+\gamma)}\left\{(R_0 - R_\infty)^2 + 2R_\infty^2\left(1+\frac{t}{\gamma}\right) + \right.\right.$$

$$\left.\left. + \frac{\gamma\cdot arc\sinh(t/\gamma)}{\sqrt{t(t+\gamma)}}\left((R_0+R_\infty)^2 + 4R_0R_\infty\frac{t}{\gamma} - 4R_\infty^2\left(1+\frac{t}{\gamma}\right)\right)\right\} - \frac{2}{3\sqrt{D}}R(t)^3\right].$$

All these dependencies define the supersaturation $\Delta(t)$ in quadrature. However the analytically calculation of residuary integrals is a difficult problem. Even integrals representation by the means of special functions is a hardly achievable problem. And integrals expression with special functions makes it difficult to research the character of supersaturation change. Therefore further we will analyze supersaturation change with time using calculus of approximations. With quadrature method $\Delta(t)$ was found that is shown in the Fig. 2. The main conclusion of calculus of approximations leads to the character law of supersaturation reduction with time (For example, 2 in the left). Such character shows the opportunity of the simple asymptotic behaviour of supersaturation with huge times. For the definition of asymptotic behaviour character the same supersaturation dependence is illustrated in the right fig. 2 in the double logarithm zoom. The well visible straight-line portion proves the power character of supersaturation behavior with huge times

$$\Delta(t) \sim t^{-\alpha} \quad \text{where} \quad t >> \gamma. \tag{4}$$

The slope ratio of straight-line portion defines exponent α. Using the least-squares method the exponent $\alpha = 1,98 \pm 0.02$ was obtained. For visualization the power law with the obtained exponent is shown by the dish line in the Pic. 2. We can watch a good coincidence of supersaturation behavior with the obtained asymptotic law (4) with huge times. Considering the obtained simple asymptotic law the exponent α can be estimated. For this purpose we use the equation that defines inclusion radius change with time under the given supersaturation obtained in [6]

$$\frac{dR(t)}{dt} = \frac{D\cdot\Delta(t)}{R(t)} + \sqrt{D}\cdot\partial^{1/2}(\Delta(t))\,. \tag{5}$$

Properly speaking the above cited solution to the inverse problem for supersaturation was obtained using this equation. Substituted the obtained law of supersaturation change (4) with huge t in this equation and used the characteristic of fractional differential operator $\partial^{1/2}$ we will get

$$\frac{dR(t)}{dt} \sim \frac{D \cdot t^{-\alpha}}{R(t)} + \sqrt{D} t^{-\alpha-1/2}. \tag{6}$$

We only have to use the character of inclusion growth change (1) with time for derivative evaluation $\frac{dR(t)}{dt}$. Comparing asymptotic leading terms of the obtained equation we can easily define the exponent α

$$\frac{1}{t^2} \sim \frac{1}{t^\alpha}, \tag{7}$$

that means $\alpha = 2$. This value was brought in correspondence with the obtained numerical solution. Thereby supervising the supersaturation change according to the proportion (4) we can obtain scatter reduction in size or dispersion in size of new phase growing inclusions. It was ascertained that at the stage of independent growth maintenance of the regime under which supersaturation is reducing with time in inverse proportion to the square of time leads to dispersion reduction. At the same time dispersion in size of new phase inclusions decreases in inverse proportion to time and the inclusions growth can be calculated with proportion (1). We have to take into account that their dispersion reduction in size also should be observed under other special speed slowdown of new phase inclusions growth. In this case the important characteristic is such change of inclusions radius that asymptotically with time becomes a constant value.

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Зменшення дисперсії за розмірами виділень нової фази зміною пересиченості розчину

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Запропоновано режим управління зростанням виділення нової фази зміною пересиченості розчину, при якому дисперсія розмірів виділень зменшується з часом. Отримано асимптотичну залежність, що визначає закон зміни пересиченості з часом для підтримки необхідного закону зростання виділення нової фази.