New phase inclusion growth control

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The task is considered of the new phase inclusion growth %control by the way of governed change of solution supersaturation. The exact solution is obtained that determines the law of supersaturation change with time for the support of required law of new phase inclusion growth.

Рассмотрена задача управления ростом выделения новой фазы контролируемым изменением пересыщенности раствора. Получено точное решение, определяющее закон изменения пересыщенности со временем для поддержания требуемого закона роста выделения новой фазы.

The growth of new phase inclusions has already for a long time become a canonical part of phase transition physics [1]. In the traditional statement of the problem, basic task is reduced to the determination of inclusion growth law under certain conditions. For this purpose, three growth stages are usually conventionally separated: nucleation, independent growth and coalescence [2]. Under modern conditions, interest for the growth of new phase inclusions has grown significantly in connection with the rapid development of nanotechnologies [3]. The cause of such interest is connected with the need to obtain nanoparticles of a certain size [4]. It is evident that in this case an inverse problem comes forward. This problem consists in answering the question: what conditions are required for the support of a given law of inclusion growth? In the simplest case, the conditions consist in the solution supersaturation degree. Of course, this is a complicated task even for the simple case of inclusions from supersaturated solution. Let us note, that the condition of independent growth can be fulfilled in practice, so that in the given work the inverse problem in the regime of independent growth of inclusions, or a one-particle problem will be considered.

In the given work, the approach proposed in [6] for describing inclusion growth under nonstationary conditions is used. As it is shown below, this approach is effective also for the solving the inverse problem. Its exact solution is obtained using results for inclusion growth in nonstationary conditions. For the given law of inclusion growth $R(t)$, the exact solution is obtained for the change of supersaturation degree with time, that provides the required growth law. This exact solution is obtained explicitly in integral form with the use of fractional derivative formalism. It is shown, that such formalism is exceptionally convenient for solving the inverse problem.

Let us consider the case of independent inclusion growth in supersaturated solution. Let us suppose that it is necessary to provide the change of inclusion radius in accordance with the given law $R(t)$. In principle, governing the inclusion growth can be achieved by the controlled changes of solution supersaturation degree. For this purpose, it is necessary to elucidate the connection of the inclusion radius with the supersaturation degree of the solution $\Delta(t)$. This means, that it is necessary to solve the inverse problem and establish the law of supersaturation degree changes for the given law of inclusion growth.

Such inverse problem is significantly complicated because of the non-local character of the supersaturation change influence on inclusion radius change. Usually, the direct problem is considered of the inclusion radius change in a supersaturated solution. The central element of solving the direct problem is the equation of diffusion growth of new phase inclusions. The physical principles of description of diffusion growth of new phase inclusions are based on the determination of the diffusion flaws on the inclusion boundary with the account of boundary conditions. Usually, for the calculation of diffusion flaws and growth equation, the assumption of quasistationary supersaturation is used (see, e.g. [5]). In other words, it is assumed that stationary flaw formation time is small in comparison with the characteristic time of inclusion growth. This supposition does not always seem to be well-grounded and can not be used, for example, for solving the inverse problem. Several cases of inclusion growth are studied. Thus, the case of constant supersaturation has been studied thoroughly enough [5]. In this case, an additive assumption about growth stationarity is also used. The approach, that allows to turn to nonstationary conditions was proposed in [6]. On the base of the developed in this work approach, the exact solution of the inverse problem was proposed.

The growth equation for new phase inclusions in nonstationary conditions obtained in [6] has the following form

$$\frac{dR}{dt} = \frac{D}{R}\Delta(t) + \frac{\sqrt{D}}{\sqrt{\pi}}\frac{d}{dt}\int_0^t \frac{\Delta(\tau)}{\sqrt{t-\tau}}d\tau, \tag{1}$$

where D – is diffusion coefficient, $R(t)$ – is radius of the new phase inclusions, $\Delta(t)$ – solution supersaturation degree. It is more convenient to consider this equation using fractional derivatives of Liouville, so that its form is simplified

$$\frac{dR}{dt} = \frac{D}{R}\Delta(t) + \sqrt{D}\partial_t^{\frac{1}{2}}\Delta(t). \tag{2}$$

Here, the operator of fractional derivation of Liouville on the semiaxis is defined according to [7]

$$\partial_t^{\alpha} f(t) = \frac{1}{\sqrt{\pi}}\frac{d}{dt}\int_0^t \frac{f(\tau)}{(t-\tau)^{\alpha}}d\tau,$$

where index $0 < \alpha < 1$. Understandably, unlike work [6], we are interested in the inverse problem. Let us assume that the law of the new phase inclusions growth $R(t)$ is determined by the initial requirements. On needs to establish the way of solution supersaturation degree changes that provides for required new phase inclusions growth regime. In order to solve this problem, let us write down equation (2), as the that for the unknown supersaturation degree $\Delta(t)$ at a given function $R(t)$ in the form

$$D\partial_t^{-\frac{1}{2}}\partial_t^{\frac{1}{2}}\Delta(t) + R\sqrt{D}\partial_t^{\frac{1}{2}}\Delta(t) = R\frac{dR}{dt}.$$

Here the well known property $\partial_t^{\alpha}\partial_t^{\beta} = \partial_t^{\alpha+\beta}$ of fractional derivation operators was used (see e.g. [7]). Let us now transform this equation as

$$\left(D\partial_t^{-\frac{1}{2}} + R(t)\sqrt{D}\right)\partial_t^{\frac{1}{2}}\Delta = R(t)\frac{dR(t)}{dt}.$$

The partial derivation operator at negative indices is defined by integral relation [7]

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

Let as denote $y = \partial_t^{\frac{1}{2}}\Delta$ and obtain linear equation of fractional order

$$\left(D\partial_t^{-\frac{1}{2}} + R(t)\sqrt{D}\right)y = R(t)\frac{dR(t)}{dt}, \tag{3}$$

that determines the law of supersaturation changes for the controlled inclusions growth. Let us bring it to the canonical form by introducing convenient definitions:

$$\left(\partial_t^{-\frac{1}{2}} + \widetilde{R}(t)\right) y = f(t). \tag{4}$$

Here $\widetilde{R}(t) = R(t)/\sqrt{D}$, $f(t) = \frac{1}{D}R(t)\frac{dR(t)}{dt}$. This equation relates to linear equations with variable coefficients of fractional order. The formal solution in the operator form can be easily written down

$$y(t) = \left(\partial_t^{-\frac{1}{2}} + \widetilde{R}(t)\right)^{-1} f(t).$$

Taking into account supersaturation degree definitions introduced above, one obtains

$$\Delta(t) = \partial_t^{-\frac{1}{2}} \left(\partial_t^{-\frac{1}{2}} + \widetilde{R}(t)\right)^{-1} f(t).$$

The basic question is how to understand and calculate action of operators in the right part. The cause of nontriviality of this expression lies in the noncommutativity of derivation operator and operator of multiplication by the function of time. Despite this difficulty in the interpretation of the formal solution, it can be quite easily used for building perturbation theory, for example, in the case of adiabatic change of inclusions size. In order to understand how this expression can be used for the exact solution analysis, let us return to equation (4) and act on it by operator $\left(\partial_t^{-\frac{1}{2}} - \widetilde{R}(t)\right)$. As a result one obtains

$$\left(\partial_t^{-1} + \partial_t^{-\frac{1}{2}}\widetilde{R}(t) - \widetilde{R}(t)\partial_t^{-\frac{1}{2}} - \widetilde{R}(t)^2\right) y = \left(\partial_t^{-\frac{1}{2}} - \widetilde{R}(t)\right) f(t).$$

Let us pay attention now to the fact that the expression in the left part $\partial_t^{-\frac{1}{2}}\widetilde{R}(t) - \widetilde{R}(t)\partial_t^{-\frac{1}{2}}$ coincides with the commutator of two operators so that it can be easily calculated as

$$\partial_t^{-\frac{1}{2}}\widetilde{R}(t) - \widetilde{R}(t)\partial_t^{-\frac{1}{2}} = \left(\partial_t^{-\frac{1}{2}}\widetilde{R}(t)\right) \equiv z(t).$$

By this way, one comes to the equation

$$\left(\partial_t^{-1} + z(t) - \widetilde{R}(t)^2\right) y = \left(\partial_t^{-\frac{1}{2}} - \widetilde{R}(t)\right) f(t).$$

This equation is considerably more convenient. Thus, its right part contains only operator of ordinary derivation and fractional derivation in the left part simply defines the given function of time. The last step is to act on the obtained equation by the operator ∂_t for reducing it to a more customary form

$$\left(1 + \partial_t(z(t) - \widetilde{R}(t)^2)\right) y = \partial_t \left(\partial_t^{-\frac{1}{2}} - \widetilde{R}(t)\right) f(t). \tag{5}$$

This equation can be easily transformed to the ordinary first order equation

$$\frac{dp}{dt} + \beta(t)p = \alpha(t), \tag{6}$$

where definitions are introduced for the unknown function $p(t) = (z(t) - \widetilde{R}(t)^2)y$, and for given coefficients $\beta(t) = 1/(z(t) - \widetilde{R}(t)^2)$ and $\alpha(t) = \partial_t \left(\partial_t^{-\frac{1}{2}} - \widetilde{R}(t)\right) f(t)$, whose dependence on time is determined only by the given law of $R(t)$growth. This equation can be solved using standard methods for ordinary differential equations. The general solution of this equation has the form

$$p(t) = e^{-F(t)}(C + \int_0^t \alpha(\tau)e^{F(\tau)}d\tau). \tag{7}$$

Here constant C is determined by the initial condition $C = p(0)e^{F(0)}$ that is connected with the initial supersaturation degree of the solution $\Delta(0)$. Function $F(t)$ is determined by the definite integral

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

Coming back to the initial variables, one can easily establish the law of supersaturation changes in integral form

$$\Delta(t) = \partial_t^{-\frac{1}{2}} \left\{ \beta(t) \cdot e^{-F(t)} \left(C + \int_0^t \alpha(\tau) e^{F(\tau)} d\tau \right) \right\}. \qquad (8)$$

Thus, relation (8) determines the law under the question of supersaturation degree changes $\Delta(t)$, that provides for the growth of new phase inclusionss according to the given law $R(t)$. Equation (8)is the exact solution of inverse problem of the control of new phase inclusions growth. Functions $F(t)$, $\beta(t)$ and $\alpha(t)$, in the solution are determined via corresponding integrals exclusively in accordance with the law of new phase inclusions growth $R(t)$.

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Керування зростанням частинки нової фази

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Розглянуто проблему керування зростанням частинки нової фази контрольованою зміною пересиченості розчину. Отримано точний розв'язок, який визначає закон зміни пересиченості розчину з часом для підтримання потрібного закону росту частинки нової фази.