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Nonlocal diffusion models: Application to rapid solidification of binary mixtures

S.L. Sobolev *

Institute of Problems of Chemical Physics, Academy of Sciences of Russia, Chernogolovka, Moscow Region 142432, Russia

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ABSTRACT

Various theoretical treatments and models for nonlocal diffusion are briefly reviewed and discussed. The nonlocal effects arise in far from equilibrium processes, which involve extremely fast heat and mass transfer at very small time and length scales. With only diffusive dynamics, the nonlocal models result in a set of transfer equations of parabolic type with an infinite velocity of diffusive disturbances. With the wavelike dynamics, the models lead to a set of transfer equations of hyperbolic type with a finite velocity of diffusive disturbances. Rapid solidification of binary alloys has been used to illustrate the influence of the nonlocal diffusion effects on solute partitioning at the phase interface.

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1. Introduction

The nonlocal effects in heat-mass transfer [1–9] arise in a wide variety of modern practical applications in materials sciences, such as metallic nanowires [1], rapid solidification of binary alloys [10–18], colloidal solidification [19], high-power laser melting [7,20], and frontal polymerization [21]. These types of problems are also of great interest for their purely mathematical content. The classical diffusion theory is based on Fick law, which suggests that the diffusion flux J at a space point x and a time moment t depends on the concentration gradient ∇C at the same space–time point, i.e. $J(x,t) = -D\nabla C(x,t)$, where D is the diffusion coefficient, and C is the concentration. But strictly speaking mass (heat) transport is an inherently nonlocal phenomenon. The heat-mass flux at a point depends on the history of the heat-mass carriers reaching the point at time t and the carriers arrive at the point in space having brought the energy or mass from other points. Thus there are essentially two important non-Fickian effects – the one related to the time lag between the flux and corresponding gradient (it can be called *time* non-local effect), the other is the space non-local effect, which takes into account that the carriers come to a point from another distant point. In many practically important cases, which occur not very far from equilibrium, Fick law gives an adequate description of diffusion phenomena. But since industrial applications strive towards higher speed, power, and miniaturization, the transport processes occur under conditions far from local

equilibrium and nonlocal effects should be taken into account. This paper concerns the non-local diffusion but the principal conclusions will be also valid for heat conduction. In Section 2 we briefly review and discuss the main non-local diffusion models. Particular emphasis is given to the space nonlocal effects, which are ruled by the ratio of the mean-free path l to the characteristic length of the system h, that is, the so-called Knudsen number. We have tried to represent the models in the relatively simple analytical form, which would allow one to use them for modeling particular processes far from equilibrium conditions. Section 3 describes the non-local diffusion effects during steady-state regimes of moving phase interface. The regimes arise in many important applications such as rapid solidification of binary alloys, colloidal solidification, frontal polymerization, combustion waves, etc. In Section 4 we use the results obtained in Section 3 to calculate the solute segregation coefficient at the phase interface, which plays the most crucial role in modeling rapid phase transformation and strongly depends on the non-local diffusion effects. We end the paper with conclusions in Section 5.

2. Non-local diffusion models

2.1. Phenomenological illustration

The simplest phenomenological illustration, which demonstrates the space–time non-local effects, can be based on the procedure described in many text-books (see, for example, [22]). Diffusion flux is a number of molecules, which move through a

* Tel.: +7 903 247 81 52; fax: +7 496 522 35 07.
E-mail address: sobolev@icp.ac.ru

plain of unit area per unit time. The net flux is due to the difference between the flow from one side of the plane and the flow from the other side of the plain. The flux from left side of the plain is proportional to $C(x - l)vdt/6$ and the flux from right side of the plain is proportional to $C(x + l)vdt/6$, where C is the particle concentration, v is the particle mean velocity. The net flux is proportional to the difference between the fluxes. Moreover we should take into account that a particle comes to a point x at a time moment $t + \tau$ from a point $(x - l)$ or $(x + l)$ where it was at a time moment t. It implies that there is a time lag τ between the diffusion flux and the particle concentration (and its derivatives), where τ is relaxation time to local equilibrium (for gases it is of the ordered of the mean collision time). In a one dimensional case one can obtain

$$J(t + \tau, x) = \frac{1}{2}(C(t, x - l) - C(t, x + l))v$$

Now each term of this equation may be expanded in a Taylor series with two small parameters l and τ

$$\sum_{n=0} \frac{\tau^n}{n!} \frac{\partial^n J}{\partial t^n} = -v \sum_{k=0} \frac{l^{2k+1}}{(2k+1)!} \frac{\partial^{2k+1} C}{\partial x^{2k+1}} \tag{1}$$

The right and the left hand side of Eq. (1) contain the terms of Taylor series with different small parameters l and τ. In the zero order approximation $n = k = 0$ this expansion yields the classical Fick law [22]

$$J = -D \frac{\partial C}{\partial x} \tag{2}$$

where $D = vl = l^2/\tau$ is the diffusion coefficient. In combination with the mass conservation law $\partial C/\partial t = -\partial J/\partial x$, Fick law results in the classical diffusion equation of parabolic type

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{3}$$

But this procedure arises two questions: (i) why we should limit ourselves with the zero order approximation $n = k = 0$ in expansion (1); and (ii) how we should compare terms with different small parameters l and τ if we consider higher order approximations of expansions (1)? The answer to the first question is that the zero order approximation to Eq. (1) is valid only for relatively slow processes when $\tau \ll t_0$ and $l \ll h$, where t_0 is the characteristic time of the process under consideration. In this case the non-local effects are small and the classical local equilibrium approach with Eqs. (2) and (3) can be used. If $\tau \propto t_0$ and /or $l \propto h$, then the nonlocal effects play significant role and higher order approximations of Eq. (1) should be used. In order to answer to the second question we should introduce the truncation procedure, which is based on the relationship between the small parameters τ and l at $\tau \to 0$ and $l \to 0$. With only diffusive dynamics, when the characteristic speed of the process under consideration $v_0 = h/t_0$ is much less than the ratio $l/\tau = v$, the small parameters τ and l are connected by the diffusion-like limiting condition [3,6]

$$\lim_{l \to 0, \tau \to 0} l^2/\tau = D = const \tag{4}$$

The first order approximation to Eq. (1) with allowance for Eq. (4) gives

$$J + \tau \frac{\partial J}{\partial t} = -D \frac{\partial C}{\partial x} - D \frac{l^2}{3} \frac{\partial^3 C}{\partial x^3} \tag{5}$$

Eq. (5) is nonlocal both in time and space due to additional time and space derivatives in comparison with Fick law (2). The need for the space nonlocal term (the last term in Eq. (5)) depends on whether $\partial^2 C/\partial x^2$ varies rapidly on the distance scale of the mean-free path

l (or correlation length). Combining Eq. (5) with the mass conservation law we obtain corresponding diffusion equation in the form

$$\frac{\partial C}{\partial t} + \tau \frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} + D \frac{l^2}{3} \frac{\partial^4 C}{\partial x^4} \tag{6}$$

This equation is nonlocal both in time and space due to the additional derivatives with parameters τ and l in comparison with local Eq. (3). Eq. (6), as well as the classical diffusion Eq. (3), is of parabolic type. Taking into account higher order approximations in a Taylor series expansion with allowance for the same limiting condition (4) one obtains a hierarchy of higher order partial differential equations of parabolic type [3,6].

With the wavelike dynamics, when $v_0 \propto v$, the limiting relation for the small parameters τ and l corresponds to a finite value of $v = l/\tau$ [3,6], i.e.

$$\lim_{l \to 0, \tau \to 0} l/\tau = v < \infty \tag{7}$$

In this case Eq. (1) results in

$$J + \tau \frac{\partial J}{\partial t} = -\frac{\tau v^2}{3} \frac{\partial C}{\partial x} \tag{8}$$

where $\tau v^2 = D$. This equation is similar to the evolution equation for heat flux known as Cattaneo-type equation [2–4]. Combining Eq. (8) with the mass conservation law, one can obtain

$$\frac{\partial C}{\partial t} + \tau \frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} \tag{9}$$

This equation, as well as higher order approximations with limiting condition (7), is of hyperbolic type. It contrasts to the classical diffusion Eq. (3) and higher order approximations with limiting condition (4), which are of parabolic type. Note that from the mathematical point of view equations of parabolic type predict an infinite velocity of diffusive disturbances because the discontinuity imposed by the sudden jump of concentration at the boundary of a semi-infinite system is felt immediately everywhere at distant points. This is inconsistent with the principle of causality and experimental data. The conceptual problem is overcome by the hyperbolic diffusion equations (Eq. (9) or higher order approximations with limiting condition (7)), which, in contrast to the parabolic equations, predict that the discontinuity imposed by the sudden jump of concentration propagates at a finite velocity V_D. The diffusive velocity corresponding to Eq. (9) is defined as $V_D = (D/\tau)^{1/2} = v$. This contradiction arises from the difference between the limiting conditions (4) and (7). At the finite value of the diffusion coefficient $D = l^2/\tau$ (see Eq. (4)), the diffusive velocity $V_D = l/\tau$ can be expressed as $V_D = D/l$, which implies that $V_D \to \infty$ at $\tau \to 0$ and $l \to 0$. The limiting condition (7) keeps a finite value of diffusive velocity $V_D = l/\tau$ at $l \to 0$ and $\tau \to 0$, which corresponds to the hyperbolic type of partial differential equations. However, in spite of this inconsistency with the principle of causality, the diffusion equations of parabolic type can be successfully used to study relatively slow processes with characteristic velocity $v_o = h/t_0 \ll V_D$. At high characteristic velocities $v_0 \propto V_D$, the diffusion equation of hyperbolic type should be used. Eq. (9) is similar to hyperbolic heat conduction equation, which is discussed in more details in the following references [2–6,20]. The hyperbolic diffusion Eq. (9) has been successfully used to describe the transition to diffusionless regimes in rapid solidification of metal alloys [12–15] and colloidal crystallization [19].

2.2. Extended irreversible thermodynamics (EIT)

In order to describe the local nonequilibrium processes the extended irreversible thermodynamics [1,2] includes the higher-order fluxes in a set of independent variables. The simplest evolution