



Diffusion–stress coupling in liquid phase during rapid solidification of binary mixtures



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ABSTRACT

An analytical model has been developed to describe the diffusion–viscous stress coupling in the liquid phase during rapid solidification of binary mixtures. The model starts with a set of evolution equations for diffusion flux and viscous pressure tensor, based on extended irreversible thermodynamics. It has been demonstrated that the diffusion–stress coupling leads to non-Fickian diffusion effects in the liquid phase. With only diffusive dynamics, the model results in the nonlocal diffusion equations of parabolic type, which imply the transition to complete solute trapping only asymptotically at an infinite interface velocity. With the wavelike dynamics, the model leads to the nonlocal diffusion equations of hyperbolic type and describes the transition to complete solute trapping and diffusionless solidification at a finite interface velocity in accordance with experimental data and molecular dynamic simulation.

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1. Introduction

Solidification under industrial conditions often involves extremely fast heat and mass transfer at very small time and length scales [1–12], which results in large thermal and concentration gradients and thus induces viscous stresses ahead of the moving solid–liquid interface. The stresses, appeared due to inhomogeneity in the field of temperature and concentration, essentially affect the structural formation of the resulting solid phase. The mechanism of the rapid solidification may be studied more completely if one takes into account the changing stress distribution during the crystallization process. The large thermal and concentration gradients accompanying the phase change processes imply that the processes occur under far from equilibrium condition and the appropriate non-equilibrium approach should be used. The deviation from equilibrium conditions can be characterized through the partition (segregation) coefficient K , which is defined as the ratio of the solid concentration C_S to the liquid concentration C_L at the interface. The local nonequilibrium diffusion model (LNDM) [6–9] uses the local–nonequilibrium diffusion equation of hyperbolic type instead of the classical local–equilibrium diffusion equation of parabolic type. This allows LNDM to describe some important features of rapid solidification at high interface velocity that cannot be explained in the framework of the classical local–equilibrium theory. For example, LNDM predicts that the transition to diffusionless solidification with complete solute trapping $K = 1$

occurs at a finite interface velocity V . The result is in agreement with experimental data [4–9] and references therein, molecular dynamic simulations [3], and phase–field–crystal model [4]. In contrast, the classical, local equilibrium approach predicts that $K \rightarrow 1$ only asymptotically when the interface velocity $V \rightarrow \infty$.

Most studies of rapid solidification to date have focused on solidification near the melting point, where the interface temperature is close to the melting temperature. In recent years, both scientific and practical interest to rapid solidification has been further motivated by the potential to fabricate more advanced materials at deep undercooling such as bulk metallic glasses and nanocrystalline materials [13]. As the sample is cooled, the viscosity increases and the viscous stresses near the interface are significant. It implies that the diffusion–stress coupling plays an important role in solidification at large interface undercooling when the solidification occurs at far from equilibrium conditions. The purpose of this work is to present an analytical model which is based of the local nonequilibrium approach and thus describes the influence of the diffusion–stress coupling on solute diffusion and solute partitioning during solidification under far from equilibrium conditions.

2. Diffusion–stress coupling model

It is well known that non-Fickian diffusion effects, such as case-II and super-case-II diffusion, two-stage sorption, and pseudo-Fickian diffusion, begin to play an important part in polymers and other viscous liquids especially near and below glass transition. The anomalous behavior is usually interpreted as the coupling of viscous stresses and diffusion. During diffusion of small molecules

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in a viscous solution, this coupling, resulting from the swelling due to the solvent, produces a relative motion between neighboring molecules of the solvent, whose mutual friction will emerge in a viscous stress [14]. With allowance for relaxation processes of both the diffusion flux J and the viscous pressure tensor P , the evolution equations for fluxes have the form [14,15]

$$J + \tau \frac{\partial J}{\partial t} = -D \frac{\partial C}{\partial x} + \beta \bar{D} T \frac{\partial P}{\partial x} \quad (1)$$

$$P + \tau_p \frac{\partial P}{\partial t} = \beta \eta_e T \frac{\partial J}{\partial x} \quad (2)$$

where τ is relaxation time of J , τ_p is relaxation time of P , ξ and η are bulk and shear viscosity, respectively, $\eta_e = 4\eta/3 + \xi$, β is a coupling constant describing interaction between diffusion and stress, D is diffusion coefficient, $\bar{D} = D(\partial\mu/\partial C)^{-1}$, μ is chemical potential. Elimination of P from these equations results in the evolution equation for diffusion flux

$$J + (\tau_p + \tau) \frac{\partial J}{\partial t} + \tau_p \tau \frac{\partial^2 J}{\partial t^2} = -D \frac{\partial C}{\partial x} - \tau_p D \frac{\partial^2 C}{\partial t \partial x} + \delta^2 \frac{\partial^2 J}{\partial x^2} \quad (3)$$

where $\delta = \beta T (\bar{D} \eta_e)^{1/2}$ is the diffusion-stress correlation length. Combining this equation with the mass conservation law $\partial C/\partial t = -\partial J/\partial x$, we obtain diffusion equation in the form

$$\frac{\partial C}{\partial t} + (\tau_p + \tau) \frac{\partial^2 C}{\partial t^2} + \tau_p \tau \frac{\partial^3 C}{\partial t^3} = D \frac{\partial^2 C}{\partial x^2} + l^2 \frac{\partial^3 C}{\partial t \partial x^2} \quad (4)$$

where $l = (\delta^2 + \tau_p D)^{1/2}$ is the effective correlation length. Eqs. (3) and (4) demonstrate that the diffusion-stress coupling leads to the nonlocal diffusion effects, which are described by the additional time and mixed derivatives. The model includes the characteristic scales of non-locality: time scales τ and τ_p – relaxation times to local equilibrium; and space scale l (or δ) – correlation length. The nonlocal diffusion equation (4) is of hyperbolic type. It predicts that the discontinuity imposed by the sudden jump of concentration at the boundary of a semi-infinite system propagates at a finite velocity

$$V_D^* = [(\delta^2 + D\tau_p)/\tau\tau_p]^{1/2} \quad (5)$$

which is usually called the diffusive velocity [4–9]. This property of the hyperbolic equation corrects the paradox of infinite propagation velocity associated with the classical diffusion equation of parabolic type, which results from Eq. (4) at $\tau_p = \tau = 0$ and $l = 0$. Let us consider some other important limiting cases of Eq. (4).

2.1. Zero correlation and diffusion relaxation effects

When nonlocal and diffusion relaxation effects can be ignored, i.e. $l = 0$ and $\tau = 0$, Eq. (4) reduces to

$$\frac{\partial C}{\partial t} + \tau_p \frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} \quad (6)$$

This equation, as well as Eq. (4), is of hyperbolic type. It is widely known in heat conduction theory [10,12,14,16–19]. The diffusive velocity associated with Eq. (6) is $V_D = (D/\tau_p)^{1/2}$, which differs from Eq. (5) due to the nonlocal and diffusion relaxation effects.

2.2. Nonzero correlation length

Usually the diffusion relaxation process is much faster than the stress relaxation process, i.e. $\tau_p > 0$ and $l > 0$, but $\tau = 0$. In this case Eq. (4) reduces to

$$\frac{\partial C}{\partial t} + \tau_p \frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} + l^2 \frac{\partial^3 C}{\partial t \partial x^2} \quad (7)$$

This equation is of parabolic type due to the addition mixed derivative (last term in Eq. (7)) in comparison with the hyperbolic equation (6), i.e. from the mathematical point of view the nonzero correlation length l transforms the type of diffusion equation from hyperbolic to parabolic. Physically it implies that the nonlocal effects, arising due to the nonzero correlation length, smooth the imposed discontinuity, creating a continuous wave structure when the information of a change in the concentration at $x = 0$ is felt everywhere immediately even at $x \rightarrow \infty$. It implies an infinite diffusive velocity. 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 $V \ll V_D$. At high characteristic velocities $V \sim V_D$, the diffusion equation of hyperbolic type (4) (or Eq. (6)) should be used. Note that Eq. (7) is analogous to the heat conduction equation, which arises in the two-temperatures systems [16–18].

3. Steady-state regimes

In this section we consider concentration profiles of solute ahead of a planar phase interface moving with constant velocity V . Such profiles arise in many practically important applications such as alloy solidification [1–9], melting phenomena [10,12,18], colloidal crystallization [11], frontal polymerization [15] etc. In a reference frame, attached to the moving interface, Eq. (4) takes the form

$$\begin{aligned} \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} + \tau_p \frac{\partial^2 C}{\partial t^2} + \tau_p V^2 \frac{\partial^2 C}{\partial x^2} \\ = D \frac{\partial^2 C}{\partial x^2} + l^2 \frac{\partial^3 C}{\partial t \partial x^2} + l^2 V \frac{\partial^3 C}{\partial x^3} \end{aligned} \quad (8)$$

This equation can be used to study the interface stability with allowance for the coupling between the diffusion and viscous stresses and this will be done elsewhere. For our purpose it is enough to consider the steady-state version of Eq. (8), which is given as

$$l^2 V \frac{d^3 C}{dx^3} + D(1 - V^2/V_D^2) \frac{d^2 C}{dx^2} - V \frac{dC}{dx} = 0 \quad (9)$$

Heat conduction equations analogous to Eq. (9) arises in the two temperature systems in connection with Stefan problem [18]. The eigenvalues for Eq. (9) are given as [18]

$$\begin{aligned} \lambda_{1,2} = \frac{D(V^2/V_D^2 - 1) \pm [D^2(1 - V^2/V_D^2)^2 + 4l^2 V^2]^{1/2}}{2l^2 V}; \\ \lambda_3 = 0 \end{aligned} \quad (10)$$

The boundary conditions for solute concentration in the liquid phase are: $C(x) \rightarrow C_0$ far from the interface ($x \rightarrow \infty$), where C_0 is the initial concentration, and $C(0) = C_i$, where C_i the concentration at the interface $x = 0$.

3.1. Classical (Fickian) diffusion

Concentration profiles for the steady-state regime $V = const$, obtained from the classical diffusion equation (Eq. (9) with $l \rightarrow 0$ and $V_D \rightarrow \infty$) has the well-known form

$$C(x) = (C_i - C_0) \exp(-xV/D) + C_0 \quad (11)$$

where D/V represents the characteristic width of the diffusion layer ahead of the moving interface. Note that in this case the diffusion layer ahead of the moving interface exists for any value of interface velocity and asymptotically goes to zero only at $V \rightarrow \infty$.

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