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

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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 viscose 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
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]

\[
J + \tau \frac{\partial J}{\partial t} = -D \frac{\partial C}{\partial x} + \beta \frac{\partial D}{\partial x} \frac{\partial P}{\partial x} \tag{1}
\]

\[
P + \tau_p \frac{\partial P}{\partial t} = \beta \eta \frac{\partial J}{\partial x} \tag{2}
\]

where \( \tau \) is relaxation time of \( J \), \( \tau_p \) is relaxation time of \( P \), \( \xi \) and \( \eta \) are bulk and shear viscosity, respectively, \( \eta_0 = 4\eta/3 + \xi \), \( \beta \) is a coupling constant describing interaction between diffusion and stress, \( D \) is diffusion coefficient, \( \bar{D} = D(\partial D/\partial C)^{-3} \), \( \mu \) is chemical potential. Elimination of \( P \) from these equations results in the evolution equation for diffusion flux

\[
J + (\tau_p + \tau) \frac{\partial J}{\partial t} + \tau_p \frac{\partial^2 J}{\partial t^2} = -D \frac{\partial C}{\partial x} + P \frac{\partial^2 C}{\partial x^2} + \beta \frac{\partial^2 J}{\partial x^2} \tag{3}
\]

where \( \delta = \beta \bar{D}(\partial D/\partial C)^{-1/2} \) 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

\[
\alpha \frac{\partial C}{\partial t} + (\tau_p + \tau) \frac{\partial^2 C}{\partial t^2} + \tau_p \frac{\partial^2 C}{\partial t^3} = D \frac{\partial^2 C}{\partial x^2} + \beta \frac{\partial^3 C}{\partial t \partial x^2} \tag{4}
\]

where \( \lambda = (\delta^2 + \tau D)^{-1/2} \) 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 nonlocality: time scales \( \tau \) and \( \tau_p \) - relaxation times to local equilibrium; and space scale \( l \) (or \( \delta \)) - 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

\[
V_D = \left( (\delta^2 + D \tau_p)/\tau \right)^{1/2} \tag{5}
\]

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

\[
\alpha \frac{\partial C}{\partial t} + \tau_p \frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} \tag{6}
\]

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 \( V_D = (D/D_p)^{1/2} \), 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

\[
\alpha \frac{\partial C}{\partial t} + \tau_p \frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} + \beta \frac{\partial^2 C}{\partial t \partial x^2} \tag{7}
\]

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 immediate even at \( x \to \infty \). 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

\[
\alpha \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} + \beta \frac{\partial^2 C}{\partial t \partial x} + \tau_p \frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} + \beta \frac{\partial^3 C}{\partial t \partial x^2} \tag{8}
\]

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

\[
\alpha V \frac{d^3 C}{dx^3} + D \left( 1 - V^2/V_D^2 \right) \frac{d^2 C}{dx^2} - V \frac{dC}{dx} = 0 \tag{9}
\]

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]

\[
\lambda_{1,2} = \left( V^2/V_D^2 - 1 \pm \sqrt{D^2 (1 - V^2/V_D^2)^2 + 4V^2 V_J^2} \right)^{1/2};
\]

\[
\lambda_3 = 0 \tag{10}
\]

The boundary conditions for solute concentration in the liquid phase are: \( C \to C_0 \) far from the interface \( x \to \infty \), 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 \( V = \text{const} \), obtained from the classical diffusion equation (Eq. (9) with \( l \to 0 \) and \( V_D \to \infty \)) has the well-known form

\[
C(x) = (C_i - C_0) \exp(-xV/D) + C_0 \tag{11}
\]

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 \( V \to \infty \).
and, consequently, the solute concentration \( \phi \) is governed by the hyperbolic diffusion equation (6) (or Eq. (12) in steady-state). Using the effective diffusion coefficient, Eq. (13), for parabolic type and the information of a change in the concentration propagates with an infinite velocity. It implies the effective diffusion coefficient, Eq. (14), is nonzero at any value of the interface velocity.

4. Partition coefficient

It is well known that the solid–liquid interface in binary alloys usually leads to solute segregation, which is quantified by the partition coefficient \( K_e = C_S / C_l \). At high interface velocity, there is substantial deviation from the local equilibrium at the interface, which results in the increasing partition coefficient. The increase in the partition coefficient with increasing interface velocity is known as solute trapping and a complete understanding of the trapping process requires the dependence \( K(V) \) on the kinetic and thermodynamic properties of the alloy. There are a number of solute trapping theories. The most widely known is the continuous growth model (CGM) [20], which in the limit of dilute concentrations leads to the following partition coefficient

\[
K(V) = \frac{K_E + V / V_I}{1 + V / V_I}
\]

(15)

where \( K_E \) is the equilibrium partition coefficient, \( V_I \) is the so-called interface diffusive speed. The CGM is based on the local equilibrium diffusion approach and can be used only at relatively low interface velocity. It should be stressed that there is a conceptual difference between \( V_I \) and \( V_D \). The interface diffusive speed \( V_I \) is a kinetic rate parameter for solute segregation at the interface. The value of \( V_I \) cannot be measured directly. Instead, values for \( V_I \) are inferred by fitting the observed dependence of \( K(V) \), Eq. (15), and it was found that \( V_I \) correlates with equilibrium partition coefficient \( K_E \). In contrast, the bulk liquid diffusive velocity \( V_D \) is a purely diffusive parameter – it is the speed of propagation of high frequency diffusive disturbances in the bulk liquid. \( V_D \) does not depend on interface kinetics and in principal can be measured by experiment.

4.1. Hyperbolic diffusion

The concept of the effective diffusion coefficients allows us to extend Eq. (15) for the local nonequilibrium case. First we consider the case when the correlation length is negligible and the solute concentration is governed by the hyperbolic diffusion equation (6) (or Eq. (12) in steady-state). Using the effective diffusion coefficient...
As shown in Fig. 2, the complete solute trapping as a function of the dimensionless interface velocity (solid line) - LNDM (hyperbolic model) \( t_0 = 0 \), Eq. (16); dashed line - diffusion-stress coupling model, Eq. (17), with \( t_0 = 0.2 \); dash-dotted line \(-\omega = 0.5\); dotted line - CGM, Eq. (15).

Coeficient, Eq. (13), one obtains the effective partition coefficient in the form [7–9]

\[
K_{\text{eff}}^H(\varphi) = \begin{cases} 
\frac{\kappa(1-\varphi^2)+\varphi\omega}{1-\varphi^2+\varphi\omega}, & \varphi < 1 \\
1, & \varphi > 1 
\end{cases}
\]

(16)

where \( \varphi = V/V_D \) is dimensionless interface velocity, and \( \omega = V_D/V_t \). Fig. 2 displays the effective partition coefficient Eq. (16) as a function of the dimensionless interface velocity (solid line). As shown in Fig. 2, the complete solute trapping \( K_{\text{eff}}^H(\varphi) = 1 \) is reached at a finite interface velocity \( \varphi \approx 1 \) (or \( V = V_D \)). The result is in agreement with experimental data ([4–9] and references therein), molecular dynamic simulations [3], and phase-field approach [4]. Note that CGM, Eq. (15), predicts complete solute trapping \( K(V) = 1 \) only asymptotically at \( V \to \infty \) (dotted line in Fig. 2).

4.2. Nonlocal effects (parabolic diffusion)

Now let us consider a case when the nonlocal effects play a significant role and the solute concentration is governed by Eq. (7) (or Eq. (9) in steady-state) with the effective diffusion coefficient Eq. (14). In this case we obtain the effective partition coefficient in the form

\[
K_{\text{eff}}^P(\varphi) = \frac{2K_D\varphi^2 + \varphi^2 - 1 + [(1 - \varphi^2)^2 + 4(\varphi t)^2]^{1/2}}{2\varphi^2 - 1 + [(1 - \varphi^2)^2 + 4(\varphi t)^2]^{1/2}} \frac{1}{\omega}
\]

(17)

Fig. 2 shows the partition coefficient, Eq. (17), as a function of the dimensionless interface velocity for different values of \( t_0 \) (dashed and dash-dotted lines). Eq. (17), as well as CGM, results in complete solute trapping \( K_{\text{eff}}^P(\varphi) = 1 \) in an asymptotic manner at \( \varphi \to \infty \). It contrasts to prediction of hyperbolic model, Eq. (16), which leads to complete solute trapping \( K_{\text{eff}}^H(\varphi) = 1 \) at a finite interface velocity \( \varphi = 1 \). When \( \varphi > 1 \), the solute atoms cannot escape the interface and solute concentration near the interface is equal to the solute concentration far from the interface, which implies the diffusionless solidification with complete solute trapping at steady-state. It should be noted that in this section we assume that \( \tau = 0 \). In case of \( \tau > 0 \), the diffusion flux relaxation effects lead to the hyperbolic diffusion equation (4) with a finite velocity of diffusive disturbances \( V_D^\tau \). In this case the complete solute trapping can be reached at \( V = V_D^\tau \) due to relaxation processes whereas the coupling effects with nonzero correlation length play the most significant role at \( V \approx V_D < V_D^\tau \).

5. Discussion

The present model, Eqs. (1)–(2), implies that the diffusion-stress coupling begins to play a significant role in solidification mechanism when the characteristic time scale of the process is comparable with relaxation times \( \tau \) and \( \tau_p \). This occurs when the sample is cooled because the relaxation times and viscosity increase dramatically with decreasing temperature. Indeed, the Maxwell relaxation time of stresses in supercooled liquids near melting temperatures is estimated as \( \tau \approx 3 \times 10^{-14} \) s [13]. If one assumes that the stress developed by the interface extends \( \approx 0.5 \) nm into the liquid, i.e., a few monolayers, then the time for the crystallization front to pass through this region is \( t_0 \approx 5–10 \times 10^{-12} \) s, which is much longer than the relaxation time. As a consequence, one can assume the liquid and solid are in quasi-equilibrium near melting point. At lower temperatures near the glass transition stress relaxation time \( \tau \approx 10^{-11} \) s, i.e. \( \tau \gg t_0 \) [13], which implies that the stress relaxation may significantly affect the solidification mechanism. The experimental date [22] and molecular dynamic simulations [13,22] demonstrate that the solidification mechanism at deep undercooling differ substantially from predictions of classical collision-limited models. The complete set of the data could be explained within the framework of a defect model of crystallization, which assumes that at low-temperature kinetic arrest leads to stresses ahead of the interface [13]. These results clearly demonstrate that the diffusion-stress coupling near the phase interface plays a decisive role in solidification of deeply undercooled melts, which justifies the present diffusion-stress coupling model (1)–(2) for binary mixtures.

Grain refinement during rapid solidification has been widely observed in experiments [1,2,21]. This phenomenon may be caused by stresses generated as a result of inter-dendritic fluid flow induced by pressure and concentration gradients [2]. It has been observed in discontinuous precipitation that a grain boundary between two matrix grains may sometimes migrate together with a new precipitating phase and the grain boundary sometimes bulges out and leaves the new phase behind [21]. One of the possible mechanisms to explain these phenomena is the change in composition that gives rise to coherency stresses, which provide a driving force for the migration of a boundary into the stressed region [21]. In polymers the super-case-II diffusion has been experimentally observed for ethanol, propanol and butanol in thin films of PMMA ([14,15] and references therein). The experimental results have been explained by taking into account the existence of the viscous stress ahead of the moving polymerization front. This has been done by using the diffusion-stress coupling model (1)–(2) adapted for super-case-II diffusion in polymers [13,14], which allows us to use the present model for studying solidification of binary mixtures.

Low temperature chemical reactions, such as hydrocarbon chlorination, olefin hydrobromination, polymerization and copolymerization, can propagate as traveling waves with velocities much higher than it is expected from Arrhenius mechanism [23]. The observed phenomena have been explained by a coupling between chemical transformation and local stress arising from high temperature gradient in the wave front [23].

Thus our diffusion-stress coupling model (1)–(2) for far from equilibrium solidification of binary mixtures is consistent with the experimental results and molecular dynamic simulation of different phase transformations, such as solidification [1,2,21,22], polymerizations [14,15], and low temperature chemical reactions [23].
6. Conclusion

The diffusion-stress coupling in the liquid phase during rapid solidification of binary mixture leads to the non-Fickian solute diffusion effects. The solute diffusion in the liquid phase is nonlocal both in time and space and can be described by the non-local diffusion equations of parabolic or hyperbolic type depending on the relation between the internal space-time scales and the characteristic scales of the process under consideration. In steady-state regimes the coupling effects can be described by the effective diffusion coefficients, which depend on the interface velocity and correlation length. In particular, the effective diffusion coefficients are used to modify the continuous growth model of solute trapping to calculate the solute partition coefficient with allowance for the diffusion-stress coupling effects. The diffusion-stress coupling plays the most pronounced role at high interface velocity or at high interface undercooling when the interface temperature is near and below glass transition.

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