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Insight into interrelation between single-particle and collective diffusion in binary melts

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HIGHLIGHTS

- A relation for self and collective diffusion coefficients in binary melts is derived.
- The relation naturally reveals cross-correlation effects in collective diffusion.
- Application of the relation for interpretation of experimental data is demonstrated.

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ABSTRACT

The interrelation between the kinetics of single-particle (tracer) and collective diffusion in a binary melt is investigated theoretically within the framework of the Mori–Zwanzig formalism of statistical mechanics. An analytical expression for the Onsager coefficient for mass transport and two self-diffusion coefficients of species in a binary melt is derived using analysis based on the generalized Langevin equation. The derived expression naturally accounts for manifestation of microscopic (dynamic) cross-correlation effects in the kinetics of collective diffusion. Hence, it presents an explicit extension of the well-known Darken equation which is currently often used for expressing collective interdiffusion in terms of the two self-diffusion coefficients. An application of our analysis for interpretation of recent experimental data on the interrelation between the kinetics of single-particle and collective diffusion in Al-rich Ni–Al melts is demonstrated.

1. Introduction

At present, reliable experimental data for the mass transport coefficients in liquid alloys are very limited. This is due to both high cost and many technical difficulties related to the diffusion measurements in the liquid state [1–8]. However, the knowledge of these coefficients is of significant importance for engineering the crystalline microstructure during solidification of the alloys [9,10]. As a result, the mass transport coefficients often remain the key assumptions in the phase field based modelling of the complex branched morphologies exhibited by dendrites during solidification from melt [9,10]. Therefore, it is highly desirable to establish theoretical relations between different mass transport coefficients in order to enable a quantitative prediction of unknown coefficients from those that can be measured most reliably in experiment [11].

It is well known that for a binary system the so-called Darken equation [12] gives a famous link between the two tracer diffusion coefficients, D_1 and D_2, and the interdiffusion coefficient, D_c, as

$$D_c = \Phi \left(c_2 D_1 + c_1 D_2 \right) , \tag{1}$$

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where c_1 and c_2 ($c_1 + c_2 = 1$) are the atomic (mole) fractions of species 1 and 2, respectively, and Φ is the thermodynamic factor. The thermodynamic factor Φ is related to the second derivative of the molar Gibbs free energy G/N with respect to the composition at constant temperature T and pressure P, as $\Phi = \frac{c_1 c_2}{k_B T}\left(\frac{\partial^2 (G/N)}{\partial c_1^2}\right)_{T,P} = \frac{c_1 c_2}{k_B T}\left(\frac{\partial^2 (G/N)}{\partial c_2^2}\right)_{T,P}$, where N is the number of atoms in the system volume V and k_B is the Boltzmann constant. This equation was originally introduced in 1948 to describe data on interdiffusion in a binary crystal coupled via the vacancy mechanism primarily on the basis of macroscopic arguments. Later, in 1961, Manning [13] put forward an extension of the Darken equation, in the general context of chemical diffusion in crystals, to the form

$$D_c = \Phi S \left(c_2 D_1 + c_1 D_2\right), \tag{2}$$

ingeniously demonstrating that a certain correction factor of the microscopic kinetic origin, S, must be included. As a result, Eq. (2) is sometimes called the Darken–Manning equation [14].

From the other side, using the Onsager formalism of the thermodynamics of irreversible processes [15,16], it can be generally shown [17] that for an isotropic binary melt the ratio D_c/Φ is related to the phenomenological coefficient L_{cc} (or renormalized coefficient $\tilde{L}_{cc}$), which links the interdiffusion flux to conjugated thermodynamic force, as

$$\frac{D_c}{\Phi} = \frac{V k_B T}{N c_1 c_2} L_{cc} = \tilde{L}_{cc}. \tag{3}$$

Therefore, generally speaking, the correction factor S characterizes cross-correlation effects that arise in collective diffusion process.

Thus, as can be seen from Eqs. (2) and (3), the central goal of a microscopic kinetic description of mass transport in a binary system is to find a reliable expression (i.e., a more sophisticated alternative to the Darken equation) for the Onsager kinetic coefficient $\tilde{L}_{cc}$ for mass transport. In particular, concerning the diffusion kinetics in binary mixing melts, which exhibit chemical ordering, we should note that both recent experimental measurements [8] and molecular dynamics (MD) simulations [2,11,18] indicate that the correction factor S is expected to be generically less than unity, $S \lesssim 1$, in such systems.

In this communication, making use of the formalism developed by Zwanzig [19,20] and Mori [21,22], we present an analysis to derive an exact analytical expression for $\tilde{L}_{cc}$ (and S) for a binary melt. This expression allows us to suggest a concept of a binary liquid random alloy for which the correction factor $S = S_0 \leq 1$ can be expressed only in terms of: (i) the ratio of the tracer diffusion coefficients D_1/D_2, (ii) the ratio of the atomic masses m_1/m_2, and (iii) the alloy composition c_1 (or c_2). We argue that for binary mixing melts exhibiting chemical ordering (such as Ni–Al melts [11]) the correction factor should typically be $S < S_0$, while for binary melts where precursors of liquid–liquid demixing are important (such as Cu–Ag melts [11]) the correction factor should be $S > S_0$. Furthermore, we point out that in thermal equilibrium the correction factor should be within the range $0 \leq S \leq 2S_0$, which is constrained by the energy of thermal fluctuations (thermal energy). Finally, we employ our theoretical findings for interpretation of recent experimental data [8] on the correction factor to the Darken equation in Al-rich Ni–Al melts.

2. Theoretical treatment

Let us consider, at thermal equilibrium, an isotropic binary liquid alloy consisting of N_1 atoms of mass m_1 and N_2 atoms of mass m_2 enclosed in a fixed volume V ($N = N_1 + N_2$, $c_1 = N_1/N$ and $c_2 = N_2/N$). Next, one can write the generalized Langevin equations for the velocities $\boldsymbol{v}_{1i}(t)$ ($i \in [1 \dots N_1]$) and $\boldsymbol{v}_{2j}(t)$ ($j \in [1 \dots N_2]$) of arbitrarily tagged atoms of species 1 and 2, conventionally decomposing the total forces $\boldsymbol{f}_{1i}(t)$ and $\boldsymbol{f}_{2j}(t)$ acting on the tagged particles according to the Mori–Zwanzig formalism [19–23], as

$$m_1 \frac{d\boldsymbol{v}_{1i}(t)}{dt} = \boldsymbol{f}_{1i}(t) = -m_1 \int_0^t K_1\left(t - t'\right) \boldsymbol{v}_{1i}\left(t'\right) dt' + \boldsymbol{R}_{1i}(t), \tag{4}$$

$$m_2 \frac{d\boldsymbol{v}_{2j}(t)}{dt} = \boldsymbol{f}_{2j}(t) = -m_2 \int_0^t K_2\left(t - t'\right) \boldsymbol{v}_{2j}\left(t'\right) dt' + \boldsymbol{R}_{2j}(t). \tag{5}$$

In these equations, $K_1(t)$ and $K_2(t)$ are the memory kernels for the evolution of the systematic, frictional forces (viscous drags) acting on the tagged atoms at time t and proportional (but opposite) to the velocities of the tagged atoms at all previous times in the past. Meanwhile, $\boldsymbol{R}_{1i}(t)$ and $\boldsymbol{R}_{2j}(t)$ are the random forces which: (i) vanish in the mean $\langle \boldsymbol{R}_{1i}(t) \rangle = 0$ and $\left\langle \boldsymbol{R}_{2j}(t) \right\rangle = 0$ ($\langle \cdots \rangle$ means the statistical time average at thermal equilibrium), and (ii) are uncorrelated with $\boldsymbol{v}_{1i}(0)$ and $\boldsymbol{v}_{2j}(0)$, respectively. In particular, the random forces describe the non-linear effects, initial transient processes and the dependence on the thermal fluctuations in the velocities of the surrounding atoms. Instantaneously, the total and random forces are the same $\boldsymbol{f}_{1i}(0) = \boldsymbol{R}_{1i}(0)$ and $\boldsymbol{f}_{2j}(0) = \boldsymbol{R}_{2j}(0)$ (see Eqs. (4) and (5)), but the two quantities evolve differently in time in such a way that the following relations $\langle \boldsymbol{R}_{1i}(t) \boldsymbol{v}_{1i}(0) \rangle = 0$ and $\left\langle \boldsymbol{R}_{2j}(t) \boldsymbol{v}_{2j}(0) \right\rangle = 0$ are preserved for all times [19–23].