



Report Number 09/05

Onsager reciprocity in premelting solids

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Received: date / Accepted: date

Abstract The diffusive motion of foreign particles dispersed in a premelting solid is analyzed within the framework of irreversible thermodynamics. We determine the mass diffusion coefficient, thermal diffusion coefficient and Soret coefficient of the particles in the dilute limit, and find good agreement with experimental data. In contrast to liquid suspensions, the unique nature of premelting solids allows us to derive an expression for the Dufour coefficient and independently verify the Onsager reciprocal relation coupling diffusion to the flow of heat.

PACS 05.70.Ln · 05.70.Np · 64.70.dm · 47.57.s

The melting of any material is normally initiated at one of its free surfaces at temperatures below the bulk melting temperature, T_m , by the formation of a thin liquid – *interfacially premelted* – film. This surface phase transition has been observed at the interfaces of solid rare gases, quantum solids, metals, semiconductors and molecular solids including ice, allowing the liquid phase to persist in the solid region of the bulk phase diagram [1]. When a premelted film forms around a foreign particle within a subfreezing solid, the particle can migrate under the influence of a temperature gradient, which produces a thermomolecular pressure gradient, a phenomenon referred to as regelation or thermodynamic buoyancy [2,3]. This has implications for many geophysical problems, such as frost heave, glacier dynamics and the interpretation of ice cores [1]. In addition, premelting and regelation play important roles in the fabrication of particle-reinforced composite structures [4, 5] and may provide a new mechanism for the tailoring of nanostructures presently of interest across materials science and engineering [6], [7]. In the general context of the statistical physics underlying diffusive motion, the study of particle motion in premelting solids provides a novel setting to explore concepts in irreversible thermodynamics in a regime not found in the classical setting where the solvent is in the liquid state.

Here we analyze regelation and associated phenomena within the framework of irreversible thermodynamics. We demonstrate that, in addition to motion under the influence of a temperature gradient, foreign

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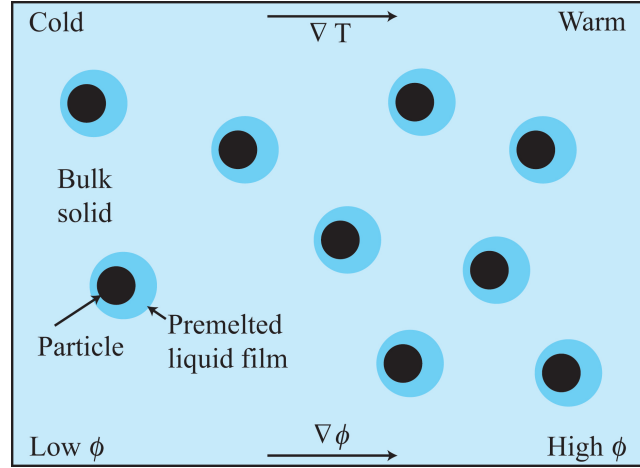


Fig. 1 Schematic diagram of a premelting solid containing foreign inclusions at local volume fraction ϕ .

particles can undergo constrained Brownian motion owing to thermal fluctuations in the premelted film. We determine the diffusivity in the dilute limit and relate it to the Stokes-Einstein diffusivity of particles in the bulk melt. Furthermore, the motion of a particle is shown to induce a reciprocal effect – a heat flux due to the release and absorption of latent heat on opposite sides of the particle. We show that this effect is described by the Onsager relation coupling mass diffusion to heat flux.

We consider a suspension of spherical particles of radius R randomly distributed in a bulk solid. For temperatures T near but less than T_m , each particle is surrounded by a premelted film of thickness d that facilitates both the particles' constrained Brownian diffusion and their directed motion parallel to temperature gradients (figure 1). From linear irreversible thermodynamics [8,9], the equations describing the flux of particles and heat are (see Appendix)

$$\mathbf{J} = -D\nabla\phi + (1 - \phi)\phi D_T \nabla T, \quad (1)$$

$$\mathbf{q} = -k\nabla T + (1 - \phi)\Pi_\phi T_m D_q \nabla\phi, \quad (2)$$

where $\mathbf{J} = \phi\mathbf{V}$ is the particle volume flux, with ϕ the volume fraction of particles and \mathbf{V} the local average particle velocity. In equation (2) \mathbf{q} is the heat flux, k is the thermal conductivity and Π_ϕ is the derivative of the osmotic pressure of the particles with respect to volume fraction. The coefficients D , D_T and D_q are, respectively, the mass diffusion coefficient, thermal diffusion coefficient and Dufour coefficient. Here, in the dilute limit, we determine these quantities as functions of the undercooling $\Delta T = T_m - T$.

The second term on the right hand side of equation (1) accounts for the Soret effect, in which a temperature gradient generates motion of the particles. We define D_T to be positive when the particles migrate towards their warm sides. Whereas in liquid suspensions the Soret effect is a complex phenomenon, with the Soret coefficient $S_T = D_T/D$ often changing sign as the temperature increases [10–12], in premelting solids, in the absence of other effects, the particles always appear to migrate towards higher temperatures. Furthermore, the Soret coefficient is several orders of magnitude *larger* than in liquid systems.

The second term in equation (2) represents the Dufour effect, in which a concentration gradient gives rise to a flow of heat. Using the principle of microscopic reversibility, Onsager proved that the Dufour coefficient D_q is equivalent to the thermal diffusion coefficient D_T [9,8]. There has, however, been significant controversy over the range of validity of the Onsager relations [13,14] and ongoing attempts to prove them in particular cases [15–17]. We show that, in the dilute limit, so long as the temperature gradient satisfies linear irreversible thermodynamics and is constant on the scale of the particle, the Onsager relation is satisfied.

Foreign particles dispersed throughout a solid near its melting temperature undergo random motion owing to thermal fluctuations in their premelted films. (As a concrete example one might consider colloidal particles in ice.) Their random walk is driven by the thermodynamic force

$$\mathbf{F}_B = -\frac{v_p}{\phi} \nabla \Pi, \quad (3)$$

where Π is the osmotic pressure of the particles and $v_p = \frac{4}{3}\pi R^3$ is the particle volume [18]. For temperatures near T_m in the dilute limit the osmotic pressure is given by the van't Hoff equation

$$\Pi = \frac{\phi}{v_p} k_b T_m, \quad (4)$$

where k_b is Boltzmann's constant.

Owing to viscous flow in the premelted films, the particle velocity \mathbf{V} is accompanied by a net lubrication force given by

$$\mathbf{F}_\eta = -v_p \frac{\eta}{K} \mathbf{V}, \quad (5)$$

where $K = d^3/6R$ is a permeability coefficient [19] and η is the dynamic viscosity of the premelted liquid film.

In mechanical and thermal equilibrium, the total force $\mathbf{F}_\eta + \mathbf{F}_B \equiv 0$, giving

$$\phi \mathbf{V} = -\frac{d^3 k_b T_m}{8\pi \eta R^4} \nabla \phi, \quad (6)$$

Comparing this result with equation (1) yields

$$D = \left(\frac{3d^3}{4R^3} \right) D_0 \quad \text{where} \quad D_0 = \frac{k_b T_m}{6\pi \eta R}. \quad (7)$$

Hence we see that the premelting-controlled Brownian diffusivity D differs from the Stokes-Einstein diffusivity D_0 of particles in bulk liquid by the factor $3d^3/4R^3$. Preliminary studies using X-ray photon correlation spectroscopy show promise in testing equation (7) [20].

In the presence of a temperature gradient variations in the thickness of the premelted film over the surface of an isolated particle lead to a thermomolecular pressure gradient force causing the particle to move [1–3]. By integrating the thermomolecular pressure over the surface of a particle this force has been obtained as

$$\mathbf{F}_T = v_p \mathcal{P}_T \nabla T, \quad (8)$$

where $\mathcal{P}_T \equiv \rho_s q_m / T_m$ is the thermomolecular pressure coefficient characterizing the magnitude of the intermolecular forces responsible for the premelted film [1], and ρ_s and q_m are the mass density and latent heat of fusion, respectively, of the bulk solid [2]. (We express Eq. (8) differently than in [2] for consistency with the present extension of that work.) In mechanical equilibrium the thermomolecular force is balanced by the viscous force \mathbf{F}_η leading to the relation

$$\mathbf{V} = \frac{K}{\eta} \mathcal{P}_T \nabla T, \quad (\nabla \phi = 0). \quad (9)$$

Comparing (1) with (9) in the limit $\phi \rightarrow 0$ yields an expression for the thermal diffusion coefficient

$$D_T = \frac{K}{\eta} \mathcal{P}_T = \frac{d^3 \rho_s q_m}{6R \eta T_m}. \quad (10)$$

The conditions for the validity of equations (7) and (10) are similar to those which apply to Stokes-Einstein descriptions of particle diffusion in liquids [21]. Specifically, the size of the particles should be much larger than the size of the liquid molecules. In premelting solids there is the additional requirement that the film thickness be small relative to the particle size in order for lubrication theory (and hence equation (5)) to apply.

We can test Equation (10) using experimental results from a study in which a $12.7 \mu\text{m}$ glass bead encased in ice was moved by imposition of a linear temperature gradient [22]. Figure 2 shows experimental measurements (stars) of $D_T = \mathbf{V}/\nabla T$ as a function of the undercooling, ΔT . Using these data the premelted film thickness at each temperature can be obtained from equation (10). The results (circles) are shown in the inset, along with the experimental measurements of $d(\Delta T)$ made by Ishizaki *et al.* [23] on porous silica glass (triangles).

In general, the premelted layer thickness will depend upon the undercooling, the interfacial curvature (through the Gibbs-Thomson effect), and the form of the particle-solid interactions according to $\Delta T =$

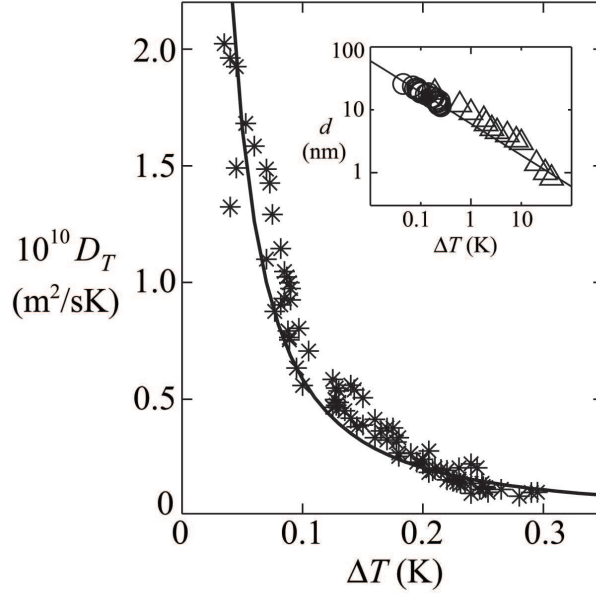


Fig. 2 Thermal diffusion coefficient of silica particles in ice. The data (stars) are from Romkens and Miller [22]. The inset shows the premelted film thickness $d(\Delta T)$ obtained from the theoretical prediction using equation (10) (circles), along with the experimental measurements of Ishizaki *et al.* [23] (triangles). The solid curve appearing in *both* the main figure and the inset is a fit to the Romkens and Miller [22] data for D_T . This demonstrates that the expression $d = 6.0\Delta T^{-0.5}(\text{nm})$ inserted in equation (10) yields a good fit to the D_T data. Moreover, because the result that $d = 6.0\Delta T^{-0.5}(\text{nm})$ does not rely on the experimental data of Ishizaki *et al.* [23] we believe that this is a demonstration of the agreement between the predictions from equation (10) and the data of Ishizaki *et al.* [23]

$\gamma\kappa/\mathcal{P}_T + T_m \left(\frac{\lambda_v}{d}\right)^{-v}$, where γ is the interfacial energy, $\kappa = 2/R$ is the interface curvature, and v and λ_v are constants that depend upon the particular intermolecular forces present [19], [24]. For a given particle size R , the Gibbs-Thomson effect can be neglected as long as $\Delta T > 2\gamma T_m/\rho_s q_m R$, which for $R \sim 10 \mu\text{m}$ is $\Delta T > 0.005 \text{ K}$ and for $R \sim 10 \text{ nm}$ is $\Delta T > 5 \text{ K}$. Whence, throughout our treatment T_m and d are independent of the particle size R . Therefore, we can fit the film thickness data (circles) according to $d = \lambda_v (\Delta T/T_m)^{-1/v}$ giving $\lambda_v/T_m = 6.0 \text{ nm}$ and $v = 2$ (solid line in inset to figure 2). This fit is extrapolated to larger ΔT and shows good agreement with the independent measurements of film thickness (triangles) from Ishizaki *et al.* [23]. It is then used in equation (10) to produce the curve in the main panel of figure 2.

The Soret coefficient S_T is defined as

$$S_T \equiv \frac{1}{\phi(1-\phi)} \frac{\nabla\phi}{\nabla T} \Big|_{\mathbf{J}=0}. \quad (11)$$

Combining (1), (7) and (10) with (11) gives

$$S_T = \frac{D_T}{D} = \frac{\mathcal{P}_T}{\mathcal{E}_T}, \quad (12)$$

in terms of fundamental quantities, where here we emphasize that $\mathcal{E}_T \equiv k_b T_m/v_p$ is the ensemble averaged kinetic energy/volume (thermal kinetic energy) of a Brownian particle. Thus in premelting solids the Soret coefficient represents the ratio of the thermomolecular pressure coefficient to the thermal kinetic energy of a Brownian particle and is predicted to be independent of premelted film thickness and undercooling. For micron sized particles in ice equation (12) yields $S_T \sim 10^8 \text{ K}^{-1}$ thereby illustrating the dominance of the thermomolecular force over the Brownian force in premelting solids. As a comparison, for μm sized particles in liquids $S_T \sim 10^{-2} \text{ K}^{-1}$ [10]. It is hoped that these forms of S_T provide an ideal experimental target. One promising method for obtaining both D and D_T simultaneously is thermal diffusion forced Rayleigh scattering [25].

When foreign particles of volume v_p are inserted into a premelting host material the heat of fusion absorbed by the solid per unit volume of particles is $\rho_s q_m$. Whereas, when particles move through an initially isothermal solid they melt material ahead, absorbing latent heat, while freezing solid behind, releasing heat. The volumetric heat of transport characterizing this phenomenon is defined by

$$Q_v^* \equiv \frac{\mathbf{q}}{\mathbf{J}} \Big|_{\nabla T=0} = -(1-\phi)\Pi_\phi T_m \frac{D_q}{D}, \quad (13)$$

where the second equality follows from (1) and (2). Hence, physically, Q_v^* represents the sensible heat released by an arbitrarily isolated part of the system per unit volume of particles diffusing into it (e.g., [26, 27]) and we obtain $Q_v^* = -\rho_s q_m$.

We verify the reciprocal relation coupling mass diffusion to heat flux in our system by inserting (4), (7), (10) and $Q_v^* = -\rho_s q_m$ into equation (13) and taking the limit $\phi \rightarrow 0$ to obtain

$$D_q = D_T. \quad (14)$$

If the Onsager relation (14) holds also at higher concentrations, (11), (13) and (14) can be used to obtain an expression for the concentration dependence of the Soret coefficient:

$$S_T = -\frac{Q_v^*}{(1-\phi)\Pi_\phi T_m}. \quad (15)$$

The Onsager relation will break down when the temperature gradient varies significantly over the surface of a particle because, as noted by Rempel *et al.* [2], under these circumstances the thermomolecular pressure gradient will vary over the surface of the particle and hence the expression (8) for the thermomolecular force will no longer hold. Such a constraint on ∇T is related to the issue of the validity of linear irreversible thermodynamics as embodied in equations (1) and (2). This is because for these relations to be applicable to this setting ∇T must not vary on the particle scale. Nonetheless, for most experimental situations envisaged the temperature gradient is sufficiently small that linear irreversible thermodynamics is valid and the Onsager relation holds.

We have shown the complimentary roles that interfacial premelting plays in both the regelation and Brownian motion of foreign particles in bulk solids. In the dilute limit, within the framework of linear irreversible thermodynamics, the Brownian diffusivity and Soret coefficient have been determined. Furthermore, in premelting solids the heat of transport can be explicitly calculated, leading to a verification of the Onsager relation coupling mass diffusion to the flow of heat.

Acknowledgements This research was supported by the Department of Energy (DE-FG02-05ER15741) and by the U.S. National Science Foundation (OPP0440841). S.S.L.P. acknowledges support from the King Abdullah University of Science and Technology (KAUST), Award No. KUK-C1-013-04. M.J.S. acknowledges support from a U.S. National Science Foundation Graduate Research Fellowship. J.S.W. is grateful for support from the Wenner-Gren Foundation, the Royal Institute of Technology and NORDITA all in Stockholm.

Mass and heat fluxes

Here we show that equations (1) and (2) can be derived from the irreversible thermodynamic treatment of the flux of mass and heat in a two-component hydrostatic mixture (cf., equations (XI.226) and (XI.227) of [8]), viz.,

$$\mathbf{J}_1 = -\rho D \nabla c_1 - \rho c_1 c_2 D_T \nabla T, \quad (16)$$

$$\mathbf{J}_q = -k \nabla T - \rho_1 \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,P} T D_q \nabla c_1. \quad (17)$$

Here $\mathbf{J}_1 = \rho_1(\mathbf{v}_1 - \mathbf{v})$ is the mass flux of component 1 relative to the barycentric velocity $\mathbf{v} = c_1 \mathbf{v}_1 + c_2 \mathbf{v}_2$, $c_j = \rho_j/\rho$ is the mass fraction of j which has a partial mass density ρ_j , $\rho = \rho_1 + \rho_2$ is the mixture density, and \mathbf{v}_j is the velocity of j with respect to the laboratory frame. The so-called reduced heat flux is \mathbf{J}_q' , where T is absolute temperature, P is the mixture pressure and μ_j is the chemical potential of j . By definition

$$c_1 + c_2 = 1 \quad \text{and} \quad \mathbf{J}_1 + \mathbf{J}_2 = 0. \quad (18)$$

With (18) equations (16) and (17) can be written as

$$\mathbf{J}_2 = -\rho D \nabla c_2 + \rho c_1 c_2 D_T \nabla T, \quad (19)$$

$$\mathbf{J}'_q = -k\nabla T - \rho_1 \left(\frac{\partial \mu_1}{\partial c_2} \right)_{T,P} T D_q \nabla c_2. \quad (20)$$

It is convenient to write equations (19) and (20) in terms of the partial density ρ_2 . To achieve this we use the thermodynamic identity (equation XI.99 of [8])

$$\left(\frac{\partial \rho_2}{\partial c_2} \right)_{T,P} = \rho^2 v_1, \quad (21)$$

where v_1 is the partial specific volume of component 1, approximately equal to

$$v_1 = 1/\rho_s, \quad (22)$$

where ρ_s is the density of pure component 1 at T and P . Additionally, we make use of the fact that the mass flux can be written in terms of the volume average velocity $\mathbf{v}^0 = \rho_1 v_1 \mathbf{v}_1 + \rho_2 v_2 \mathbf{v}_2$ using the thermodynamic identity $\rho_1 v_1 + \rho_2 v_2 = 1$ to obtain

$$\mathbf{J}_2^0 = \rho v_1 \mathbf{J}_2 \quad (23)$$

where $\mathbf{J}_2^0 = \rho_2(\mathbf{v}_2 - \mathbf{v}^0)$.

With (21), we rewrite (19) in the form of (23) and this and (20) become

$$\mathbf{J}_2^0 = -D\nabla \rho_2 + v_1 \rho_1 \rho_2 D_T \nabla T, \quad (24)$$

$$\mathbf{J}'_q = -k\nabla T - \rho_1 \left(\frac{\partial \mu_1}{\partial \rho_2} \right)_{T,P} T D_q \nabla \rho_2. \quad (25)$$

For a dispersion of hard spherical particles $v_2 = 1/\rho_p$, where ρ_p is the constant mass density of an individual particle, in which case (24) and (25) can be written as

$$\mathbf{J} = -D\nabla \phi + \phi(1 - \phi) D_T \nabla T, \quad (26)$$

$$\mathbf{q} = -k\nabla T - \rho_1 \left(\frac{\partial \mu_1}{\partial \phi} \right)_{T,P} T D_q \nabla \phi, \quad (27)$$

where $\mathbf{J} = \phi(\mathbf{v}_2 - \mathbf{v}^0)$ is the particle volume flux, $\phi = \rho_2/\rho_p$ is the volume fraction of particles and $\mathbf{q} = \mathbf{J}'_q$. As shown by de Groot and Mazur, in closed systems in which v_1 and v_2 are constant, the volume average velocity \mathbf{v}_0 is zero, in which case (26) reduces to (1). Inserting the thermodynamic relation $(\partial \mu_1 / \partial \phi)_{T_m, P_m} = -(1/\rho_s) \Pi_\phi$ into (27) gives equation (2), where $1 - \phi = \rho_1/\rho_s$ and $\Pi_\phi = (\partial \Pi / \partial \phi)_{T_m, P_m}$ at a reference state of bulk coexistence.

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