Onsager reciprocity in premelting solids

S. S. L. Peppin$^1$, M. Spannuth$^1$, and J. S. Wettlaufer$^{1,2}$

$^1$Department of Geology and Geophysics and $^2$Department of Physics
Yale University, New Haven, CT, 06520

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The diffusive motion of colloidal 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.

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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. When $T \approx T_m$, the premelted film is thicker than the correlation lengths of the solid-liquid interfaces and hence the total free energy of the (planar-planar) system is represented as a linear combination of bulk and interfacial terms (this latter contains both the interfacial energy and the long ranged volume-volume interactions which are also forces/area in such a system). The total free energy of a curved interfacially melted system includes in addition the Gibb-Thomson effect, which, while contributing to the premelted film thickness $d$, one can prove produces no net thermodynamic force over a closed surface. Nonetheless, 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. Here we analyze this and related phenomena within the framework of irreversible thermodynamics and demonstrate that in addition to motion under the influence of a temperature gradient, the particle 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). From linear irreversible thermodynamics, the equations describing the flux of particles and heat are

$$J = -D\nabla \phi + (1 - \phi)\phi D_T \nabla T,$$

$$q = -k \nabla T + (1 - \phi)\Pi_\phi T_m D_\phi \nabla \phi,$$

where $J = \phi V$ is the particle volume flux, with $\phi$ the volume fraction of particles and $V$ the local average particle velocity. In equation (2) $q$ is the heat flux, $k$ is the thermal conductivity and $\Pi_\phi$ is the derivative of the osmotic pressure of the particles with respect to volume fraction. The coefficients $D$, $D_T$ and $D_\phi$ 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 \[6\ [7\], in premelting solids 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 \(D_N\) is equivalent to the thermal diffusion coefficient \(D_T\) \[4\ [5\]. There has, however, been significant controversy over the range of validity of the Onsager relations \[8\ [9\] and ongoing attempts to prove them in particular cases \[10\ [11\ [12\]. 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.

Colloidal particles dispersed throughout a solid near its melting temperature undergo random motion owing to thermal fluctuations in their premelted films. Their random walk is driven by the thermodynamic force

\[ F_B = -\frac{\nu_T^2}{\phi} \nabla \Pi, \] (3)

where \(\Pi\) is the osmotic pressure of the particles and \(\nu_T = \frac{4}{3} \pi R^3\) is the particle volume \[13\]. For temperatures near \(T_m\) in the dilute limit the osmotic pressure is given by the van’t Hoff equation

\[ \Pi = \frac{\phi}{\nu_T} k_b T_m, \] (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

\[ \mathbf{F}_n = -\nu_T \eta \mathbf{V}, \] (5)

where \(K = d^3/6R\) is a permeability coefficient \[13\] and \(\eta\) is the dynamic viscosity of the premelted liquid film.

In mechanical and thermal equilibrium, the total force \(\mathbf{F}_n + \mathbf{F}_B \equiv 0\), giving

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

Comparing this result with equation \[1\] yields

\[ D = \left( \frac{3d^3}{4R^3} \right) D_0 \quad \text{where} \quad D_0 = \frac{k_b T_m}{6 \pi \eta R}. \] (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 \[7\ [15\].

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 \[1\ [2\ [3\]. By integrating the fluid pressure over the surface of a particle this force has been obtained as

\[ \mathbf{F}_T = \nu_T \mathcal{P}_T \nabla T, \] (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 \(\rho_s\) 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 \(\mathbf{F}_n\) leading to the relation

\[ \mathbf{V} = \frac{K}{\eta} \mathcal{P}_T \nabla T, \] (9)

Comparing \[1\] with \[9\] in the limit \(\phi \to 0\) yields an expression for the thermal diffusivity coefficient

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

This relation can be tested experimentally using the results of a study in which a 12.7 \(\mu m\) glass bead encased in ice was moved by imposition of a linear temperature gradient \[16\]. Figure 2 shows experimental measurements (stars) of \(D_T = \mathcal{V}/\nabla T\) as a function of the undercooling. Using measurements of \(d = d(\Delta T)\) \[17\ [18\] in equation \[10\] we can predict \(D_T(\Delta T)\) which is shown by the solid lines. Clearly the agreement between theory and experiment is good. The deviation at small \(\Delta T\) may be due to an overestimation of the film thickness by Ishizaki et al. \[17\] owing to curvature effects in their system, which become important as \(\Delta T\) approaches 0.

The Soret coefficient \(S_T\) is defined as

\[ S_T \equiv \frac{1}{\phi(1 - \phi)} \left. \nabla \phi \right|_{T=0}. \] (11)

Combining \[1\], \[7\] and \[10\] with \[11\] gives

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

in terms of fundamental quantities, where here we emphasize that \(\mathcal{E}_T \equiv k_b T_m/\nu_T\) 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 \(S_T \sim 10^8 K^{-1}\) thereby illustrating the dominance of the thermomolecular force over the Brownian force in premelting solids. As a comparison, for \(\mu m\) sized particles in liquids \(S_T \sim 10^{-2} K^{-1}\)
and we obtain

\[ Q \] unit volume of particles diffusing into it (e.g., [20, 21]) leased by an arbitrarily isolated part of the system per traversions, (11), (13) and (14) can be used to obtain an If the Onsager relation (14) holds also at higher concentration to heat flux in our system by inserting (4), (7), (10) into the expression (8) for the thermomolecular force will no longer hold. Such a constraint on \( \nabla T \) is independent of the issue of the validity of linear irreversible thermodynamics as embodied in equations (1) and (2). This is because while \( \nabla T \) may be sufficiently small for these relations to be satisfied it may still vary on the particle scale, say, for large particles. Nonetheless, for most experimental situations envisaged the temperature gradient is sufficiently small that the Onsager relation holds.

We have shown the complimentary roles that interfacial premelting plays in both the regelation and Brownian motion of colloidal 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.

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**APPENDIX: 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 [4]), viz.,

\[ \mathbf{J}_1 = -\rho D \nabla c_1 - \rho c_1 c_2 D_T \nabla T, \]

(A.1)

\[ \mathbf{J}_q' = -k \nabla T - \rho_1 \left( \frac{\partial \mu_1}{\partial c_1} \right)_{T,P} T D_q \nabla c_1. \]

(A.2)

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 \( \rho_j \), \( \rho = \rho_1 + \rho_2 \) 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

\[ S_T = -\frac{Q^*_v}{(1 - \phi) \Pi_T T_m}. \]  

(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 [3] for the thermomolecular force will no longer hold. Such a constraint on \( \nabla T \) is independent of the issue of the validity of linear irreversible thermodynamics as embodied in equations (1) and (2). This is because while \( \nabla T \) may be sufficiently small for these relations to be satisfied it may still vary on the particle scale, say, for large particles. Nonetheless, for most experimental situations envisaged the temperature gradient is sufficiently small that the Onsager relation holds.

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 [19].

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

\[ Q^*_v \equiv \frac{q}{\eta} \bigg|_{\nabla T=0} = -\rho \Pi_T T_m \frac{D_q}{D}, \]  

(A.3)

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., [20, 21]) 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 \( \phi \to 0 \) to obtain

\[ D_q = D_T. \]  

(A.4)

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:

\[ S_T = -\frac{Q^*_v}{(1 - \phi) \Pi_T T_m}. \]  

(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 [3] for the thermomolecular force will no longer hold. Such a constraint on \( \nabla T \) is independent of the issue of the validity of linear irreversible thermodynamics as embodied in equations (1) and (2). This is because while \( \nabla T \) may be sufficiently small for these relations to be satisfied it may still vary on the particle scale, say, for large particles. Nonetheless, for most experimental situations envisaged the temperature gradient is sufficiently small that the Onsager relation holds.

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(A.1)

\[ \mathbf{J}_q' = -k \nabla T - \rho_1 \left( \frac{\partial \mu_1}{\partial c_1} \right)_{T,P} T D_q \nabla c_1. \]  

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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 \( \rho_j \), \( \rho = \rho_1 + \rho_2 \) 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 \( \mu_j \) is the chemical potential of \( j \). By definition

\[
c_1 + c_2 = 1 \quad \text{and} \quad J_1 + J_2 = 0. \tag{A.3}
\]

With (A.3) equations (A.1) and (A.2) can be written as

\[
J_2 = -\rho D \nabla c_2 + \rho c_1 c_2 D_T \nabla T, \tag{A.4}
\]

\[
J'_q = -k \nabla T - \rho_1 \left( \frac{\partial \mu_1}{\partial c_2} \right)_{T, P} TD_q \nabla c_2. \tag{A.5}
\]

It is convenient to write equations (A.4) and (A.5) in terms of the partial density \( \rho_2 \). To achieve this we use the thermodynamic identity (equation XI.99 of [4])

\[
\left( \frac{\partial \rho_2}{\partial c_2} \right)_{T, P} = \rho^2 \nu_1, \tag{A.6}
\]

where \( \nu_1 \) is the partial specific volume of component 1, approximately equal to

\[
\nu_1 = 1/\rho_s, \tag{A.7}
\]

where \( \rho_s \) 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 \( v^0 = \rho_1 \nu_1 v_1 + \rho_2 \nu_2 v_2 \) using the thermodynamic identity

\[
J^0_2 = \rho \nu_1 J_2. \tag{A.8}
\]

where \( J^0_2 = \rho_2 (v_2 - v^0) \). With (A.6), we rewrite (A.4) in the form of (A.8) and this and (A.5) become

\[
J^0_2 = -D \nabla \rho_2 + \nu_1 \rho_1 \rho_2 D_T \nabla T, \tag{A.9}
\]

\[
J'_q = -k \nabla T - \rho_1 \left( \frac{\partial \mu_1}{\partial \rho_2} \right)_{T, P} TD_q \nabla \rho_2. \tag{A.10}
\]

For a dispersion of hard spherical particles \( \nu_2 = 1/\rho_p \), where \( \rho_p \) is the constant mass density of an individual particle, in which case (A.9) and (A.10) can be written as

\[
J = -D \nabla \phi + \phi (1 - \phi) D_T \nabla T, \tag{A.11}
\]

\[
q = -k \nabla T - \rho_1 \left( \frac{\partial \mu_1}{\partial \phi} \right)_{T, P} TD_q \nabla \phi, \tag{A.12}
\]

where \( J = \phi (v_2 - v^0) \) is the particle volume flux, \( \phi = \rho_2 / \rho_p \) is the volume fraction of particles and \( q = J'_q \). As shown by de Groot and Mazur, in closed systems in which \( \nu_1 \) and \( \nu_2 \) are constant, the volume average velocity \( v_0 \) is zero, in which case (A.11) reduces to (1). Inserting the thermodynamic relation \( (\partial \mu_1 / \partial \phi)_{T, m, \rho_m} = -(1/\rho_s) \Pi_{\phi} \) into (A.12) gives equation (2), where \( 1 - \phi = \rho_1 / \rho_s \) and \( \Pi_{\phi} = (\delta \Pi / \delta \phi)_{T, \rho, \rho_m} \) at a reference state of bulk coexistence.