Interfacial Premelting and the Thermomolecular Force: Thermodynamic Buoyancy

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(Received 20 March 2001; published 7 August 2001)

The presence of a substrate can alter the equilibrium state of another material near their common boundary. Examples include wetting and interfacial premelting. In the latter case, temperature gradients induce spatial variations in the thickness of the premelted film that reflect changes in the strength of the repulsion between the substrate and the solid. We show that the net thermomolecular force on a macroscopic substrate is equivalent to a *thermodynamic buoyancy* force—proportional to the mass of solid that can occupy the volume enclosed by the substrate and the temperature gradient.

DOI: 10.1103/PhysRevLett.87.088501 PACS numbers: 92.40.Sn, 64.70.Dv, 68.08.Bc, 68.37.Ps

At temperatures approaching, but still lower than their bulk melting temperatures, the surfaces of many solids are separated from foreign substrates by thin fluid layers known as premelted films [1]. Interfacial premelting has been shown to exert a controlling influence in such diverse problems as the solidification of composite materials [2], sliding and debris entrainment by cold-based glaciers [3], thundercloud electrification [4], atomic force microscopy [5], thermal regelation [6,7], and frost heave [7,8]. The intermolecular forces that cause premelting also exert a repulsive force between the solid and a foreign substrate. Over the surface of the substrate, spatial variations in the strength of this repulsion can lead to a net thermomolecular force that must be balanced by counteracting forces (such as those due to gravity, viscous dissipation and/or elastic deformation). Here we provide a generalized method for quantifying the net thermomolecular force acting on a closed surface that is wetted by premelted films, showing that it is independent of the particularities of the interfacial forces (e.g., van der Waals, electrostatic, ...).

For example, we shall show that a foreign particle in ice that is subjected to a uniform temperature gradient ∇T, as shown in Fig. 2(a), has a net thermomolecular force acting on it equal to

$$\mathbf{F}_T = -m_s \nabla(\Delta\mu) \approx m_s \frac{q_m}{T_m} \nabla T, \tag{1}$$

where q_m is the latent heat of fusion per unit mass, T_m is the bulk melting temperature, and m_s is the mass of ice that could occupy the particle volume. The thermomolecular force appears as a buoyancy force with the departure of the chemical potential, at temperature T, from bulk coexistence $\Delta\mu \approx q_m(T_m - T)/T_m$ taking the place of the gravitational potential. We therefore coin the phrase "thermodynamic buoyancy" and identify a principle analogous to Archimedes' principle—that the thermodynamic buoyancy on a finite body immersed in a premelting solid is equal to the mass of solid displaced by the body times the gradient of the substrate-induced shift of the chemical potential. We emphasize that this force is generated by intermolecular interactions between the substrate and the solid; it is not caused by the action of gravity.

Interfacial premelting is accompanied by a pressure difference between the solid and melt phases, given by $\Delta P \equiv p_s - p_l = \gamma_{\mathrm{sl}}\mathcal{K} + p_T(d)$, where $\mathcal{K}$ and γ_{sl} are the curvature and surface energy of the solid-liquid interface, and $p_T(d)$ accounts for the force per unit area with which the solid and the substrate repel each other (often referred to in the wetting literature as the disjoining pressure). The dependence of p_T on the film thickness d is determined by the type of intermolecular interactions that dominate the system—for dispersion forces, for example, $p_T = \mathcal{A}/(6\pi d^3)$ where $\mathcal{A}$ is the Hamaker constant. At equilibrium, the chemical potentials in the solid and melt phases are equal. A consequence of the Gibbs-Duhem relation [9] is that $\Delta P \approx \rho_s q_m \Delta T/T_m$, where ρ_s is the solid density, and the undercooling $\Delta T \equiv T_m - T$ is the temperature depression from the melting temperature of the bulk solid. The thermomolecular force on the surface S of a substrate is defined as

$$\mathbf{F}_T \equiv -\int_S p_T\, d\mathbf{S} \approx \int_S \left(\gamma_{\mathrm{sl}}\mathcal{K} - \frac{\rho_s q_m \Delta T}{T_m}\right) d\mathbf{S}, \tag{2}$$

where the vector element $d\mathbf{S}$ points in the direction of the normal to the surface $\mathbf{n}$ (see Fig. 1).

We examine the two terms on the right side of Eq. (2) separately. The first term is the contribution of interfacial curvature to the pressure difference between the phases; it can be written in terms of the surface stress tensor, defined as $\boldsymbol{\sigma}^s \equiv \gamma_{\mathrm{sl}}(\mathbf{I} - \mathbf{nn})$, so that $\int_S \gamma_{\mathrm{sl}}\mathcal{K}\, d\mathbf{S} = \int_S \nabla^s \cdot \boldsymbol{\sigma}^s\, dS$, where $\nabla^s \equiv (\mathbf{I} - \mathbf{nn}) \cdot \nabla$ is the surface gradient operator (e.g., see Ref. [10]). We apply the surface version of the divergence theorem to write this surface integral in terms of the integral over the bounding curve

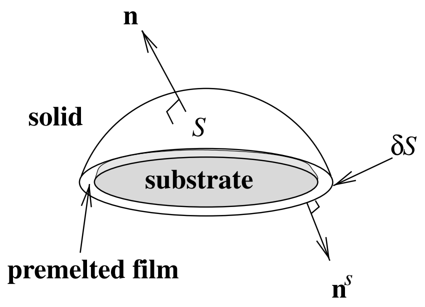

FIG. 1. A schematic diagram of a surface S showing the outward normal $\mathbf{n}$. The boundary of S has normal $\mathbf{n}^s$, which is tangent to S along δS. As shown in the text, curvature effects produce no net force over a closed surface. For an open surface, curvature effects lead to a force that can be calculated from a line integral along δS with contributions in the $\mathbf{n}^s$ direction.

$\int_S \gamma_{\mathrm{sl}} \mathcal{K}\, d\mathrm{S} = \int_{\delta S} \mathbf{n}^s \cdot \sigma^s d\,(\delta S)$, where $\mathbf{n}^s$ is the normal to δS, which is tangent to S along its boundary (see Fig. 1). When S is closed, the integral is over a curve of length zero and hence this curvature term disappears; *curvature effects over a closed surface produce no net force.*

For a substrate that is completely surrounded by premelted liquid, the first term in Eq. (2) integrates to zero. We apply the divergence theorem on the remaining term to obtain

$$\mathbf{F}_T \approx -\int_V \nabla\left(\frac{\rho_s q_m \Delta T}{T_m}\right) dV, \tag{3}$$

where V is the volume contained within S. We define $\mathbf{G} \equiv (q_m/T_m)\nabla T$ and treat the case where the substrate is small compared to the length scale over which changes in the temperature gradient occur, so that the net thermomolecular force is

$$\mathbf{F}_T \approx m_s \mathbf{G}, \tag{4}$$

which is equivalent to Eq. (1). This result is independent of the nature of the interfacial forces that are responsible for the presence of the film and hence it is applicable to all premelting systems. As noted above, Eq. (4) implies that $\mathbf{F}_T = -m_s \nabla(\Delta\mu)$ where $\Delta\mu$ is the increase in the chemical potential above that at bulk coexistence, which is induced by the presence of the substrate. To be more precise, $\Delta\mu \equiv \mu_l(T, P_l) - \mu_s(T, P_l)$, where the subscripts s and l refer to the solid and liquid phases and the indices indicate the temperature and pressure at which each chemical potential is evaluated.

The thermomolecular force is important in many natural and industrial settings, for instance, as the underlying cause of frost heave [7,8] and particle rejection from solidification fronts [2]. Its effect on an isolated substrate particle provides a useful and geophysically relevant illustration of our result. For example, dust particles that are trapped in the polar ice sheets are viewed as indicators of past climate conditions [11], but thermal regelation can cause particle migration into ice of a different age from that with which they were deposited. To demonstrate this, we return to the case of a substrate that is separated by a premelted film from a surrounding solid, such as ice, and subjected to a uniform temperature gradient, as shown in Fig. 2(a). The thermomolecular force is given by Eq. (4), and the gravitational buoyancy force is $\mathbf{F}_g = (\rho_p - \rho_l)V\mathbf{g}$, where ρ_p and ρ_l are the densities of the particle and the liquid, respectively. The particle remains stationary with respect to the solid if $\mathbf{G} = -\mathbf{g}(\rho_p - \rho_s)/\rho_s$, otherwise the resultant force is balanced by dissipative processes that resist the particle motion. (Experimental observations [6] are consistent with the theoretical prediction [7] that the

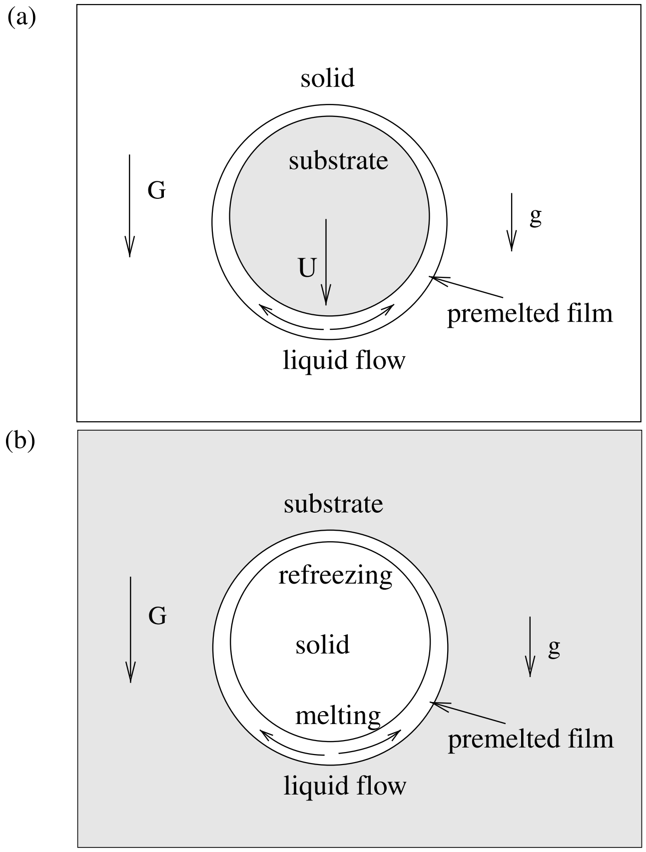

FIG. 2. Schematic diagrams showing two examples of thermal regelation. (a) A substrate surrounded by a premelted film and moving at velocity $\mathbf{U}$ up a temperature gradient. For a spherical substrate particle of radius $a \gg d$, we have [7] $\mathbf{U} \approx d^3[\rho_s\mathbf{G} + (\rho_p - \rho_s)\mathbf{g}](6\mu a)^{-1}$ where $\mu \approx 1.8 \times 10^{-3}$ Pa s is the fluid viscosity. When $\mathbf{G} \approx 3\mathbf{g}$, a micron-sized particle with $\rho_p \approx 2\rho_s$ moves downwards relative to the solid at 1 μm per year when the average film thickness is a few nanometers. (b) A premelted solid crystal surrounded by a rigid substrate and subjected to a temperature gradient. The viscous resistance to fluid flow must balance the sum of $\mathbf{F}_T$ and $\mathbf{F}_g$, as in (a). Here, however, the crystal cannot move so the flow results in a continuous recrystallization with melting on the lower (warm) side and freezing on the upper (cold) side. Using the same parameter values as in (a), we find that the solid crystal is completely reformed every two years.

viscous resistance to fluid flow determines the particle velocity for this system.) Even for the relatively small temperature gradients experienced by dust particles in an ice sheet, roughly 0.025 $\mathrm{K\,m^{-1}}$, the magnitude of $\mathbf{G}$ is roughly 3 times the normal gravitational acceleration ($q_m \approx 3.3 \times 10^5$ $\mathrm{J\,kg^{-1}}$, $T_m \approx 2.7 \times 10^2$ K, and $|\mathbf{g}| \approx 10$ $\mathrm{m\,s^{-2}}$). An interesting variation on this problem is the reverse case in which a premelted film separates a solid crystal from the rigid substrate that surrounds it [see Fig. 2(b)]. Since the substrate prevents the solid crystal from moving, the sum of $\mathbf{F}_T$ and $\mathbf{F}_G$ is balanced by the force associated with viscous resistance to fluid flow in the premelted film as the crystal melts and refreezes on opposite sides. This suggests that grain-boundary melting [12], as can occur between ice grains [13], should be accompanied by continuous recrystallization at a rate proportional to the local temperature gradient.

For isothermal systems, Eq. (4) implies that there is no net thermomolecular force over a closed surface. This insight can be used to obtain $\mathbf{F}_T$ acting on a force microscope tip that is partially inserted into a premelted solid sample [see Fig. 3(a)]. The solid-liquid interface joins the solid surface in the horizontal plane so the interfacial curvature produces no net vertical force on the tip. The net thermomolecular force is equal and opposite to that force which would be present on its cross section if the tip were completely surrounded by the premelted solid, as shown in Fig. 3(b). This implies that the repulsive force exerted by the sample on the tip has a magnitude of $|\mathbf{F}_T| \approx \pi a^2 p_T(d)$, where a is the radius of the tip at the solid surface and d is the thickness that the premelted film would attain in the absence of interfacial curvature. On a planar surface $p_T = \Delta P$ so the dependence of ΔP on the undercooling dictates that $|\mathbf{F}_T| \approx \pi a^2 \rho_s q_m \Delta T / T_m$. Since $\mathbf{F}_T$ depends on a^2, it is more sensitive to irregularities in the tip shape than are other forces in this system such as the line tension, which is proportional to a. The magnitude of the "bumps" in the force-depth curves observed during recent indentation experiments on ice crystals (see Fig. 4 of Ref. [5]) suggests that they were generated by variations in $|\mathbf{F}_T|$, which are associated with repulsive pressures of about 60 bars when $\Delta T \approx$ 5 K. A static force experiment using a probe with a well-characterized geometry would be more amenable to a quantitative test of this theory.

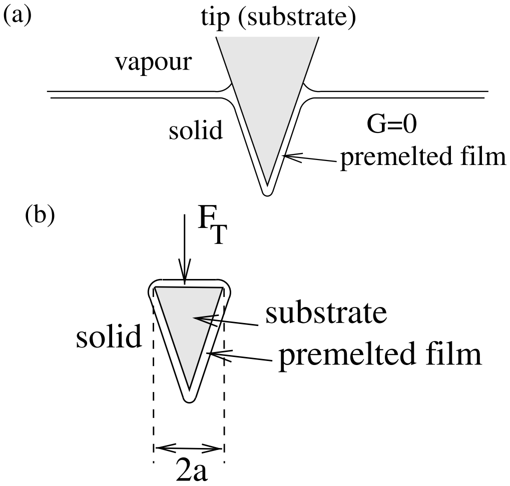

FIG. 3. The thermomolecular force on a force microscope tip. (a) Schematic of a force microscope tip inserted into an isothermal solid (i.e., $\mathbf{G} = 0$) that is coated with a premelted film. The thermomolecular force on the tip is equivalent to that which would be present on its planar cross section if it were truncated at the solid-vapor interface and completely surrounded by the premelted solid, as shown in (b). Small variations (not shown) in the radius a cause relatively large variations in $|\mathbf{F}_T|$ that are the most likely cause of the "bumps" in the force-depth curves obtained in a recent force microscopy study of the surface of ice [5].

It is instructive to employ a similar analysis to investigate the net force on a wetted substrate, where the effects of interfacial curvature and intermolecular interactions alter the chemical potentials of two fluid components [14]. The chemical potentials admit expansions in terms of deviations from reference temperature and pressure conditions. Gradients in either of these control parameters can generate a net force between the substrate and the nonwetting component (see Fig. 4). Interfacial curvature plays no role in the generation of this force when the nonwetting component is completely enveloped by the wetting component. We find that the force exerted by a substrate on a nonwetting component of volume V is given by

$$\mathbf{F} = \int_V \left[\frac{\rho_{\mathrm{w}} - \rho_{\mathrm{nw}}}{\rho_{\mathrm{w}}} \nabla P_{\mathrm{w}} + \rho_{\mathrm{nw}}(s_{\mathrm{w}} - s_{\mathrm{nw}}) \nabla T \right] dV , \tag{5}$$

where s is the specific entropy and the subscripts "nw" and "w" refer to the nonwetting and wetting components, respectively. When the pressure gradient in the wetting fluid is $\nabla P_{\mathrm{w}} = -\rho_{\mathrm{w}} g$, the first term in Eq. (5) [which was

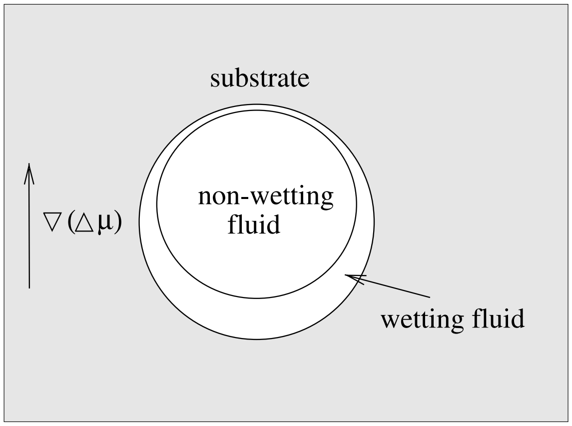

FIG. 4. Schematic diagram showing a nonwetting fluid component that is surrounded by a second fluid that wets the substrate.

neglected in deriving Eq. (3) because of the small density contrasts between most solids and their melts] exactly counteracts the gravitational buoyancy that acts on the nonwetting component. The second term leads to Eq. (4) for the thermomolecular force when the entropy difference is between a solid and its melt.

The intermolecular interactions that act between a solid and its substrate to cause interfacial premelting also produce dynamic consequences in diverse natural and laboratory settings, ranging from frost heave in frozen soils [8] and thermal regelation [6,7] to particle rejection from solidification fronts [2] and tip-sample repulsion during atomic force microscopy [5]. Our analysis predicts that the net thermomolecular force that results from these intermolecular interactions can be viewed as an equivalent body force—the thermodynamic buoyancy. Treating $\mathbf{F}_T$ in this way greatly simplifies its calculation and provides insight into the dynamics of numerous phenomena. Our theory is in agreement with the observations of experimental studies that have indirectly measured the thermomolecular force by focusing on the effects produced by counteracting viscous forces and the accompanying fluid flow in premelted films [2,5–8]; more direct experimental proof and a clear exclusion of other effects might be provided by a static force experiment.

This work is supported by the National Science Foundation under Grant No. OPP9908945.

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