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Frost heave in physisorbed films: Vapor flow and substrate effects

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The magnitude of vapor flow accompanying the surface-melted liquid flow in physisorbed multilayer films due to thermomolecular pressures was estimated. It was found that the vapor flow is significant compared to the flow of the surface-melted liquid in thick films. As the flows continue, the film thickness profile evolves into one determined by a dynamic equilibrium of vapor pressure. The flow of surface-melted liquid stops when the dynamic equilibrium is reached.

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It has recently been demonstrated that undercooled liquid films, existing due to interfacial melting or finite-size effects at a solid-wall interface, will flow upon application of a temperature gradient parallel to the interface [1–8]. This flow has been explained as a consequence of the interaction between the interfaces sandwiching the liquid film. The interaction induces a thermomolecular pressure P_T, which, together with hydrodynamic pressure P_h, balances the external pressure P applied to the system, $P=P_T+P_h$ [1–6]. Applying a Gibbs-Duhem relationship to the solid and liquid layers yields a relation between the maximum value of P_T and temperature T [2]:

$$P_T=\rho_s q_m\left(\frac{T_m-T}{T_m}\right)=\rho_s q_m\frac{\Delta T}{T_m}, \tag{1}$$

where T_m is the bulk melting temperature, and ρ_s and q_m are the solid-state density and the latent heat of fusion of the material, respectively. Under a constant external pressure, P_T decreases and P_h increases in the direction of the temperature gradient. The variation of P_h drives liquid flow toward the lower-temperature region. The flowed-in liquid must be converted into a solid in order to maintain a constant liquid thickness at any given location. This process results in the accumulation of solid material in the low-temperature region [6].

Melting of a physisorbed multilayer film typically starts from the top layer and proceeds layer by layer toward the bottom as T_m is approached [9–13]. For temperatures below, but close to, T_m, a multilayer film can be in a stratified melting stage with the surface layer(s) in a liquid state and the bottom layer(s) in a solid state [9–13]. Applying the same thermodynamic argument described above to such a film suggests that the surface-melted layer(s) will flow toward regions of lower temperature when a temperature gradient is applied parallel to the film. Such a possibility might open a new avenue for studying the dynamic properties of two-dimensional liquids.

However, there are differences between the two systems: (a) an undercooled liquid film at a solid-wall interface and (b) a surface-melted liquid layer(s) in a physisorbed film. The former is a three-layer system consisting of a wall, liquid, and solid; the latter is a four-layer system consisting of a substrate, solid, liquid, and vapor. A complete treatment of the latter case requires consideration of the chemical potential and the dynamics of all three layers of the adsorbate (solid, liquid, and vapor) and their interfaces [14], under the influence of a temperature gradient and a substrate potential. The main difference, however, is the involvement of the vapor and liquid-vapor interface in the case of flow of surface-melted liquid layer(s) in an adsorbed film. The vapor can flow, together with the surface-melted liquid, under the same temperature gradient. The liquid and vapor flows cause the solid-liquid and liquid-vapor interfaces, which sandwich the surface-melted liquid, to evolve and thus change the substrate-adsorbate interaction. In this Brief Report, only a *qualitative* analysis of the accompanying vapor flow and the substrate effect on the thermomolecular flow of the surface melted layers in a physisorbed multilayer film is intended.

Consider a surface-melted multilayer film adsorbed on a substrate in a closed experimental cell, as shown in Fig. 1(a). When a temperature gradient is applied parallel to the substrate of such a system, the surface melted liquid will flow in the direction opposite to the gradient. Assuming that the flow can be described as lubrication flow [2–4,15], the volume flow flux per unit breadth in the liquid layer, with thickness L_l, is given by

$$\begin{aligned}Q_l&=-\frac{L_l^3}{12\mu_l}\left(\frac{dP_l}{dx}\right)\\&=-\frac{L_l^3}{12\mu_l}\left(\frac{\rho_l q_m}{T_m}+\frac{\rho_l}{\rho_s}\frac{dP}{dT}\right)\left(\frac{dT}{dx}\right)\\&\equiv -a_l L_l^3\left(\frac{dT}{dx}\right),\end{aligned} \tag{2}$$

where μ_l is the liquid viscosity, ρ_l the liquid density, and P_l the pressure exerted on the liquid.

The same temperature gradient causes the vapor pressure in the warmer region to rise, creating a pressure gradient which drives the vapor to flow toward colder regions. Assuming the local vapor pressure of the film follows a Frenkel-Halsey-Hill (FHH) relation [16]

$$P=P_0(T)\exp\left(-\frac{\alpha}{k_B T L^3}\right), \tag{3}$$

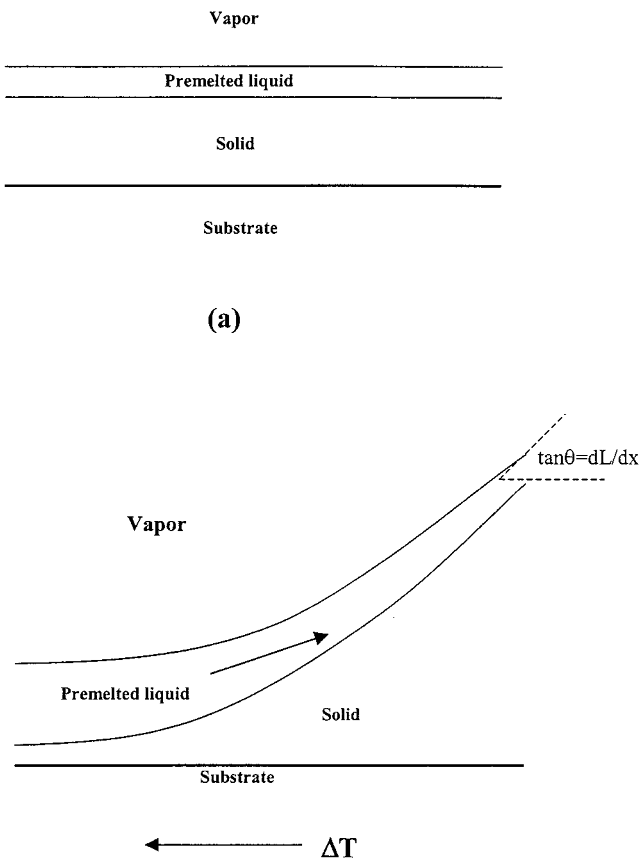

FIG. 1. (a) A multilayer film with top layer(s) melted at temperatures below the bulk melting temperature. The film is thus in a stratified state. (b) When a temperature gradient is applied parallel to the substrate, both the surface melted liquid and vapor flow toward lower temperature, resulting in an increase of film thickness in the colder region. When vapor pressure reaches a dynamic equilibrium, the film thickness profile evolves to that determined by Eq. (8). The angle between the slope of the thickness profile and the temperature gradient, *θ*, is related to the local thickness variation tan *θ*=*dL*/*dx*.

where P_0 is the saturated vapor pressure, L the film thickness, k_B the Boltzmann constant, and α is a constant characterizing the adsorbate-substrate interaction, the gradient of vapor pressure along the substrate is then

$$\frac{dP}{dx}=\left[\left(\frac{dP_0}{dT}+P_0\frac{\alpha}{k_BT^2L^3}\right)\frac{dT}{dx}+P_0\frac{3\alpha}{k_BTL^4}\frac{dL}{dx}\right]\times\exp\left(-\frac{\alpha}{k_BTL^3}\right). \tag{4}$$

In the thick-film limit, this equation reduces to $dP/dx \cong (dP_0/dT)(dT/dx)$. The flow in the vapor could be more complex than that in the liquid and probably should be treated as a potential flow in some cases [18]. However, in order to estimate the low limit of the vapor flow rate and to make a direct comparison to that of a surface-melted liquid, the lubrication approximation is also applied to the vapor flow [17,18]. Thus the flow flux per unit length of the vapor is then given by

TABLE I. The values of flow coefficient for several rare gas systems. All the viscosity data used are for bulk phases and are at the melting temperature under a pressure of 1 bar, except liquid Kr and liquid Ne for which the values of viscosity used are at the melting temperatures under a pressure of 70 and 0.8 bars respectively [22].

Substances	μ_1 (μPa s)	μ_v (μPa s)	a_l (10^7/s K)	a_v (10^7/s K)
Ne	1600	46.2	45.7	34.0
Ar	2798	74.5	19.8	10.5
Kr	4270	108.6	6.8	5.6
Xe	5400	133.7	4.2	3.6

$$\begin{aligned}Q_v&=-\frac{L_v^3}{12\mu_v}\left(\frac{dP}{dx}\right)\\&=-\frac{L_v^3}{12\mu_v}\left(\frac{dP}{dT}\right)\left(\frac{dT}{dx}\right)\\&\equiv -a_vL_v^3\left(\frac{dT}{dx}\right),\end{aligned} \tag{5}$$

where μ_v is the vapor viscosity and L_v is the height of open space above the film adsorbed on a substrate. It should be noted that the vapor-liquid interface in an adsorbed film is moving when frost heave occurs. The motion of the interface increases the flow rates of both the liquid and vapor, but their relative importance should not change significantly [18]. The magnitudes of a_l and a_v, together with L_l and L_v of Eqs. (2) and (5), provide an estimate of the significance of the vapor flow relative to the flow of surface-melted liquid. Table I lists the values of a_l and a_v calculated for several rare gas systems in the thick-film limit and using the bulk viscosity data. The viscosity of thin liquid films is known to be greater than that of the bulk liquid, due to the layerlike ordering at an interface [19,20]. Thus the values for a_l could be overestimated. Table I shows that the calculated values of a_l and a_v are all comparable for rare gas systems. The liquid layer thickness (L_l) is usually much smaller than the height (L_v) of the open space that the vapor occupies above the film. Therefore, at the initial stage of the application of a temperature gradient, vapor flow is significant comparing to the flow of the surface-melted liquid in a thick film.

The vapor flow caused by a temperature gradient is essentially a process in which some of adsorbate desorb from the warmer region, flow to the colder region, and then readsorb. This process increases the film thickness in the colder region and reduces the pressure gradient, because local vapor pressure increases with the local film thickness [see Eq. (3)]. The vapor flow stops when the vapor pressure in the system reaches a dynamic equilibrium, in which the combined effect of the temperature gradient and the film thickness variation makes the vapor pressure uniform throughout the system [17]. The condition of the dynamic equilibrium is determined by Eq. (4) in which the first and second terms (the local film thickness L is a function of both position and time) cancel each other, so that $dP/dx=0$. The dynamic equilibrium should not affect the thermomolecular pressure generated by the temperature gradient. If the flow of surface-melted liquid would sustain, then the dynamic equilibrium of vapor pressure provides a favorable condition for unambiguously detecting and studying frost heave in an adsorbed film.

However, when the condition of the dynamic equilibrium is reached, the flow of surface-melted liquid is not in a direction parallel to the substrate, but rather along a path close to the film thickness profile, as illustrated by Fig. 1(b). The film thickness profile is determined by requiring $dP/dx=0$ in Eq. (4):

$$\frac{\delta L}{\delta x}=-\frac{\delta T}{\delta x}\left(\frac{L}{3T}+\frac{k_BTL^4}{3\alpha}\frac{\delta\ln P_0(T)}{\delta T}\right). \tag{6}$$

The saturated vapor pressure can be expressed as [21]

$$\ln P_0(T)\approx-\frac{q_l}{k_BT}+\text{const}, \tag{7}$$

where q_l is the latent heat of sublimation of the substance. Combining Eqs. (6) and (7) yields

$$\frac{\delta L}{\delta x}=-\frac{\delta T}{\delta x}\left(\frac{L}{3T}+\frac{q_lL^4}{3\alpha T}\right). \tag{8}$$

The surface-melted liquid needs to climb in opposition to the substrate potential, moving from the region near the substrate (warmer region) to region far from it (cooler, thicker region), in order to maintain the flow, as illustrated by Fig. 1(b). When the liquid layer is thin, the flow can be considered to be approximately along the liquid-vapor interface. Thus the additional energy cost per unit volume for sustaining such a flow is

$$\delta E\approx\rho_l\frac{3\alpha}{L^4}\,\delta L\approx-\rho_l\frac{\delta T}{T}\left(\frac{\alpha}{L^3}+q_l\right), \tag{9}$$

where δL is the distance a unit of liquid is displaced normal to the substrate. Combining Eqs. (1) and (9) gives the pressure required to induce flow in a surface-melted film:

$$\Delta P=\rho_l\left(\frac{\rho_s}{\rho_l}q_m-q_l-\frac{\alpha}{L^3}\right)\frac{\Delta T}{T}. \tag{10}$$

The difference between the latent heat of sublimation and the latent heat of fusion of a substance is much greater than the difference between the densities of its solid and liquid phases. So the thermomolecular pressure cannot overcome the energy cost of climbing in opposition to the substrate potential when the dynamic equilibrium is reached.

Under the dynamic equilibrium condition, the local slope of the film thickness profile is determined by Eq. (8) ($\tan\theta=dL/dx$). A strong adsorbate-substrate interaction results in a smaller angle θ, but gives rise to a stronger adsorbate-substrate potential for the flowing liquid to overcome. A weak adsorbate-substrate interaction results in a larger angle. The extreme case $\alpha=0$ corresponds to films with infinite thickness or surface melting on a bulk material. In this case, the angle between the temperature gradient and the liquid-vapor interface is 90° [the second term in Eq. (8) diverges], when the dynamic equilibrium is established. So the vapor flow accompanying the flow of surface-melted liquid on a bulk surface will continue until the liquid-vapor interface changes to a position which is perpendicular to the temperature gradient.

The qualitative analysis presented above demonstrates that frost heave in a surface-melted physisorbed thick film is accompanied by a significant vapor flow. As the flows continue, the film thickness profile evolves and, eventually, a dynamic equilibrium of vapor pressure can be reached. When this condition is established, vapor flow stops, but the flow of surface-melted liquid stops as well. Whether there exits a time window during which vapor flow is dramatically reduced, while liquid flow is still sustained as the film thickness profile evolves toward the dynamic equilibrium, is an interesting subject for further exploring.

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[1] L. A. Wilen and J. G. Dash, Phys. Rev. Lett. **74**, 5076 (1995).
[2] J. S. Wettlaufer and M. G. Worster, Phys. Rev. E **51**, 4679 (1995).
[3] J. S. Wettlaufer, M. G. Worster, L. A. Wilen, and J. G. Dash, Phys. Rev. E **76**, 3602 (1996).
[4] M. G. Worster and J. S. Wettlaufer, in *Fluid Dynamics at Interfaces*, edited by W Shyy (Cambridge University Press, Cambridge, England, in press).
[5] D. M. Zha *et al.*, Phys. Rev. Lett. (to be published).
[6] J. G. Dash, Science **246**, 1591 (1989).
[7] J. S. Wettlaufer and J. G. Dash, Sci. Am. (Int. Ed.) **282**, 50 (2000).
[8] M. Hiroi, T. Mizusaki, T. Tsuneto, A. Hirai, and K. Eguchi, Phys. Rev. B **40**, 6581 (1989).
[9] M. J. Lysek, M. A. LaMadrid, P. K. Day, and D. L. Goodstein, Phys. Rev. B **47**, 7389 (1993); P. Day, M. LaMadridm, M. Lysek, and D. L. Goodstein, *ibid.* **47**, 7501 (1993); P. Day, M. Lysek, M. LaMadrid, and D. L. Goodstein, *ibid.* **47**, 10 716 (1993).
[10] H. S. Young and G. B. Hess, Phys. Rev. Lett. **64**, 918 (1990).
[11] J. M. Phillips, Q. M. Zhang, and J. Z. Larese, Phys. Rev. Lett. **71**, 2971 (1993); J. M. Phillips and J. Z. Larese, Phys. Rev. B **56**, 6462 (1997).
[12] Da-Ming Zhu and J. G. Dash, Phys. Rev. Lett. **57**, 2959 (1986); **60**, 432 (1988).
[13] Da-Ming Zhu and J. G. Dash, Phys. Rev. B **38**, 11 673 (1988).
[14] J. Krim and J. G. Dash, Surf. Sci. **162**, 421 (1985); D. Pengra and J. G. Das, J. Phys.: Condens. Matter **4**, 7317 (1992).
[15] The derivation of the first part of the equation (from Darcy's law) can be found in O. M. Phillips, *Flow and Reaction in*

Permeable Rocks (Cambridge University Press, Cambridge, England, 1991); the derivation of the second part of the equation can be found in Ref. [2].

[16] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, New York, 1946).

[17] The mean free path of gas molecules for most physisorbed films near their bulk triple points is less or around a few thousand Å. Thus the thermal transpiration effect [T. Takaishi and Y. Sensui, Trans. Faraday Soc. **59**, 2503 (1963)] within an adsorption cell made of commonly used substrates, such as graphite foam, is negligible.

[18] P. C. Carman, *Flow of Gases Through Porous Media* (Ademic, London, 1956); R. E. Collins, *Flow of Fluids Through Porous Materials* (Chapman & Hall, London, 1961).

[19] J. Q. Broughton, A. Bonissent, and F. F. Abraham, J. Chem. Phys. **74**, 4029 (1979).

[20] R. Evans, Adv. Phys. **28**, 143 (1979).

[21] R. K. Crawford, in *Rare Gases Solids II*, edited by M. L. Klein and J. A. Venables (Academic, New York, 1988).

[22] N. B. Vargaftik, Y. K. Vinogradov, and V. S. Yargin, *Handbook of Physical Properties of Liquids and Gases* (Begall House, New York, 1996).