Dependence of Quasiliquid Thickness on the Liquid Activity: A Bulk Thermodynamic Theory of the Interface

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Studies of the phenomenon of quasiliquid formation span systems as diverse as noble gases, complex organic molecules, and metals, and span triple point temperatures from 25 to 933 K. We show that when viewed as a single phenomenon essentially all published measurements of the quasiliquid layer thickness on solids below the melting point can be plotted as a function of the thermodynamic activity. Two classes of behavior are then observed: one for molecular systems and one for atomic systems. We derive a dependence on activity through a grand canonical lattice gas calculation. This is the only such unifying theory of this phenomenon.

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The presence of an equilibrium liquid layer on the surface of a solid at temperatures below the triple point has been observed in one-component systems as diverse as, e.g., noble gases [1,2], small polyatomic molecules [3,4], large organic molecular crystals [5,6], metals [7–10], and, most particularly, water [11–20]. Variously named a quasiliquid, a premelt layer, or surface disordered layer, this layer has been implicated in macroscopic phenomena as diverse as frost heave, thundercloud electrification, bulk melting, and ice skating. We call it an interfacial liquid in this Letter. An observation of this phenomenon common to published studies is an increasing liquid thickness with a power law or logarithmic dependence on a relative temperature, $T_t - T$, where T_t is the triple point temperature. In all of the theoretical approaches applied to this problem the chemical potential of the interface, μ_i, is minimized by the formation of a liquid layer of some thickness. Landau type theories using either a generic free energy functional [21] or one based on surface excess energies [10,22] reproduce the logarithmic divergence, while Ising mean field treatments [23] reproduce the power law behavior. Recent approaches include treating the interface as a static dielectric [24] or, most recently for ice, accounting for impurity molecules [25] or non-bulk-like structures at the surface [26] in electrostatic calculations of μ_i. These theories have enabled calculations of thickness as a function of temperature in agreement with observation. They also, however, imply that the observed temperature dependence and form of the intermolecular forces capture the inherent physics of the phenomenon.

It is common in discussions of this phenomenon to reference the work on ice regelation by Faraday [27] and his original observations. Toward a more fundamental understanding of the phenomenon we suggest a broader reference from Fowler and Guggenheim [28]: “Since the phenomenon of condensation-evaporation is common to all substances, it should be possible to give a general explanation essentially independent of the detailed form of the intermolecular forces. . . .” In this spirit we utilize the classic chemical physics of sublimation and vaporization to formulate a theory of the interfacial liquid which is exactly that: “. . .independent of the detailed form of the intermolecular forces. . . .” This is accomplished by analyzing the data not as a function of temperature but rather as a function of the liquid activity, defined using the sublimation and vaporization pressures. In so doing we show that it is the balance of bulk thermodynamic free energies that is the fundamental property of the system. In addition, a new mystery is revealed, that atomic and molecular systems behave as two distinct classes with respect to this phenomenon.

We first present a compilation of interfacial liquid data from the literature where the thickness is plotted as a function of the liquid activity. We show that in this representation data from atomic systems, whose triple points vary from 24.5 (neon) to 933.5 K (aluminum), all follow one common functional dependence of thickness on activity while the data from molecular systems, whose triple points vary from 54.35 (oxygen) to 342.61 K (biphenyl), follow a second functional dependence. We also present a new calculation of the liquid thickness based on a lattice calculation in the grand canonical ensemble. We construct the system free energy from bulk thermodynamic properties and show that the liquid activity is a natural reduced variable of the system and that the liquid thickness may be calculated to first order as a polynomial in this activity. This calculation is performed from first principles with no degrees of freedom and reproduces the thickness as a function of activity exhibited by the molecular systems.

Measurements of liquid layer thickness on a number of atomic and molecular systems are reproduced in Fig. 1. The data are plotted as the calculated layer thickness, θ, in layers, as a function of the difference temperature from the triple point. All data were originally reported as a function of the temperature, and measurements of the thickness have been interpreted as follows. Data points

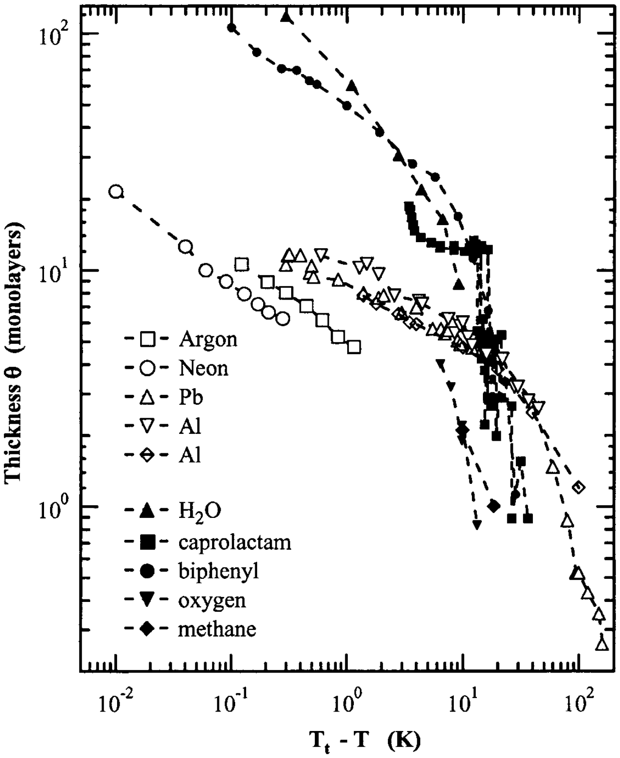

FIG. 1. Compilation of quasiliquid data from the literature plotted as the thickness in layers as a function of the difference temperature from the triple point. Studies are referenced in the text and include Ar (open squares), Ne (open circles), Pb (open triangles), Al (open inverted triangles and open diamonds), CH_4 (solid diamonds), O_2 (solid inverted triangles), H_2O (solid triangles), caprolactam (solid squares), and biphenyl (solid circles). The dashed lines are guides for the eye.

for argon [1] were obtained in a calorimetric study of multilayer adsorption on graphite where the melting temperature is measured as a function of layer thickness. Data for neon [2] were obtained in the same way. Data for lead [8] were obtained by ion scattering in shadowing and blocking experiments. These data were originally reported as the number of disordered atoms per unit area. We have divided by a surface density of 0.577×10^{15} Pb atom/cm^2 to arrive at a thickness in layers. The same experimental technique was applied to aluminum [9], and these data were divided by a surface density of $0.5 \times 0.863 \times 10^{15}$ Al atom/cm^2 in order to plot the thickness in layers. We multiply by 0.5 as the data were originally reported in bilayers. Data from another study on aluminum [10] using core electron photoemission are plotted as originally reported. Glancing angle x-ray scattering data for water [16] are plotted as reported, as are the ellipsometric data for biphenyl [6] and the x-ray reflectivity data for caprolactam [5] using $T_t = 342.3$ K. Data for molecular oxygen in the fluid II regime obtained by neutron diffraction [3] are plotted as originally reported. Finally, low thickness data for methane [4,29] are plotted as reported using $T_t = 90.65$ K.

There are a number of other data sets for the systems compiled in Fig. 1. For the data on lead [8], there is good agreement with other data [7]. The situation for water is more complicated [11–20]. We have presented the data of Dosch *et al.* [16] as most representative due to the careful attention to equilibrium conditions in that experiment. The atomic force microscopy (AFM) data for water from Doppenschmidt and Butt [17] are also in good agreement. There is considerable disagreement with many of the other studies [30]. Finally, where one crystal face presented a much thicker interfacial liquid than the others we have used the data for that face.

In Fig. 2, the data are replotted as a function of the liquid activity, x. The pressure above a sample is the solid sublimation pressure, as has been confirmed directly for water [16]. At equilibrium, therefore, the activity is a fixed function of the temperature through the sublimation and vaporization free energy as

$$x = \frac{P_{\mathrm{sol}}}{P_{\mathrm{liq}}} = \exp\left(-\frac{(\Delta G_{\mathrm{sub}} - \Delta G_{\mathrm{vap}})}{RT}\right), \tag{1}$$

where the liquid pressures are extrapolated to temperatures below T_t. The activity can thus be calculated directly from the sublimation and vaporization pressures.

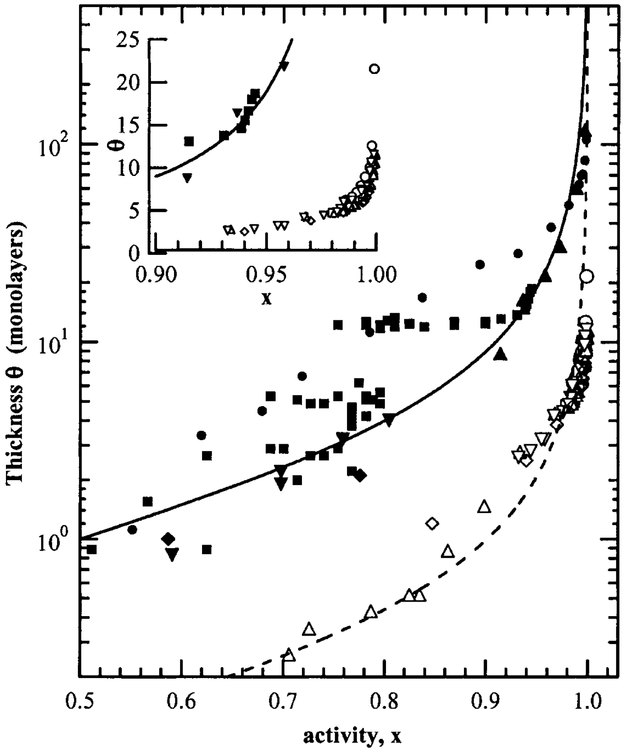

FIG. 2. Same compilation of data as for Fig. 1, with the same labeling of systems, now plotted as a function of the activity through Eq. (2) and the parameters of Table I. The solid line is a calculation of the thickness as a function of activity from Eq. (6). The inset is simply an expanded scale view.

For many substances studied here, however, the sublimation data are not available, and instead we use the direct integration of the Clausius-Clapyron equation for each phase with integration limits from the triple point state to p, T, which leads to

$$x = \frac{P_{\mathrm{sol}}}{P_{\mathrm{liq}}} = \exp\left[-\frac{\Delta H_{\mathrm{fus}}}{R}\left(\frac{1}{T} - \frac{1}{T_t}\right)\right]. \tag{2}$$

The data of Fig. 2 are plotted as a function of x by using the reported temperature and Eq. (2), with the heats of fusion and triple point temperatures compiled in Table I. When replotted in this way, these data are well described by two curves in θ as a function of x. We are aware of only one exception to this, gallium [31]. This model independent observation is the principle result of this Letter.

We now derive this dependence on activity using a lattice gas calculation in the grand canonical ensemble. The derivation is based on classic lattice statistics calculations of Hill [32]. Consider a macroscopic grand partition function, Θ, composed of M subsystems, each described by a subsystem partition function ξ. The average number of molecules in the macroscopic system is

$$\overline{N} = \lambda\left(\frac{\partial \ln\Theta}{\partial \lambda}\right)_{M,T} = M\lambda\left(\frac{\partial \ln\xi}{\partial \lambda}\right)_T, \tag{3}$$

where $\lambda = \exp(\mu/kT)$ is the absolute activity. The average occupancy per site is just

$$\frac{\overline{N}}{M} = \lambda\left(\frac{\partial \ln\xi}{\partial \lambda}\right)_T. \tag{4}$$

In this model of the interfacial liquid layer, we adopt the one-dimensional liquid model wherein our system is the solid surface comprised of the M independent, distinguishable and equivalent sites, on each of which a one-dimensional liquid resides of height (in layers) $\theta = N/M$. If we assume that molecules in all layers, including the first, are equivalent, with molecular partition function q, then each subsystem partition function takes the form [32]

$$\xi = 1 + q\lambda + q^2\lambda^2 + q^3\lambda^3 + \cdots = \sum_i^m q^i\lambda^i, \tag{5}$$

where m molecules occupy the site. From Eqs. (4) and (5) the thickness is then

$$\theta = \frac{q\lambda}{1 - q\lambda} = \frac{x}{1 - x}, \tag{6}$$

where we have used the typical redefinition of the activity, $x = q\lambda$ [32]. Equation (6) thus predicts a relationship between thickness and liquid activity. The solid line of Fig. 2 is calculated from Eq. (6), and this curve is consistent with the data for the molecular systems. The theory also indicates that, by the definition of the bulk free energy, the interfacial liquid layer is thermodynamically equivalent to the bulk liquid for the molecular systems. The popular term "quasiliquid" may, therefore, be a misnomer and better reserved for atomic systems or systems with a layer thickness less than a few monolayers.

We do not yet know the reason for the two classes of behavior distinguishing the atomic and molecular species. One can calculate a curve to match the dependence on activity exhibited by atomic systems by taking higher powers of the activity in Eq. (6), but we are not aware of any expansion or other justification of such a formula. Previous classifications of systems according to logarithmic or power law dependence on temperature are now mixed, with systems exhibiting both types of temperature dependence represented in each class. Furthermore, the classes include strikingly different species, with the atomic species represented by both metals and noble gases, and molecular species by strongly hydrogen bonding systems and methane. One obvious distinguishing feature is the polyatomic nature of the molecular systems. The resulting differences in partition functions may provide a theoretical starting point to understand this difference.

Finally, Eq. (6) indicates behavior that is symmetric about the triple point, in that an inversion of the definition of x leads to the prediction of solid layers on the liquid surface at temperatures above the triple point. This effect has, indeed, been observed by surface tension [33] and x-ray scattering [34] measurements for a series of normal alkanes. We have calculated the predicted interfacial layer thickness, both liquid and solid, for a series of n-alkanes in the inset of Fig. 3. The thickness is plotted as a function of temperature above and below the triple point, and the carbon number (e.g., 1 = methane, 4 = n-butane). The divergent thickness at $\Delta T = 0$ has been suppressed. The thickness has been calculated using the activity from Eq. (2) (inverted for $T > T_t$), tabulated values of ΔH_{fus} and T_t for the n-alkanes, and Eq. (6). The calculations are based solely on the measured thermodynamic quantities of these alkanes and show two interesting features relative to the measurements of the solid on

TABLE I. Heats of fusion and triple point temperatures used in Eq. (2).

	ΔH_{fus} (kJ/mole)	T_t (K)
Neon[a]	0.43	24.54
Argon[a]	0.99	83.81
Lead	4.80	600.65
Aluminum	10.69	933.52
O_2	0.73	54.35
Methane	1.55	90.65
H_2O	4.59	273.15
Caprolactam	16.10	342.30
Biphenyl	18.69	342.61

[a] Determined from measured vapor pressures.

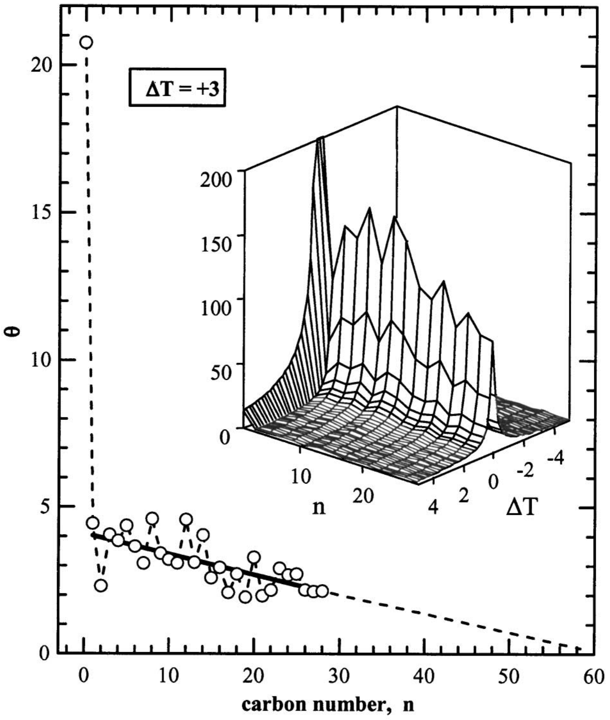

FIG. 3. Solid layer thickness at 3 K above the triple point for the n-alkanes, as a function of carbon number. The solid line is a fit to the data, extrapolated to zero thickness. The calculation indicates that a solid layer on the liquid should no longer be observed at carbon number greater than 58, in agreement with measurements [33]. Inset: Surface plot of the calculated layer thickness for the family of normal alkanes as a function of both the difference temperature, $\Delta T = T - T_t$, and the carbon number.

liquid layer. With the exception of $n = 1$ we note that the thickness peaks at $n \sim 10$ and begins to reduce with increasing n. In fact, this reduction can be extrapolated to predict the loss of a measurable surface layer. This is done in the main panel of Fig. 3 at $\Delta T = +3$, corresponding to measurements made in Ref. [33]. The predicted loss of the detectable layer occurs at ~58 layers. This peak of thickness at $\sim n = 10$ and loss of the phenomenon at $\sim n = 60$ is consistent with Ref. [33] for $14 > n > 50$. Thus, the theory also quantitatively reproduces the most recent observations with regard to symmetry about the triple point.

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