

Melting at Grain Boundaries and Surfaces

In a recent Letter, Broughton and Gilmer¹ studied melting at grain boundaries (GB) in a system of particles interacting via truncated Lennard-Jones forces. They observed the growth of a disordered, liquidlike film within the GB as the temperature, T , was raised towards the triple point with $T = T_3$. In this Comment, I show that the analogy between these melting phenomena and related interfacial phase transitions, such as complete wetting in fluids^{2,3} and surface-induced disorder in solids,⁴ leads to new predictions for melting at boundaries.

On any point of the crystal-liquid (CL) coexistence curve with pressure P and $T = T_m(P)$, the GB with interfacial tension γ_{GB} may contain a droplet of the melt bounded by the CL interface with tension γ_{CL} . In equilibrium, the interfacial tensions must balance which implies $\gamma_{GB} = 2\gamma_{CL}\cos(\phi)$, where ϕ is the contact angle. In a fluid context, this is known as Antonow's rule.⁵

When $\phi = 0$, the droplet spreads out and the GB is wetted by the melt. In this case, a disordered, liquidlike film appears in the GB when the CL coexistence curve is approached from $T < T_m(P)$. The Landau free energy per unit area for a film of thickness l is^{3,4,6,7}

$$V(l) = Atl + V_0(l), \quad (1)$$

with $t \equiv (T_m - T)/T_m$, and $A \equiv T_m(S_L - S_C)$, where S_L and S_C are the bulk entropies per unit volume of the liquid and of the crystal at T_m . The term $V_0(l)$ depends on the intermolecular forces. If these forces decay faster than exponentially, $V_0(l) \approx \gamma_{CL}\exp(-l/\xi_L)$ for large l , where ξ_L is the bulk liquid correlation length at T_m . This applies to *truncated* Lennard-Jones potentials as studied in Ref. 1. Then, for three-dimensional systems, the l dependence of the equilibrium thickness, l_{eq} , follows from mean-field theory, i.e., from $\partial V/\partial l = 0$.³ Thus, $l_{eq} \propto \ln(1/t)$ as $t \rightarrow 0$. The same divergence follows for the excess energy. This is consistent with the molecular-dynamics data obtained in Ref. 1.

In real solids, nonretarded and retarded van der Waals forces lead to² $V_0(l) \approx -W/l^2$ and $V_0(l) \approx -\bar{W}/l^3$ in (1) for large l , respectively. However, it follows from the general theory of van der Waals forces that the Hamaker constants W and \bar{W} are always positive for a liquidlike film intruding between two crystals which differ in their orientation but not in their density. Therefore, the effective van der Waals force between the two CL interfaces is *always attractive*. Furthermore, interfacial fluctuations cannot overcome this attraction in three-dimensional systems.³ This implies that the liquidlike film has a finite thickness, l_{eq} at $T = T_m$, and the GB *can only be wetted incompletely by the melt*. Nevertheless, the liquidlike film can consist of many atomic layers and will have interesting physical properties since the quasiliquid is strongly perturbed by the vicinity of the

two CL interfaces.

For surface melting, on the other hand, the effective van der Waals force between the CL and the liquid-vapor interface can be repulsive. Indeed, W and \bar{W} are expected to be negative in this case when the density in the solid phase is larger than in the melt.⁴ Then, $l_{eq} \propto 1/t^\psi$ as $t \rightarrow 0$ with $\psi = \frac{1}{3}$ and $\frac{1}{4}$ for nonretarded and retarded van der Waals forces, respectively.

For GB melting, the two CL interfaces bounding the liquidlike layer differ in their orientation and, thus, can differ in their roughening temperature T_R . So far, I have tacitly assumed that at least one CL interface is rough. If both were smooth, the growth of the liquidlike film would occur in a layer-by-layer mode. This would lead to (rounded) steps in the excess energy as a function of T . Therefore, GB melting can be used to *determine* T_R for the CL interface. The data in Ref. 1 for the (310) system seem to indicate that at least one $T_R < T_3$ in this case.

Finally, *equilibration* of thick, liquidlike layers within a GB or at a surface will be rather slow: The layer growth is controlled either by the free-energy gradient, $\partial V/\partial l$, or by diffusion in the same way as for wetting layers.⁸ For short-range forces, for instance, $l(\tau) \propto \ln(\tau)$ with time τ as long as $l(\tau) \ll l_{eq}$. The final approach to equilibrium is given by $l_{eq} - l(\tau) \propto \exp(-\tau/\tau_0)$ if the growth is controlled by the free-energy gradient, and by $l_{eq} - l(\tau) \propto 1/\sqrt{\tau}$ if it is limited by thermal diffusion.

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