

Roles of grain boundary melting in the search for supersolid helium

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Topics

Adsorption and wetting

Premelting

Incomplete wetting of solid He

Grain boundary melting

Slippage of bulk solid; viscous coupling

Crystalline interfaces

Speed of crystal growth

Critical velocity; temperature dependence

He3 effects

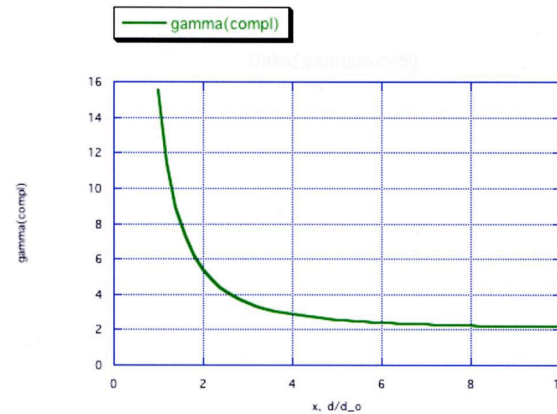
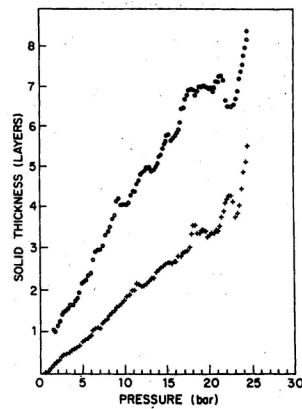
Pressure-driven flow

Porous media

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Adsorption and wetting



Strong adsorption forces from most solid substrates should cause preference for solid deposit during solid-liquid coexistence. Observations of He4 adsorption on graphite by Gridin, et al. , and by Eckstein, et al. confirm such expected behavior. Many experiments show that He monolayers on graphite form highly ordered states. Monotonically thickening solid grows with increasing pressure. The graph of surface energy shows how $\gamma(d)$ decreases with increasing thickness when adsorption is dominated by dispersion forces.

Adsorption on typical substrates

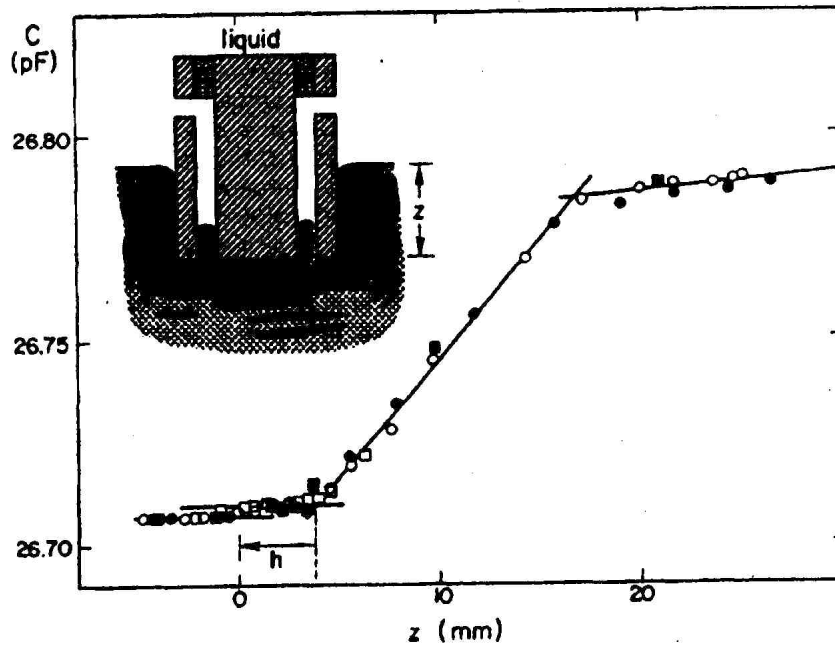
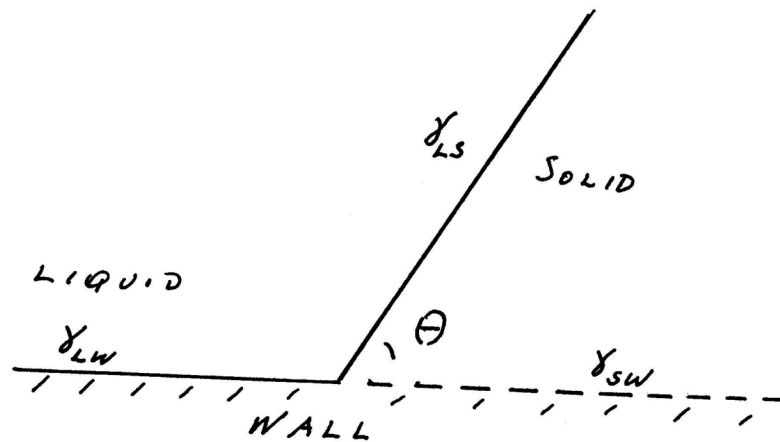


FIG. 1. Measurement of the capillary depression $-h$ at 1.31 K: capacitance C versus z . The inset shows a cylindrical capacitor immersed in the solid to a depth z . The small increase in C at $z=0$ is due to the edge capacitance as the solid reaches the bottom of the capacitor; the solid enters the annular space at $z=-h=3.9$ mm, and the capacitor is full at $z=16.7$ mm. Filled circles, initial decrease of 2 ; open circles, first subsequent increase of 2 ; filled and open squares, a second cycle, decreasing and increasing z , respectively.

In contrast to behavior on graphite, solid He at coexistence incompletely wets typical substrates. The solid nucleates abruptly on copper (Balibar, et al.), and on glass (Landau, et al.) The illustration shows observations on copper; an appreciable offset and finite contact angle. The cause of partial wetting is substrate heterogeneity, which imposes strains and disorder on the film. The disorder propagates to higher layers, hence the crystalline solid cannot evolve smoothly from the disordered film. Solid nucleates abruptly, leaving a grain boundary with appreciable surface energy. No substrate other than graphite has shown complete wetting of solid He₄ at coexistence.

Grain boundary energy

The finite contact angle between solid and substrate gives a measure of the grain boundary* energy γ_{sw} :



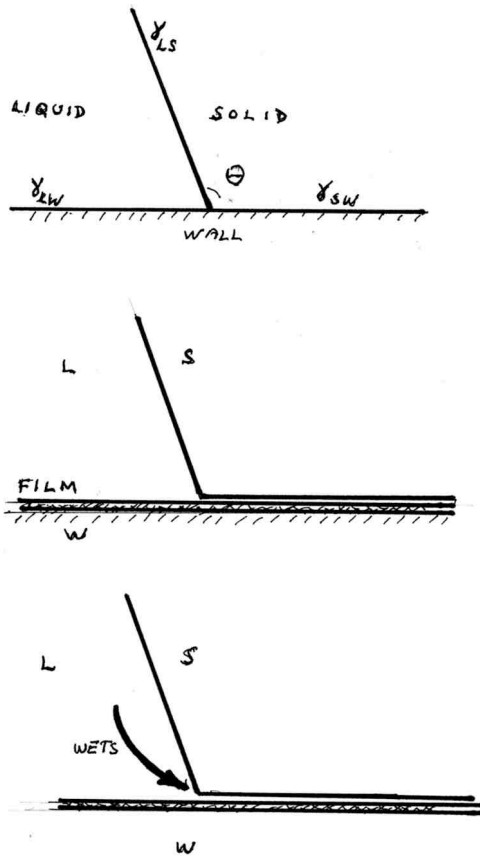
$$\gamma_{sw} = \gamma_{lw} - \gamma_{ls} \cos\theta$$

From Balibar's data we estimate the grain boundary energy at coexistence

$$\gamma_{sw} = 1.1 \text{ erg/cm}^2$$

*The term *grain boundary* is apt because the actual interface is between the solid He and a film of adsorbed He. In more typical cases *grain boundary* refers to interfaces between crystallites of the same substance.

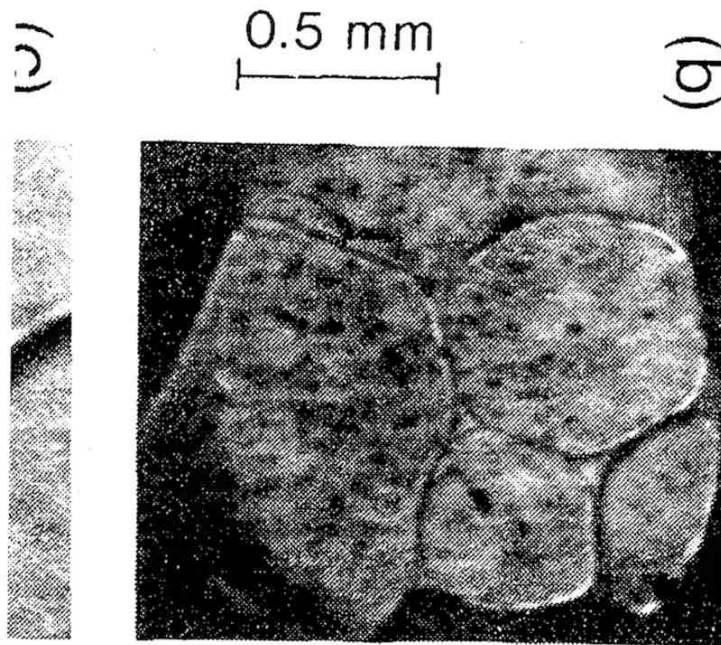
Liquid invades



Liquid is isotropic, compressible and can more easily adapt to the irregularities of the grain boundary surfaces. It reduces the gb energy; if liquid is present it will invade the grain boundary. But after the liquid thickness grows to a few layers, the attraction of the walls prefers the higher density solid, so the liquid growth is terminated. Thus, the wetting of the grain boundary is incomplete.

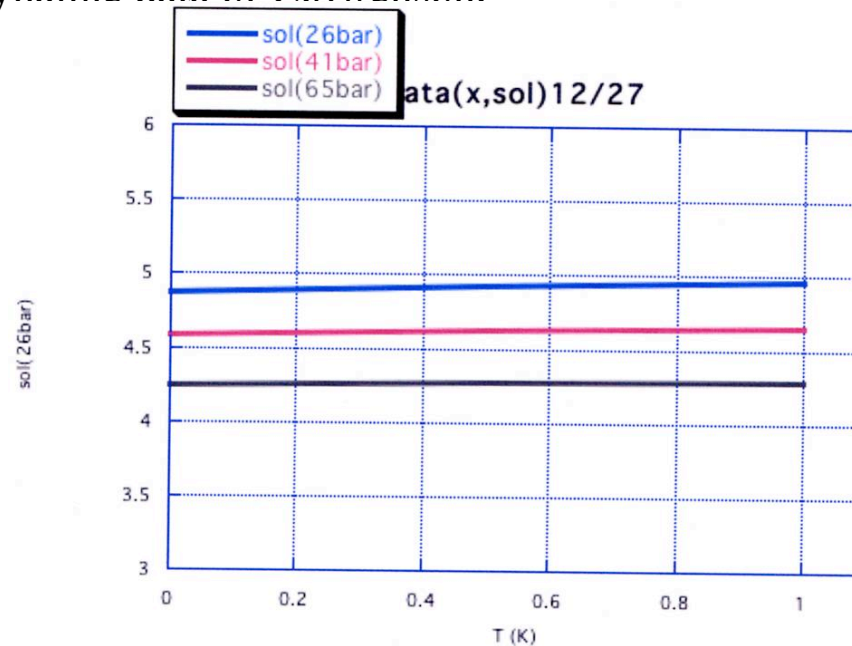
Grain boundary melting

If the liquid phase can lower the surface energy of an interface with a foreign substrate, or an interface between grains of the same substance, it will invade the boundary. If the conditions are not too far from the phase boundary, the solid will ***premelts*** to provide the wetting liquid. Franck, et al. observed the grain boundary melting of solid He4.



Thickness of the melt liquid

The thickness of the melt liquid at the bulk solid He-dense film interface is estimated by an expansion in P,T from a point on the phase coexistence line. The free energy of the melt is the sum of surface and bulk terms, and its chemical potential is equal to that of the solid. We calculate the thickness of the melt liquid at the pressures and temperatures of the Kim and Chan measurements on bulk solid. The reference state is taken from the thermodynamic data of C. Swenson.



Slippage and viscous drag

We propose that in the Kim and Chan experiment with bulk solid He, the grain boundary melt allows the solid to slip against the wall of the container. In our 2005 PRL the slippage was limited by viscous drag. We assumed that the melt liquid acts as a Newtonian fluid, and calculated the slippage for a thin walled cylinder bathed on both sides by a liquid layer of thickness d and viscosity η . The fractional slippage was identified with the missing rotational inertial fraction:

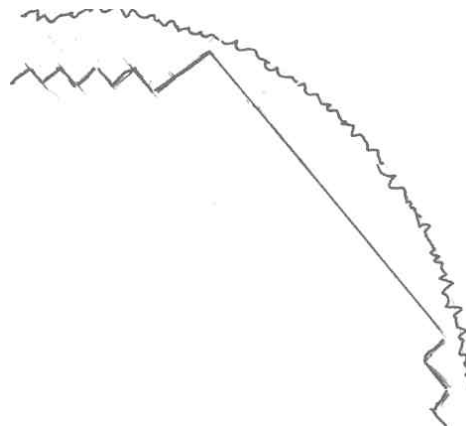
$$\text{NCRIF} = (\theta - \theta_o) / \theta_o = (\rho_{\text{sol}} / \rho_{\text{liq}}) sd / \lambda^2; \quad \lambda = (2\eta / \rho\omega)^{1/2}$$

Fitting to the observed NCRIF, the empirical viscosity is about 300 microPoise, an order of magnitude greater than the viscosity of liquid He4 at the λ point. The large factor was attributed to the combined effects of superfluid depletion at the walls and confinement.

We are now proposing a different primary drag mechanism.

The grain boundary surfaces

We now focus on the grain boundary surfaces, and recognize that they are rough. On the wall side, the disordered film is rough on a molecular scale. On the solid He side, the roughness is due to crystallinity. The solid adapts to the curvature of the cell walls by a combination of smooth facets and stepped vicinal facets.



Crystal growth rate

During torsional oscillations, as the solid tends to lag the motion of the cell, the local gb thickness fluctuates from the equilibrium value. If the motion is slow and/or T is low, crystal growth and melting can keep the gb close to equilibrium. As T rises, crystal growth rate decreases due to the increasing latent heat. Therefore, crystal growth cannot keep the system in equilibrium if shear velocity is too large or T rises; the surfaces interfere, or “scrape”, and slippage, decreases. Thus, critical velocity and T dependence of NCRIF are linked.

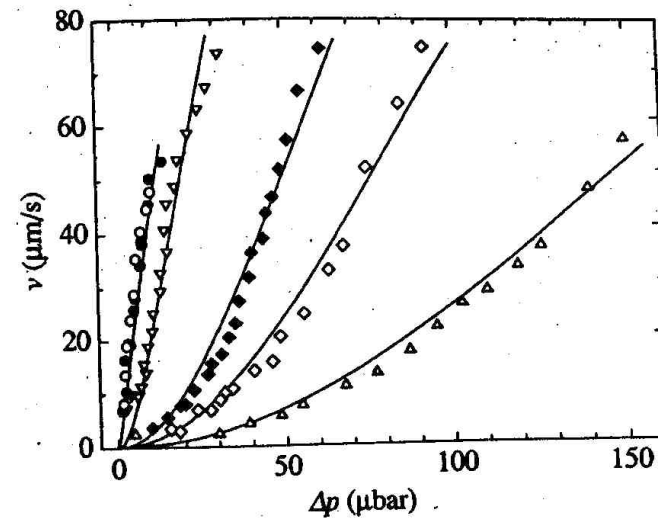
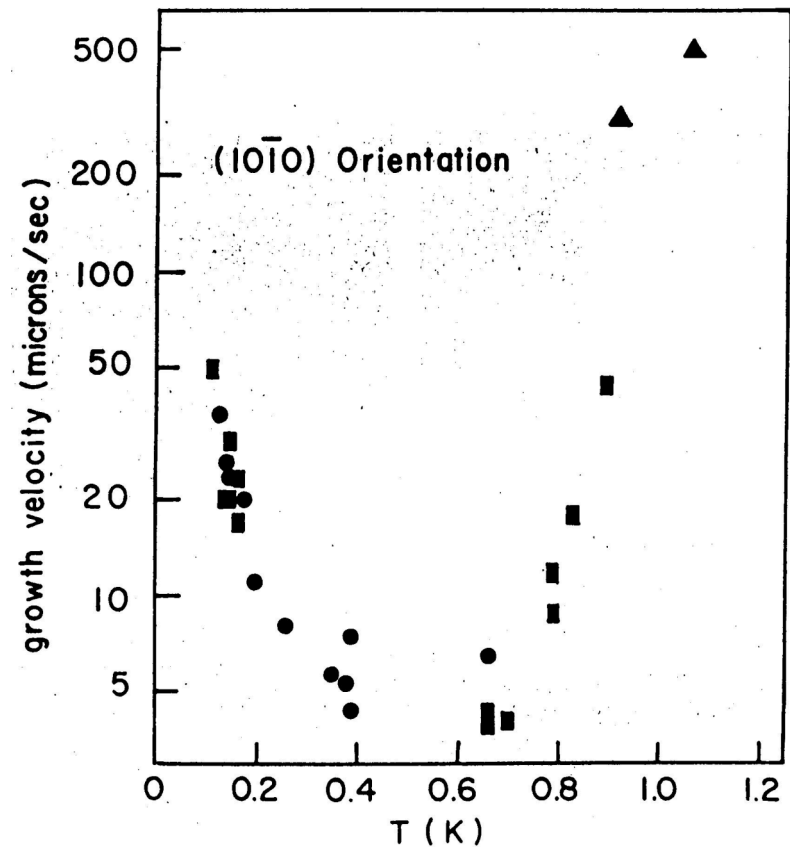


FIG. 55. Velocity of the c facet on ^4He crystals as a function of the driving pressure Δp : \circ , $T=2$ mK; \bullet , 20 mK; ∇ , 50 mK; \blacklozenge , 100 mK; \diamond , 150 mK; \triangle , 200 mK. Solid lines are guides to the eye. From Ruutu *et al.*, 1996.

Crystal growth speed vs T

The measurements of Wolf, et al. show the strong T dependence of growth rate below the roughening temperature. We note that the rates are comparable to the critical velocities detected in the torsional oscillation studies. We calculate that the growth rate necessary for the facets in the gb to avoid scraping (~ 1 nm/ms) can be induced by the chemical potential differences due to the torsional oscillations at the lowest temperatures.



Vortex excitation

We think it unlikely that new vortex lines can be excited in the grain boundary fluid by the oscillatory motion. However, trapped lines that had been created during the filling and cooling process may be extended. Relative motion of the background superfluid, which exerts a Magnus force on the trapped lines, may draw out loops of line. These loops move through the normal fluid fraction, which causes a 'mutual friction' drag force adding to the coupling between the solid He and the cell walls. It is even possible that some of the loops become attached to the opposite wall of the gb. These effects add to the mechanisms that decrease NCRIF at large velocities.

Possible He³ effects

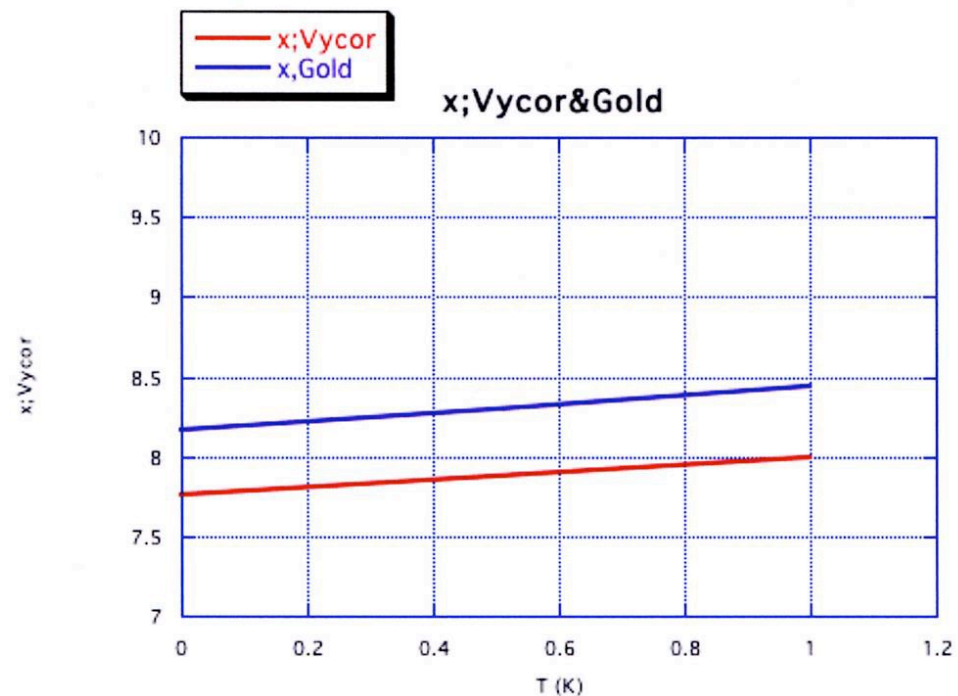
- Preference interfaces, grain boundaries, dislocations, vortex lines
- Inhibits grain growth, tends to stabilize small crystals
- Enhanced concentration in gb superfluid lowers T_c
- Pinning of dislocations

Pressure driven flow

- Very sensitive pressure driven flow experiments in Vycor by Day, et al, and in glass capillaries by Day and Beamish, detect no flow.
- If NCRI is due to bulk supersolidity, flow rate should be calculable (expected?) from chemical potential gradient and superfluid density.
- If NCRI is due to slippage at wall interfaces, flow rate may be calculable if detailed geometry is available.

Grain boundaries in porous media

Grain boundary thicknesses in Vycor and porous gold are calculated for the pressures of the Kim and Chan experiments. The effective pressures are expanded beyond the P,T of threshold freezing in the two media. It is important to note that the geometry of the media is much more complicated and heterogeneous than the simple computational model: a network of cylindrical tubes of uniform diameter and length.



NCRIF in porous media

We speculate on two possible mechanisms for missing rotational inertia in porous media.

Free circulation of superfluid in the grain boundary melt liquid
Slippage of a stiff skeleton of solid relative to the porous matrix.

But the NCRIF results in Vycor and in porous gold, i.e. the near equality of NCRIF, in spite of a factor of 200 in surface area, is difficult to explain by gb melting.

Experimental test: Is it a bulk or a surface phenomenon?

Test whether the missing inertia occurs in the bulk solid, or at wall-solid interfaces.

A cell filled with Grafoil, (sheets of oriented high area exfoliated graphite). Orient the sheets with the graphite xtal c-axis parallel to the rotation axis. Since solid He completely wets graphite at coexistence, there would no grain boundaries or disordered layers between the solid and the walls. If supersolidity appears in such a cell, the only locus for NCRIF would have to be the solid He.

Addendum on H₂

During discussion of the Penn State experiments that show very small but finite NCRI in a cell filled with solid H₂, I claimed that grain boundary melting could not be contributing to the effect, because the temperature was much too far from the phase boundary. I must now qualify that claim. If there is a disordered layer between the wall and solid hydrogen, as in the case of solid He, (and I think it likely), then its surface energy should scale with the latent heat. If it is wetted by the liquid phase, and the surface energy is lowered by a scaled amount, then grain boundary melting should occur, and extend down to very low temperatures.

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