Layer-by-Layer Growth of Solid \( ^4\text{He} \) on Graphite

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Recent experiments by Maynard et al on fourth sound in a Grafoil-filled \( ^4\text{He} \) cell show a periodic dependence of the resonant frequency on the average number of solid layers. We interpret their sharp minima as resulting from the inherent smoothness of complete layers, which inhibits the propagation of waves of melting and freezing, and reduces their damping and their coupling to fourth sound. Using a lattice-gas model, we study the roughness of incomplete surface layers, and suggest how this can lead to the observed broad maxima. We predict that the maxima of damping and of resonant frequency coincide.

1. INTRODUCTION

Maynard et al\(^1\) have reported experiments on fourth sound in a Grafoil/\( ^4\text{He} \) cell under pressure. They find a sequence of sharp minima in the resonant frequency, which is interpreted as evidence for layer-by-layer epitaxial crystallization of solid \( ^4\text{He} \) on the surface of the graphite platelets with increasing pressure. Their work is still the only evidence of layer-by-layer growth of the solid, and independent confirmation would be welcome. Nevertheless, despite the circumstantial nature of the evidence, their explanation in terms of layered growth is attractive. However, Maynard et al comment, “exactly how the fourth sound velocity is affected by the formation of solid layers is not clear.” The present paper attempts to clarify this question.

Qualitatively, it is plausible that fourth sound is affected differently by a complete solid \( ^4\text{He} \) layer and an incomplete one. The complete layer should be quite rigid and inert, while an incomplete layer is capable of partial crystallization and melting in the varying pressure field of the fourth sound. The situation is reminiscent of the difference between rough and smooth solid–liquid interfaces\(^2\) in bulk \( ^4\text{He} \).

The temperature in these experiments\(^1\) was between 1.0 and 1.5 K—mostly above the reported roughening temperature for bulk \( ^4\text{He} \). However,
external force fields extend the region of stability of smooth surfaces, and at a distance of only a few atomic layers from the graphite surface there is a strong van der Waals field. The possible formation of smooth surfaces well above the bulk roughening temperature is therefore not surprising.

We stress that our picture does not involve a roughening transition—we believe that close to the graphite substrate the interface is naturally smooth, and that the roughness of incomplete layers is a constraint arising directly from their incompleteness. Nevertheless, this constrained roughness is enough to endow the interface with dynamical properties.

A simple way to picture the experimental cell of Maynard et al. 1 is that it is composed of two coupled dynamical systems: (a) the interstitial liquid helium, whose dynamics is governed by the usual two-fluid hydrodynamics,3 leading to fourth-sound propagation, and (b) the solid–liquid interface, which can support waves of melting and freezing ("paglyons," from παγγωνω, "freeze," and λυωνω, "melt"). Each system has resonant modes, which may be regarded as damped harmonic oscillators. Let the complex frequency of a bulk fourth-sound mode be \( \omega_1 = \omega_1' + i \omega_1'' \); \( \text{Im}(\omega_1) = \omega_1'' < 0 \) describes the intrinsic damping. The dissipation associated with the motion of the liquid should not depend on the interface structure; the tangential component of the superfluid velocity \( v \), need not vanish on a glass surface, a fortiori not on a rough solid helium surface. Hence, if we characterize the solid–liquid interface by a roughness parameter \( \alpha \) (defined more precisely later), \( \omega_1'' \) is independent of \( \alpha \).

However, the dissipation associated with a paglyon mode should depend on \( \alpha \) and be maximal when the surface is roughest (i.e., when the surface layer is half full). For simplicity, we assume linearity; \( \text{Im}(\omega_2) = -\kappa \alpha \), where \( \kappa \) is a constant. Let \( \omega_2' \) denote Re \( (\omega_2) \).

The two modes are coupled, since the surface layer will melt and freeze with pressure fluctuations. The coupling should be strongest when the interface is roughest; the simplest assumption is again linearity in \( \alpha \), with a proportionality constant \( \lambda \).

The frequencies of the coupled system are the eigenvalues of the matrix

\[
\begin{pmatrix}
\omega_1 & \lambda \alpha \\
\lambda \alpha & \omega_2' - i \kappa \alpha
\end{pmatrix}
\]

namely

\[
\Omega_\pm = \frac{1}{2}(\omega_1 + \omega_2' - i \kappa \alpha) \pm \sqrt{\left[\frac{1}{4}(\omega_1 - \omega_2' + i \kappa \alpha)^2 + \lambda^2 \alpha^2\right]^{1/2}}
\]

We find (see below) that the roughness parameters \( \alpha \) has a rather flat maximum for a half-filled surface layer, and a sharp minimum when the number of layers is an integer. Expanding Eq. (2) for small \( \alpha \), we find for
the shift $\Delta(\omega_1 - \omega_2) \equiv \Omega_+ - \Omega_- - (\omega_1 - \omega_2)$ in the frequency difference,

$$\Delta(\omega_1 - \omega_2) = \alpha^2 (4\lambda^2 - \kappa^2)/(\omega_1' - \omega_2') + O(\alpha^3)$$

(3)

The frequencies "repel" if $2\lambda > \kappa$ and $\omega_1' - \omega_2' > 0$, or if both inequalities are reversed. Since $\omega_2'$ is considerably larger than $\omega_1'$, the observation that the fourth-sound frequency increases for incomplete layers implies that $\kappa > 2\lambda$, i.e., the damping is more important than the direct coupling. (An alternative possibility is that $\kappa < 2\lambda$, but that in solid layers of only a few atoms thickness the paglyon modes are drastically slowed. This could occur because in two dimensions melting becomes a transition of higher than first order.)

2. THE LATTICE-GAS MODEL

To estimate the dependence of $\alpha$ on the incompleteness of the surface layer, we model this layer and its most relevant neighbor by a lattice gas on a pair of triangular lattices*; the two layers are displaced so as to represent the positions of atoms on the surface of a growing hcp crystal. Let the average layer coverage be $\theta$, and let $n$ be the integer nearest to $\theta$. If $\theta$ is greater (smaller) than $n$, the lower layer is almost full (upper layer is almost empty) and plays only a minor role. We use magnetic terminology, and let "spin up" represent a filled site. Let $\sigma_u^U$ and $\sigma_u^L$ designate spin variables (with values $\pm 1$) on the upper and lower layers, respectively, and let $J$ be an Ising coupling constant, modeling the tendency for two neighboring sites to be both filled or both empty. The solid-on-solid approximation is used. This approximation neglects "overhanging" solid, as well as droplets of foreign phase. It thus fixes the number of unsatisfied bonds between sites on different layers, and enables us to ignore interlayer interactions. (It also neglects the effect of the gradient of the van der Waals field of the substrate.) The model Hamiltonian is thus

$$H = -J \sum_{R=U,L} \sum_{\langle \alpha, \beta \rangle} \sigma_\alpha^R \sigma_\beta^R$$

(4)

where the sum is over nearest neighbors only. The total number of spins per layer is $V$, and we take periodic boundary conditions.

The fractional coverage $c = \theta - n$ is modeled by the magnetization of the two layers:

$$c' = \frac{1}{2}(M_L + M_U)$$

(5)

*In restricting our attention to two layers, we rely on the surface not being rough on the scale of many layers (i.e., in the sense of the roughening transition). Also, the smallness of the latent heat of $^4$He melting in the experimental temperature range makes the lattice gas an appropriate model.
Fig. 1. The dependence of the surface roughness parameter $s$ on the fractional coverage $c'$ for several temperatures. Each point represents the mean of at least $1.2 \times 10^6$ attempted pairs of spin flips on a two-layer system with 400 spins per layer. For clarity, only a few typical error bars are shown; they represent 2.6 standard deviations. $T_c = 3.64 \text{ J}$ is the Onsager temperature for an infinite plane triangular lattice. Three points near $c' = 0$ lay outside the area of the graph, and were omitted. Note that the maxima do not occur precisely at $c' = \frac{1}{2}$. This fact (and more generally the inequivalence between the points $c' = -a$ and $c' = 1 - a$) reflects the limitations of the two-layer model; they could have been avoided by using a three-layer model.
where

$$M_R = V^{-1} \sum_\alpha \sigma_\alpha^R, \quad R = L, U$$  \hspace{1cm} (6)

As a measure of our roughness parameter $\alpha$, we take the sum $s$ of the perimeters of all the solid (i.e., spin-up) regions in both layers, i.e., if $E$ is the energy (4) of a particular configuration, then for that configuration $s = E/J - 6V$.

We have studied the dependence of $s$ on $c'$ by Monte Carlo simulation and analytically.\textsuperscript{7} In the simulation, we keep $c'$ constant, by considering only pairs of opposing spin flips. The temperatures for the simulation were chosen sufficiently below the Ising critical temperature to avoid macroscopic fluctuations, but sufficiently above zero to allow spontaneous droplet formation. The results are shown in Fig. 1. The sharp kink at $c' = 0$ is important, since we believe that it is responsible for the sharp minima in resonance frequencies described in Ref. 1. However, near $c' = 0$ the error bars of the Monte Carlo calculation appear to be anomalously large, and for that reason we have also studied the region of small $c'$ analytically.

For $c' = 0$, the solid-on-solid condition can be ignored; each layer will take a “magnetization” close to the spontaneous Ising magnetization, but the two layers will take opposite signs. For small but positive $c'$, a change of $M_L$ has a free energy cost of order $V \delta M_L$. However, because of the formation of bigger than critical droplets, the cost of a change $M_U$ in the upper layer is only of order $(V \delta M_U)^{1/2}$. The same argument applies, mutatis mutandis, for small negative $c'$. Arguing along the lines of Ref. 7, we find, for small $c'$, that

$$s(c') = s_T + \gamma |c'|^{1/2}$$  \hspace{1cm} (7)

where $s_T$ is a monotonically increasing function of $T$, and $\gamma$, which is related to the surface tension, decreases with $T$. Similarly, for $c' = \frac{1}{2}$, the arguments of Ref. 7 show that $s$ is nearly independent of $c'$.

### 3. DISCUSSION

While this manuscript was in preparation, we received an article\textsuperscript{8} which extends the experimental results of Ref. 1. As in Maynard et al.,\textsuperscript{1} Ramesh and Maynard make the connection between the applied pressure $p$ and the number of solid layers by using Franchetti’s theory\textsuperscript{9} of helium near a substrate. The relation is

$$\theta_F = (6.7 \text{ layers bar}^{1/3})(p_0 - p)^{-1/3}$$  \hspace{1cm} (8)

where $p_0$ is the bulk solidification pressure.
Ramesh and Maynard\textsuperscript{8} also give an interpretation of their experimental results; this interpretation is conceptually similar to ours, but differs in several respects. In particular, one important difference is that Ramesh and Maynard believe that the minima of frequency correspond to half-filled layers and the maxima to complete ones. In their interpretation, the sharpness of the minima follows from a postulated relation between $c$ and $s$:

$$s \propto |c| = |\theta - n|$$

Their explicit postulate is that the density of surface "kinks" is proportional to $c$. Although this density is not defined exactly, it seems to us that $s$ is a good measure of it. Equation (9) implies a discontinuity in the derivative $ds/d\theta$ for both integer and half-odd values of $\theta$. (Note that $n$ is the nearest integer to $\theta$, and not the integer part of $\theta$.)

Ramesh and Maynard introduce a semiempirical correction, relating the coverage $\theta$ to the "Franchetti coverage" $\theta_F$. Their expression, which contains two adjustable parameters, is

$$c = \theta - n = 2^{i-1}(1 - \gamma)(\theta_F - n)^i + \gamma(\theta_F - n)$$

When the parameters $i$ and $\gamma$ satisfy the conditions $i > 1$, $\gamma \neq 0$, the correction weakens the influence of the singularities in $s(\theta)$ for integral $n$, but not of the half-integral singularities. The half-integral singularities therefore contribute the sharpness required to fit the observed minima, while the integer ones are smoothed, to reproduce the broad maxima. A priori, the form (9) does not seem plausible to us. The density of kinks is presumably closely related to our roughness parameter $s(c)$—a quantity that we have found to be flat near $c = \frac{1}{2}$ (consistent with the results of Ref. 7).

It is difficult to decide which postulate fits the experimental data better—minima of frequency at integer or at half-odd-integer layer coverage; the Franchetti\textsuperscript{9} relation [Eq. (8)] used by Maynard et al. is only reliable some distance from the substrate, and the choice of its zero is uncertain. It should, however, be possible to resolve the question by comparing the positions of the resonant frequency minima with the maxima of damping. According to our interpretation, the damping should be maximal half-way between the sharp frequency minima, while according to the interpretation of Ref. 8, maximum damping should coincide with minimum frequency. A comparison with some preliminary attenuation data (Maynard, private communication) is inconclusive. Other checks of the form (3) can be made by varying $\omega_0$—e.g., by looking at higher fourth-sound resonances or by changing the size of the cell.
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REFERENCES