Title
Studies of the Melting of a 2D Solid

Journal
Journal of Phys C. Solid State Physics, 15

Authors
Sinha, S. K.
Vora Purohit, Parul
Dutta, P.
et al.

Publication Date
1982

Peer reviewed

J. Phys. C: Solid State Phys., 15 (1982) L275–L281. Printed in Great Britain

LETTER TO THE EDITOR

Studies of the melting of a 2D solid

S K Sinha†, P Vora†‡, P Dutta§ and L Passell‖

† Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

‖ Department of Physics, Brookhaven National Laboratory, Upton, NY 11973, USA

Received 31 December 1981

Abstract. We have made a detailed numerical analysis of neutron diffraction lineshapes across the constant-coverage melting transition of incommensurate monolayers of methane on graphite. We find that in the liquid phase the liquid lineshape is well fitted with a lorentzian structure factor. While the exact nature of the transition very close to T_m cannot be commented upon, the 'freezing' of the liquid appears to be initially continuous, with an increase in correlation length to hundreds of Ångstroms before the appearance of a solid phase.

Recent theoretical work has emphasised the unique nature of the melting transition in two-dimensional (2D) systems (Dash and Ruvalds 1979, Sinha 1980). The dislocation-mediated theory of melting (Kosterlitz and Thouless 1973, Young 1979, Nelson and Halperin 1979) predicts a continuous melting transition from a 2D solid to a 'hexatic' liquid phase with only an essential singularity in the specific heat. However, a more definitive signature for this transition is predicted in the pair correlation length, which is expected to diverge continuously as the temperature is lowered towards the liquid–solid transition temperature T_m. On the other hand, several computer simulations (Abraham 1980, Toxvaerd 1980, Kalia and Vashishta 1981) appear to yield the result that the 2D melting transition is first order, as in 3D.

Monolayer films physisorbed on relatively smooth substrates provide good physical realisations of two-dimensional solids and fluids. (The effect of the lateral periodic potential of the substrate is minimised when the monolayer periodicity is *incommensurate* to that of the substrate, although an orientational ordering field may still be present.) In this Letter we present a quantitative study of the behaviour of the structure factor of CD_4 monolayers on a graphite substrate through the melting transition, using neutron diffraction techniques. In order to do this, it is necessary to carry out a more detailed and rigorous analysis of the diffraction lineshape in terms of an arbitrary $S(K)$, rather than the 'Warren' lineshapes (Warren 1941, Kjems *et al* 1976) used previously. We have done this, and the general expression for the observed lineshape in terms of $S(K)$, the orientational distributions of the graphite crystallites and the instrumental resolution has been given elsewhere (Dutta *et al* 1980, Sinha *et al* 1982). The results presented here will represent least-squares fits to those lineshape expressions using

‡ Present address: Department of Physics, Michigan State University, East Lansing, MI 48824, USA.

§ Present address: Department of Physics and Astronomy, Northwestern University, Evanston, IL 60201, USA.

0022-3719/82/100275 + 07 $01.50

suitably parametrised forms for $S(K)$. Details of the experimental technique may be found elsewhere (Dutta *et al* 1980, Sinha 1981). The diffraction experiments were performed with an experimental wavevector resolution of about 0.01 $Å^{-1}$.

The phase diagram of CD_4 on graphite is known from recent neutron diffraction studies (Vora *et al* 1979). At temperatures up to 50 K and up to a critical coverage (here denoted by $\rho = 1.0$), a registered $\sqrt{3} \times \sqrt{3}$ solid phase exists, while at higher coverages or temperatures the solid phase is incommensurate with the substrate, being expanded relative to the $\sqrt{3} \times \sqrt{3}$ structure for $\rho < 1.0$ and compressed for $\rho > 1.0$. From the earlier measurements (Vora *et al* 1979), it was deduced that melting from the *expanded* 2D solid proceeded through a coexisting solid–liquid phase region as the temperature was raised, indicative of a first-order melting transition. On the other hand for $\rho > 1.0$ no coexistence region could be identified, and for these constant coverage experiments it was surmised that the transition was continuous (the coverage on the surface was not quite constant owing to losses to the ambient vapour in the sample container with increasing temperature, but this effect is small). Since CD_4 on graphite always melts from an incommensurate (IC) solid phase, this system allows us to study the melting of a 2D solid on a smooth surface over a range of coverages. Accordingly, a detailed set of neutron diffraction measurements was performed as a function of temperature using a grafoil substrate and at two nominal values of the coverage ($\rho = 0.92$ and $\rho = 1.09$).

Results for the structure factor in the vicinity of (10) reflection for the IC solid phase are presented elsewhere (Sinha *et al* 1982). They are consistent with the power-law structure factor expected theoretically, with the exponent η increasing rapidly near T_m. This is ascribed (Nelson and Halperin 1979) to the renormalisation of the elastic moduli near T_m.

Figure 1 shows the integrated intensity of the (10) diffraction peak (with the empty grafoil scattering subtracted) as a function of temperature for the two coverages studied. It may be seen that for the higher coverage there is an abrupt decrease in the peak height, indicative of a solid–liquid transition. For $\rho = 0.92$, a more gradual rise is noted with decreasing temperature. This is similar to the behaviour observed for Kr on graphite (Birgeneau *et al* 1980) and is ascribed to the presence of a two-phase coexistence region. Although the temperature at which the solid phase first appears cannot be precisely

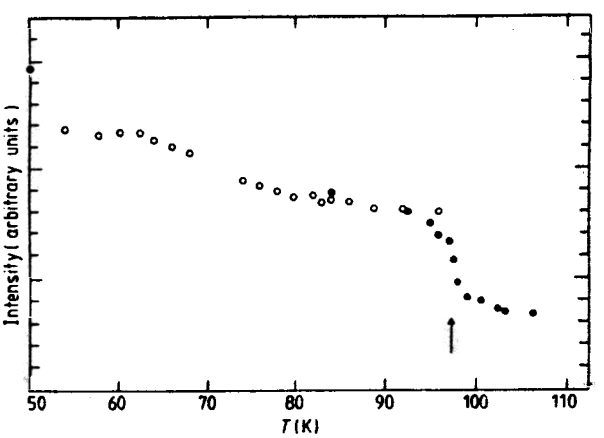

Figure 1. Integrated intensity of (10) diffraction peaks (with background subtracted) from CD_4 on grafoil (○ $\rho = 0.92$; ● $\rho = 1.09$) as a function of temperature across the melting transition.

determined from the plot, it reveals temperature ranges over which the liquid phase certainly exists. Accordingly, starting from the highest temperatures, a fit to the observed peaks was made, assuming a liquid structure factor.

No attempt was made here to verify directly the existence of a hexatic phase, since the random orientation of the crystallites around the c axis precludes observation of orientational order in the plane. It is believed that the orientational field of the substrate also eliminates the isotropic-liquid to hexatic transition. Accordingly, for the fitting procedure, we chose the structure factor given by Nelson and Halperin (1979):

$$S(\boldsymbol{K}) = \sum_{\boldsymbol{G}} \bar{S}_{\boldsymbol{G}}(\boldsymbol{K} - \boldsymbol{G}) \tag{1}$$

where

$$S_{\boldsymbol{G}}(\boldsymbol{q}) = A(q^2\xi^2 + 1)^{-(1-\eta^*_{\boldsymbol{G}}/2)} \tag{2}$$

where $\boldsymbol{G}$ is a reciprocal lattice vector of the 2D solid, ξ is a correlation length in the fluid, A is an amplitude factor and $\eta^*_{\boldsymbol{G}}$ is the value of the exponent in the power-law structure

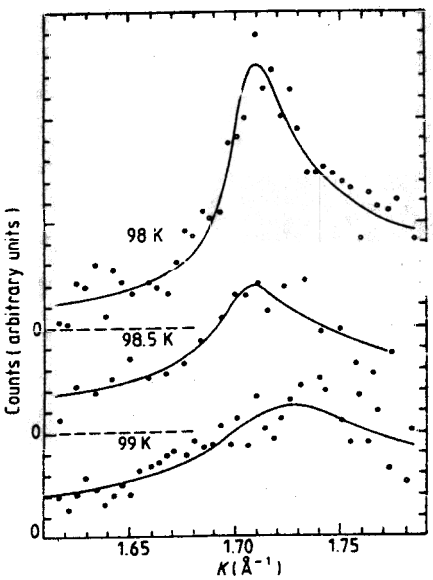

Figure 2. Diffraction lineshapes for the (10) peak of CD_4 on grafoil at a coverage of $\rho = 1.09$ as a function of temperature just above the melting transition. The full lines represent fits using a lorentzian $S(\boldsymbol{K})$ as in equation (2).

factor of the solid at T_m (for the (10) peak, η cannot exceed 1/3 (Nelson and Halperin 1979)). In practice, the exponent of equation (2) was approximated by unity (i.e. a lorentzian line shape was assumed), and contributions from reciprocal lattice vectors other than (10) were neglected. $S(\boldsymbol{K})$ was then averaged over all possible orientations of $\boldsymbol{G}$ in the plane, to obtain an effective isotropic $\bar{S}(\boldsymbol{K})$. It should be noted that the expression in equation (2) is approximate, being rigorously valid only at $q = 0$. Also, equation (2) is valid only for infinite 2D crystals. Modifications of the Kosterlitz–Thouless transition due to finite size effects have not yet been calculated theoretically. However, one would expect equation (2) to be valid provided $\xi < L$, the crystallite size.

Figure 2 shows the observed and fitted lineshapes in the high-temperature region for

a coverage of $\rho = 1.09$. The asymmetric form of the peak shapes is well known (Kjems *et al* 1976) and is due to the combination of the distribution of orientations of the crystallite planes and the nature of the diffraction process from 2D systems. Figure 3 shows the behaviour of the correlation lengths with temperature. Several features are to be noted. First, at high temperatures the correlation length is at a roughly constant value, which for all coverages is significantly larger than typical ranges of atomic correlation in 3D liquids. As the temperature is decreased, ξ rises rapidly and at still lower temperatures behaves rather differently. We interpret the lower-temperature regime as that in which the system has become a finite-sized 2D solid (for $\rho = 1.09$) or has passed into the regime of solid–liquid coexistence, i.e. a first-order transition has taken place (for $\rho = 0.92$). In these regimes, we are no longer justified in using equation (2). Thus only the higher-temperature points, as shown, were used in discussing the behaviour of ξ with temperature in the liquid. Unfortunately, since the exact T_m cannot be determined because of the above effects, the number of observed values of $\xi(T)$ are not sufficient to

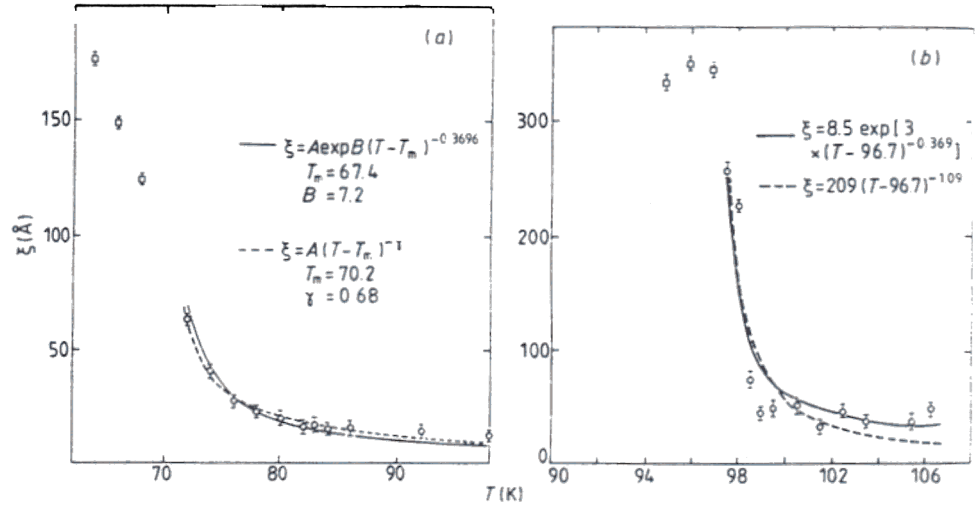

Figure 3. (*a*) Temperature dependence of ξ for CD_4 on grafoil at a coverage of $\rho = 0.92$ (fluid), based on fits using a lorentzian $S(K)$; (*b*) as in (*a*) but for a coverage of $\rho = 1.09$. Open circles are the data.

characterise definitively the critical behaviour. Shown in figure 3 are fits of $\xi(T)$ of the form (Nelson and Halperin 1979)

$$\xi(T) = \xi_0 \exp[b(T - T_m)^{-0.3696}] \tag{3}$$

where ξ, A, T_m were taken as adjustable parameters. Also shown are straight power-law fits of the form

$$\xi(T) = a(T - T_m)^{-\nu}. \tag{4}$$

It may be seen that it is not possible on the evidence of the data to decide which is to be preferred

(i) It may be shown by computer simulation of lineshape profiles using different values of ξ that the present instrumental resolution (including crystallite misorientation effects) does not prevent us from distinguishing ξ values up to 800 Å. Although the overall width of the curve is not very sensitive to ξ beyond 150 Å or so, the ratio of the height of the peak to the height of the 'tail' at large q is still quite sensitive to ξ. However, this assumes a unique model (lorentzian lineshape) for $S(\boldsymbol{K})$.

(ii) Computer simulations show that, in principle, the lineshapes for a power-law (solid-like) structure factor ($\eta < \frac{1}{2}$) and lorentzian (liquid-like) structure factor are distinguishable for $\xi < 1/\Delta K$, where ΔK is the halfwidth of the effective leading edge due to instrumental resolution. However, the distinguishability requires counting statistics far better than obtained in the present experiments. Thus, there remains the troublesome question of whether the apparent increase of ξ on lowering T may be due to the continuous but rapid increase of a solid phase coexisting with a liquid phase. This may, however, be resolved by means of the following further test. Let us suppose there

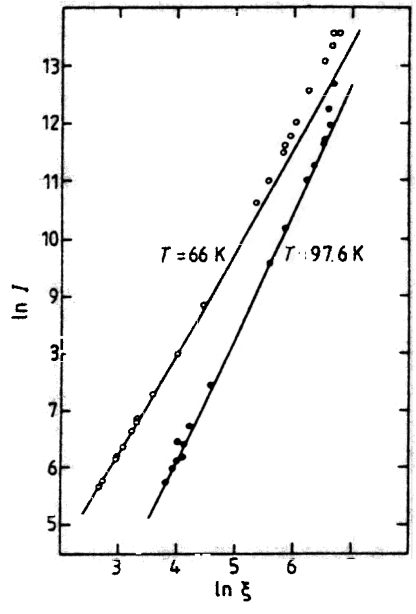

Figure 4. Dependence of the amplitude factor A of the fitted lorentzian form of $S(\boldsymbol{K})$ on ξ, for CD_4 on grafoil at $\rho = 0.92$ (open circles) and $\rho = 1.09$ (full circles).

exists a fraction f of solid and $(1-f)$ of liquid, where f may be a function of temperature. The structure factor may then be written as

$$S(\boldsymbol{K}) = fS_{\text{solid}}(\boldsymbol{K}) + (1-f)S_{\text{liq}}(\boldsymbol{K}) \tag{5}$$

where we assume a constant size L for the solid regions, and a characteristic $\eta (\simeq \eta^*$, since we are in the vicinity of T_m) which is also slowly varying with temperature relative to f. For $S_{\text{solid}}(\boldsymbol{K})$ we take the expression derived by Dutta and Sinha (1981) for a finite crystal. For $S_{\text{liq}}(\boldsymbol{K})$ we use equation (2), where $A = \xi^{2-\eta^*}$ as required by general scaling arguments. It is reasonable to assume that the amplitude A of the effective lorentzian fitted to equation (5) is proportional to the value of $S(\boldsymbol{K})$ at $q \equiv \boldsymbol{K} - \boldsymbol{G} = 0$, while the fitted ξ is proportional to the value of q at which $S(\boldsymbol{K})$ drops to half its maximum value.

Figure 4 shows a plot of ln A against ln ξ obtained from fits to the experimental data for both coverages. It can be shown that a pure liquid ($f = 0$) or a pure solid ($f = 1$) yields a straight line of slope $|2 - \eta^*|$. However, if f increases as T is lowered the fitted values would follow a curve of increasing slope with increasing ξ, as can be shown by direct computation of equation (5). It is seen that, for $\rho = 0.92$, the points do fall on a straight line of slope 1.68 until the point where solid–liquid coexistence is entered, at which point the slope increases as expected. Although the solid–liquid coexistence region precluded a measurement of η^* from the solid structure factor just below T_m, the value of 0.32 obtained from the slope is not inconsistent with extrapolation from values of η obtained at lower temperatures in the pure solid phase (Sinha *et al* 1982). For $\rho = 1.09$, a similar straight line was obtained in the regions which have been taken as 'liquid' phase in figure 3. The slope ($\simeq$2.0) was again consistent, within experimental error, with the much smaller value of η obtained as $T \rightarrow T_m$ in the solid phase for this coverage. The absence of a change in slope at T_m is consistent, as discussed above, with the absence of any appreciable solid–liquid coexistence region at this coverage.

On the basis of these measurements, one can thus say with a considerable degree of certainty that:

(i) the 'freezing' of a 2D liquid appears to be initially continuous, with an increase of the correlation length to hundreds of Ångstroms before the appearance of a true 2D solid phase;

(ii) any temperature region of coexistence of solid and liquid must be confined to a very narrow region, if any, around T_m for $\rho = 1.09$;

(iii) the predicted critical behaviour, i.e. the divergence of the structure factor as some power of the correlation length, appears to be obeyed;

(iv) the exact nature of the transition cannot be commented upon, particularly in the absence of predictions for the behaviour of ξ close to T_m for finite crystals.

Similar results have recently been obtained using synchrotron radiation for Ar monolayers on graphite by J P McTague, M Nielsen and J Bohr (private communication) and for Xe monolayers on graphite by P A Heiney, R J Birgeneau, G S Brown, P M Horn, D E Moncton and P W Stephens (private communication).

This work was supported by the US Department of Energy

References

Abraham F F 1980 *Phys. Rev. Lett.* **44** 463

Birgeneau R J, Hammonds E M, Heiney P, Stephens P W and Horn P M 1980 *Ordering in Two Dimensions* ed S K Sinha (Amsterdam: North-Holland) p 69

Dash J G and Ruvalds J (ed.) 1979 *Phase Transitions in Surface Films* (New York: Plenum)

Dutta P and Sinha S K 1981 *Phys. Rev. Lett.* **47** 50

Dutta P, Sinha S K, Vora P, Nielsen M, Passell L and Bretz M 1980 *Ordering in Two Dimensions* ed S K Sinha (Amsterdam: North-Holland)

Kalia R K and Vashishta P 1981 *J. Phys. C: Solid State Phys.* **14** L643

Kjems J K, Passell L, Taub H, Dash J G and Noraco A D 1976 *Phys. Rev.* B**13** 1446

Kosterlitz J M and Thouless D J 1973 *J. Phys. C: Solid State Phys.* **6** 1181

Nelson D R and Halperin B I 1979 *Phys. Rev.* B**19** 2456

Sinha S K (ed.) 1980 *Ordering in Two Dimensions* (Amsterdam: North-Holland)

Sinha S K, Vora P, Dutta P and Nielsen M 1982 to be published
Toxvaerd S 1980 *Phys. Rev. Lett.* **44** 1002
Vora P, Sinha S K and Crawford R K 1979 *Phys. Rev. Lett.* **43** 704
Warren B E 1941 *Phys. Rev.* **59** 693
Young A P 1979 *Phys. Rev.* B**19** 1855