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A first order two-dimensional melting transition: methane adsorbed on (0001) graphite (*)

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Résumé. — La diffraction neutronique permet de mesurer la perte de l’ordre à longue distance d’un solide bidimensionnel localisé de méthane adsorbé lors de sa fusion. Les expériences montrent que la fusion est une transition du premier ordre et que l’on peut définir le point triple de la couche, soit 56 ± 0,4 K.

Abstract. — The variation of long range order of a registered solid submonolayer of methane adsorbed on the graphite basal plane is measured at melting by neutron elastic scattering. The sudden loss of order indicates a first order melting transition and defines the two-dimensional triple point of the layer, namely 56 ± 0.4 K.

Among the phase transitions in monolayer films discovered a few years ago [1], melting involves long standing theoretical questions [2]. For an incommensurate monolayer, melting corresponds to the loss of long-range directional [3] or topological [4] order. For such systems, the melting transition can be either continuous or first order [4-7]. In the case of registered films with long-range positional order, melting to a disordered fluid phase can occur via a continuous transition, as, for example the order-disorder transition of the $\sqrt{3} \times \sqrt{3}$ registered phase of He on graphite [8, 9]. However, it is also possible that such phases could melt via a sharp first order phase transition. Experimental results for various solid monolayers adsorbed on graphite indicates that solid-fluid phase transitions are more or less abrupt, depending on the adsorbate and/or substrate quality [10-22]. It has been emphasized that size effects and substrate heterogeneity can blur a first order phase change and make it appear to be continuous [19]. Other characteristics of first order phase changes, which may be less subject to heterogeneity, are the coexistence of two distinct phases, and a linear dependence of extensive variables on the total quantity of adsorbate [2].

A recent Letter reported a coexistence region between 2D incommensurate solid and 2D liquid for a monolayer of NO adsorbed on graphite [23]. Here we report a more complete study of melting of methane adsorbed on graphite, where we find a coexistence region between 2D registered solid and 2D liquid, and at lower coverage a sudden loss of long range order within a narrow temperature interval, indicative of a first order melting transition at a 2D triple point. The liquid phase is characterized by its density, short range order and lateral mobility.

Our experimental system was deuterated methane ($\text{CD}_4$) adsorbed on Papyex [24], a compressed and partially aligned powder of exfoliated graphite similar to Grafoil [2, 10, 12]. It has large specific adsorption area ($\sim 20 \text{ m}^2/\text{g}$, $1.1 \text{ g/cm}^3$) predominantly of basal plane (0001) surfaces, with mean orientation parallel to the plane of the sheet. It has been used previously for neutron or X-ray scattering studies of films [23, 25-27].

The neutron diffraction experiments were performed in such a way that the incident beam and the scattering vector $\mathbf{Q} = 4\pi \sin \theta/\lambda$ were parallel to the mean orientation of the graphite basal planes (in-plane geometry). We used the deuterated form of methane ($\text{CD}_4$) which is a good coherent scatterer. Almost all the measurements were done for a coverage $x = 0.6$ monolayer within the 51.6-60.8 K tempera-

(*) Experiments performed at I.L.L. Grenoble.
ture range. Two other experimental conditions were also chosen, \( x = 0.83, T = 55.8 \text{ K} \) and \( T = 58.7 \text{ K} \). The interest of this choice will be obvious in the course of the discussion. In our notation, \( x = 1 \) corresponds to a 0.07 Å\(^{-2}\) molecular density, i.e. to a compressed out-of-registry monolayer.

For \( x = 0.60 \) and \( 51.6 \leq T \leq 55.7 \), the diffraction pattern exhibits a sharp peak (Fig. 1a) characteristic of an in-registry \( \sqrt{3} \times \sqrt{3} \text{ R } 30^\circ \text{ 2D solid illustrated in the inset. The same diffracted peak is observed for } x = 0.83 \text{ and } T = 55.8 \text{ K}. \) For both coverages (\( x = 0.60 \) and \( x = 0.83 \)), all the graphite surface cannot be occupied by a CD\(_4\) registered solid whose completion corresponds to \( x \approx 0.9 \). Hence a low density, disordered phase coexists with the 2D solid. This phase is a 2D gas and of course cannot be detected by neutron diffraction.

Fig. 1. — Neutron diffraction spectra from CD\(_4\) adsorbed on graphite. Background scattering from the substrate has been subtracted. Typical background level is \( 2-3 \times 10^4 \) counts for the present experimental conditions. Both curves are normalized to the same incident flux. The solid curve represents the best fit with the standard theoretical line [12] and yields the nearest neighbor distance and the correlation range \( L \). a) 01 peak of the in-registry \( \sqrt{3} \times \sqrt{3} \text{ R } 30^\circ \text{ 2D solid (inset), } T = 52.6 \pm 0.4 \text{ K and coverage } = 0.60, \) parameters of the fit : \( a = 4.26 \text{ Å}, L = 250 \text{ Å}. \) b) At melting the preceding peak broadens \( (T = 56.9 \pm 0.1 \text{ K, coverage } = 0.60) \) indicating a short spatial correlation range. Parameters of the fit : \( a = 4.33 \pm 0.3 \text{ Å}, L \approx 20-25 \text{ Å}. \)

The Bragg peak has been interpreted with the current theory (see for instance [12]) of 2D diffraction and the experimental data have been corrected for the instrumental resolution \( (\Delta \theta = 0.3^\circ) \) and for the distribution of crystallite angles about the preferential orientation. The width of the peak enables us to determine the spatial correlation range \( L \) of the 2D crystals, i.e. the mean size of the diffracting arrays. Its value is about 250 Å, nearly constant within the 51.6-55.7 K temperature range. Such a ∼ 250 Å correlation range has previously been observed for Kr [26] and NO [23] solids adsorbed on Papyex. The limited size of the 2D crystals is probably due to the existence of defects on the graphite surface preventing a larger extension of the 2D lattice.

Above \( T = 56 \text{ K}, \) the diffracted pattern for \( x = 0.60 \) changes drastically. It broadens and the correlation range decreases. Figure 1b presents a typical diffracted peak observed between 56.4 and 60.8 K. It defines a condensed phase with a short spatial correlation range \( (L \approx 20-25 \text{ Å}). \) Mobility measurements [27] have shown that this phase is a 2D liquid which, in these \( T \) and \( \theta \) ranges, coexists with a 2D gas.

In figure 2, the spatial correlation range is plotted as a function of \( T \). It drops abruptly by a factor 10 within 0.7 K indicating a clear-cut melting transition.

This result is confirmed by two experimental facts:

i) At melting, the distance between CD\(_4\) molecules jumps from 4.26 Å (\( \sqrt{3} \) in-registry structure) to 4.33 ± 0.03 Å. As in three dimensions, there is a sudden expansion when a 2D solid melts.

ii) At \( T = 58.7 \text{ K} \) and for \( x = 0.83 \), we observe a diffracted peak which can be interpreted as resulting from the scattering of a mixture of 2D liquid and solid. Figure 3 shows this peak and a comparison with a composite of 1/3 of 2D solid and 2/3 of 2D liquid.

The sharpness of our observed melting transition appears to be related to the graphite quality. Melting of 0.7 monolayer of CD\(_4\) adsorbed on graphon has been studied previously by neutron scattering [14]. In this case, the submonolayer melts continuously.
between 40 and 60 K. Graphon is a graphitized carbon black showing crystallites with very small (0001) uniform domains which prevents the developments of long range order; Marlow et al. report that their diffraction lines indicated coherence lengths of about 35 Å.

In summary, we experimentally demonstrated by neutron diffraction that $T = 56 \pm 0.4$ K is a phase boundary between the 2D gas-solid and the 2D liquid-solid coexistence domains. Hence $56 \pm 0.4$ K is the 2D triple point of the first layer of methane adsorbed on the (0001) graphite plane.

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[24] Papyex is the trade name of the product of Carbone Lorraine, 37-41 rue Jean-Jaurès, 92231 Gennevilliers (France).