

Evidence of Two Kinds of Two-Dimensional Adsorbed Fluids by Mobility Measurements

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(Received 22 January 1979)

The diffusion coefficient of a mobile CH₄ submonolayer adsorbed on graphite (0001) is systematically measured by quasielastic neutron scattering. Its behavior with coverage is used to distinguish clearly two kinds of adsorbed fluids; a two-dimensional liquid and a two-dimensional liquid and a two-dimensional hypercritical fluid.

The existence of phase transitions on physisorbed monolayers was observed about ten years ago by Thomy and Duval¹ and the names "two-dimensional (2D) gas," "2D liquid," and "2D solid" were justified by analogy with the three-dimensional phases in interpreting entropy determination obtained from adsorption isotherm measurements. More recently microscopic probes have been used in order to observe the actual mobility of these different phases, especially to distinguish between a solidlike and a fluidlike behavior. Different techniques, including NMR,²⁻⁴ Mossbauer resonance,⁵ or neutron scattering,⁶ have been used to detect 2D melting by measuring an enhancement in the mobility of the adsorbed phase. The large mobility observed in these experiments gives no information about the nature of the 2D fluid. It is not easy to make a precise distinction between a hypercritical fluid with a high compressibility, occupying the whole surface which is available for it, and a liquid whose domains are limited by a well-defined boundary.

We believe the results reported here answer the question in the case of a submonolayer of methane adsorbed on the basal plane of graphite. We measured the diffusion coefficient of the 2D CH₄ fluid by incoherent quasielastic neutron scattering at constant temperature as a function of coverage, and in addition we have shown that the type of variation of the 2D diffusion coefficient with coverage enables us to distinguish between two kinds of mobile phases, 2D liquid and 2D hypercritical fluid.

The CH₄-graphite (0001) system has several advantages: The (0001) graphite surface is highly uniform; methane has a strong incoherent neutron cross section and can be considered as a spherical molecule at the temperature at which

the experiment was performed; its rotation frequency is very large ($\omega_r \approx 10^{13}$ s) and does not result in a quasielastic effect in the range where the translational diffusion is observed. Furthermore, the phase diagram of the CH₄ adsorbed layer is fairly well known.¹ The condensation occurs in a layer-by-layer mode and the first layer undergoes two first-order phase transitions within a triple point and a critical temperature range. The 2D critical temperature (~ 72 K) is determined by adsorption isotherm measurements and the triple point is about 56 K as found by neutron scattering.^{6,7}

A graphite "powder" called Papyex⁸ is used to increase the surface per unit volume and obtain a measurable neutron signal. This powder is a recompressed exfoliated graphite having almost nothing but uniform (0001) surfaces with a preferential orientation. This product is very similar to Grafoil, which has been extensively used in surface phase studies.⁹

The quasielastic scattering experiment is currently employed to measure the diffusion coefficient of bulk liquids.¹⁰ A monochromatic neutron beam interacts with molecules executing Brownian movements and gains or loses energy, resulting in a broadening of the neutron energy distribution. According to theory, this broadening is Lorentzian and for small scattering vector Q the width ΔE of the peak is proportional to the translational diffusion coefficient D

$$\Delta E = 2\hbar D Q^2. \quad (1)$$

The experiment was carried out on the IN5 time-of-flight spectrometer at the Institut Laue-Langevin in Grenoble using an incident neutron beam of wavelength $\lambda = 8$ Å and a geometry where the scattering plane is parallel to the mean orientation of the graphite basal plane. This in-plane geometry

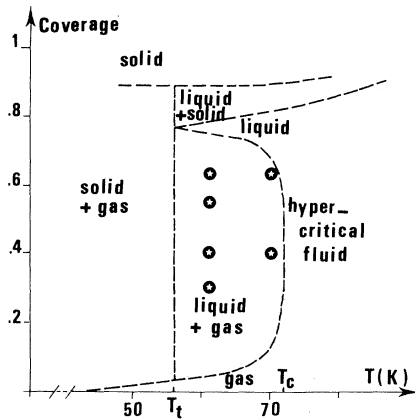


FIG. 1. Schematic phase diagram of the CH_4 first monolayer adsorbed on (0001) graphite. Our actual experimental conditions are represented by stars. The limit of the coexistence regions are not well known and the T_t two-dimensional triple point and the T_c two-dimensional critical temperature have been determined within ± 1 K. $\theta = 1$ corresponds to a $0.07\text{-}\text{\AA}^{-2}$ molecular density.

enables us to measure the mobility mainly parallel to the layer. The experimental resolution is $35\ \mu\text{eV}$. The scattering function is measured as a function of the energy E for a given scattering vector \vec{Q} ranging from 0 to $1\ \text{\AA}^{-1}$.

As is standard in monolayer neutron scattering physics, for each experimental condition the bare graphite spectrum was subtracted from the spectrum obtained with a given coverage of methane. Experiments have been performed at $T = 61$ K and coverages $\theta = 0.3, 0.4, 0.55,$ and 0.63 ; and at $T = 70$ K, $\theta = 0.4$ and 0.63 (see Fig. 1). The experimental conditions are reported in Fig. 1, which gives a schematic phase diagram of the CH_4 first adsorbed layer and the operating conditions (i.e., T and θ). It has been drawn with information obtained from adsorption isotherm and neutron scattering measurements.^{1,6,7} A few examples of the resultant spectra are shown in Fig. 2. All the quasielastic peaks measured at $T = 61$ K, $Q = 0.585\ \text{\AA}^{-1}$ and various coverages exhibit a broadening which is clearly larger than the instrumental resolution and whose widths are very similar. We also verified that the solid, which is stable below 56 K, does not show any broadening whatsoever.

As suggested by theoretical models¹⁰ the experimental data can be fitted with Lorentzian curves (solid curves in Fig. 1). The full width at half-maximum, ΔE , is plotted as a function of the

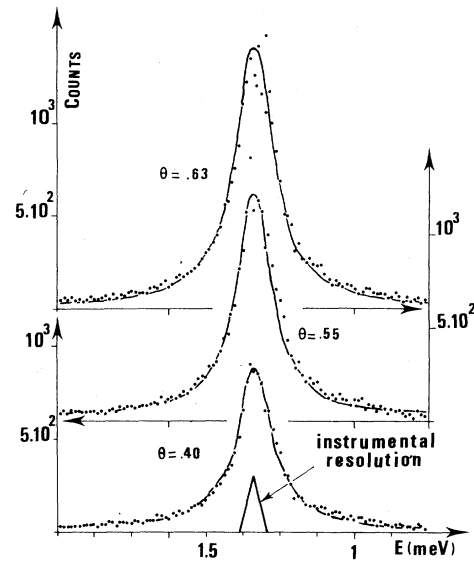


FIG. 2. Difference of the CH_4 -covered and bare graphite incoherent quasielastic spectra at 61 K and $Q = 0.585\ \text{\AA}^{-1}$ for three coverages ($\theta = 0.40, 0.55, 0.63$). All the spectra are normalized to the same incident flux. Typical background level (bare graphite spectra) is 6000 counts for E_0 the neutron incident energy. The broadening is coverage independent. The solid curves represent the best fits with a Lorentzian line convoluted by the instrumental resolution.

square of the scattering vector. Relation (1) is fulfilled for each coverage. Figure 3 illustrates the straight line obtained at $T = 61$ K and $\theta = 0.63$.

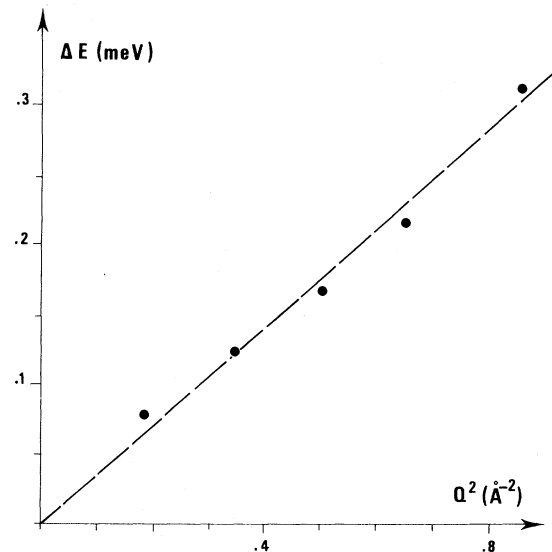


FIG. 3. Full width at half maximum as a function of Q^2 [Eq. (1)] for $\theta = 0.63$ and $T = 61$ K. The slope of the straight line yields the 2D diffusion coefficient.

TABLE I. Diffusion coefficient D of the saturated 2D liquid for two temperatures and different coverages θ . D is coverage independent.

θ	D (10^{-5} cm 2 s $^{-1}$)	
	61 K	70 K
0.30	2.2 ± 0.4	
0.40	2.5 ± 0.3	4.9 ± 0.5
0.55	2.6 ± 0.3	
0.63	2.7 ± 0.3	4.9 ± 0.5

The slope of the straight line yields the diffusion coefficient of the overlayer; the results given in Table I emphasize a striking fact: At constant temperature, mobility is coverage independent within the limit of the experimental uncertainty. This behavior is drastically different from that of the 2D hypercritical fluid studied previously⁶ and reproduced in Table II.

Between the 2D triple point (~ 56 K) and the 2D critical temperature (~ 72 K) and for our coverage range one should be in the coexistence domain of dense and diluted 2D phases. In our neutron scattering experiment we cannot observe the 2D diluted phase (2D gas) because of its high mobility and small density which yield a very flat and broad spectrum. Our peaks are mainly due to the most dense phase. This is confirmed by the observation of a proportionality between the amplitude of the Lorentzian curve and the coverage at constant \bar{Q} and T . Hence, the constant value of the diffusion coefficient is proof that the coverage change only produces an increase of the surface occupied by the densest phase whose mobility is an intensive property. This is precisely the property of a liquid. Furthermore, the measured value of D is the same order of magnitude as the bulk liquid¹¹ within the temperature range for which this 3D liquid is stable, namely above 90 K.

This can be illustrated by a set of 2D liquid islands bathing in a sea of very low-density 2D gas. Our experimental results show that the diffusion coefficient does not depend on the fraction of the graphite surface covered with the 2D liquid. This behavior is quite different from that of the 2D hypercritical fluid,⁶ i.e., the fluid stable above the 2D critical temperature. In this case, molecules tend to occupy all the available surface and the mobility is strongly coverage dependent (see Table II).

If we look at the value of D for $T = 61$ and 70 K

TABLE II. Diffusion coefficient of the 2D hypercritical fluid at 90 K (Ref. 6). D is coverage dependent.

θ	D (10^{-5} cm 2 s $^{-1}$)
0.45	13 ± 1.3
0.7	7 ± 0.7
0.9	2.2 ± 0.3

(Table I), we see a significant variation of the diffusion coefficient with temperature. This can be due to an activation energy of diffusion or as suggested recently¹² to the possible existence of two kinds of 2D liquids.

As recalled in the introduction, only a few properties of the 2D liquid were known; for example, the thermodynamics^{1,9} and the correlation range order.¹³ Incoherent neutron scattering enables us to obtain a precise and valuable knowledge of the 2D liquid through the important dynamical property which is the 2D diffusion coefficient.

We would like to thank IN5's staff for technical assistance. We appreciated helpful discussions with C. Marti, B. Croset, and J. G. Dash. The experiments were performed at Institut Laue-Langevin in Grenoble.

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⁸Trade name of the product processed by Carbone Lorraine. Its specific surface is about 20 m 2 /g.

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