

tum transfer of accelerated quasiparticles to the lattice.

There is a further possible excitation mechanism which is truly incoherent. If the oxide is considered to be an amorphous material, it should contain two-level systems which absorb the electromagnetic waves resonantly.<sup>13</sup> The excited two-level systems will relax quantitatively via emission of phonons of the same frequency, because of the large phonon density of states. In this case, the absorbed photon power is<sup>13</sup>

$$P = 2\pi A \omega \mu'^2 n(E) V_{ac}^2 / d,$$

where  $\mu'$  is the dipole moment,  $n(E)$  the density of states of the two-level systems, and  $d \approx 1$  nm the oxide thickness. In a dirty glass (BK7),  $p^2 n(E) / 4\pi \epsilon_0 = 3 \times 10^{-4}$  was observed.<sup>13</sup> Since the oxide was grown under fairly dirty conditions, we may use this value, and obtain  $Y \approx 100 \Omega^{-1}$ , again the right order of magnitude.

In conclusion, we have discovered a new source of tunable monochromatic phonons with frequencies up to the energy gaps of superconductors. The frequency resolution of the source should prove to be extremely high, because it depends only on the stability of the Josephson frequency. As yet, there are two possible ways to explain the effect quantitatively, namely, by the assumption of piezoelectricity or of two-level systems

in the oxide. A decision may be made by experiments on the angular distribution of phonons emitted by smooth junctions.

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## Dynamics of Methane Monolayers Adsorbed on Graphite

J. H. Quateman<sup>(a)</sup> and M. Bretz

Department of Physics, The University of Michigan, Ann Arbor, Michigan 48109

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Pulsed-NMR measurements of methane on graphite have been performed between 45 and 105 K for 0.2 to 1.1 monolayers. Spin-relaxation times show first-order melting at 57 K, sensitivity to the hypercritical fluid, and continuous transitions where an incommensurate solid displaces the registered phase at both higher temperature and coverage. These measurements, plus activation-energy comparisons, provide a significant clarification of methane's high-temperature behavior.

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The widespread interest in adsorbed films on graphite is sustained by a continual unfolding of novel predictions and observations. In particular, registry and associated commensurate-incommensurate transitions (CIT's) have inspired studies of Potts model analogies, orientational phases, dislocation models, domain-wall configura-

tions, possible low-temperature liquids, and chaotic phases for coverage-driven CIT's.<sup>1</sup> In addition, transitions from a registered phase into a higher-temperature incommensurate (floating) solid have been proposed.<sup>2</sup> The phase diagram of adsorbed krypton<sup>3</sup> possesses a well-developed registered phase which melts directly into a two-

dimensional (2D) liquid. In contrast, xenon forms no registered monolayer but condenses into a close-packed 2D solid.<sup>3</sup> Methane ( $\text{CH}_3$  or  $\text{CD}_4$ ), being intermediate between Kr and Xe in both hard-core diameter and incompatibility of the 3D solid with the graphite lattice,<sup>4</sup> possesses *both* coverage- and temperature-driven CIT's<sup>5</sup> making it an inherently richer system than these noble-gas adsorbants. The  $\text{CD}_4$  phase diagram as determined by neutron scattering<sup>5,6</sup> contains a low- $T$  ( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$  commensurate phase, a CIT to the *expanded* solid above 50 K, a 56-K first-order transition to the fluid, and at 0.87 layer a CIT to the *compressed* solid.

Nuclear magnetic resonance complements neutron scattering and thermodynamic studies<sup>7</sup> by providing dynamic molecular information. In this Letter we report pulsed-NMR measurements of  $\text{CH}_4$  which verify solid condensation, delineate the liquid-gas transition, and give activation energies in the vicinity of the CIT's. Our results are summarized in the monolayer phase diagram of Fig. 1. We observe first-order melting along the triple-point line at 57 K for coverages less than 0.80 layer and continuous temperature-driven (between 0.80 and 0.87 layer) and pressure-driven (across 0.87 layer) CIT's. To within our coverage resolution, 0.03 layer, these phase lines

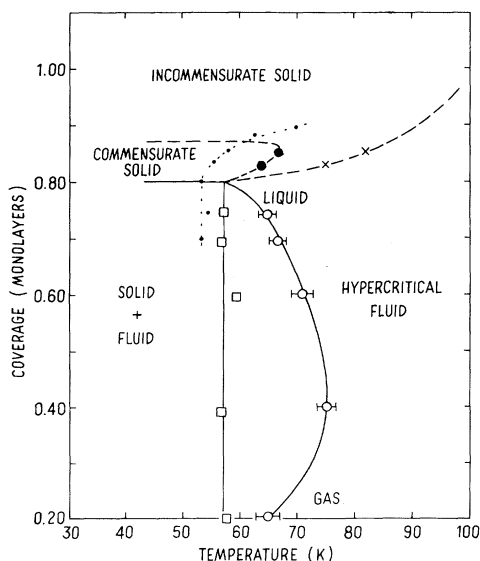


FIG. 1. Phase diagram of methane. Phase boundaries (full lines, first order; dashed lines, continuous) were determined as follows: from  $T_2$  break, squares;  $T_1$  slope discontinuity, solid circles and crosses;  $T_1$  liquid analysis (Ref. 16), open circles. Locus of  $T_1$  minima is the dotted line. Monolayer completion is defined in text.

meet the triple line at a multicritical point at 57 K and 0.80 layer. Inelastic neutron scattering<sup>6</sup> has indicated a critical point near 75 K. We find a high- $T$  boundary between a hypercritical fluid (2D gas above its critical point) and a liquid/gas two-phase region. These NMR results, then, provide a clarification of methane's high- $T$  behavior. Of particular importance are our findings that the high-coverage registered phase endures to 68 K (versus  $\sim 50$  K from neutron scattering<sup>5</sup>), and that above 68 K the expanded and compressed solids coalesce into a single incommensurate (floating) solid phase.

Our sample was constructed from 19 g of baked ( $800^\circ\text{C}$  for 24 h *in vacuo*) Grafoil wafers and Mylar spacers in an epoxy cylinder mounted in a 1–300 K cryostat. To ensure uniform adsorption the sample cell was filled via a vacuum-isolated line and films were annealed at 110 K for 6 h. A small quantity of  $^4\text{He}$  gas ( $0.072\text{ cm}^3$  STP) was added to maintain temperature equilibrium. A 77-K adsorption isotherm showed well-defined steps and verified cell cleanliness. Monolayer coverage ( $93.3\text{ cm}^3$  STP) was determined from the isotherm inflection point in comparison with previous work.<sup>5</sup> We note that Thomy and Duval<sup>8</sup> use a different criteria for monolayer capacity. Our microcomputer-controlled pulsed-NMR spectrometer was tuned to a low frequency, 4.586 MHz, to avoid Grafoil eddy-current heating and rf shielding. We used Meiboom-Gill pulse sequences to measure spin-spin relaxation times,  $T_2$ , and  $180^\circ$ - $90^\circ$ - $180^\circ$  sequences to determine spin-lattice relaxation,  $T_1$ .<sup>9</sup> Decays were exponential, and  $T_2 \ll T_1$  as expected for 2D relaxation.<sup>10</sup> Methane orientational relaxation times are very short at all temperatures of this study. Spin relaxation is via intramolecular dipolar interactions where the axis of molecular rotation changes as a result of collisions.<sup>11,12</sup>

The results for  $T_1$  and  $T_2$  at several monolayer coverages of  $\text{CH}_4$  are presented in Fig. 2. For 0.2 layer [inset to Fig. 2(a)]  $T_1$  rises as  $\sqrt{T}$ , consistent with a polyatomic gas with dipolar interactions.<sup>13</sup> Film solidification at 57 K is marked by a discontinuity in the  $T_1$  and  $T_2$  data [see Fig. 2(a)]. The discontinuity in  $T_1$  appears broader than in  $T_2$  ( $\sim 3$  K) since it is masked by the strong  $T$  dependence near the  $T_1$  minima. An intermediate phase from 68 to 82 is readily apparent in the 0.85-layer  $T_1$  data of Fig. 2(b).  $T_1$  slope changes without accompanying  $T_2$  structure suggest that these transitions are of higher order. Data taken at 2.107 MHz (not shown) give identi-

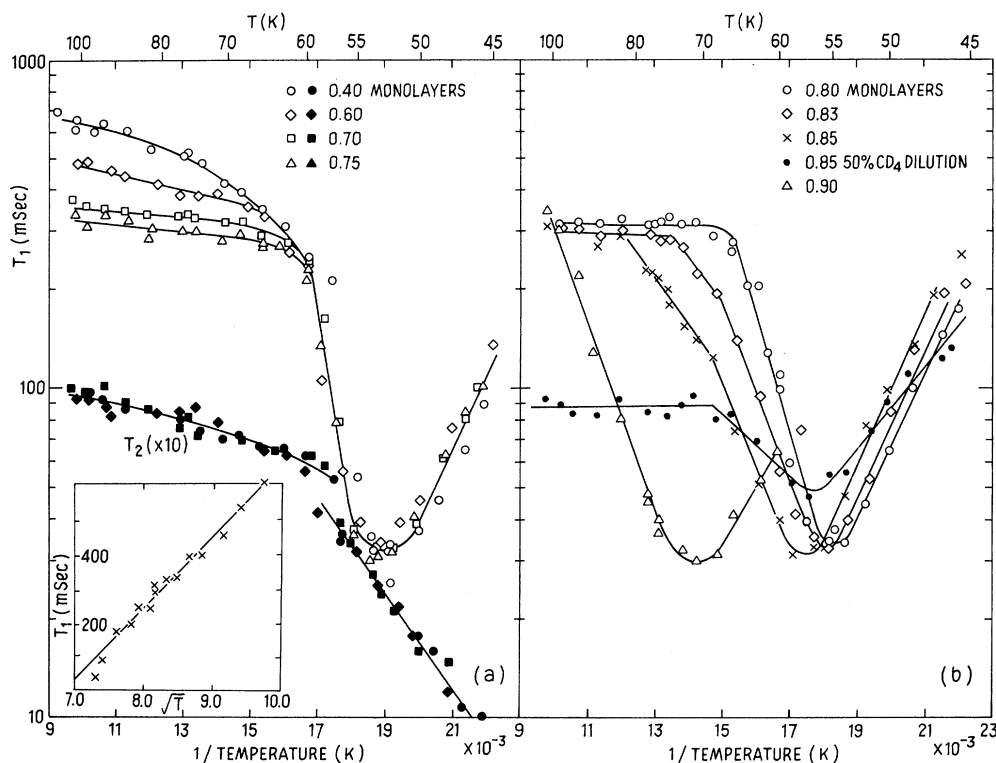


FIG. 2. (a)  $T_1$  (upper data) and  $T_2$  (lower data,  $\times 10$ ) for monolayer coverages in the two-phase region vs inverse temperature with 4.586 MHz. Inset:  $T_1$  vs  $\sqrt{T}$  for 0.20-layer data. Solid lines guide the eye. (b)  $T_1$  data for near-monolayer coverages at 4.586 MHz. For 0.85 layer, data with 50% isotopic mixture are shown.

cal temperature boundaries for the discontinuous and intermediate phases. We also measured  $T_1$  for protons in a 50%  $\text{CH}_4/\text{CD}_4$  mixture [Fig. 2(b)]. The broadening and rising of the minimum reflects a *spread* in activation free energies associated with *intramolecular* interactions.<sup>14</sup> The 68-K transition is present and actually enhanced in the mixture data since  $T_1$  remains short above 68 K. We follow the neutron-scattering identification<sup>5</sup> of a registry-expanded solid CIT for 0.85 layers with melting occurring at a higher  $T$ . As coverage increases toward layer completion the film compresses and the  $T_1$  minima move to higher  $T$ . This compression is evidently continuous, indicating that the pressure-driven CIT at 0.87 layer is of higher order, for the locus of the  $T_1$  minimum (dotted line of Fig. 1) varies smoothly through the CIT.<sup>15</sup> NMR senses this phase boundary by an abrupt activation-energy change, to be discussed shortly.

The liquid-phase  $T_1$  data [above 57 K, Fig. 2(a)] appear to change from a coverage-independent liquidlike curve to coverage dependence with rising  $T$  as expected for a compressible hyper-

critical fluid. We analyze these data elsewhere<sup>16</sup> but do include a suggested phase boundary in Fig. 1. The diffusion constant  $D$  of the liquid is proportional to  $T_1$ .<sup>13</sup> For  $T_1 = 300$  msec (0.70-0.85 layer) we calculate  $D = 2.3 \times 10^{-5}$  cm<sup>2</sup>/sec, agreeing with  $D = (2.6 \pm 0.3) \times 10^{-5}$  cm<sup>2</sup>/sec obtained at 0.7 layer from inelastic neutron scattering.<sup>6</sup>

The position, shape, and depth of the  $T_1$  minima contain important information. We have found that the  $T_1$  minima are fitted well by the form for two-proton intramolecular interactions<sup>13, 17</sup>

$$\frac{1}{T_1} = \frac{2\gamma^4 \hbar^2 I(I+1)}{5b^6} \left( \frac{\tau}{1 + (\omega\tau)^2} + \frac{4\tau}{1 + 4\omega^2\tau^2} \right).$$

The spin correlation time  $\tau(T)$  and therefore  $T_1(T)$  is extracted through an Arrhenius plot of the function  $\tau(T) = \tau_0 e^{\epsilon/kT}$ . Here,  $\epsilon$  represents a barrier activation energy for molecular motion. It is customary<sup>18</sup> to rewrite  $\tau_0^{-1}$  as a product of attempt frequency  $\nu$  and a factor depending on entropy difference  $\Delta s$  between ground and activated states, giving  $\tau(T) = 1/\nu \times e^{-\Delta s/k} \times e^{\epsilon/kT}$ . In the two-phase solid/fluid region  $\epsilon$  is nearly constant at 650 K (Fig. 3). Simple model calculations indi-

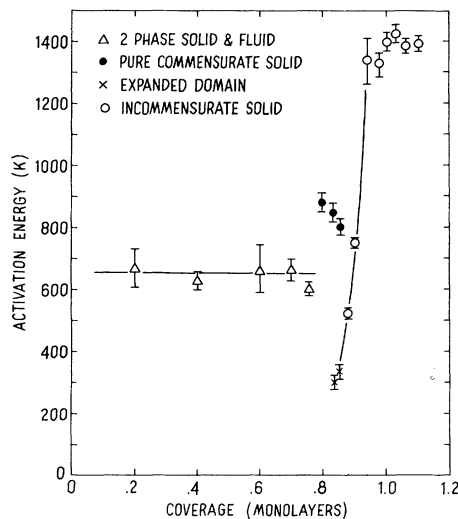


FIG. 3. Activation energies obtained from Arrhenius plot of correlation times as determined from shape of the  $T_1$  minima.

cate that the activation mechanism is evaporation of ordered-phase atoms.<sup>16</sup> For comparison the calculated molecular interaction potential for  $\sqrt{3}$  packing is 914 K and the heat of desorption from a commensurate monolayer is 2577 K.<sup>19</sup> At 0.80 layer commensurate islands merge and both  $\epsilon$  and  $\Delta s$  (not shown) change abruptly, signaling a different activation process. The  $\epsilon$  varies across the commensurate phase as voids, interstitials, and other defects rearrange. Activation energies for the expanded domain [from slopes of Fig. 2(b)] are included in Fig. 3. They are *much* lower than the  $\epsilon$ 's for the commensurate phase but are comparable to the activation energy of the compressed solid at 0.88 layer. The precipitous fall and smooth progression of  $\epsilon$  between 0.83 and 0.94 layer convince us that the expanded domain and compressed phase are actually a *single* incommensurate phase bounding the commensurate solid. On nearing monolayer completion, activation processes are inhibited by compression, the  $\epsilon$  dramatically rises from 300 to 1350 K ( $\epsilon = 1609$  K for a 3D solid<sup>20</sup>), and  $\Delta s$  increases by about 3.5/activation (in units of Boltzmann's constant).

The actual dynamic mode cannot be determined from the activation free energy alone. Domain-wall unpinning,<sup>21</sup> dislocation dynamics,<sup>18</sup> and grain boundary generation<sup>22</sup> are all activated processes in 2D solids. Furthermore,  $\Delta s$  is subject to considerable extrapolation uncertainties making numerical comparisons unwise. We ap-

plied the Frank and Van der Merwe model<sup>23</sup> of misfit dislocations to our system. Using  $\text{CH}_4/\text{graphite}$  Lennard-Jones potentials,<sup>24</sup> and an 11-K well depth,<sup>19</sup> we find a commensurate region capable of enduring a 2.3% lattice mismatch  $\delta_c$ , beyond which  $\epsilon$  is calculated to be 125 K. This  $\delta_c$  places the unstressed registered monolayer at 0.85 actual layer with a Frank and Van der Merwe model activation energy of  $\sim 700$  K for unpinning dislocations. The agreement with our value of  $\epsilon = 800$  K indicates that unpinning is a reasonable activation mechanism. We note that behavior analogous to dislocation-mediated melting is predicted when entering the registered phase at 0.85 layer and 68 K (point "B" in Fig. 4 of Ref. 2).

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<sup>(a)</sup>Present address: Bell Laboratories, Holmdel, N. J. 07733.

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