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Specific heat and phase diagrams of H_2 adsorbed on D_2- or HD-plated graphite

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Heat-capacity measurements are used to investigate the phase diagram of H_2 adsorbed on exfoliated graphite (gr) plated with approximately one monolayer of either D_2 or HD, in the range $3.7< T <13$ K. The added H_2 dosages are all within the equivalent of one monolayer coverage on the bare graphite. For the system $H_2/D_2/gr$ a narrow transition at 5.74 ± 0.03 K seems to indicate triple line melting. This transition shows a very small shift to lower temperatures with increasing coverage. For each coverage within the triple line densities, this transition is followed, at higher temperatures, by another transition culminating at a critical point at 9.44 ± 0.30 K. The melting line of a H_2 compressible solid is traced at coverages above the end of the triple line. For the H_2/HD/gr system though, the apparent triple line melting temperature occurs at a higher temperature than for $H_2/D_2/gr$ and decreases from 6.58 ± 0.03 K at low densities, to a somewhat constant 6.25 K near monolayer completion. The critical point of the higher temperature phase is at 10.17 ± 0.2 K. We present a simple model of interlayer isotopic mixing used to explore the origin of the triple line tilting in both systems.

I. INTRODUCTION

Due to their small mass and relatively weak molecule-molecule interaction, hydrogen (H_2), deuterium (D_2), and deuterium hydride (HD) form excellent systems for the study of quantum effects in the condensed state. Their solid-liquid-vapor triple-point temperatures are the lowest ones occurring in nature for three-dimensional (3D) systems,[1,2] in good agreement with expectations from the quantum theorem of corresponding states.[3]

Unsaturated films of H_2, HD, and D_2 allow us to investigate the effects of dimensionality and substrate fields on thermodynamic and transport properties. Dimensionality alone reduces the triple-point temperatures of single-monolayer films (2D) of "classical" gases to about 60% of their 3D values;[4] thus we should expect for a monolayer film of H_2, $T_t(2D)\approx8.3$ K. The quantum theorem of corresponding states predicts that this temperature should move further down since the de Boer parameter for H_2, $\eta = \hbar^2/m\sigma^2\epsilon$ (for atoms or molecules of mass m interacting via a Lennard-Jones potential of depth ϵ and hard core σ), is very close to its maximum calculated value for the existence of a triple point for 2D bosons at $T = 0$ K.[5–7]

The phases occurring in the first monolayer of H_2, HD, and D_2 adsorbed on graphite (we will abbreviate the terminology by H_2/gr, etc., for single-layer films, and H_2/H_2/gr, etc., for bilayer films) are well known. Extensive reviews[8,9] have been written recently. At low and intermediate densities all of the molecular isotopes condense into a solid structure commensurate with every third adsorption site of the graphite basal plane. The condensation temperatures at densities up to a quarter of a monolayer vary from 10 to 13 K as the density increases, and grow up to 17–20 K at perfect commensuration (surface density $n = 0.0636$ Å^{-2}). At monolayer completion the three molecules form a triangular solid incommensurate with the graphite lattice. Surface densities at monolayer completion are $n = 0.094$ Å^{-2} for H_2 and 0.099 Å^{-2} for D_2, both higher than the densities of the (111) planes of their 3D solids, respectively 0.0823 and 0.0907 Å^{-2}.[10] By contrast, D_2 adsorbed on MgO forms a 2D solid in uniaxially commensurate troughs in the [110] direction of the MgO(100) surface. This solid can be compressed along the troughs forming various rectangular cells with lattice parameters compatible with commensuration every four, six, or more D_2 molecules [$(2\times n)$ structures],[11] until at monolayer completion it is in an accidental equilateral triangular structure of density slightly lower than on graphite at the same point. The actual condensation temperature at low densities is not known, but at higher densities the solid condenses at temperatures comparable to those on graphite.

H_2, HD, and D_2 monolayers formed on top of the first solid layer of their own type of hydrogen molecule show phase diagrams similar to those of conventional matter, with a 2D solid-liquid-vapor triple point and liquid-vapor coexistence region ending at a critical point. For H_2/H_2/MgO, $T_t = 7.2$ K,[12] for H_2/H_2/gr, $T_t = 5.96$ K,[10] for D_2/D_2/gr, $T_t = 11.04$ K,[10] and for HD/HD/MgO, $T_t = 9.9$ K.[7] Quasielastic neutron scattering (QENS) measurements on the second layer of HD/MgO (Ref. 13) found that for a coverage equivalent to 1.6 layers, the translational diffusion coefficient D was essentially zero (all solid) at 7 K, while at 10.2 K the equivalent of half a layer had $D\approx1.2\times10^{-5}$ cm^2/s, about 1/4 of the diffusion coefficient of liquid HD at its 3D triple point (16.61 K). Nuclear magnetic resonance measurements of Jeong[14] for a bilayer HD film on MgO show rapid interlayer exchange above 7 K. While the correspondence between the QENS and NMR measurements has not been explored in detail, both measurements point to rather good mobility at low temperatures, consistent with the thermodynamic data. It thus appears that on the much less strongly bound second layer,[15] molecular hydrogen remains mobile to substantially lower temperatures than on the first layer on graphite or MgO.

An interesting possibility is to study the phases of one of the hydrogen molecules when adsorbed on a different kind of hydrogen molecule. Given their somewhat different surface and bulk densities and different binding energies to a substrate, we would expect that H_2 on top of a D_2-plated solid adsorber may behave like a single H_2 monolayer over a different species, weaker binding substrate surface.[15] It should be impossible for H_2 to make a simple commensurate structure on the denser D_2. In addition, measurements on HD/D_2/MgO and H_2/HD/MgO by NMR show that the larger mass molecules deposit next to the substrate at relatively low temperatures, with layer promotion and intermixing starting at about 7 K.[14,16] In this paper we report heat-capacity measurements over the entire H_2 monolayer range of H_2/D_2/gr and of H_2/HD/gr. We briefly describe the experimental setup and the various platings. The results show for H_2/D_2/gr a $T_t(2D)\approx5.74$ K, slightly lower than the $T_t(2D)$ found for H_2/H_2/gr,[10] and a critical temperature $T_c(2D)\approx9.44$ K. For H_2/HD/gr, $T_t(2D)$ is higher than for H_2/H_2/gr, and $T_c(2D)\approx10.17$ K. Furthermore, we find strong evidence of interlayer mixing of the different pairs of molecules as shown by shifting "triple-point temperatures" with H_2 dosing.

II. EXPERIMENTAL DETAILS

The measurements were performed with a computer-controlled adiabatic dc calorimeter. The experimental cell was designed to satisfy the somewhat conflicting requirements of minimum area for easy changing of coverages, fast internal time constant for rapid data acquisition, minimum dead volume, and enough sensitivity for about 0.5% accuracy in the total heat capacity. It consisted of two sheets of graphite foam (exfoliated graphite),[17] each one of about 0.5 cm thickness and 3.75 cm diameter, pressure fitted into a very thin wall (0.025 cm) copper calorimeter suspended from a reference temperature plate by a 0.32 cm o.d. glass tube with a pair of glass-metal (Kovar) joints, the lower one soft soldered to the cell. The support tube also served as the gas dosing line. The total area of the graphite was 47±1 m^2, determined by a N_2 isotherm at 77.6 K.[18] Temperature was measured by a carbon resistor, calibrated against a factory calibrated CryoCal germanium thermometer at the start of every cooldown. Heat pulses were provided with an Evanohm wire heater. A detailed description of the calorimeter and how it operates has been written by one of us (F.C.L.).[19]

The gases used for the experiments were (a) H_2, Union Carbide, 99.99% purity, (b) D_2, Linde (Union Carbide) CP grade, minimum purity 99.5%, and (c) HD, MSD Isotopes (Merck-Frost, Montreal, Canada), which had 98.9% atomic deuterium. Gas dosings were done from the tanks at room temperature, filtered by a liquid nitrogen trap. Molecular H_2 and D_2 exist in ortho and para varieties. We did not attempt to determine the ortho-para composition of our films. In earlier adsorption isotherm experiments on H_2/MgO using a quartz cell with a Kovar joint we noted that the magnetic properties of the Kovar appear to catalyze the ortho-para conversion of H_2, at significant vapor pressures, in about 0.5 h. All our films were annealed overnight at about 12–13 K (see below), where the bilayer film vapor pressure is in the 10^{-1} Torr range.

The gas dosing procedure for the two major sets of runs was the following.

H_2/D_2/gr. A total of 16.62 cc STP (Nk_B=6.17 mJ/K) of D_2 gas was introduced at 30 K which, at lower temperatures, corresponds to a 0.095 Å^{-2} surface density. This dose, which is about 4% less than the densest D_2/gr monolayer, was an accidental choice due to an uncertain initial calibration of the graphite area.[10] This film was cooled (and annealed) overnight to 13 K. The calorimeter was then cooled to the lowest desired temperature over several hours where a heat-capacity run was started. The total heat capacity of the calorimeter plus the D_2 plating served as the background for the H_2 measurements. Small doses of H_2 were introduced at 13 K starting at coverage Nk_B=3.09 mJ/K (about 0.5 monolayer), and were annealed at this temperature for several hours, usually overnight. The calorimeter was again cooled over 3–4 h, and the heat capacity was measured. A heat-capacity run took about 20 h to reach 13 K where it stopped for a new shot. After reaching monolayer H_2 completion, the cell was pumped out at high temperature and a new identical D_2 plating was dosed. After the background was remeasured, H_2 dosings started from zero with shots of about 0.05 monolayer until the coverages overlapped the first experiment. No differences in the data were found in the overlap region.

H_2/HD/gr. We measured two adsorption isotherms of HD at 12.0 and 20.0 K to determine the amount of HD gas needed for a complete monolayer. As a result, 17.72 cc STP (Nk_B=6.57 mJ/K) of HD gas was introduced. We then followed the same experimental procedure as above for the D_2 plating, except that the annealing temperature was 12 K instead of 13 K. A total of 18 heat-capacity runs were measured for H_2 coverages from 0.05 to 1.0 monolayer.

We estimate the density of a complete HD monolayer to be around 0.101(± 0.002) Å^{-2}. This density seems somewhat high, since we expected the HD/gr monolayer density to be in between those of D_2/gr (0.099 Å^{-2}) and H_2/gr (0.094 Å^{-2}) reported in Ref. 10. It is possible that the HD we used contains a few percent of a condensable impurity which froze on the fill line walls and did not reach the graphite, but nevertheless added to the room temperature volumetric dosing. A structural determination of lattice parameters at and above monolayer completion should clarify this point. For internal consistency, we measured the heat capacity of a few coverages of H_2/gr, HD/gr, and D_2/gr around monolayer completion and found for H_2 and D_2 that the minimum total film heat capacity (usually associated with monolayer solid completion) occurred within 1% of the coverages expected for our cell as scaled from Ref. 10.

As reported in the discussion below, we also measured one heat-capacity run for H_2/H_2/gr, HD/HD/gr, and D_2/D_2/gr in the 1.2–1.3 layer region. These films were plated using a similar procedure to the one described for the mixed isotopes systems.

III. RESULTS

Our results are fairly different depending on whether D_2 or HD is plating the graphite substrate. Heat-capacity data for several coverages of H_2/D_2/gr are shown in Fig. 1, and likewise for H_2/HD/gr in Fig. 2. The phase diagrams (location of heat-capacity peaks or rounded anomalies as a function of coverage and temperature) resulting from the two sets of platings are shown in Figs. 3 and 4.

D_2 plating. For reference, one monolayer close-packed H_2/gr on our cell corresponds to coverage Nk_B=6.10 mJ/K. For the H_2/D_2/gr system, heat-capacity peaks around 5.8 K appear at H_2 coverages as low as 1.24 mJ/K, Figs. 1 and 3 (horizontal error bars). We can identify an apparent triple line that with increasing coverage has a slight tilt towards lower temperatures at an average temperature of 5.74 K, and a higher-temperature transition, probably denoting the boundary of a $L+V$ coexistence region ending at a critical point at 9.44 K. Heat-capacity isotherms were used to map the boundaries of linear regions in a heat-capacity vs coverage plot. Regions of phase coexistence require that the total heat capacity be linear with coverage. The boundary edges determined this way are shown in Fig. 3 with vertical error bars.

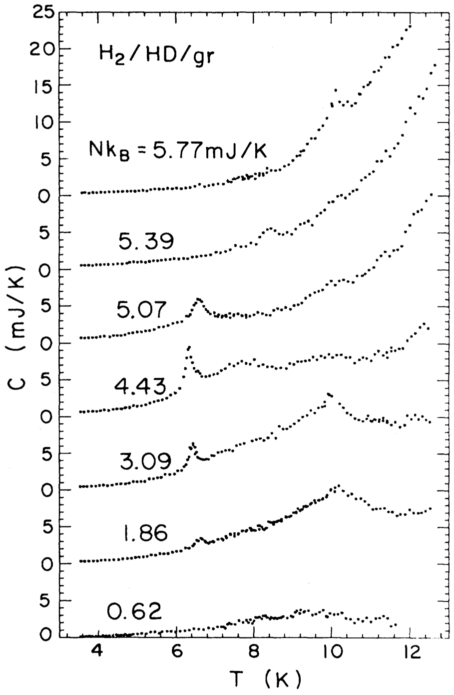


FIG. 2. Measured heat capacity of H_2/HD/gr for a few selected coverages, after the HD/gr background subtraction.

For T <10 K, the phase diagram looks similar to that of the *second* layer H_2 in H_2/H_2/gr. The triple-point temperature T_t=5.74 K is about 0.22 K lower than for H_2/H_2/gr. This can be easily seen in Fig. 5 where we

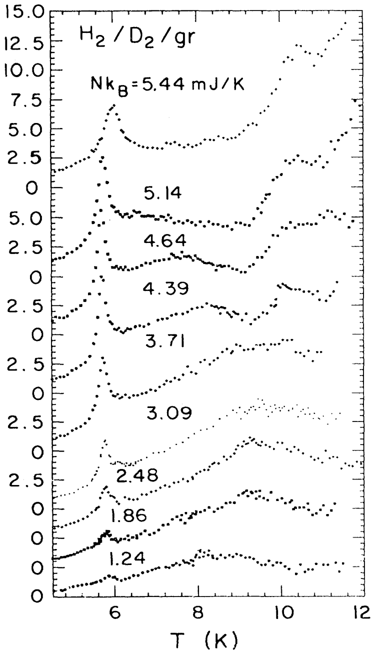


FIG. 1. Measured heat capacity of H_2/D_2/gr for a few selected coverages, after the D_2/gr background subtraction.

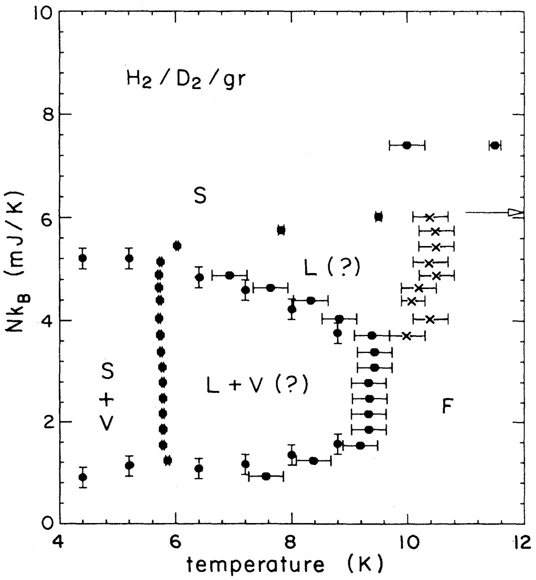


FIG. 3. Location of heat-capacity peaks (horizontal arrow bars) and end of coexistence regions (vertical arrow bars) for H_2/D_2/gr, from all the heat-capacity runs measured. Crosses indicate location of rounded feature observed in heat capacity of Fig. 1.

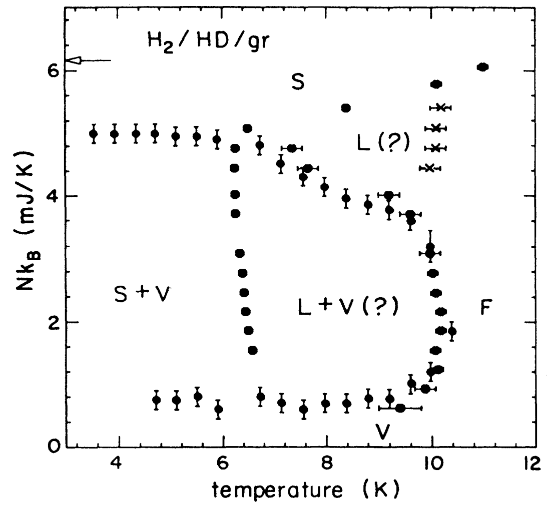


FIG. 4. Location of heat-capacity peaks (horizontal arrow bars) and end of coexistence regions (vertical arrow bars) for H_2/HD/gr, from all the heat-capacity runs measured. Crosses indicate location of very rounded, small feature observed in heat capacity of Fig. 2.

compare two heat-capacity runs taken in our cell, one for each system, at comparable total coverage.

We note that since the D_2 plating is about 4% less dense than a full monolayer (ML), it is likely that the first 0.04 ML (0.24 mJ/K) of H_2 goes next to the graphite and compresses the D_2 plating. After subtracting this 0.24 mJ/K from the total H_2 dose, the critical point coverage, the coverage at which the triple-point peak appears, and the coverage span of the $L+V$ coexistence region all match very well (within 0.01 ML accuracy) their counterparts in the phase diagram of the *second* layer H_2 on bare graphite.[10]

For T around 10.4 K, there is a series of very weak and rounded peaks at coverages Nk_B>3.6 mJ/K. We do not know what they represent. Although they may signal the existence of possible commensurate phases, we note that similar features are not observed for the pure bilayers of H_2/H_2/gr and D_2/D_2/gr.

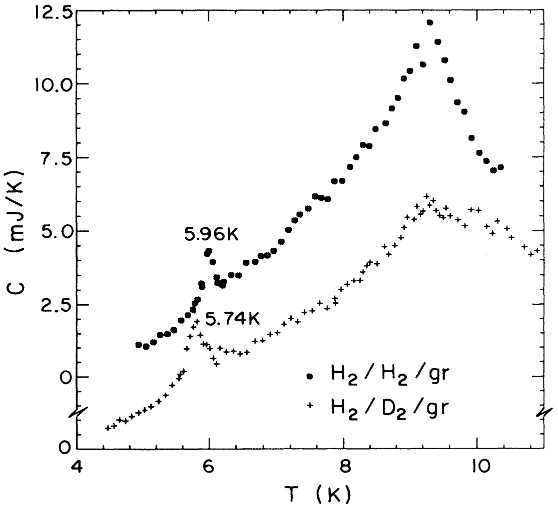


FIG. 5. Heat capacity of H_2/H_2/gr and H_2/D_2/gr for similar second layer coverages.

Finally, the run with H_2 coverage Nk_B=3.71 mJ/K was measured both with the normal D_2 plating described above, and with the addition of an extra 0.666 cc STP (about 4% of the previous 16.62 cc STP plating) D_2 gas. The heat-capacity data after the 4% D_2 introduction shows its T_t(2D) at about 5.80 K, slightly higher than before the addition, and the peak at 10.4 K becomes somewhat stronger.

HD plating. The H_2/HD/gr measurements, Fig. 4, result in a phase diagram similar to the one of H_2/D_2/gr but with "skewed" phase boundaries. The apparent T_t(2D) moves to lower temperature with increasing coverage, starting at $T \approx 6.58$ K at the low-density end of the coexistence region, and shifting to $T \approx 6.25$ K at the top end. The coexistence region ends at about 10.17 K. All these temperatures are noticeably higher than their counterparts in H_2/H_2/gr and H_2/D_2/gr. A series of weak peaks also appears at densities above the critical density (4.4 mJ/K< Nk_B <5.4 mJ/K) at around 10.1 K, a temperature 0.3 K *lower* than the similar feature in H_2/D_2/gr, and the peaks appear weaker than those in the D_2 plating.

It is interesting to compare the H_2 dosings for the lower and upper boundaries of the S-V coexistence region in the two different platings. The results, determined by heat-capacity isotherms, are, respectively, Nk_B=0.75 mJ/K and 5.00 mJ/K for the HD plating, and 0.86 mJ/K and 4.96 mJ/K for the D_2 plating (after the 0.24 mJ/K correction, explained above). Since our random dosing uncertainty is about 1%, both the absolute density of the S and V phases of H_2 and the density difference between them, regardless of the plating, are very similar.

IV. ANALYSIS AND DISCUSSION

In this section we report on calculations of the change in entropy across the apparent triple point, the latent heat of fusion per particle, and the density of the solid phase at the triple point, and show estimates from a simple model for the origin and tilt of the triple line of H_2/HD/gr which indicate that interlayer mixing is the likely cause.

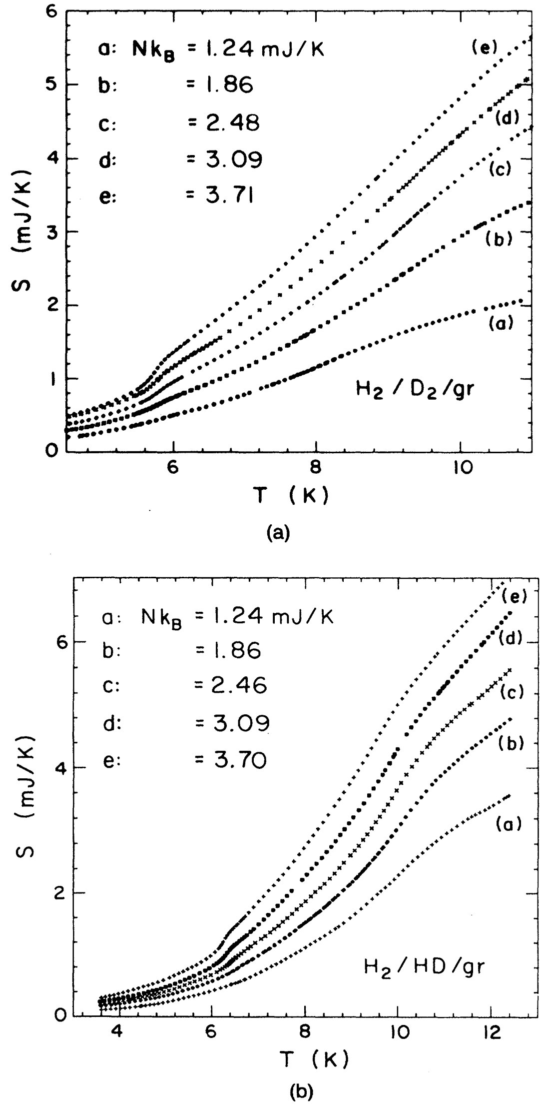
A. Entropies and heats of transition

We calculate the entropy as a function of temperature from

$$S(T) = \int_0^T \frac{C(T')}{T'} dT'. \quad (1)$$

Since we do not have data to very low temperatures (where the total heat capacity is small), we assume $C \propto T^2$ below the lowest measured point. Figure 6(a) shows the calculated entropy for the five lowest coverages of $H_2/D_2/gr$ depicted in Fig. 1. The sharp increases near 5.74 K are due to the triple-point peaks, and the upswings at or below 9.44 K that are somewhat hard to resolve are due to the broad boundary of the $L + V$ region. Figure 6(b) shows results of a similar calculation for $H_2/HD/gr$.

To estimate the entropy change at the triple point, per molecule, we must consider that not all H_2 molecules contribute to the triple-point heat-capacity peaks. Only those H_2 molecules in the solid phase of the $S + V$ coexistence region, denoted by V_s (or $N_s k_B$), are involved in the melting transition across the triple line.[22] In the following paragraphs we estimate V_s assuming no interlayer mixing.



(a)

(b)

FIG. 6. (a) Calculated entropies for $H_2/D_2/gr$ from the five lowest heat-capacity coverages shown in Fig. 1. (b) Calculated entropies for $H_2/HD/gr$ at similar coverages.

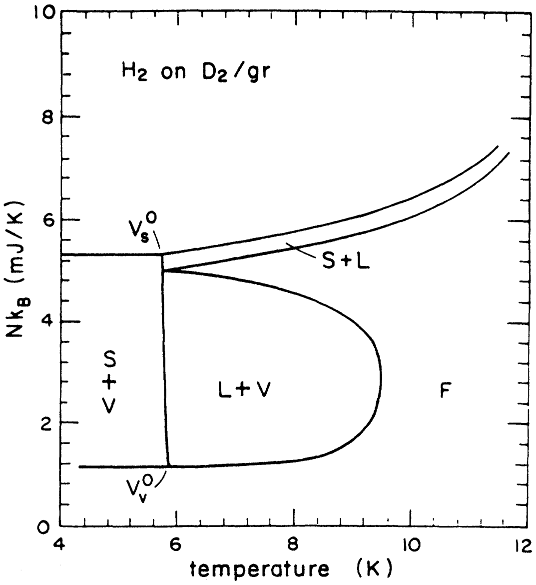


FIG. 7. Outline of the phase diagram for the first layer of $H_2/D_2/gr$.

Figure 7 shows a schematic trace of Fig. 3 where V_s^0 and V_v^0 represent the H_2-dosed volumes at the upper and lower phase boundaries at the triple-point temperature. Assuming a total surface area A, of any H_2 dose V for which $V_v^0 < V < V_s^0$ below $T_t(2D)$ the amount V_s is in the 2D solid-phase-covering surface area A_s, and the amount V_v is in the vapor-phase-covering surface area A_v. Thus

$$A = A_s + A_v, \quad V = V_s + V_v. \tag{2}$$

From the density equivalence, we also have

$$\frac{V_s}{A_s} = \frac{V_s^0}{A}, \quad \frac{V_v}{A_v} = \frac{V_v^0}{A}. \tag{3}$$

Thus it is straightforward to derive

$$V_s = \frac{V_s^0}{V_s^0 - V_v^0}(V - V_v^0) \tag{4}$$

and

$$V_v = \frac{V_v^0}{V_s^0 - V_v^0}(V_s^0 - V). \tag{5}$$

Figure 8 shows the entropy change for the $H_2/D_2/gr$ coverage Nk_B=3.71 mJ/K. Linear extrapolations from both sides are used to calculate the entropy change across the triple line, $\Delta S \approx$0.27 mJ/K, although linear extrapolations are only approximate. The extrapolations cover the entire width of the heat-capacity peak. Again assuming that 0.04 ML (0.24 mJ/K) H_2 goes to the plating layer next to the graphite, we have V = 3.47 mJ/K, V_v^0=0.86 mJ/K, and V_s^0=4.96 mJ/K. Thus Eq. (4) gives V_s=3.19 mJ/K. The entropy change per molecule is therefore given by $\Delta S/V_s = 0.084k_B$, which corresponds to 0.96 cal/mol for the heat of fusion. We have repeated this procedure for six coverages along the triple line of $H_2/D_2/gr$

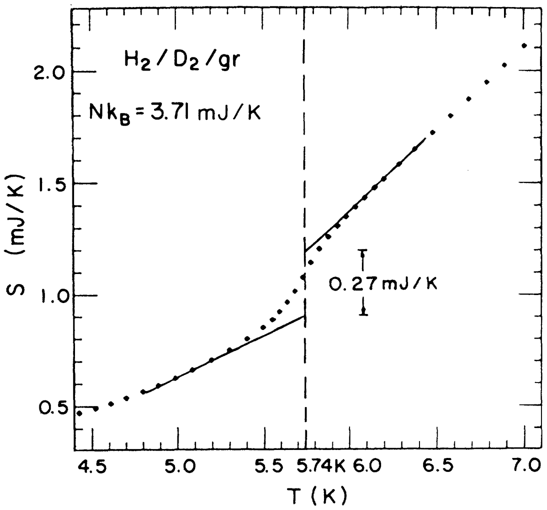


FIG. 8. Entropy change across the triple line for H_2 coverage Nk_B=3.710 mJ/K, on D_2/gr.

and nine coverages of H_2/HD/gr and obtain for the heats of fusion, respectively, 0.90±0.08 cal/mol and 0.84±0.06 cal/mol. Wiechert deduced from a single coverage of his data a heat of fusion of 0.93 cal/mol for H_2/H_2/gr.[10] The agreement is remarkable considering that different methods of substracting a background will produce differences much larger than the statistical errors quoted.

These heats of fusion are only about, or less than, 1/30 of the bulk H_2 heat of fusion, and even a factor of 3 smaller than for the second layer H_2 on MgO reported by Ma *et al.*[12] The small heats of fusion and entropy changes at melting indicate that the 2D liquid density must be almost the same as the 2D solid density, and the liquid must retain some ordering from the solid.

Finally, our estimates show that at T_t(2D) the density of 2D solid H_2 in equilibrium with its 2D vapor, on top of any of the hydrogens/gr substrates, is approximately 0.077 $Å^{-2}$, 3–5 % lower than the densest planes of 3D hydrogen.

B. Condensation temperatures

Part of the interest in films of H_2 is related to the possibility that if a liquid film is produced at low enough temperature, a Kosterlitz-Thouless transition to the superfluid state should occur. By analogy with ^{4}He films[20,21] but with the free mass of H_2, the transition temperature should be about 2 K for a monolayer with density 0.08 $Å^{-2}$. Assuming that the liquid identification in our experiment is correct, it is obvious that these systems solidify at temperatures more than twice higher than the expected T_{onset}. On the other hand, the change in substrate from H_2/MgO to D_2/gr makes for a 1.4–1.5 K *decrease* in T_t(2D) on changing from the *weaker* to the *stronger* binding. We believe that this large change between the results with MgO to the results with graphite is related to the proximity of the quantum parameter η for H_2 to the limiting quantum parameter for solidification for bosons mentioned in the Introduction. The different substrates must affect the effective η through changes in m, σ, and ϵ for an H_2 molecule in a periodic potential. Several years ago, and in connection with the study of helium adsorbed on rare-gas-plated graphite, Rehr and Tejwani[23] calculated for a triangular lattice of adsorption sites, and de Mello[24] for a honeycomb lattice of sites, the second virial coefficient for ^{4}He and ^{3}He on periodic substrates. The honeycomb lattice can be formed by plating graphite with rare gases. Knowing the density of states for the two isotopes on several helium–rare-gas combinations, and estimating from somewhat analogous systems for those combinations for which no calculations existed, they were able to account for the large variations observed experimentally in the condensation temperatures at about 1/4 monolayer coverage. Similar calculations for H_2 adsorption do not exist, but they would be extremely interesting since they may be able to point out the way to an appropriate substrate for reduced condensation (and perhaps solidification) temperatures. We show in Fig. 9 the Lennard-Jones H_2-H_2 intermolecular potential. On this potential we have placed the measured distances between second and third nearest neighbor (NN) adsorption sites on the honeycomb lattice formed by one monolayer of either H_2 or D_2,[10] plus the actual distances between H_2, HD, and D_2 molecules in the close-packed planes of the 3D materials. The only structural evidence available for the second layer H_2 is on H_2/gr, where it seems to form a floating incommensurate solid.[10] It is thus very likely that on the low-density 2D gas phase the effective site interaction distance of Ref. 22 is the one corresponding to the third NN, leading to a weaker effective ϵ.

Calculations have been published recently regarding the adsorption of ^{4}He, ^{3}He, and H_2 on very weak binding substrates, and possible effects on the two-dimensional

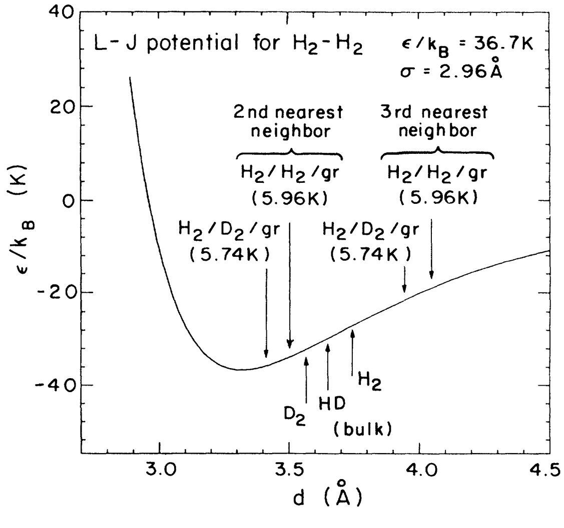


FIG. 9. H_2-H_2 Lennard-Jones potential with known or estimated distances between the second and third nearest neighbor adsorption sites on the monolayer plating as seen by the second layer. In parentheses, T_t(2D) for various H_2 films; see text.

condensation temperature.[25–27] The weak binding has a profound effect on the wetting behavior of thin and thick films, but provided that the film forms, the weak binding tends to *enhance* 2D condensation.[26] One prediction is that provided that a H_2 film forms, its ground state at $T=0$ K is a 2D solid, in agreement with previous calculations.[6]

C. Interlayer mixing

Both systems studied show triple lines which tilt towards lower temperatures as the H_2 coverage increases, with the tilting in H_2/HD/gr being the most pronounced. This feature, not seen by Wiechert in his pure H_2 and D_2 heat-capacity measurements[10] or us in ongoing studies of bilayer HD, may be attributed to interlayer mixing between H_2 and HD at the triple-point temperature.

Experiments with NMR directly support the fact that in a mixture of hydrogen isotopes adsorbed on MgO and at temperatures below 7 K the larger-mass molecules deposit next to the substrate.[14,16] At 0 K we expect complete isotopic separation. However, at finite temperatures isotopic mixing may lower the free energy of the system. In this section we present a simple classical estimate of the free energy change upon mixing, which allows us to calculate the concentration of either HD or D_2 on the second (the H_2) layer as a function of temperature. The model includes three contributions: the mixing entropy in both the first and the second layers, the binding energy difference resulting from the exchange of type of isotopic molecule between the first and second layers, and the change in 2D Debye temperatures of the first and second layer solids due to "impurity" mixing. The results of the calculation, when combined with regular solution theory, adequately describe features of the H_2/HD/gr system for which the triple-line tilting is the largest and the triple-point temperature falls in between those of pure H_2/H_2/gr and HD/HD/gr, and suggests the reason for the smaller tilting of T_t(2D) in the H_2/D_2/gr system.

Using H_2/HD/gr for the notation (replace D_2 for HD in every equation to describe the H_2/D_2/gr system) except where mentioned, the quantities involved in the calculation are defined as follows: N_{HD} and $N_{\mathrm{H_2}}$ are the total number of HD molecules and H_2 molecules in the system H_2/HD/gr. We assume that at $T = 0$ K, all HD molecules N_{HD} are in the first layer to form a complete monolayer and all H_2 molecules $N_{\mathrm{H_2}}$ are in the second layer. Neglecting the few percent first and second layer density differences, the ratio $y = N_{\mathrm{H_2}}/N_{\mathrm{HD}}$ represents the H_2 monolayer fraction. $x_{\mathrm{H_2}}$ and x_{HD} are the concentrations of H_2 in the HD (first) layer and HD in the H_2 (second) layer. If we assume that equal amounts of H_2 and HD are exchanged, then we have the relation $x_{\mathrm{HD}} = x_{\mathrm{H_2}}/y$. We define $\epsilon^{(i)}_{\mathrm{H_2}}$ and $\epsilon^{(i)}_{\mathrm{HD}}$ as the binding energies of each H_2 and HD molecule in the ith layer to the graphite substrate. The following terms are then taken into account.

Mixing entropy: The classical entropy of mixing is given by

$$\begin{aligned}\Delta S = &-N_{\mathrm{HD}}k_B[x_{\mathrm{H_2}}\ln(x_{\mathrm{H_2}}) + (1-x_{\mathrm{H_2}})\ln(1-x_{\mathrm{H_2}})]\\ &-N_{\mathrm{H_2}}k_B[x_{\mathrm{HD}}\ln(x_{\mathrm{HD}}) + (1-x_{\mathrm{HD}})\ln(1-x_{\mathrm{HD}})].\end{aligned} \tag{6}$$

Binding energy change: The interactions between hydrogen molecules of the same kind or between hydrogen molecules of different kinds are very similar. Based on this, we can reasonably assume $\epsilon_{\mathrm{H_2\text{-}H_2}} = \epsilon_{\mathrm{HD\text{-}HD}} = \epsilon_{\mathrm{H_2\text{-}HD}}$. Neglecting kinetic energy effects, the energy change resulting from interlayer exchange is mainly due to the binding energy difference between H_2/gr and HD/gr:

$$\begin{aligned}\Delta E &= N_{\mathrm{HD}}x_{\mathrm{H_2}}[(\epsilon^{(1)}_{\mathrm{H_2}} - \epsilon^{(1)}_{\mathrm{HD}}) + (\epsilon^{(2)}_{\mathrm{HD}} - \epsilon^{(2)}_{\mathrm{H_2}})]\\ &= N_{\mathrm{HD}}x_{\mathrm{H_2}}\Delta\epsilon,\end{aligned} \tag{7}$$

where $\Delta\epsilon$ is the binding energy change associated with one molecule exchanged.

Energy change due to changes in Debye temperature: In the temperature range 4–13 K a completed first layer of any of the hydrogens is always in the incommensurate solid form. Below the second layer triple point, the H_2 in the H_2/HD/gr system is also solid. We approximate behavior of either the first or second layer by a 2D Debye solid. The very-low-temperature free energy can be expressed in term of a Debye temperature Θ_D as

$$F(T) = N_{\mathrm{HD}}k_B\left[\frac{2}{3}\Theta_D - 4.8\left(\frac{T}{\Theta_D}\right)^2 T\right]. \tag{8}$$

When H_2 molecules dissolve into the HD first layer, $\Theta_{D(1)}$ will be altered due to the modified energy spectrum. When the H_2 concentration is small, one can treat H_2 molecules as mass defects because the replacement of HD by H_2 only changes the mass at that particular lattice site; the interactions among the molecules remain the same. The new Debye temperature in the mass defect model is approximately[29]

$$\Theta_{D(1)}(x_{\mathrm{H_2}}) = \Theta_{D(1)}(0)[1 - a x_{\mathrm{H_2}}]^{-1/2}, \tag{9}$$

where $a = (M_{\mathrm{HD}} - M_{\mathrm{H_2}})/M_{\mathrm{HD}} = 1/3$. Then the free energy change can be estimated as follows:

$$\begin{aligned}\Delta F_{\Theta_{D(1)}} = N_{\mathrm{HD}}k_B\Bigg[&\frac{2}{3}\Theta_{D(1)}(0)\left(\frac{1}{\sqrt{1-a x_{\mathrm{H_2}}}} - 1\right)\\ &+4.8 a x_{\mathrm{H_2}}\left(\frac{T}{\Theta_{D(1)}(0)}\right)^2 T\Bigg].\end{aligned} \tag{10}$$

A similar calculation to the one above, but now with HD as the impurity in the 2D solid (second layer) H_2, yields Eq. (10) but with $\Theta_{D(2)}$, x_{HD}, and $a = (M_{\mathrm{H_2}} - M_{\mathrm{HD}})/M_{\mathrm{H_2}} = -(1/2)$.

Summing up all the four contributions, the total free energy change resulting from the interlayer mixing is given by

$$\Delta F = \Delta F_{\Theta_{D(1)}} + \Delta F_{\Theta_{D(2)}} + \Delta E - T\Delta S. \tag{11}$$

The mixing fractions $x_{\mathrm{H_2}}$ and x_{HD} are obtained by minimizing the total free energy change with respect to x_{H_2} for each T and y, and then solving numerically the resulting equation. In order to calculate x_{H_2}, three parameters $\Delta\epsilon$, $\Theta_{D(1)}(0)$, and $\Theta_{D(2)}(0)$ need to be given. From the literature,[30] we have the binding energies $\epsilon^{(1)}_{H_2}/k_B \approx -483$ K and $\epsilon^{(1)}_{D_2}/k_B \approx -517$ K. We estimate the binding energy $\epsilon^{(1)}_{HD}/k_B \approx (\epsilon^{(1)}_{H_2}/k_B+\epsilon^{(1)}_{D_2}/k_B)/2$. The adsorption potential of the graphite substrate is $\propto 1/r^3$, with r being the distance from a molecule to the graphite surface.[30] Therefore the binding energy difference in the second layer can be estimated to be 1/8 of that in the first layer. From our own heat-capacity measurement of HD/gr at monolayer completion, we obtain $\Theta_{D(1)}(0) \approx 150$ K, while our measurements on H_2/HD/gr shown in Fig. 2 give a second layer $\Theta_{D(2)}(0) \approx 50$ K. We show in Fig. 10 our calculated concentration of HD molecules in the H_2 (second) layer at $T = 6.5$ K, close to the triple-point temperature. In the coverage range of the triple line (1.54 mJ/K< Nk_B <4.75 mJ/K or $0.23 < y < 0.72$), the HD concentration on the second layer decreases from 26% to 15% with increasing H_2 coverage if we consider the complete model as outlined, and from 16% to 9% if we do not include the change in Debye temperature of the second layer (solid lines).

Although the magnitude of interlayer mixing voids the simple treatment of the solid layers as pure phases with added impurities, we believe that mixing occurs and is responsible for the triple-line tilting. In 3D, the hydrogen isotopes are completely soluble in each other and the melting temperature of a mixture approximately follows the ideal solution lever rule $T_m \approx \sum c_i T_m(i)$, where c_i and $T_m(i)$ are the ith isotope concentration and melting temperature.[2] If the same rule holds for a 2D system, the tilted triple line can be qualitatively explained.

In reality the mixed system does not have a "triple line." One should add a third axis showing x_{HD}. For every x_{HD} there is a different S-L-V coexistence point. The lower end of the triple line is expected to be at higher temperature because of the higher HD concentration. Meanwhile, it is also expected that the triple point of H_2/HD/gr is in between those of H_2/H_2/gr at 5.96 K and HD/HD/gr at 8.44 K. We show in Fig. 11 our lever rule calculation of the shift in triple-point temperature with H_2 coverage. The experimental data fall in between the calculated lines without (solid line) and with consideration (dashed line) for changes of the Debye temperature of the second layer.

We believe that interlayer mixing is also responsible for the slight shift to lower T of the triple line in H_2/D_2/gr, but the actual temperature at which the triple line occurs can not be found by a simple lever rule since this temperature is lower than the T_t(2D) of the single-component systems. Nevertheless, we can still estimate the degree of mixing. The concentration of D_2 in the second layer is also shown in Fig. 10, lower curves, with only first layer Debye temperature changes, or with both first and second layer changes. For H_2/D_2/gr, $a = (M_{D_2} - M_{H_2})/M_{D_2} = 1/2$ for the first layer, and $a = -1$ for the second layer. We do not have a good value for the Debye temperature of D_2/gr, and so we still use $\Theta_{D(1)}(0) \approx 150$ K for the first layer and $\Theta_{D(2)}(0) \approx 50$ K for the second layer, which are good enough for our estimate. Due to the binding energy difference between H_2/gr and D_2/gr, larger than between H_2/gr and HD/gr, the D_2 concentration in the second layer is considerably lower than for the bilayer system with HD in the first layer.

While these estimates show possible interlayer mixing, a comparison between the entropies of the two-component films and the entropies found by integration of C/T, as in Sec. IV A, for measurements done in our adsorption cell of monolayer films of the single-component systems H_2/H_2/gr, HD/HD/gr, and H_2/HD/gr at about 1.4 layer coverages (not shown) fails to find the expected excess (mixing) entropy corresponding to this large degree of mixing. This may not necessarily void our model; it may be possible that our very slow cooling method allows for unmixing to occur in the gas, liquid, and solid phases, while our fast heat-capacity acquisition (heating pulses of about 10 s and about 3–5 min per point) does not allow for mixing in the solid phase to take place.

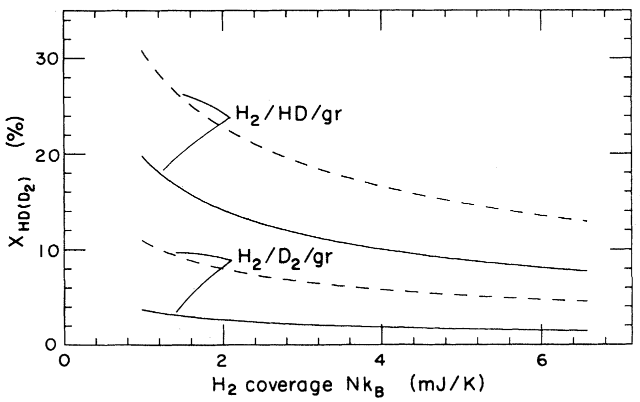


FIG. 10. Estimated HD and D_2 concentrations in the second layer at $T = 6.5$ K as a function of the H_2 coverage for the two systems studied. Dashed lines correspond to the full calculation described in text, solid lines to the same calculation excluding the change in $\Theta_{D(2)}$.

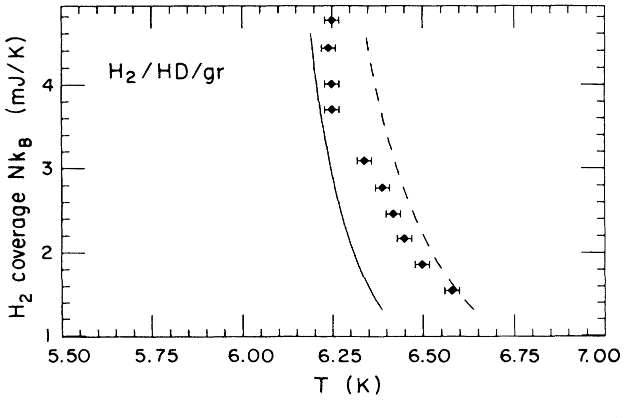


FIG. 11. Calculated tilt in the triple line for H_2/HD/gr due to interlayer mixing and application of regular solution theory, compared to experimental points (circles). Solid line calculated without considering change in $\Theta_{D(2)}$, and dashed line with the inclusion of the estimated change.

A study of HD on D_2, H_2 on bilayer HD and D_2, and mixing in multilayers of various combinations of isotopic molecules should be rather fascinating, and it would shed information on many of the results reported in this paper.

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