

## Heat capacity of the commensurate phase and ordering transition of para-H<sub>2</sub> monolayers on graphite

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Heat-capacity data for the  $\sqrt{3} \times \sqrt{3} R 30^\circ$  commensurate-solid phase and commensurate ordering transition of para-H<sub>2</sub> monolayers on graphite show striking similarities to He monolayers. The commensurate-solid disordered-fluid phase boundaries have similar shapes and the transitions show similar critical behavior. A value of  $0.36 \pm 0.05$  is observed for the critical exponent  $\alpha$ . At low temperatures the commensurate-solid phase behaves like an Einstein solid with a characteristic temperature of  $53.4 \pm 1.2$  K.

### INTRODUCTION

Diffraction studies of para-H<sub>2</sub> monolayers physisorbed on graphite<sup>1,2</sup> indicate the presence of a  $\sqrt{3} \times \sqrt{3} R 30^\circ$  commensurate structure on the graphite basal plane over a range of submonolayer coverage and  $T < 20$  K. A heat-capacity study<sup>3</sup> comparing low-density para-H<sub>2</sub> with <sup>4</sup>He suggests analogous phase diagrams for the two systems. Current work by Lerner *et al.*,<sup>4</sup> on para-H<sub>2</sub> and recent work by Ecke *et al.*<sup>5</sup> on <sup>4</sup>He should permit more detailed comparisons at low densities. The correspondence between para-H<sub>2</sub> and <sup>4</sup>He on graphite is a consequence of their molecular properties. Both are small, light, effectively spherical molecules that are weakly interacting and strongly influenced by quantum zero-point motion. Thus, para-H<sub>2</sub> provides another physical system with which to test theories developed for <sup>4</sup>He. This paper reports results of a heat-capacity study of the commensurate-solid phase of para-H<sub>2</sub> on graphite and its ordering transition. The results show remarkable similarities to the corresponding phase and transition for <sup>4</sup>He on graphite.

### EXPERIMENTAL RESULTS

A high-precision adiabatic calorimetric technique was used in this heat-capacity study.<sup>6-8</sup> The basic apparatus is that used by Ecke, but includes significant experimental modifications made possible by an improved computer-controlled electronics system. These modifications reduce measurement scatter from roughly 1.0% of the total measured signal plus background to about 0.2%. The advantage of using the same calorimetry cell is that the substrate is well characterized by the previous work, allowing accurate comparison of the <sup>4</sup>He and para-H<sub>2</sub> systems. The substrate is a single piece of graphite foam<sup>9</sup> with mass of 16.47 g and surface area of 486.9 square meters. Surface-area calibration is determined by assuming that maximum peak height and critical temperature of the <sup>4</sup>He commensurate order transition occur at  $\rho = 1.0$  ( $n = 0.0637 \text{ \AA}^{-2}$ ),<sup>6,7</sup> A disadvantage of this experimental cell is the relatively large background heat capacity due to a massive copper container. For the <sup>4</sup>He

system the monolayer heat capacity is roughly equal to the copper container heat capacity. For the para-H<sub>2</sub> system, the higher temperature of the study reduces the relative monolayer heat capacity to roughly 2–10% of the container background. The experimental modifications compensate for most of the reduction in signal to background, but the H<sub>2</sub> film heat-capacity results are still less precise than for <sup>4</sup>He. Further details will be published elsewhere.

Our study consists of nine monolayer densities from  $n = 0.0634 \text{ \AA}^{-2}$  to  $0.0690 \text{ \AA}^{-2}$ . Figure 1 shows net heat-capacity data for  $0.0645 \text{ \AA}^{-2}$  after background subtraction. To reduce the effects of scatter in the data, the transition was traced twice with 1.0% temperature steps and three times with 0.3% temperature steps. This density has the highest specific-heat peak of all of our samples,  $11.7 C/Nk_B$  at 20.42 K. The critical temperature  $T_c$  is identified as the temperature of the maximum of the heat-capacity peak. The transition region scales closely to the corresponding region for the <sup>4</sup>He order-disorder transition measured in the same cell.<sup>6</sup> For para-H<sub>2</sub>, full width at half maximum (FWHM) of the heat-capacity peak with the highest critical temperature is 2.1% of  $T_c$ , compared to a FWHM for <sup>4</sup>He of 2.2%. At higher and lower densi-

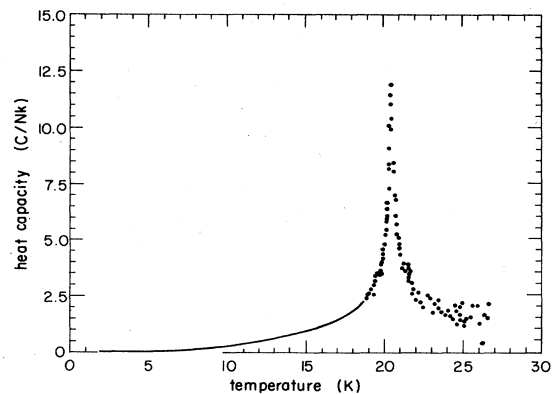


FIG. 1. Heat capacity of para-H<sub>2</sub> monolayer on graphite at density  $n = 0.0645 \text{ \AA}^{-2}$ .

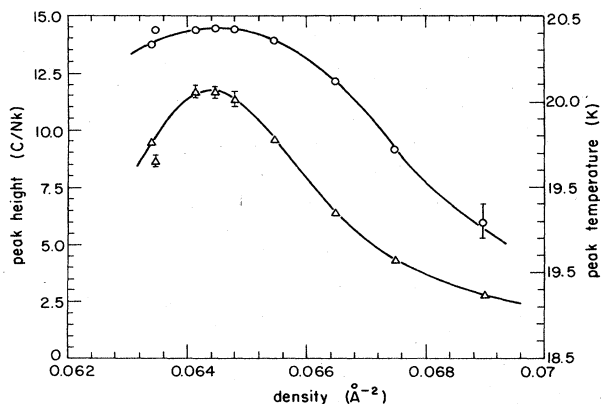


FIG. 2. Commensurate-solid disordered-fluid transition specific-heat peak height versus density ( $\Delta$ , left axis). Transition critical temperature versus density ( $\circ$ , right axis).

ties the peak height drops rapidly and  $T_c$  decreases, as illustrated in Fig. 2. One of the samples,  $n = 0.0635 \text{\AA}^{-2}$ , was studied before the apparatus modification was complete and hence these data have somewhat larger uncertainties. Vapor pressure was monitored with a thermocouple gauge calibrated against a capacitance manometer with normal  $\text{H}_2$  gas. Desorption is not significant for any of the densities until several degrees K above the transition.

The commensurate-solid disordered-fluid phase boundary is very similar to that for  $^4\text{He}$ . Figure 3 compares the phase boundaries of para- $\text{H}_2$ ,  $^4\text{He}$ ,<sup>6,10,11</sup> and the results of a triangular Ising-model calculation.<sup>12</sup> The para- $\text{H}_2$  and  $^4\text{He}$  data have been shifted so that their maximum critical temperatures occur at a coverage of  $\rho = 1.012$ , the ideal coverage of maximum  $T_c$  for the triangular Ising model. Agreement between the shifted experimental results is excellent, but their critical temperatures fall more rapidly than the theoretical curve on both sides of the maximum. A significant difference between the para- $\text{H}_2$  and  $^4\text{He}$  systems is that the monolayer of

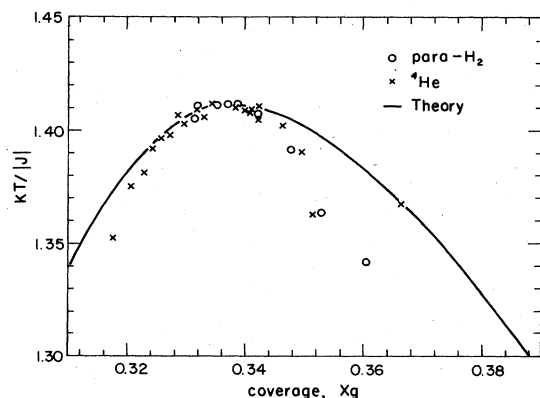


FIG. 3. Comparison of commensurate-solid disordered-fluid phase boundaries of para- $\text{H}_2$ ,  $^4\text{He}$  (Refs. 6, 10, and 11) and a triangular Ising-model calculation (Ref. 12). The coverage scale corresponds to  $x_g = \frac{1}{3}$  at the density of perfect  $\sqrt{3} \times \sqrt{3}$  structure.

maximum critical temperature and heat-capacity peak height is about 1.3% denser for para- $\text{H}_2$  than it is for  $^4\text{He}$ . Analysis<sup>12</sup> of the  $^4\text{He}$  results yielded a value for the interaction term  $J/k_B$  equal to 2.08 K. On the same basis, we find 14.53 K for para- $\text{H}_2$ . This results in a nearest-neighbor repulsion term of 8.32 K for  $^4\text{He}$  and 58.1 K for para- $\text{H}_2$ .

We determined the critical exponent  $\alpha$  by a fit to Eq. (1):

$$C(T) = A |t|^\alpha + B + DT, \quad (1)$$

where  $t = (T - T_c)/T_c$ . Data in the region  $0.008 < |t| < 0.12$  are included in the fit. Our data are consistent with Eq. (1) in that all of the peaks are symmetrical about  $T_c$  in the region of fit. The coefficients  $A$ ,  $B$ , and  $D$  were determined by a least-squares fit for each trial set of  $\alpha$  and  $T_c$ . Final values of  $\alpha$  and  $T_c$  were determined by a grid search for the minimum total squared deviation of the data points from Eq. (1). For the sample with the highest peak height,  $n = 0.0645 \text{\AA}^{-2}$  ( $\rho = 1.013$ ), the empirical exponent is  $\alpha = 0.331 \pm 0.026$ . This is in excellent agreement with the theoretical value  $\frac{1}{3}$  and with  $^4\text{He}$  data.<sup>5,10,13</sup> For the three samples with densities closest to  $\rho = 1$ , we obtain an average exponent  $\alpha = 0.36 \pm 0.05$ . Exponents for all of the samples are plotted in Fig. 4, which shows that the effective  $\alpha$  is monotonically reduced as  $\rho$  moves away from  $\rho = 1$ . Qualitatively this is expected as the heat-capacity peak becomes lower and more rounded away from  $\rho = 1$ .

The temperature dependence of the commensurate-solid heat capacity below the transition is different from that of He. The para- $\text{H}_2$  signal resembles that of an Einstein solid with characteristic temperature  $\Theta_E = 53.4$  K. A plot of effective Einstein temperature  $\Theta_E$  versus  $T$  for  $n = 0.0645 \text{\AA}^{-2}$  is presented in Fig. 5. The empirical  $\Theta_E$  is essentially constant over the range 6–12 K. Above this range  $\Theta_E$  decreases due to the influence of the order-disorder transition. The decrease of  $\Theta_E$  below 6 K is consistent with the effect of a small concentration of ortho- $\text{H}_2$ . Similar anomalous low-temperature behavior is observed in bulk solid  $\text{H}_2$  measurements.<sup>14</sup> The empirical  $\Theta_E$  is in excellent agreement with inelastic neutron-scattering measurements on in-plane excitations.<sup>1</sup> The

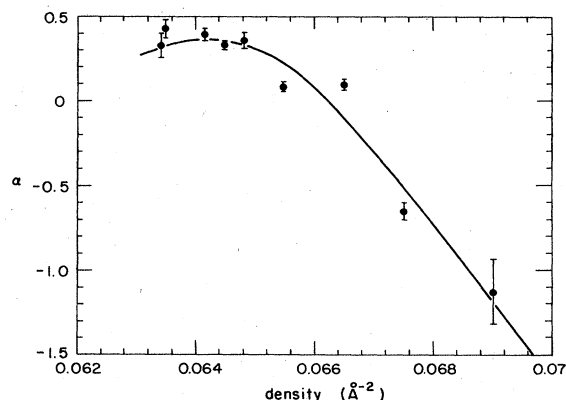


FIG. 4. Specific-heat critical exponent  $\alpha$  versus density.

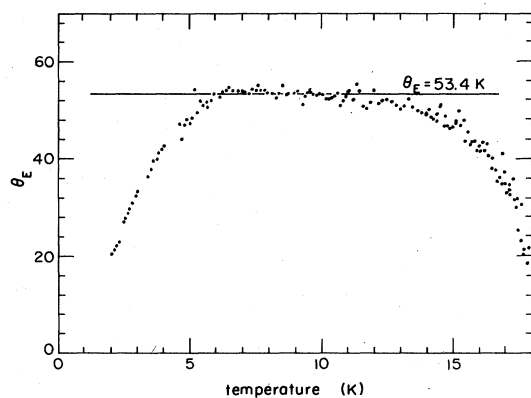


FIG. 5. Characteristic temperature  $\Theta_E$  determined from specific heat, for  $n=0.0645 \text{ \AA}^{-2}$ .

scattering measurements indicate an excitation mode of narrow-energy width at 4.9 meV. This energy corresponds to  $\Theta_E=57 \text{ K}$ . Since the Einstein model works well, the mode is evidently a type of independent particle motion. The fact that the excitations are seen by in-plane neutron scattering and not by out-of-plane scattering indicates that the mode is the in-plane oscillation of molecules within each adsorption site. Our measurements of vapor pressure show why only in-plane modes are excited. A series of measurements were made on monolayers with densities near  $\rho=1$  and temperatures in the range 25–30 K. The isosteric heat  $Q_{st}=k_b T^2(d \ln P/dT)_n$ ,<sup>15</sup> obtained from these measurements is  $500 \pm 50 \text{ K}$ . This is an order of magnitude greater than the thermal  $\Theta_E$ , and more than an order of magnitude greater than the temperatures of this study. Thus, the out-of-plane mode is essentially in its ground state in the experimental temperature range.

In contrast to this simple spectrum of the registered phase of para- $\text{H}_2$ , the registered phase of He monolayers cannot be described by a single frequency Einstein oscillator. For both  $^4\text{He}$  and  $^3\text{He}$   $\log [C(T)/Nk_b]$  is linear with temperature over the range  $0.08 < T/T_c < 0.89$ .<sup>16</sup> Although this empirical dependence fits  $^4\text{He}$  and  $^3\text{He}$  data quite well, it has not received any theoretical interpretation. We believe that it is an artifact of a broad distribution of excitation energies, and we will present an analysis of the energy distribution in a future paper.<sup>8</sup>

A possible explanation of the specific-heat critical behavior away from  $\rho=1$  is provided by Ecke *et al.*<sup>5</sup> The two-dimensional (2D) three-state Potts model predicts  $\alpha=1/3$  only for paths of constant chemical potential. All heat-capacity measurements are made at or near constant density. Any difference between the constant chemical potential and constant density paths tends to reduce the empirical  $\alpha$  determined by a curve fit to constant density

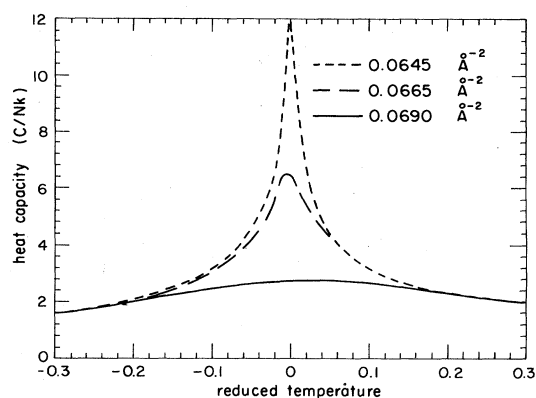


FIG. 6. Heat capacities of films  $n=0.0645$ ,  $0.0665$ , and  $0.690 \text{ \AA}^{-2}$  in the critical region versus reduced temperature.

data. Ecke *et al.* argue that data further from the critical temperature are affected less by constant density paths. Their arguments are valid only for densities less than  $\rho=1$ . Our results for  $\rho > 1$  appear to behave in a similar fashion, and this is illustrated by Fig. 6, which shows para- $\text{H}_2$  data in the critical region. For the sake of clarity only  $0.0645$ ,  $0.0665$ , and  $0.690 \text{ \AA}^{-2}$  are plotted together. As with  $^4\text{He}$  monolayers on graphite for  $\rho < 1$ , the film heat capacities overlap away from the critical temperature.

## CONCLUSIONS

The data presented here provides striking evidence of the similarity of para- $\text{H}_2$  monolayers on graphite to  $^4\text{He}$  monolayers on graphite. In the immediate neighborhood of  $\rho=1$  a value of the specific-heat critical exponent  $\alpha$  of  $0.36 \pm 0.05$  is observed. This is consistent with the critical exponent of  $1/3$  given by the 2D three-state Potts model, making para- $\text{H}_2$  monolayers on graphite another physical realization of the Potts model. The para- $\text{H}_2$  commensurate solid, however, behaves much more like an Einstein solid with a single excitation energy than does the  $^4\text{He}$  system. Further analysis of these measurements, together with the results on the incommensurate-solid phase and the intermediate density region between the commensurate- and incommensurate-solid phases, will be reported in a later paper.

## ACKNOWLEDGEMENTS

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