Experimental Determination of a Two-Dimensional Liquid-Vapor Critical-Point Exponent

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The liquid-vapor coexistence boundary of submonolayer CH_4 adsorbed on graphite was mapped out in an extensive ac heat-capacity study. The order-parameter exponent β that describes the shape of the liquid-vapor coexistence boundary was found to be 0.127 ± 0.020. This is in good agreement with $\frac{1}{8}$, the exact value calculated for a two-dimensional Ising-model system.

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One of the central ideas of modern critical-phenomena theory is the concept of universality.[1] The critical behavior as exhibited in the value of the critical exponents is expected to be the same for all systems in the same universality class. The classification of the universality classes depends on only a very few relevant parameters, namely, the spatial dimensionality of the system and the dimensionality of the order parameter that characterizes the transition. Since the order parameter of the liquid-vapor transition, the density difference in the liquid and vapor phases, and the order parameter of the Ising model, the magnetization, are both scalars, it is expected that the liquid-vapor transition should fall in the same universality class as the Ising-model system. This is confirmed convincingly in bulk simple-fluid systems: The critical exponents found for the bulk liquid-vapor transitions in recent experiments are in excellent agreement with those calculated for a three-dimensional Ising-model system.[2,3] We shall report in this Letter the first determination of a critical exponent of a two-dimensional liquid-vapor system. The order-parameter exponent β is extracted from an extensive heat-capacity study of submonolayer methane adsorbed on graphite. Our value for β, 0.127 ± 0.020, is in good agreement with $\frac{1}{8}$, the value calculated for the two-dimensional Ising-model system.[4]

The various phase transitions of submonolayer CH_4 and CD_4 adsorbed on graphite have been studied by neutron scattering,[5,6] NMR,[7] and calorimetric[8] methods. These studies showed that submonolayer methane melts from an incommensurate structure to a liquid-vapor coexistence region at a two-dimensional triple temperature. In addition to methane on graphite, this two-dimensional liquid-vapor coexistence region has also been reported for other adsorbates on graphite.[9] However, very little quantitative information concerning the nature of the liquid-vapor transition and especially the critical behavior is available from these experiments. Quantitative results are difficult to obtain because signatures of this transition are broad and weak as compared, for example, with those near a first-order melting transition at the two-dimensional triple temperature.

We decided to attempt another heat-capacity study of this transition because the ac calorimetry techniques used in our laboratory[10] have been shown to have resolution superior to that of conventional adiabatic methods. In order to reduce the broadening and smearing effects due to finite size and heterogeneity in the substrate potential,[11] a more homogeneous substrate, Graphite Foam (instead of Grafoil) is used in our experiment.[10]

Since the experimental arrangements of this experiment are similar to earlier studies from our laboratory, most of the details will be omitted here. Following the convention of other studies of methane on graphite,[5-7] we defined the methane coverage at the inflection point between the first and second vertical steps of the vapor-pressure isotherm (performed at 78 K) to be monolayer ($n = 1$) coverage. The resolution in coverage determination with our gas-handling system is 0.5% of a monolayer. The resolution in temperature determination of the calorimeter is 0.01 K and there is no observable temperature shift upon repeated thermal cycling of the sample cell. The coverage and the temperature scales are estimated to be accurate to 1% of a monolayer and 0.20 K.

In Fig. 1, heat-capacity traces of nine of the 23 submonolayer films used in studying the liquid-vapor transition are shown. The background due to the calorimeter has been subtracted and the heat capacity is shown in reduced units, C/Nk_B. N is the total number of molecules adsorbed on graphite and k_B is Boltzmann's constant. A sharp heat-capacity anomaly with a full width at half maximum of 0.15

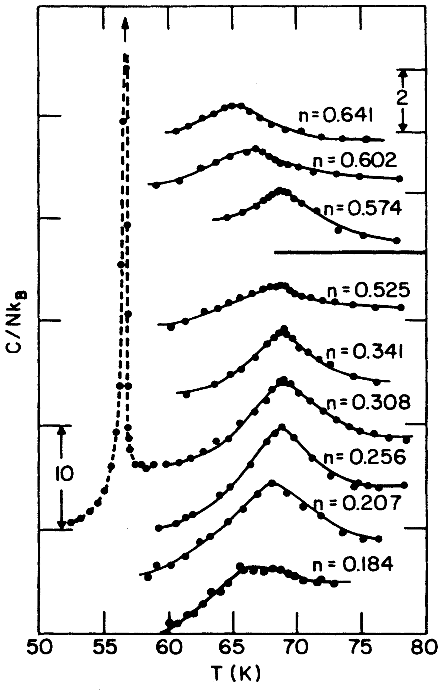

FIG. 1. Heat-capacity traces of nine submonolayer methane films in the liquid-vapor transition region. Each vertical division corresponds to either ten units (low coverages) or two units (high coverages) in C/Nk_B. The two-dimensional triple-point peak height for the $n = 0.308$ is 110 in C/Nk_B. Solid lines are results of a least-squares analysis.

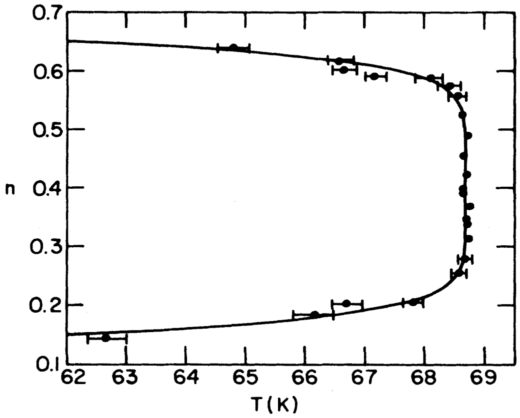

FIG. 2. Peak positions of the liquid-vapor heat-capacity anomaly as a function of methane coverages. These data points trace out the liquid-vapor coexistence boundary. Error bars show the expected uncertainty of the transition temperatures at each coverage according to a nonlinear least-squares analysis of the heat-capacity scan. These uncertainties are comparable with the size of dots for intermediate coverages. Solid line is drawn with $\beta = 0.127$.

K is found at the same temperature (56.58 ± 0.02 K) for all submonolayer coverages studied. For the sake of clarity, this peak is shown for only one of the coverages. The constancy of the peak temperature and the narrow width of these peaks are consistent with a triple-line interpretation at this temperature. In addition to the triple-line-temperature peak, an additional much smaller and broader (full width at half maximum ~5 K) heat-capacity anomaly due to the crossing of the liquid-vapor coexistence boundary is seen for each of the 23 films with coverage between $n = 0.145$ and $n = 0.640$.

The position of the maximum in these peaks, T_p, appears to be well defined. It is determined with the following procedure: The measured heat capacity for each coverage as a function of temperature is fitted with a nonlinear-least-squares program[12] by the following phenomenological form:

$$C/Nk_B = A \exp[-|T-T_p|^2/L] + D(T-T_p) + E, \quad (1)$$

where A, L, D, E, and T_p are parameters of the fit. The Gaussian term is chosen for its simplicity; the terms $D(T-T_p)$ and E are included to account for the regular (not related to transition) contribution of adsorbed film to the heat capacity and possible incorrect subtraction of the background. The values of T_p determined according to Eq. (1) are in good agreement (generally within ± 0.10 K) with the value obtained from the assumption of a quadratic function in T for the heat capacity in a narrower range around T_p. The solid lines shown in Fig. 1 are the fitted heat-capacity traces. The statistical uncertainty in T_p determined with this procedure ranges from 0.3 K for low and high coverages to 0.1 K for coverages in the intermediate region where T_p is near the critical temperature. The difference is due to the fact that at low and high coverages the heat-capacity scan follows a path that is almost parallel to the coexistence boundary. The transition temperature T_p extracted with this procedure is plotted as a function of the coverage n in Fig. 2. In what follows, we shall assume that the data points in Fig. 2 lie on the coexistence boundary. The most striking feature of Fig. 2 is the extreme flatness of the boundary on the high-temperature side. Such a shape was also observed in a recent vapor-pressure study of the second layer of Ar adsorbed on cadmium chloride[13] and a more recent adiabatic heat-capacity study, also of methane on graphite.[14] The phase boundaries obtained in these studies, however, are not of sufficient quality for careful quantitative analysis.[13,14]

Along the coexistence boundary, the coverage n_i at a specific temperature T_{pi} falls either in the liquid branch (n_l, T) or the vapor branch (n_v, T). The data points shown in Fig. 2 should follow a power law of the form

$$(n_l - n_c) = (n_c - n_v) = B_0[(T_c - T)/T_c]^{\beta}, \qquad (2)$$

where B_0, T_c, and β are respectively the critical amplitude, the critical temperature, and the order-parameter exponent. We have assumed in Eq. (2) that the coexistence boundary is symmetrical about the critical coverage n_c.

Because of the flatness of the coexistence boundary near T_c, the expected uncertainty in the transition temperature prevents the power-law analysis over a wide range of coverages near $n = n_c$. Between $n = 0.28$ and $n = 0.5$, the actual variation in the transition temperature T_p of the ten methane coverages, on the order of 0.06 K, is comparable with the expected statistical uncertainty in T_p (0.1 K) determined for each film coverage. Although the data from these ten coverages cannot be used for power-law analysis, their average transition temperature, 68.67 ± 0.06 K, serves as an excellent estimate for the critical temperature.

The remaining thirteen data points outside $0.28 < n < 0.5$ were analyzed according to Eq. (2) with a nonlinear-least-squares program.[12] In order to limit the number of free parameters, these data points were fitted with B_0, T_c, and β as free parameters and with the value of n_c changed systematically. In Fig. 3(a), the χ^2 value as a function of n_c is shown for such a fit. At the minimum χ^2 value (normalized to be one), $n_c = 0.402$ and $T_c = 68.67 \pm 0.04$ K, $B_0 = 0.332 \pm 0.024$, and $\beta = 0.127 \pm 0.020$ (uncertainties quoted here are the one-sigma value). It should be noted that the critical temperature found in this fit is in complete agreement with the estimate from the ten intermediate coverages. If a value of $n_c = 0.388$ is used, the χ^2 value increases to 3 and the best-fit parameters are $B_0 = 0.326$, $T_c = 68.70$, and $\beta = 0.121$. On the other side of the minimum, also at $\chi^2 = 3$, the best-fit parameters are $B_0 = 0.341$, $T_c = 68.65$, and $\beta = 0.136$ for an n_c value of 0.417. We have repeated the analysis by fixing one, two, or three of the parameters among n_c, T_c, and B_0 at the values found above, and in each case the best-fit value for β changes by less than 0.002 from 0.127. In Fig. 3(b), the χ^2 value as a function of β is shown with n_c, T_c, and B_0 fixed at the respective best-fit values, namely, 0.402, 68.67 K, and 0.332. The solid line shown in Fig. 2 is drawn with these best-fit values and with $\beta = 0.127$.

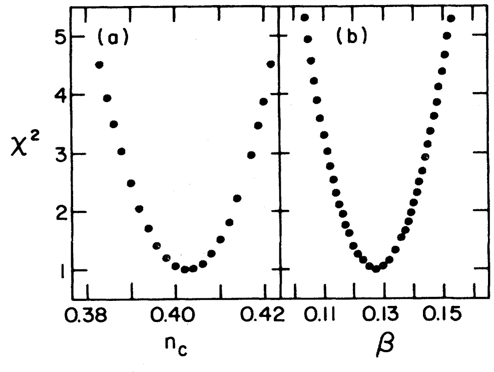

FIG. 3. (a) χ^2 as a function of the imposed critical coverage n_c. T_c, B_0, and β are free parameters of this fit. (b) χ^2 as a function of the imposed β. T_c, B_0, and n_c are fixed at the best-fit values given in (a). In both (a) and (b) the best-fit value for β is 0.127. See text for more discussion.

We have also fitted the data with the values of T_c fixed at 68.61 and at 68.73 K, the limit of probable high and low estimates of T_c according to the average transition temperature of the ten coverages near n_c. In these fits, B_0 and β are left as free parameters and the value of n_c is changed systematically. We found that with T_c fixed at 68.61 K, the best-fit value of β is 0.111, and with T_c fixed at 68.73 K, $\beta = 0.146$.

We have complemented the exponent β analyses by examining the shape of the heat-capacity traces of eight coverages (between $n = 0.308$ and $n = 0.455$) near the critical value. In Fig. 4 we have plotted for the $n = 0.395$ and $n = 0.424$ coverages the measured heat-capacity values, with the regular contribution not related to the transition [the $D(T - T_p)$ and E terms in Eq. (1)] subtracted, as a function of the logarithm of the absolute reduced temperature, $t = |T - T_c| T_c^{-1}$. At these coverages T_p, the peak temperature, is indistinguishable from T_c. The fact that the heat-capacity values for $T > T_c$ and $T < T_c$ appeared to be merged as a single curve indicated that the assumption of an identical (subtracted) regular contribution below and above T_c is reasonable.[15] Figure 4 shows clearly, in spite of the scatter, a linear dependence of the heat capacity on $\ln|t|$ between $|t| = 2.5 \times 10^{-2}$ and $|t| = 1 \times 10^{-1}$. Similar dependences are found for the other six coverages. This linear dependence indicates that the shape of these heat-capacity anomalies appears to be consistent with the Ising-model prediction that the specific-heat exponent, α, is close to zero.[15,16] The broad half-widths found in the heat-capacity anomalies are consistent with the

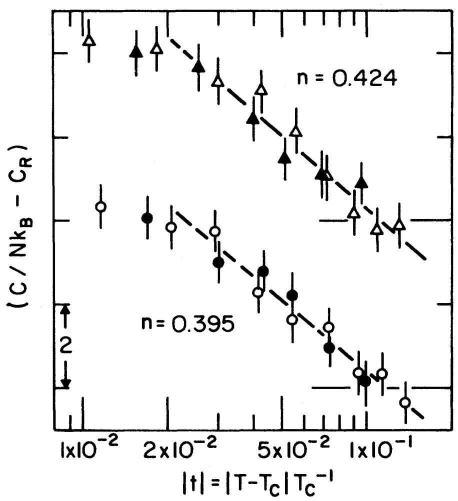

FIG. 4. Heat capacity due to transition as a function of absolute reduced temperature. C_R represents regular (not related to transition) contribution to the heat capacity. Note the shift in the y axis for the two different coverages. Open and closed symbols represent respectively data above and below T_c. Dashed straight lines are drawn to aid the eyes.

significant rounding observed up to $|t| = 2.5\times10^{-2}$. The fact that rounding in our data sets in at a significantly larger (more than a factor of 2.5) reduced temperature than those found in the order-disorder transitions of ^{4}He on graphite[15] and ^{4}He on Kr-plated graphite[16] suggested that the liquid-vapor transition is particularly sensitive to substrate inhomogeneity effects.[11]

Since the shape of our heat-capacity traces are consistent with $\alpha \sim 0$, and the values of β from our studies and from the neutron study of two-dimensional magnetic systems[17] (at 0.119 and 0.123) are all in good agreement with $\frac{1}{8}$, we are led to conclude that both of these experimental systems belong to the same universality class of the two-dimensional Ising model. We can further conclude that although substrate attraction is solely responsible for keeping the adsorbate molecules on the surface, it is an unimportant or irrelevant parameter in determining the critical behavior of the two-dimensional liquid-vapor transition.

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