

Experimental Evidence of Continuous Melting of Ethylene on Graphite

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Heat-capacity measurements of ethylene on graphite in both the submonolayer and monolayer regions reveal a weak and broad anomaly relating to the melting transition of the overlayer. The findings in the submonolayer are in contrast to all previous studies in physisorbed systems, where sharp heat-capacity signals were observed. These results suggest that the melting of ethylene on graphite is a continuous transition for submonolayer as well as monolayer coverages.

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The possibility of a continuous and, in particular, Kosterlitz-Thouless-Nelson-Halperin-Young (KT-NHY)¹ type of melting transition is one of the most important motivations for the studies of phase transitions of overlayers physisorbed on attractive surfaces. Although the most likely realization of continuous melting is that of a solid overlayer that is incommensurate with the substrate, experimental results on these systems to date have found a range of different behaviors. Melting transitions of Ne,² O₂,³ Xe,⁴ and CH₄⁵ adsorbed on graphite in the submonolayer region are found to be first-order transitions that occur at triple points. At higher surface coverage, the submonolayer solid-vapor coexistence region in these systems is replaced by a pure solid phase and the melting temperature shifts upward with coverage. Recent synchrotron x-ray studies of Xe on graphite⁶ found evidence suggesting that the melting transition may change from first-order-like to continuous at a sufficiently high surface coverage. Smooth and broad heat-capacity and two-dimensional spreading-pressure anomalies were found at the melting of high-coverage compressed-monolayer ⁴He on graphite.⁷ These results could be considered signatures of continuous melting, as well as being consistent with first-order transitions broadened by heterogeneities.^{7,8}

The melting transition of Ar on graphite exhibits interesting behavior.^{9,10} A small (peak height is $3k_B$ per molecule) but sharp heat-capacity peak with a half-width (FWHM) of 0.3 K is found at the melting temperature.⁹ This peak is situated on the low-temperature side of a broad (FWHM 6 K) anomaly. The most straightforward interpretation of these results is that the sharp peak is a signal of "weak" first-order melting from the solid to a well-correlated fluid and the broad anomaly is related to the gradual loss of order in the well-correlated fluid.

In this paper we shall report heat-capacity evidence of the continuous melting of a physisorbed overlayer in the submonolayer as well as monolayer-completion regions. The system studied is that of ethylene and deuterated ethylene adsorbed on graphite. Heat-capacity scans as a function of temperature of twelve different coverages of C₂D₄ on graphite from $n = 0.45$

to $n = 1.15$ and four coverages of C₂H₄ on graphite from $n = 0.3$ to $n = 0.61$ were made to study their melting behavior. The ac calorimetric technique used in this study has been described elsewhere^{9,11} and will not be repeated here. In this study $n = 1$ is defined to be the coverage at the top of the vertical substep, corresponding to the completion of the $\sqrt{3} \times \sqrt{3}$ overlayer, in the N₂ vapor-pressure isotherm taken at 74 K.¹¹ This coverage scale is similar to that used in earlier studies¹¹⁻¹⁴ of ethylene on graphite.

In Fig. 1, the phase diagram of submonolayer and monolayer C₂D₄ on graphite based on this study is shown. The nature of the various phases and the loca-

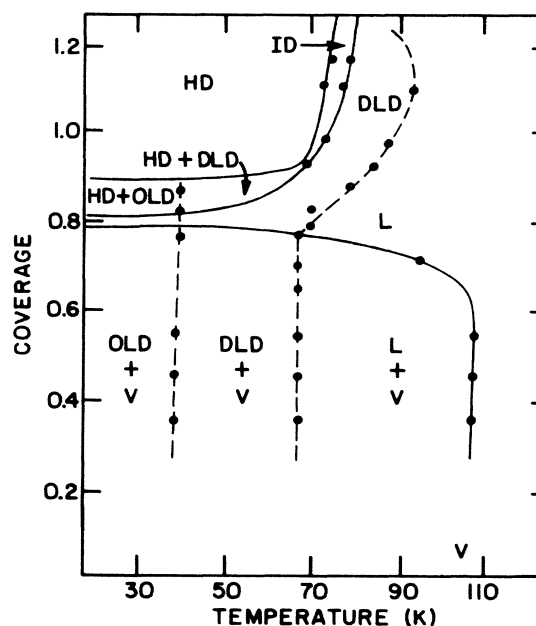


FIG. 1. Phase diagram of monolayer ethylene on graphite. Solid circles are locations of observed heat-capacity anomalies; solid and dashed lines represent respectively boundaries of first-order and continuous phase transitions. HD, ID, OLD, and DLD stand for high-, intermediate-, orientationally ordered low-, and orientationally disordered low-density solids. L and V stand for liquid and vapor. Precise location of the phase boundaries parallel to the temperature axis is more speculative.

tion of the phase boundary as shown in Fig. 1 are consistent with existing NMR,¹² x-ray,¹³ neutron,¹⁴ and vapor-pressure–isotherm¹⁵ results. The melting temperature in the submonolayer and monolayer-completion regions determined in our study is in very good agreement with that determined in the scattering and NMR studies.^{12–14} These experiments also show that the ethylene overlayer in the submonolayer and monolayer-completion regions always melts from the (orientationally) disordered low-density solid (DLD) phase. It is called the low-density phase because by comparison to the two other solid phases in the monolayer, this phase was found to have the lowest density. In the DLD phase the C=C bonds of the ethylene molecules are thought to be parallel to the graphite surface but randomly oriented with respect to each other.^{12–14} In Figs. 2 and 3, heat-capacity scans near the melting transition of C₂D₄ and C₂H₄ in the submonolayer region and C₂D₄ at higher surface coverage are shown. Figure 2 shows that in the submonolayer region the melting temperature is not sensitive to the coverage and that the melting behaviors of C₂H₄ and C₂D₄ are not different. The height of the heat-capacity signal is less than $5k_B$ per molecule. This is about a factor of 20 less than that due to triple-point melting of Xe, Ne, O₂, and CH₄ on graphite.^{2–5} The width (FWHM) of the ethylene melting anomaly is about 3 K, which is 20 times larger than that in the systems mentioned above. For $n \geq 0.8$, Fig. 3 shows that the melting temperature of C₂D₄ on graphite also increases with coverage as seen with other overlayer systems. The melting signals for coverages above $n = 0.8$ appear to be even weaker than that for $n < 0.8$. This may be a reflection of the fact that the heat-capacity scan is made along a path that is not perpendicular to the

phase boundary.

Since this weak and broad heat-capacity anomaly related to melting is unexpected, we have been very careful to eliminate any possible systematic effect. In addition to the C₂D₄ sample (99% deuteration), two different samples of C₂H₄ (99.99% purity) from different sources were used and no difference was observed in the melting behavior. Since the sharp melting peaks seen in our laboratory for the CH₄-on-graphite⁵ and Ar-on-graphite⁹ systems were carried out with adsorbate gases of comparable purity, it is unlikely that the residual impurity in the ethylene adsorbate is responsible for the broad anomaly. The sample cell was evacuated after the ethylene experiment and methane gas was introduced at 90 K. The characteristic sharp delta-function-like melting peak with a half-width (FWHM) of 0.15 K was found.⁵ This indicates that the calorimeter was clean during the ethylene experiment. One possible interpretation of the broad melting signals is that this is a result of broadening by the substrate heterogeneity.⁷ Since the half-width of the ethylene peaks is respectively a factor of 20 and 10 times larger than that observed for the melting of CH₄ and Ar in submonolayer coverage, one must invoke the unlikely possibility that ethylene is unusually sensitive (compared to other adsorbates) to heterogeneity effects. This is, however, not consistent with the observed heat-capacity behavior near 2D liquid-vapor critical points: The half-width of this peak in C₂D₄ is about 3 K,¹⁶ on the order of but smaller than that in CH₄ and Ar.^{5,9} The same substrate, namely Graphite Foam, with a single-crystallite domain of $\sim 10^6 \text{ \AA}^2$, was used in the CH₄, Ar, and ethylene experiments. The half-width of the melting peak of ethylene remains on the order of 3 K from the low-

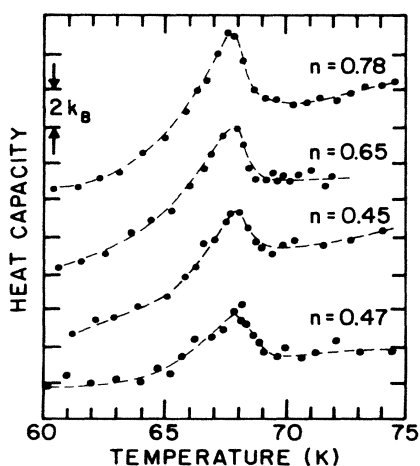


FIG. 2. Heat-capacity scans of the melting of submonolayer C₂D₄ (top three scans) and C₂H₄ (bottom scan) on graphite. Heat capacity is shown in units of C/Nk_B , where N is the total number of ethylene molecules on graphite.

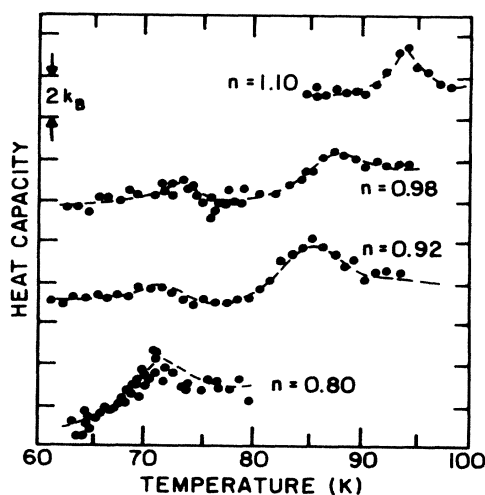


FIG. 3. Heat-capacity scans of melting of C₂D₄ on graphite above submonolayer coverage. The heat-capacity anomalies near 70 K for $n = 0.92$ and $n = 0.98$ are related to structural changes in the solid phase.

submonolayer region with coexisting vapor to the high-monolayer pure-solid region. If the heterogeneity interpretation is correct, one would expect a significant increase in the broadening in the high-coverage region.⁷

The area under the anomaly provides a measure of the change in entropy ΔS related to melting. In the submonolayer region, the ΔS values are $0.7k_B$ per molecule for CH_4 and $0.4k_B$ for C_2D_4 . Although the similarity is expected, it is striking considering the difference in the half-widths of the peaks. The absence of any sharp heat-capacity peak, according to the Clausius-Clapeyron equation, suggests that there is no observable discontinuous change in the solid and liquid densities at melting. For Ar on graphite, it was estimated that the sharp heat-capacity peak of $3k_B$ per molecule with a half-width of 0.3 K at the melting temperature corresponds to a density discontinuity of 0.2%. If the melting of ethylene on graphite is similar to that of Ar on graphite,⁹ any possible sharp feature, as shown in Figs. 2 and 3, would be smaller than $0.5k_B$ per molecule. This places an upper bound of about 0.05% on the density discontinuity at melting over a temperature range of 0.3 K. Within this resolution, the melting of ethylene on graphite appears to be continuous for both the submonolayer and monolayer coverages.

Since the shape of the heat-capacity signature at the KTNHY melting transition is not expected to be universal,^{1,17} it is not possible to deduce from our data whether the melting of ethylene on graphite is describable by the KTNHY model. We have made an analysis of the temperature dependence of the heat-capacity anomaly related to melting according to an activation model, similar to that performed by Ecke and Dash for helium on graphite.⁷ An activation energy of $2000 \pm 300 k_B \cdot \text{K}$ is found for all submonolayer C_2D_4 coverages ($n < 0.78$) and an energy of $5600 \pm 800 k_B \cdot \text{K}$ is found for $n = 1.10$. For coverages between $n = 0.8$ and $n = 1.1$, smaller activation energies are found; this is likely to be due to the fact that the experimental paths in this coverage range do not cross the melting boundary perpendicularly. If the unbinding of the dislocation pairs is the appropriate mechanism for the melting of ethylene on graphite, then the dislocation core energy E_c is $1000 k_B \cdot \text{K}$ in the submonolayer region. The simulation study of Saito¹⁸ shows that the melting of a two-dimensional overlayer can change from first-order-like, with dislocations of small core energy, to continuous for sufficiently large core energy. The value found here for ethylene is almost 4 times Saito's critical value of $E_c/k_B T_m \cong 4$. We have also examined and compared the measured spin-lattice relaxation times (T_1) near the melting of submonolayer CH_4 on graphite¹⁹ and submonolayer C_2H_4 on graphite.¹² In both experiments, a minimum in T_1

is found in the vicinity of the melting transition. The change in T_1 through the melting transition in C_2H_4 is about 4 times more gradual than that in CH_4 . The T_1 results in C_2H_4 were attributed by the authors to be a signature of first-order melting broadened by substrate inhomogeneity.¹² We are not entirely convinced of this interpretation since the CH_4 and CH_2H_4 NMR experiments were performed with the same substrate, Grafoil. Although the T_1 results cannot be considered as evidence of continuous melting for C_2H_4 on graphite they do show that the melting in C_2H_4 on graphite is clearly more gradual than that of CH_4 on graphite.

Quasielastic neutron scattering has been used to measure the diffusion coefficient of methane²⁰ and more recently ethylene²¹ on graphite. Whereas in the methane case a discontinuous jump is found at melting, the diffusion coefficient in ethylene on graphite was found in a recent high-resolution study to change continuously through the melting transition.²¹

In conclusion, we note that there is a pattern in the

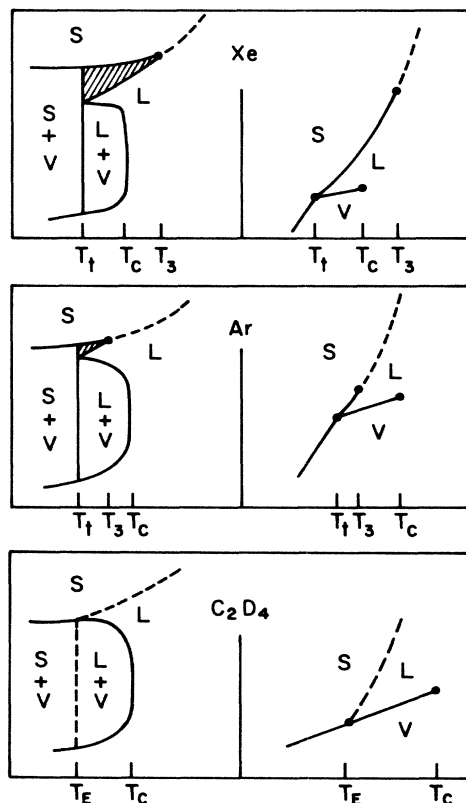


FIG. 4. Schematic phase diagrams of Xe, Ar, and C_2D_4 on graphite in both the n - T (left) and μ - T (right) planes. Solid and dashed lines represent respectively first-order and continuous boundaries. T_t , T_c , T_3 , and T_E represent respectively triple, critical, tricritical, and critical end points. For clarity, the solid-liquid (crosshatched) regions in the n - T phase diagrams are enlarged.

melting of incommensurate overlayers of classical molecules. The schematic phase diagrams of Xe, Ar, and C₂D₄ on graphite are shown in Fig. 4. For Xe on graphite, the large solid-to-liquid density drop at the triple point is reflected by a strong delta-function-like heat-capacity anomaly at melting. The phase diagrams of CH₄, O₂, and Ne on graphite are similar to that of Xe on graphite with the exception that there is, to date, no evidence of a change to continuous melting at high coverage. For Ar on graphite, the small heat-capacity peak at melting is consistent with a much smaller solid-to-liquid density drop at the triple point. The melting transition in the Ar case also appears to change from first-order-like to continuous at the tricritical point, the end point of the solid-liquid coexistence region. For ethylene on graphite, our data indicate the absence of a solid-liquid coexistence region. There are no triple and tricritical points for ethylene on graphite and the melting for submonolayer coverages occurs at a critical end point.

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