# Combined Neutron Diffraction and Adsorption Isotherm Study of the Anomalous Wetting Properties of $NH_3$ on Graphite

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The wetting properties of $NH_3$ films on graphite have been examined over a temperature range of approximately 50 K (centered about the bulk triple point of 195.4 K) using a combination of high-resolution vapor pressure isotherms and elastic neutron diffraction. Between 172 and 215 K, a single adsorption step appears at reduced pressures above 0.5. As the system is cooled, the position of this step (which is shown to be associated with the formation of a thin liquid film) increases smoothly between 0.5 and 0.95. Evidence is put forward that there is a transition from complete wetting to incomplete wetting to nonwetting. Also, the role of cluster formation and hydrogen bonding is discussed. [S0031-9007(97)03608-9]

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Vapor pressure isotherms have been employed for nearly a century to characterize the adsorptive properties of porous media but, thus far, only limited efforts have been directed toward combining them with diffraction studies to obtain a detailed microscopic characterization of wetting phenomena. There is an extensive literature devoted to the discussion of vapor pressure measurements and to the classification schemes into which they fall [1–3]. An important feature of these studies has been the derivation of empirical formulas to describe the shape of the observed isotherms and to determine from them various macroscopic quantities such as the heats of adsorption, adsorption capacity, and porosity. In general, thermodynamic measurements rely on models and on induction to connect macroscopic observations to the microscopic properties of the systems responsible for producing them, leading to significant latitude in interpretation. There is a need to develop a more definitive, atomic-scale, understanding of the wetting properties of adsorbed-phase systems because many technologically important processes depend on them.

Developing a detailed understanding of the adsorption properties of $NH_3$ is of particular interest because it is a simple polar molecule used extensively in the production of numerous nitrogen-based chemical products and because this system seems to exhibit all of the possible wetting modes. Both high-resolution adsorption isotherm and powder neutron diffraction techniques were employed in this study to probe the physisorption process. This approach has also been used in the past—in conjunction with computer simulations—to provide a simple, microscopic interpretation of the phenomena associated with multilayer adsorption and melting [4,5].

Terms like "complete wetting," "incomplete wetting," and "nonwetting" are widely used to describe different growth modes. Complete wetting refers to layer-by-layer film formation from a monolayer up to macroscopic thicknesses (where coexistence of the bulk phase occurs). Incomplete wetting takes place when only a finite number of layers form before bulk condensation occurs, resulting in coexistence of a uniform film with the bulk phase. In the nonwetting case, only bulk condensation occurs. It is possible for a system to exhibit a "wetting transition" from incomplete wetting at low temperatures to complete wetting at higher temperatures. Much attention has previously been paid to wetting transitions in the neighborhood of the bulk triple point, $T_{\mathrm{tr}}$ [6]. It is also relevant to mention that the term "prewetting" describes a finite change in film thickness in the neighborhood of, but away from, the bulk coexistence line [3]. Evidence of prewetting behavior has been seen in studies of inert gases and molecular hydrogen interacting with alkali metal surfaces [7].

An earlier study of $NH_3$ adsorption on graphitized carbon blacks has been reported [8]. The main conclusion of those investigations was that ammonia exhibits type III adsorption; i.e., the system tends to favor the formation of multilayer films and that the $NH_3$ adsorption behavior is strongly influenced by the heterogeneous sites. Carbon blacks are not the substrate of choice for accurate determinations of the adsorption characteristics of molecules on graphite surfaces. Because surface inhomogeneities and pore condensation act to obscure the true wetting properties. The high-quality, exfoliated graphite-foam substrate used in this study was degassed at 1000 °C using an Er getter to remove all traces of oxygen, loaded into an aluminum sample cell in a helium filled glove box and mounted on a APD Displex refrigerator. Sample temperatures were regulated to within 5 mK and all isotherms were corrected for the gas which occupied the dead space. The monolayer capacity of the graphite foam cell was determined to be 8.24 $\mathrm{cm}^3$ STP, using a $N_2$ isotherm at 77.0 K. (We will refer to this quantity of gas as $X = 1.00$.) Altogether, more than 30 high-resolution volumetric adsorption isotherms were measured in the temperature range $161 \leq T \leq 244$ K using an automated gas-handling system [9] that employed commercial

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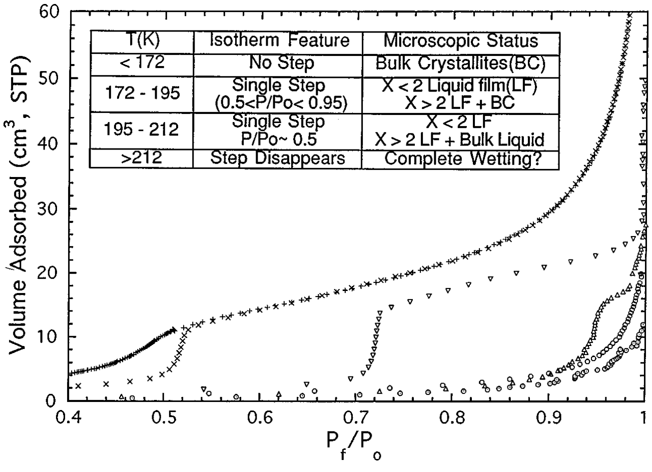
capacitance manometers (MKS Instruments). A representative subset of these isotherms is shown in Fig. 1.

The adsorption data in Fig. 1 divide naturally into the four temperature regions delineated in the inset to Fig. 1. At the lowest temperatures, $161 < T < 172$ K, there is only a small, monotonic increase in the number of $NH_3$ molecules adsorbed as the reduced pressure $p/p_0$ increases ($p_0$ is the saturated vapor pressure). Careful measurements in this temperature regime are required because even 10 mK temperature fluctuations result in pressure excursions large enough to cause a spontaneous jump to the bulk vapor pressure, especially at reduced pressures above 0.95. This behavior presumably reflects the extremely small free energy difference between the bulk (solid) phase and the adsorbed phase in this temperature regime. We believe that at $T < 160$ K the isotherms would be essentially "horizontal."

A single "adsorption step" is observed between 172 and 195 K. Nearly constant in height ($\sim 12$ cm$^3$), the step moves from $p/p_0 = 0.55$ towards $p/p_0 = 0.92$ as the temperature decreases. *This behavior is remarkable because the first step in an isotherm usually appears near zero in reduced pressure units.* Furthermore, only small incremental changes in the amount of adsorbed gas are necessary to produce an almost immediate displacement of the isotherm toward the bulk vapor pressure (i.e., to $p/p_0 = 1$) once the first step is completed. The appearance of the step at reduced pressure units near one is consistent with a prewetting transition and prewetting line [3,7].

In the temperature interval ($195 < T < 212$ K), which includes the bulk triple point of $NH_3$, the position of the adsorption step is less sensitive to changes in temperature (it remains near $p/p_0 \sim 0.5$) and, unlike the behavior at lower temperatures, the isotherm grows monotonically towards the bulk vapor pressure with increasing coverage after the first step is completed.



| T(K) | Isotherm Feature | Microscopic Status |
|---|---|---|
| < 172 | No Step | Bulk Crystallites(BC) |
| 172 - 195 | Single Step<br>(0.5<P/Po< 0.95) | X < 2 Liquid film(LF)<br>X > 2 LF + BC |
| 195 - 212 | Single Step<br>P/Po~ 0.5 | X < 2 LF<br>X > 2 LF + Bulk Liquid |
| >212 | Step Disappears | Complete Wetting? |

FIG. 1. Adsorption isotherms of $NH_3$ on graphite as a function of temperature. Moving from left to right the isotherms were measured at 243.97, 212.09, 182.99, 172.13, 170.25, and 161.02 K, respectively. The table shown in the inset summarizes the various wetting regimes.

Finally, above 212 K the single adsorption step gradually disappears with increasing temperature (changes in the slope of the isotherm were used to establish this temperature boundary). These higher temperature isotherms also exhibit a gradual, monotonic rise in the amount of gas adsorbed and proceed smoothly toward the saturated vapor pressure.

We have found that the heat of adsorption is roughly $5.7 \pm 0.2$ kcal/mole between 172 and 195 K over the coverage range of the vertical riser. At temperatures between 200 and 212 K there is a small gradual reduction in the heat of adsorption toward $5.5 \pm 0.2$ kcal/mole.

Understanding this unusual thermodynamic behavior is greatly aided by the neutron diffraction measurements we now describe. Powder diffraction traces were recorded using the fifteen-detector, medium-resolution, powder diffractometer, TAMPA, on the H5 beam line at the High Flux Beam Reactor at Brookhaven National Laboratory. Operated in transmission at a fixed wavelength of 2.440 Å, TAMPA had a $Q$ resolution of about 0.01 Å$^{-1}$ in the neighborhood of 1.9 Å$^{-1}$. All of the diffraction patterns described here are *difference* traces obtained by subtracting the diffraction pattern of the graphite-filled sample cell from the signal recorded after the film has been deposited on the substrate. $ND_3$ was used rather than $NH_3$ because deuterium has a relatively large coherent and small incoherent neutron scattering cross section.

Two different types of diffraction measurements were made. In the "isotherm" measurements the substrate temperature was kept fixed while the number of adsorbed molecules was increased: In the "constant coverage" measurements, the number of molecules within the cell was kept constant while the temperature of the cell was varied. In Fig. 2 diffraction patterns are shown for a constant $NH_3$ coverage of $X = 0.7$, recorded between 220 and 150 K. At higher temperatures a broad, symmetric, diffraction pattern consistent with a signal from a disordered, presumably liquid phase is observed. When the sample is cooled below about 175 K a set of weak, broad, *symmetric* peaks appear at $Q$'s near 1.7, 2.1, and 2.5 Å$^{-1}$. Further cooling leads to peaks that increase in intensity, decrease in width, and move to larger $Q$. These changes are *all* consistent with the formation of bulk solid $NH_3$. Similar constant coverage measurements were made as low as $X = 0.3$ with essentially the same result. There are several points to be made concerning these scans. First, a coverage of $X = 0.7$ is significantly less than the amount of $NH_3$ needed to complete a *single* layer. Second, bulk $ND_3$ freezes at about 200 K. Third, the diffraction peaks recorded here are of the symmetric shape associated with bulk solid phases; i.e., they do not have the characteristic asymmetric sawtooth-like shape associated with adsorbed (2D), monolayer-solid films [10,11]. Finally, there is the observed narrowing of the symmetric bulk diffraction peaks indicating the nucleation and growth of bulk $NH_3$ crystallites. Nothing in these data indicates the formation of an adsorbed two-dimensional *solid* film.

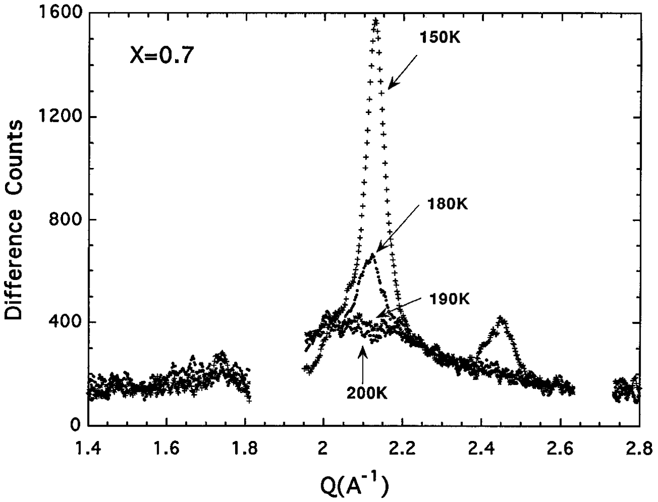


FIG. 2. "Constant coverage" neutron diffraction difference scan performed at $X = 0.7$ for $ND_3$ on graphite as a function of temperature. The data at $Q$'s near 1.9 and 2.7 Å$^{-1}$ have not been included because these are locations where large peaks due to the graphite substrate and sample cell appear.

Figures 3(a)–3(c) show three different constant temperature neutron diffraction scans made at coverages ranging from $X = 0.3$ to approximately four nominal layers. These scans are representative of the temperature regimes mentioned above. At *all* temperatures *above* 175 K and coverages *below* $X = 2.0$ there is a single, broad peak centered near $Q = 2.1$ Å$^{-1}$. The shape of this peak remains fairly constant but its intensity grows linearly with coverage. Figure 3(a) shows that at 230 K this peak (which is characteristic of a liquid phase) continues to grow without change of shape over the entire coverage range examined. Figure 3(b) shows that at 185 K a narrow, *symmetric* peak appears at the same position ($Q \sim 2.1$ Å$^{-1}$) once the coverage exceeds $X = 2.0$ as was found in the constant coverage scans. This feature, which we identified earlier as indicating bulk solid formation, grows in size once the coverage is increased beyond $X = 2.0$. Finally at 174 K, Fig. 3(c) clearly illustrates that the formation of bulklike solid occurs at coverages as low as $X = 0.66$, and that further increases in the $NH_3$ concentration at this temperature are coupled with an increase in intensity of the (bulk) Bragg peaks.

In order to understand the microscopic properties of the $NH_3$/graphite system one must first identify the microscopic phases that are responsible for the temperature dependence of the isotherms (i.e., the shape and location of the vertical riser). The neutron and isotherm measurements have established that a disordered, liquidlike layered film forms on the graphite surface at all temperatures between 175 and 212 K and at coverages below $X \sim 2.0$. At temperatures above the triple point of $NH_3$, the graphite substrate appears to be completely wet by a liquid $NH_3$ film. This is clearly evident from the way the adsorption isotherm asymptotically proceeds toward the saturated vapor pressure and from the unchanged shape and progressive growth of the liquidlike neutron diffraction profile. In the neighborhood of the bulk triple point changes occur in the functional form of the isotherm that reflect changes in the microscopic behavior of the adsorbed system. Neutron measurements indicate that the sharp-vertical step appearing at $p/p_0 = 0.5$ is the result of a dense adsorbed liquid film forming on the substrate. In this temperature

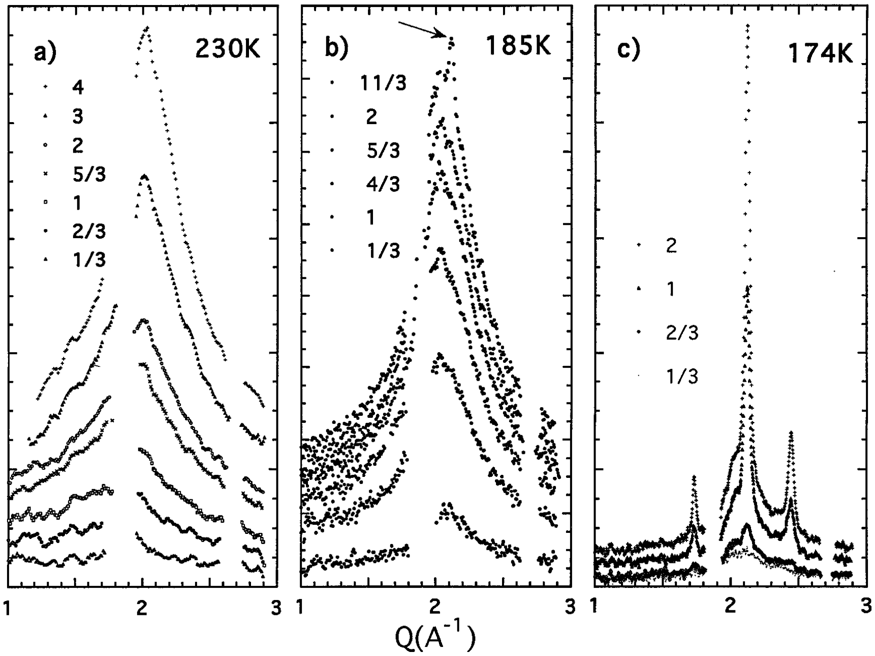


FIG. 3. "Constant temperature" neutron diffraction difference scans of $ND_3$ adsorbed on graphite performed at (a) 230 K, (b) 185 K, and (c) 174 K as a function of coverage, $X$ (decreasing thickness from top to bottom). The arrow in (b) points to the location of the bulk Bragg peak discussed in the text.

regime, once the coverage exceeds $X \sim 2$ diffraction signals consistent with bulk solid formation appear. Decreasing the temperature below roughly 175 K suppresses the formation of a *liquid film* and favors the nucleation of a bulklike solid phase. This suggests that wetting transitions must occur near 175 K and also at the bulk triple point. Since wetting transitions near the bulk triple point have been extensively examined in the past (see, e.g., Refs. [2,3,6]) and because our ability to differentiate between 2D and 3D liquid diffraction profiles is limited, we will focus our attention here on the interpretation of the data in the neighborhood of 175 K.

Computer simulation studies of $NH_3$ films on graphite performed by Spurling and Lane [12] indicated that at 195 and 251 K $NH_3$ films in the monolayer regime formed large clusters with radial distribution functions characteristic of a dense "liquidlike" surface phase. We also make note of the helium atom scattering measurements of Rowntree, Scoles, and Xu [13]. The authors suggested that a large degree of orientational disorder must be present in the $NH_3$-on-graphite system to explain the diffraction rings they recorded. They were also puzzled by the fact that even when enough $NH_3$ was adsorbed to cover the entire surface, scattering from the graphite substrate was always present. This is an unusual situation since helium atoms scatter from the tails of the electronic distribution of the outermost layer. We believe that it is indicative of the fact that at low temperatures ($T \sim 35$ K) the graphite single crystal surface is partly covered with small mesas of preferentially ordered "bulklike" solid $NH_3$ crystallites. Computer simulations of how the elastic strain might drive the "clustering" of elastic films on graphite surfaces have been reported recently by Phillips [14]. There is other evidence which suggests that cluster formation takes place in the $NH_3$/graphite system. By comparing equivalent isotherms for the $NH_3$ and $CH_4$ on the same graphite substrate we could determine the number of molecules of each needed to complete the first layer. Using the molecular volumes of the two molecules (as determined from bulk densities near the critical point of both species) we then found that there was insufficient space on the graphite surface to accommodate all of the $NH_3$ molecules in a "flat" single plane (i.e., requires at the *absolute minimum* 10% more $NH_3$ molecules than there is space for at the same distance above the substrate). Thus, in order for all of the $NH_3$ molecules to adsorb in the "first" layer some modulation of the adsorption distance from the substrate must occur. This could be accomplished if small agglomerates or "3D-like clusters" of molecules were to form within the liquid film. This clustering effect is most likely related to the hydrogen bonding known to occur between $NH_3$ molecules. Certainly at lower temperatures, an orientationally ordered solid structure forms due to the strong hydrogen bonding between $NH_3$ molecules.

The picture presented above invokes the tendency of $NH_3$ films to cluster as the mechanism for understanding the crossover in wetting properties of $NH_3$ on graphite near 172 K. The coexistence of the liquid film and bulk solid signals at $X > 2.0$ and temperatures between 175 and 195 K may also be an indication of surface melting where a thin liquid film coats the outer surface of the small $NH_3$ crystallites. Such a description was used in a model developed by Béal-Monod and Mills [15].

In conclusion, $NH_3$ on graphite exhibits all three types of wetting behavior and that only formation of liquid films is possible. At temperatures below 172 K the strong interaction (as a result of hydrogen bonding) between $NH_3$ molecules favors the formation of solid bulklike crystallites. This mechanism preempts the formation of a uniform solid monolayer phase and hence leads to nonwetting. Similar effects have been seen for $NH_3$ adsorption on BN and MgO [16] and should also be present in other polar, molecular systems where hydrogen bonding plays a role.

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