

Inadequacy of Lifshitz Theory for Thin Liquid Films

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We have studied the adsorption of cyclohexane and water on molecularly smooth mica using an angle-averaging, refractive-index-matching ellipsometric technique. The isotherms are linear for sub-monolayer coverages, showing the importance of entropy effects, and give finite thicknesses (≈ 2 nm) at saturation. The similarity of the two isotherms suggests that the adsorption is governed by nonspecific interactions. There is no evidence of layering but the isotherms do not agree with the Lifshitz theory of van der Waals forces.

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The adsorption of gases to solid surfaces has long been the subject of extensive experimental and theoretical investigations.¹ More recently, the phase behavior of adsorbed films has been the focus of attention.²⁻⁴ Two-dimensional phase transitions and layering transitions have been observed with solid films of inert gases,⁵⁻⁷ such as ethylene⁸ and oxygen⁹ on graphite, but less information has been obtained on liquid films, especially at room temperature.¹⁰ Most such studies have concentrated on comparisons of the observed film thickness with the predictions of continuum theories of surface forces. The thickness as a function of the relative vapor pressure p/p_s , and thereby the chemical potential, yields information on the interactions between the solid and the vapor phase across adsorbed liquids such as water,^{11,12} hydrocarbons,^{13,14} or other organic liquids.¹⁵

Closely related phenomena include surface wetting in binary liquid systems, the spreading of liquids on solid substrates, and surface melting (see, for example, reviews by Dietrich,¹⁶ de Gennes,¹⁷ and Dash¹⁸).

The interpretation of many adsorption experiments is complicated by porosity, roughness, and chemical inhomogeneity of the solid substrate. Muscovite mica is one of the few molecularly smooth substrate surfaces available and constitutes an ideal model system for the study of surface interactions.¹⁹ Ellipsometry has been widely employed to measure the thickness of layers adsorbed on solid surfaces. It has recently been used to study the spreading of liquids on solid substrates and effects due to the molecular nature of the liquid have been resolved by using near smooth substrates (silicon) and liquids with large molecules.^{20,21} Unfortunately, the optical anisotropy and interference effects from the layered structure of mica make the interpretation of ellipsometric measurements difficult, although it has been used by one of us to study spreading.²²

The low-temperature work on gas adsorption and layering has until now been quite isolated from investiga-

tions of adsorbed film thicknesses at room temperature. One class of experiments has been carried out at temperatures below or close to the bulk triple point of the fluid where the adsorbed films are mainly solid, the other at temperatures above the triple point along the vapor-liquid coexistence line. In this Letter we present data on the adsorption of cyclohexane and water to mica and our hope is that such measurements at room temperature will contribute to a more unified approach to gas adsorption.

The vapor pressure was controlled by direct introduction of vapor into an evacuated glass chamber and monitored with a transducer (Datametrix capacitance gauge). The chamber was completely immersed in a bath (fitted with glass windows to allow the passage of light) with a continuous flow of temperature-controlled water (18.1 °C). Measurements with water were also performed using solute (LiCl) control of the water vapor pressure in an atmosphere of laboratory air. These measurements were carried out at 20 °C in a sealed chamber of stainless steel with a glass hemisphere, enclosed in a thermal shield of copper. The temperature was monitored at several points inside the chamber and variations with time and position were ≤ 0.1 °C.

The freshly cleaved mica (≈ 50 μm thick) was glued with an epoxy resin (5 min Araldite) to a black anodized aluminium disk. With solute control the mica was placed in the chamber and dried over P_2O_5 for several hours before the liquid was introduced. In the vapor introduction method the chamber was first evacuated through a liquid-nitrogen cold trap. The cyclohexane was dried over a molecular sieve and any residual water pumped off through a cold trap immediately before admitting vapor to the chamber. In both cases measurements were performed with both increasing and decreasing p/p_s and no hysteresis was observed.

The extent of adsorption was measured with a phase-modulated ellipsometer. It measures directly both the

real and imaginary components of the complex ratio of the p -polarized and s -polarized reflection amplitudes, r_p/r_s , for a given angle of incidence. In the vicinity of the Brewster angle [$\text{Re}(r_p/r_s) = 0$] a thin dielectric layer on the surface results in a displacement of the r_p/r_s locus strictly along the imaginary axis by an amount related to the dielectric thickness of the layer. The film thickness can be calculated if the dielectric profile of the layer is known. The predicted locus of r_p/r_s for an optically anisotropic substrate such as mica is, however, in general very complex because of interference effects. Approximate refractive-index matching at the back side is achieved through the use of the Araldite glue, but perfect matching is impossible because of the anisotropy of mica.²³ Measurements and calculations by one of us²⁴ show that the residual signal which has interference effects as the angle of incidence is varied, is shifted as a whole to larger values of $\text{Im}(r)$ by an amount calculated for a thin film on an equivalent isotropic substrate. A measure of the *angle-averaged* ellipticity signal thus removes the residual interference effects and leaves a signal that can easily be interpreted in terms of the adsorbed layer thickness. The appropriate angle averaging ($\pm 5^\circ$) is achieved very simply by using a lens to give a converging incident light beam. The ellipticity signal also depends on the rotational orientation of the mica and we have used the orientation that gives the smallest ellipticity signal (optical axis in the p direction). The adsorbed layer thickness was deduced from the change in ellipticity from the bare mica value upon the introduction of vapor. The sensitivity of the ellipticity measurements with our setup was 10^{-5} , which corresponds to a thickness sensitivity of about 0.005 nm (using bulk refractive indices).

The measured film thicknesses of cyclohexane and wa-

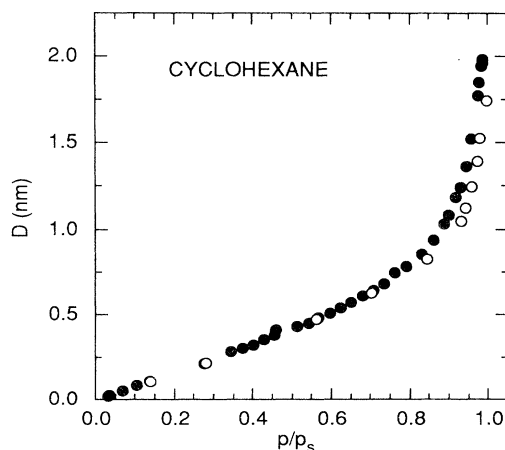


FIG. 1. Ellipsometrically determined film thickness D of cyclohexane adsorbed on molecularly smooth mica vs the relative vapor pressure p/p_s at 18°C . The different symbols are measurements with two different mica sheets. No hysteresis was observed.

ter adsorbed on mica at 18°C for $p/p_s = 0-0.99$ are shown in Figs. 1 and 2. The different symbols are the results of independent sets of measurements with mica sheets of different thicknesses. Also shown are the measurements with solute control of p/p_s for water (triangles in Fig. 2). We note in particular the linear regime at low vapor pressures and the increase in adsorption at higher values of p/p_s for both liquids, but that the thickness appears to remain finite close to saturation. From these results the disjoining pressure of the film Π_D (the interaction free energy per unit area between the solid substrate and vapor in the presence of the adsorbed film) can be calculated according to

$$\Pi_D = -\mu(D, T) = (kT/v_m) \ln(p/p_s), \quad (1)$$

where $\mu(D, T)$ is the chemical potential per unit volume of a thin film of thickness D and v_m is the molecular volume of the liquid. The results are shown in Figs. 3 and 4 for cyclohexane and water, respectively.

The salient features of the experimental isotherms (Figs. 1 and 2) may be summarized as follows: (i) a linear pressure dependence of the mean film thickness for low vapor pressures, (ii) a more rapid increase in the adsorbed amount at higher pressures, (iii) the complete absence of layering or structural effects, and (iv) no wetting close to saturation.

The linear behavior persists up to about 1 (statistical) monolayer (0.5 nm) for cyclohexane but only to about $\frac{1}{2}$ a monolayer for water (≈ 0.15 nm). This means that the data can be fitted with a Langmuir or Brunauer-Emmett-Teller-type isotherm in this regime and the adsorption is consequently driven by entropy effects. (We note here that use of the bulk dielectric constant in the calculations from the ellipsometric data is not strictly

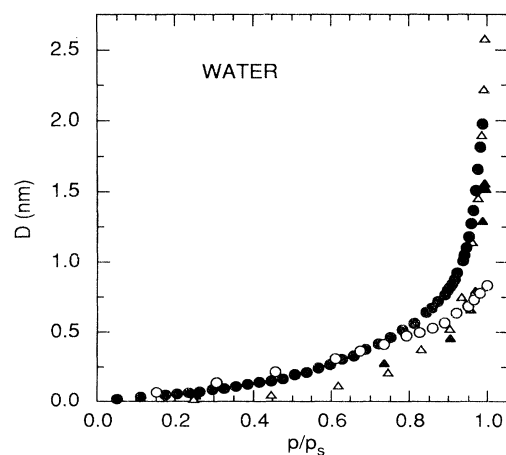


FIG. 2. Film thickness D of water adsorbed on mica vs the relative vapor pressure p/p_s . The results of four series of measurements using different mica sheets are presented. Circles represent data obtained with direct vapor pressure control at 18°C and triangles are results using solute control at 20°C .

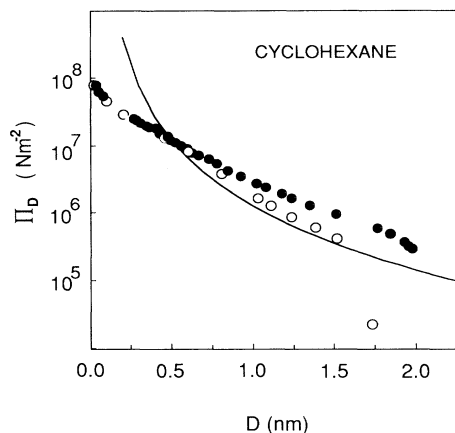


FIG. 3. Disjoining pressure Π_D [calculated according to Eq. (1)] vs the film thickness D of cyclohexane on mica. For symbols see Fig. 1. The experimental error is represented by the symbol size. The solid line is the prediction of the Lifshitz theory of van der Waals forces (with retardation) (Ref. 31).

correct, but there is evidence to suggest that this does not lead to any significant error.^{25,26}

At higher p/p_s the adsorption deviates from linearity and increases more rapidly with pressure. The similarity of the water and cyclohexane isotherms is striking, when scaled by the mean molecular diameter the results are almost indistinguishable for p/p_s below about 0.8. This is perhaps an indication that specific lateral interactions such as hydrogen bonding are not of major importance, at least for thicknesses below 2 monolayers. Similarly, the results of force measurements across liquids between mica surfaces¹⁹ show that hard-sphere interactions dominate and dipolar and hydrogen-bonding effects are of secondary importance.

The differences between the curves for the same vapor are not large in absolute terms but well outside the thickness-measurement error. The difference is most likely due to slight variations in the adsorption of contaminants from the atmosphere during the necessary 2-min exposure between cleavage and installation in the chamber. Mica is a very-high-energy surface and thus extremely susceptible to variations in surface properties due to adsorption.²⁷ Nevertheless, the shapes of the different curves are the same, even when solute control is used in the case of water.

Neither cyclohexane nor water wets mica—the isotherms appear to tend toward a finite thickness at saturation. This is in agreement with the finite contact angles ($\approx 6^\circ$ – 7°) of both liquids on air-cleaved mica. (Water wets freshly cleaved mica but an instant of exposure to air is sufficient to give a finite contact angle.²⁸)

The Lifshitz theory of van der Waals forces²⁹ (solid lines in Figs. 3 and 4) does not fit the experimental isotherms over any significant part of the thickness regime.

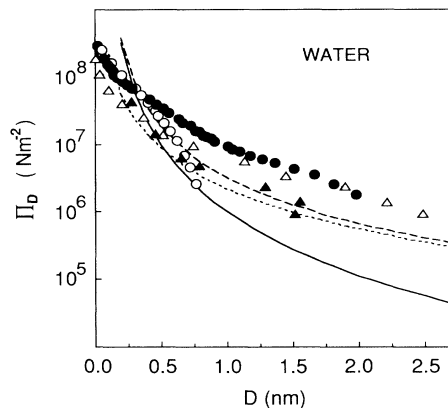


FIG. 4. Disjoining pressure Π_D vs the film thickness D of water on mica. For symbols see Fig. 2. The experimental error is represented by the symbol size. The solid line is the prediction of the Lifshitz theory and the dotted line is a double-layer interaction (Ref. 32). The dashed line shows the sum of these two contributions.

By assuming the existence of an electrical double-layer repulsion across the adsorbed water film, it is, in principle, possible to obtain a slightly better fit (Fig. 4) but the similarity of the isotherm to that of cyclohexane, where no double-layer forces would exist, renders such a fitting procedure highly questionable. Although Lifshitz theory should in principle be accurate in the limit of large film thicknesses D , this does not necessarily imply wetting. A lower-energy state at small thicknesses where the theory does not hold might well lead to a finite-film thickness and a contact angle, as observed.²⁹

There are numerous claims in the literature that adsorption data fit Lifshitz theory.^{13,14} On closer examination it becomes clear that the agreement for films of comparable thickness is no better than what we obtain here. The thickness at a given p/p_s may be correct within a factor of 2, but the shape of the isotherm is very different or indistinguishable only because of insufficient experimental accuracy (cf. data in Ref. 14). Measurements by Sabisky and Anderson³⁰ on helium films showing good agreement with Lifshitz theory were for thicknesses greater than 1.2 nm (≈ 5 layers of helium atoms, whereas our cyclohexane films are less than 5 molecular diameters thick).

Various theoretical treatments^{2,3} have demonstrated that the type of adsorption isotherm expected varies depending on the relative strengths of the substrate-molecule and molecule-molecule interaction potentials, as well as the temperature. Some progress has been made in identifying and rationalizing the experimentally observed behavior in the case of low-temperature adsorption of inert and other simple gases.^{2,5-9} At a given temperature complete wetting (infinite film thickness), partial wetting (finite films, as in our case), or the complete

absence of adsorption is predicted. Transition from partial wetting to complete wetting occurs at the wetting temperature T_w , which is characteristic of both the liquid and the substrate used. One interpretation of the finite-film thicknesses observed by us is that the experimental temperature is below T_w , although T_w is usually assumed to lie below the triple point T_t , where the wetting behavior is dominated by energy considerations. The complete absence of structural effects or layering indicates that we are far above the roughening temperature. This is not surprising, the roughening temperature has been shown to be at about $0.8T_t$ for several systems⁷ (T_t is 0.01°C for water and 5.4°C for cyclohexane). Nevertheless, the absence of layering does not mean that Lifshitz theory can be used to predict the film thickness.

The main features described in this Letter (linear isotherms at low p/p_s and lack of agreement with Lifshitz theory) have also been found with other liquids on both mica and silicon. These results, including some on wetting systems, will be reported in an extended publication.

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