Adsorption Isotherms of Hydrogen: The Role of Thermal Fluctuations

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It is shown that experimentally obtained isotherms of adsorption on solid substrates may be completely reconciled with Lifshitz theory when thermal fluctuations of the free film surface are taken into account. This is demonstrated for hydrogen adsorbed on gold as a model system. Analysis of the fluctuation contributions allows one to determine the surface tension of the free hydrogen film as a function of film thickness. It is found to decrease sharply for film thicknesses below seven atomic layers.

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Solid surfaces exposed to a gaseous environment attract the gas molecules by virtue of molecular forces, giving rise to a thin film of adsorbed molecules under almost any condition. The most important attractive force involved is the van der Waals force, which is due to the quantum mechanical zero point fluctuations of the electron shells of the molecules. It is present for all materials and extends over distances much larger than a molecular diameter. It was thus tacitly accepted for a long time that the theory of Frenkel, Halsey, and Hill (FHH) [1–3], which is based on the van der Waals force alone, accurately describes adsorption isotherms, i.e., the dependence of the thickness of the adsorbed film as a function of the partial pressure of the adsorbed species in the surrounding medium. It predicts that the thickness, d, of the adsorbed film varies as

$$d = \left(\frac{\alpha}{k_B T \ln \frac{p_0}{p}} \right)^{1/3}, \tag{1}$$

where α is the van der Waals constant of the system, p is the gas pressure, and p_0 is the saturated vapor pressure of the film material. The power $1/3$ on the right-hand side of Eq. (1) stems from the fact that, according to the Lifshitz theory of dispersion forces, the adsorption energy should scale as the inverse third power of the film thickness [4,5]. This holds for the film thicknesses to be discussed here, for which retardation effects can be safely neglected [5,6]. Deviations from FHH theory are to be expected only when the temperature is close to the critical point of the adsorbing substance, such that the width of the free film surface may be comparable to the film thickness.

On the contrary, experimentally determined adsorption isotherms revealed considerable deviations from FHH theory for virtually all systems studied [7–10]. Although it has been mentioned before that thermal fluctuations may be the cause for the observed discrepancies [10,11], this possibility has not yet been studied in detail experimentally. It is the purpose of the present paper to show that thermal fluctuations of the free film surface are very probably the cause of the above-mentioned discrepancies. If these fluctuations are taken into account, the adsorption isotherms may be completely reconciled with theory.

As a model system, we have chosen hydrogen films adsorbed on gold substrates. Films have been prepared in a helium flow cryostat at temperatures around the triple point, ranging from 10 to 14 K ($T_3 = 13.952$ K). The thickness of the adsorbed films has been determined via surface plasmon resonance spectroscopy, as it was done successfully before [12]. The substrates consisted of approximately 50 nm thick gold films prepared by evaporation onto polished glass. The adsorbed hydrogen shifts the surface plasmon resonance of the metal surface, which allows one to determine the coverage, i.e., amount of material adsorbed per unit area [12,13]. This can be converted into an effective film thickness assuming the film to have bulk material density.

Inspection of the gold substrates by scanning tunneling microscopy revealed a roughness and a lateral correlation length similar to what was found before by other authors [14,15]. The surfaces exhibit large crystal facets, such that, at temperatures below the roughening transition of hydrogen (≈9 K [16]), two dimensional phase transitions in adsorbed single layers of hydrogen [16,17] could be easily observed. From the substrate topography, it could be estimated by the Kelvin equation [18] that measurements of coverage might lose reliability at thicknesses well above 5 nm due to capillary condensation effects. Consequently, only films with a thickness up to 5 nm were used for analysis. As will be seen below, effects of fluctuations are most important at much smaller thickness, where roughness effects can be safely neglected.

To start with, we mention that both above and below the triple point temperature, T_3, the thick hydrogen film which adsorbs close to saturation is in the liquid phase [12,19]. This is seen qualitatively from the fact that, if one takes for $p_0(T)$ in Eq. (1) the saturated vapor pressure of the *liquid* phase, which must below T_3 be obtained by extrapolation of the liquid/vapor coexistence line, all isotherms fall onto a single master curve. This is demonstrated in Fig. 1, which shows the data of ten isotherms obtained for

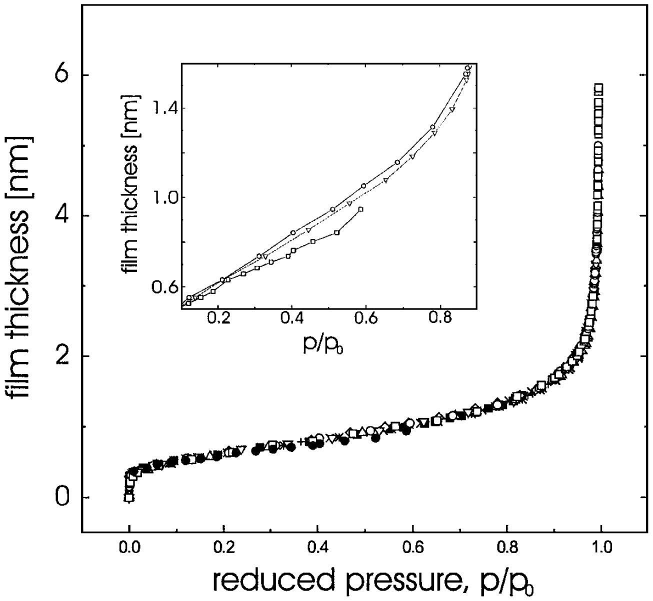

FIG. 1. Assuming the adsorbed film to be liquid, it is natural to use the saturated vapor pressure of the liquid phase in the FHH equation. In fact, this makes all isotherms fall onto a single master curve, independent of temperature. The slight deviations in the flat parts of the curve (around $p = 0.5p_0$) are significant and may be well explained by thermal fluctuations. They are shown clearly in the inset, which displays isotherms for 10.190 K (squares), 13.939 K (triangles), and 13.964 K (circles).

temperatures ranging from 10.190 to 14.067 K, plotted as a function of reduced pressure, $p/p_0(T)$. Since the saturated vapor pressure of the solid phase is always below that of the liquid phase, the divergence of the isotherm is not reached for temperatures below T_3, such that the film thickness at solid/vapor coexistence is finite. This thickness at saturation increases with increasing temperature, and diverges for $T \rightarrow T_3$. This is triple point wetting [12].

As one can see in Fig. 1, the mutual agreement of the isotherms is very good for sufficiently thick films. The van der Waals constant is found to be 7 ± 3 K(nm)^3, which is consistent with the theoretical estimate of 8 K(nm)^3 [20]. However, closer inspection of the data reveals systematic discrepancies which are particularly obvious at thicknesses below 2 nm, as can be seen from the inset. This is revealed more clearly in Fig. 2, where the data of a single isotherm ($T = 13.964$ K) are plotted such that the behavior described by Eq. (1) would yield a straight line. The characteristic negative curvature of the isotherm in this plot demonstrates the deviation, and is similar to what has been described before by other authors [8,10].

The data are very well represented by the solid curve, which is obtained from a refined model taking into account thermal fluctuations in film thickness [11]. The statistical approach is based on a solid-on-solid (SOS) model which has extensively been applied to multilayer-stepped adsorption isotherms [21–23]. We assume the substrate to consist of a square lattice of N adsorption sites $i = 1, \ldots, N$ and thickness $d_i = a_0 n_i$ of the adsorbed film at the site i allowing $n_i \geq 0$ to be any non-negative integer, where a_0 denotes the monolayer thickness. The restriction of gas molecules to certain lattice sites is well proven for a monolayer and seems to be justified for films only a few layers thick, i.e., the regime on which we are focusing. The vapor is considered to be a homogeneous reservoir of molecules with chemical potential $\mu = k_B T \log(p_0/p)$ and the adsorbed molecules are assumed to pile up at each site in columns, without forming overhangs or vapor bubbles, which is reasonable for thin films and temperatures well below the critical point. The statistics of the film thickness is then given by the partition sum $Z = \sum_{\{n_i\}} \exp[-\beta \mathcal{H}(\{d_i\})]$, where the sum runs over all configurations n_i $(i = 1, \ldots, N)$ of the film. The Hamiltonian reads [11]

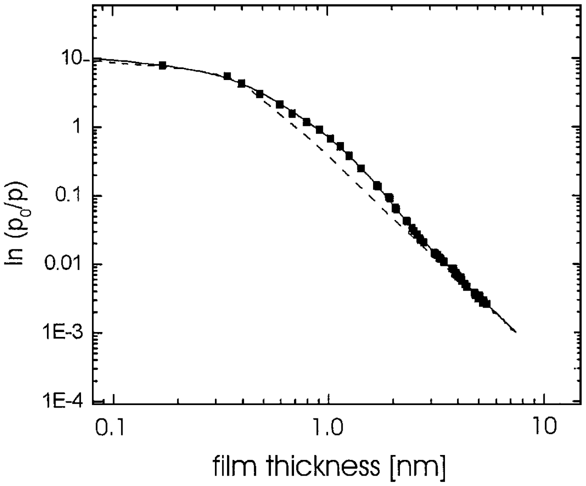

FIG. 2. A typical isotherm, obtained at $T = 13.964$ K, plotted such that an FHH isotherm according to Eq. (1) would yield a straight line. The negative curvature is clearly visible. The solid curve is a fit of our model. For the dashed curve, the surface tension has been set to infinity in the model, in order to suppress fluctuation effects. The difference between the data and the dashed curves thus demonstrates the significant impact of fluctuations.

$$\mathcal{H}(\{d_i\}) = \sum_i^N \left(d_i k_B T \log\frac{p_0}{p} - \sum_{\nu=1}^{n_i} \frac{\alpha}{z_\nu^3} \right) + \frac{\gamma}{2} \sum_{\langle ij \rangle} (d_i - d_j)^2, \qquad (2)$$

where z_ν is the distance of the νth layer to the substrate. The surface tension γ of the film-vapor interface takes into account the molecular interactions within the film, where the sum runs over nearest-neighbor sites $\langle ij \rangle$ only.

Assuming that fluctuations in the film thickness are not relevant, one may minimize the energy (2) yielding the most probable thickness d given by the FHH isotherm, Eq. (1). But the film-vapor interface is always undulated due to thermal fluctuations which become important for thin films where fluctuations are hindered by the substrate. Thus, in order to perform the partition sum, we apply a mean-field approximation, replacing d_j in Eq. (2) with its mean value $\bar{d}$. One obtains a self-consistent equation for the mean thickness, which can be solved by standard numerical procedures and can be applied to the experimental data in a straightforward manner (see Fig. 2). The solution is the adsorption isotherm $\bar{d}(\mu; \alpha, a_0, \gamma)$ depending on the Hamaker constant α, the monolayer thickness a_0, and the surface tension γ. Of course, $\gamma(\bar{d})$ is dependent on the mean film thickness and may be determined experimentally when vapor pressure p and thickness $\bar{d}$ are measured.

This SOS model reproduces the results of Brunnauer, Emmett, and Teller [24] as well as the FHH model in the monolayer and thick-film regimes, respectively, but for intermediate coverages a qualitatively different behavior is found which is governed by thermal fluctuations of the film thickness, and is therefore determined by the surface tension, γ. As one can see in Fig. 2, the substrate-induced hindrance of such fluctuations increases significantly the mean thickness $\bar{d}$ as compared to the most probable thickness d given by the FHH isotherm. Most importantly, the isotherms obtained experimentally are well described taking fluctuations into account, without any further assumptions. Qualitatively, the effect of the fluctuations, i.e., the deviation from the FHH isotherm, increases with increasing temperature, as expected. For illustration, we have included in Fig. 2 what is obtained from our model if fluctuations are absent (dashed line). This was done by setting $\gamma \to \infty$ in the calculations. The impact of the fluctuations becomes particularly obvious this way.

Let us now go a step further and use the fluctuation contributions identified above to determine the surface tension, γ, of the hydrogen/vapor interface. This turns out to be mathematically difficult on the basis of Eq. (2). Therefore, we used a somewhat simpler approach based on the fluctuation-dissipation theorem, which directly yields a more convenient expression for the excess chemical potential due to capillary waves [25], and also contains γ as a parameter. It is less accurate than Eq. (2) because it neglects the geometric limitation of the fluctuation amplitude by the finiteness of the film thickness, but it suffices for a rough evaluation of γ.

The result is shown in Fig. 3. While one would naively expect γ to be constant, we see that it is dramatically reduced for small thickness. The jump at 0.7 nm may well indicate the boundary between the solidified part of the film close to the wall [12,19] and the liquid. At a higher film thickness, a strong increase of the surface tension is seen, which approaches the bulk value above 25 Å, corresponding to about 6.5 molecular layers (one layer is 3.8 Å thick). In fact, the notion of a film thickness dependent surface tension has been introduced before, and even shown to be a conceptual necessity close to a phase transition [26,27].

We tend to be cautious as to the actual amount by which the surface tension of the thin films is reduced, because the method used for its determination is not as accurate as Eq. (2), as mentioned above. However, there is no doubt according to our qualitative result that the surface tension is considerably less for the thin film than for the bulk. It is desirable to develop an analysis based on Eq. (2) to check the result displayed in Fig. 3.

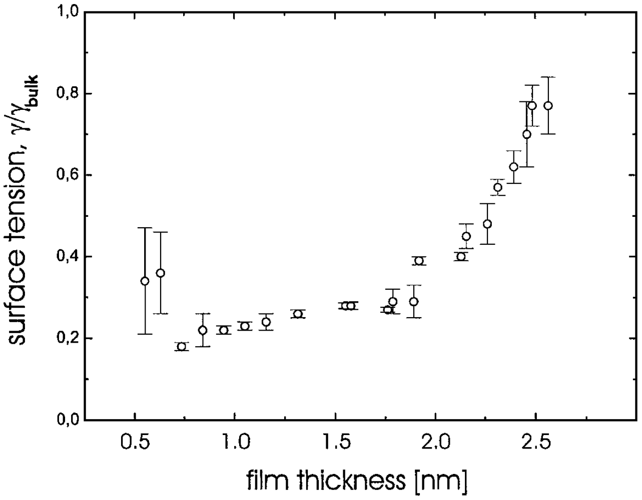

FIG. 3. The surface tension of hydrogen as a function of film thickness, as obtained from the analysis of the fluctuation contribution to the equilibrium film thickness. At small thickness, the surface tension is dramatically reduced, and approaches the bulk value only above 2.5 nm (about 6.5 monolayers).

In conclusion, we have demonstrated, with hydrogen adsorbed on gold as a model system, that adsorption isotherms may be completely reconciled with Lifshitz theory if thermal fluctuations of the free film surface are taken into account. This seems to resolve a long-standing discussion in the field of wetting forces, and also provides a means of determining the surface tension of molecularly thin liquid films. For hydrogen, we found a substantial reduction of the surface tension with respect to the bulk value. The exact physical nature of this effect must be left to further studies.

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