

Adsorption isotherms and thermal fluctuations

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The influence of thermal fluctuations on adsorption isotherms is calculated within the context of a self-consistent mean-field theory, and it is found that such fluctuations cannot be neglected in the analysis of adsorption data. This result arises from our observation that substrate-induced hindrance of thermal fluctuations can significantly alter the form of an adsorption isotherm, particularly in the thin-film regime ($\approx 0-5$ nm) which is most commonly probed by adsorption experiments. Previous experiments involving room-temperature adsorption on flat surfaces have been reanalyzed, and the reported discrepancies with the Lifshitz theory of van der Waals forces are found to be much reduced when thermal fluctuations of the thickness of the adsorbed layer are taken into account. Recently published data for nitrogen adsorption on rough substrates have also been reanalyzed, and the thermal fluctuations are found to be more important for thin adsorbed layers than undulations of the film induced by the roughness of the substrate. The analysis reveals that, as long suspected, the scaling regime of asymptotic divergence has not yet been reached for film thicknesses remaining below 5 nm.

I. INTRODUCTION

The technique of adsorption¹⁻⁴ has recently given rise to a lively discussion about the interpretation of data for film adsorption on rough substrates.^{5,6} At issue is not only whether the substrate is fractal or self-affine, but whether adsorption experiments are even suitable as probes of substrate roughness. Early measurements on flat substrates,^{7,8} moreover, remain a matter of discussion, with recent experiments^{9,10} claiming significant discrepancies with theory. Despite significant levels of theoretical activity in this area, the impact of thermal fluctuations of the thickness of the adsorbed film on the form of an adsorption isotherm has received very little attention in attempts to remove these discrepancies. But fluctuations are one of the most important phenomena in nature. They are particularly essential for the understanding of experimental data, whether or not such data are collected at high temperatures or near a critical point. Calculations of the influence of thermal fluctuations on adsorption isotherms within the context of a self-consistent mean-field theory are presented here.

Although measurements of monolayer adsorption¹¹⁻¹⁹ have been extensively analyzed, few theoretical approaches have emerged for interpreting data recorded for thicker films. The usual approach is based on the work of Frenkel, Halsey, and Hill (FHH),²⁰⁻²² extended to account for fractal^{1,23-25} or self-affine surface geometries.⁵ The FHH approach does not incorporate the effects of thermal fluctuations, and the authors are aware of only a very few papers which deal with the finite thickness of the film-vapor interface to describe adsorption data on flat substrates.^{26,27} Within the closely related area of film wetting phenomena,²⁸ numerous theoretical approaches are concerned with the properties of fluctuation surfaces near a wall²⁹⁻³⁴ (overviews of this topic can be found, for example, in Refs. 28 and 35-37). None of these works has, however, been applied to interpret the type of experimental data for multilayer adsorption mentioned above. The goal of this paper is thus a statistical theory of adsorption on a rough surface which both incorporates ther-

mal fluctuations and can be readily applied to measurements. In the following, we first consider the effect of thermal fluctuations on adsorption on flat substrates, and then extend the model to the case of substrates which exhibit self-affine surface roughness.

The best-known approaches to describe the thickness of physically adsorbed films on flat substrates are the Brunauer-Emmett-Teller (BET) theory³⁸⁻⁴⁰ for low coverages and the Frenkel-Halsey-Hill theory²⁰⁻²² for the asymptotic behavior of thick films. We start our analysis with a short overview of their results in order to emphasize the shortcomings of such approaches even for adsorption on flat substrates (Sec. II). Since the FHH theory neglects fluctuations of film thickness and the BET theory does not take into account long-range van der Waals interactions we have combined aspects of each in a statistical theory (Sec. III). Our model reproduces the results of the BET and FHH models in the monolayer and thick-film regimes, respectively, but for intermediate coverages a qualitatively different behavior occurs which is governed by thermal fluctuations. Our approach is well known in the literature as the solid-on-solid (SOS) model, and it has already been applied to multilayer-stepped adsorption isotherms.^{31,32} But it has not been applied to the fluctuation-dominated, thin-liquid-film regime of interest here. Our approach, furthermore, yields a self-consistent equation [Eq. (3.7)] for the adsorption isotherm which can be directly implemented in the analysis of experimental data.

Despite the simplicity of our approach of a self-consistent mean-field approximation, the results match the quantitative behavior of measured data quite well. Reanalyzing data recorded on flat surfaces^{9,10} where the Lifshitz theory of van der Waals forces was found to be inadequate,⁴¹ we find far better agreement between theory and experiment.

For the case of adsorption on rough substrates, the measurements cannot be described by thermal fluctuations alone (Sec. IV). In Sec. V we present comparisons of the theory to actual experimental data for adsorption on smooth and rough substrates. In particular, we focus on liquid-nitrogen data on silver film substrates which are believed to exhibit self-affine

surface roughness.¹⁻³ In order to obtain quantitative agreement with these experiments, we extend the theory for rough substrates by introducing an effective film-substrate potential taking into account the change of the adsorbate-substrate potential due to roughness. In contrast to other approaches,^{5,6} we ignore the dependence of the local film thickness on surface tension and roughness, which may be important for thicker films. The reported data extend only to ten monolayers and can be fitted quite well without taking into account the scaling behavior of the asymptotic divergence. In particular we find that the previously observed scaling over half a decade^{1-3,5} turns out to be a crossover behavior and that the scaling regime of asymptotic divergence has not yet been reached. This has long been suspected without explaining the transition in terms of thermal fluctuations hindered by the substrate.⁵

II. BET AND FHH ADSORPTION THEORIES FOR FLAT SUBSTRATES

In order to introduce our nomenclature, we first define the BET theory in a manner somewhat different from the usual approach. On a flat substrate, there exist well-defined lattice sites where gas molecules can be adsorbed. Therefore, for simplicity, we assume the substrate to consist of a square lattice of N adsorption sites $i = 1, \dots, N$ and numbers n_i of gas molecules adsorbed at the site i , allowing $n_i \geq 0$ to be any non-negative integer. 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 which we are focusing on. Our assumed geometry is depicted in Fig. 1. The vapor is considered to be a homogeneous reservoir of molecules 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 low temperatures. The substrate-film interface

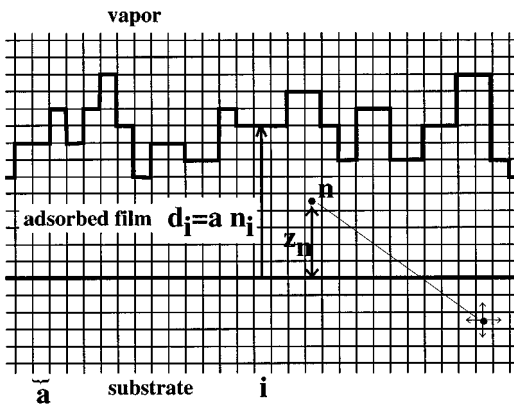


FIG. 1. A flat substrate is shown with N surface sites in thermal equilibrium with a vapor and covered by a film consisting of n_i adsorbed molecules at site i . A molecule in the vapor phase with distance z from the surface of the substrate experiences an attractive force $U(z)$ due to the van der Waals interaction with molecules within the substrate, which yields an adsorbed film with thickness $d_i = a n_i$ depending on temperature T and pressure p . The lattice constant a is given by the microscopic size of the molecules. In contrast to the solid substrate, the film-vapor interface is subjected to thermal fluctuations.

is assumed to be flat, while the film-vapor interface is undulated due to thermal fluctuations.

If one considers only monolayer adsorption, one must restrict the number of gas molecules per site to be 1 or zero, $n_i \leq 1$, whereas in the case of multilayer adsorption n_i can take on values larger than 1. Assuming a typical molecular size a , the thickness of the adsorbed film $d_i = a n_i$ at the substrate site i can be directly related to the total number of adsorbed molecules.

For most experiments the vapor is well described as an ideal gas, i.e., by a chemical potential

$$\beta \mu_{\text{vapor}}(p, T) = -\ln \frac{p}{p_0}, \quad (2.1)$$

where p_0 is a reference pressure, k_B the Boltzmann constant, and $\beta = 1/k_B T$. Whereas the homogeneous vapor is thermodynamically defined by its temperature T and pressure p , our task here is to calculate the thermodynamic behavior of the film, and in particular the dependence of the mean thickness $d = \langle d_i \rangle$ on temperature and pressure. The statistics of the film thickness within the BET theory is given by the partition sum

$$Z = \sum_{\{n_i\}} e^{-\beta \mathcal{H}(\{n_i\})}, \quad (2.2)$$

where the sum runs over all configurations n_i ($i = 1, \dots, N$) of the film. The BET theory assumes that the energy of each configuration

$$\mathcal{H}(\{n_i\}) = \sum_i^N H(n_i) \quad (2.3a)$$

is a sum of the independent contributions $H(n_i)$ from each adsorption site i , i.e., the molecules at different sites do not interact. The local energy

$$H(n_i) = n_i \mu_{\text{film}} + \sum_{\nu=1}^{n_i} U_{\nu} \quad (2.3b)$$

is given by the chemical potential μ_{film} of the film and the adsorption energy U_{ν} of the ν th adsorbed molecule.

The BET theory furthermore assumes a difference in the adsorption energy

$$U_{\nu} = \begin{cases} \epsilon, & \nu = 1 \\ \epsilon', & \nu \geq 2, \end{cases} \quad (2.4)$$

between particles in the first layer and in subsequent layers, but particles in all subsequent layers are assumed to have equal adsorption energy. The partition sum (2.2) can then be calculated exactly, yielding

$$Z = \left(1 + \frac{e^{-\beta \mu_{\text{film}} - \beta \epsilon}}{1 - e^{-\beta \mu_{\text{film}} - \beta \epsilon'}} \right)^N. \quad (2.5)$$

Since the vapor and film are in thermodynamic equilibrium the chemical potentials of both phases are equal,

$$\mu_{\text{film}} = \mu_{\text{vapor}}. \quad (2.6)$$

Defining the free energy of the film as

$$f := \frac{\beta F}{N} = -\frac{1}{N} \ln Z, \quad (2.7)$$

one obtains the mean thickness by

$$\bar{n}_{\text{BET}}(p, T) = \frac{\partial f}{\partial \beta \mu_{\text{film}}} = \frac{c(T)x}{[1-x]\{1+[c(T)-1]x\}}, \quad x = \frac{p}{p_s},$$

$$c(T) = e^{-\beta(\epsilon - \epsilon')} > 1, \quad (2.8)$$

where the saturation pressure $p_s(T) = p_0 e^{\beta \epsilon'}$ depends only on the temperature. In contrast to Eq. (2.1), we now define the chemical potential

$$\beta \mu = -\ln \frac{p}{p_s} \quad (2.9)$$

with respect to the saturation pressure p_s , so that the thickness in Eq. (2.8) diverges,

$$\bar{n}_{\text{BET}} \xrightarrow{\mu \rightarrow 0} (\beta \mu)^{-1}, \quad (2.10)$$

if μ goes to zero, i.e., the pressure p approaches p_s . For small pressures $x \ll 1$, or in the limit $\beta \epsilon \ll -1$ with $e^{-\beta \epsilon} p / p_0$ fixed, we can derive from Eq. (2.8) the well-known Langmuir isotherm

$$\bar{n}_L(p, T) = \frac{p}{p_0 e^{\beta \epsilon} + p} \quad (2.11)$$

for monolayer adsorption. We note that the same result could have been obtained immediately by restricting the partition sum (2.2) to values $n_i \leq 1$.

The BET result (2.8) provides an excellent description of much adsorption data at low pressure, but it fails to describe the behavior near saturation, $\mu \rightarrow 0$. In contrast to Eq. (2.10), the measured film thicknesses frequently diverge with an exponent $s > 1$,^{2,3,7-10,28,42}

$$\bar{n}_{\text{expt}} \sim (\beta \mu)^{-1/s}. \quad (2.12)$$

In order to account for such thick-film adsorption behavior, FHH proposed a different adsorption energy U_ν to be used in the Hamiltonian (2.3b). Recognizing that the relevant interaction of the molecules is not a nearest-neighbor contact energy ϵ' , FHH suggested a long-ranged van der Waals interaction

$$U_\nu = -\frac{\alpha}{(z_\nu)^s}, \quad \alpha > 0, \quad (2.13)$$

between substrate and molecules with $s=3$, where z_ν is the distance of the molecule ν from the substrate (see Fig. 1). This potential can be obtained by the elaborate Lifshitz theory⁴¹ or more simply by summing the van der Waals force

$$U_{\text{vdW}} = -\frac{24}{\pi} \frac{\alpha}{r^6} \quad (2.14)$$

over the half space covered by the substrate,

$$U_\nu = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy \int_{-\infty}^0 dz U_{\text{vdW}}[\sqrt{x^2 + y^2 + (z - z_\nu)^2}]$$

$$= -\frac{\alpha}{z_\nu^3}. \quad (2.15)$$

The constant α is related to the difference of the polarizations of the substrate and the adsorbed liquid. Its value can be found for some substances in the literature.⁴³

Assuming that fluctuations in the thickness of the film n are not relevant, one can minimize the energy given by Eqs. (2.3b) and (2.13) in order to find the most probable thickness as the mean thickness

$$\bar{n}_{\text{FHH}} = \left(\frac{\alpha}{\mu} \right)^{1/s} \quad (2.16)$$

with $s=3$ in perfect agreement with certain experimental data.⁴² Slopes such as $s=2$ (Refs. 7–9) and $s \approx 1$ (Ref. 10) have nevertheless been routinely reported. They have usually been interpreted as evidence for substrate-adsorbate interactions which did not vary as z_ν^{-3} . But an explanation for such an “effective” interaction potential has never been provided. The interaction energy $U_\nu = \alpha' z_\nu^{-2} \ln z_\nu$ proposed by Prosen and Sachs⁴⁴ has been quoted repeatedly⁷⁻⁹ in order to explain deviations in adsorption data from Lifshitz theory. Their result is only valid, however, for very small distances z_ν and is thus not applicable to the multilayer regime. A detailed discussion of interaction energies between molecules and substrates can be found in Ref. 45.

For low pressure, i.e., thin films, the FHH theory makes no predictions. In contrast to the previously discussed BET theory the FHH approach does not take into account thermal fluctuations of the thickness—despite the fact that they are actually there. But fluctuations do in fact influence the shape of adsorption isotherms even for thicker films. This can be demonstrated by employing the potential (2.13) in the Hamiltonian (2.3b) and performing the partition function (2.2). It is interesting to note that in this case one obtains

$$\bar{n}(p, T) \xrightarrow{\mu \rightarrow 0} (\beta \mu)^{-1} \quad (2.17)$$

as saturation is approached, even for $s \neq 1$ [see Eq. (2.10)]. The reason for the difference in the asymptotic behavior in Eq. (2.16) and (2.17) is that the mean thickness \bar{n} has been shifted away from the most probable value \bar{n}_{FHH} in Eq. (2.16) on account of thermal fluctuations.

Thermal fluctuations can, of course, be suppressed by phenomena such as adsorbate-adsorbate interactions, which have been entirely neglected so far. It is particularly important to consider adsorbate-adsorbate interactions in the thick-film regime, where the influence of substrate-adsorbate interactions progressively decreases. Since these interactions generally decrease thermal fluctuations, they influence the adsorption data towards FHH-like behavior. Thus the self-energy of the film appears to be the reason for the validity of FHH theory. But for thin films the self-interaction of the molecules in the film is expected to become progressively less important, allowing fluctuations to potentially dominate the shape of the isotherm.

III. A STATISTICAL THEORY OF ADSORPTION ON FLAT SUBSTRATES

One very direct approach to include thermal fluctuations and self-energies of the film would be to incorporate adsorbate-adsorbate interactions in the Hamiltonian in Eq. (2.3) as well as the adsorbate-substrate potential given by Eq. (2.13). The partition sum in Eq. (2.2) would then be performed. A more convenient way to consider such interactions is through the introduction of a surface tension γ' associated with the film-vapor interface. The long-ranged portion of the adsorbate-adsorbate interaction, as well as the dependence of the film energy on the thickness, are thus neglected. These approximations could be improved in future refinements of the theory, should discrepancies with data remain.

In a continuum description, the existence of surface tension leads to an energy contribution proportional to the interface area A ,

$$\begin{aligned} \mathcal{H}_s &= \gamma' A = \gamma' \int_{-\infty}^{\infty} \sqrt{1 + [\nabla d(x,y)]^2} dx dy \\ &= \frac{\gamma'}{2} \int_{-\infty}^{\infty} [\nabla d(x,y)]^2 dx dy + O([\nabla d(x,y)]^4), \end{aligned} \quad (3.1)$$

where $d(x,y)$ is the thickness at the surface site (x,y) . Discretizing the substrate surface $(x,y) \rightarrow i$ and the thickness $d(x,y) \rightarrow an_i$, we obtain

$$\mathcal{H}_s = \frac{\gamma}{2} \sum_{\langle ij \rangle} (n_i - n_j)^2, \quad n_i \geq 0, \quad (3.2)$$

with $\gamma = \gamma' a^2$, where the sum runs over nearest-neighbor sites. Thus the Hamiltonian (2.3) now reads

$$\mathcal{H}(\{n_i\}) = \sum_i H(n_i) + \frac{\gamma}{2} \sum_{\langle ij \rangle} (n_i - n_j)^2 \quad (3.3)$$

with

$$H(n) = n\mu + \sum_{\nu=1}^n U_\nu \quad (3.4)$$

and

$$U_\nu = -\frac{\alpha}{z_\nu^3}, \quad \alpha > 0. \quad (3.5)$$

We thus arrive at a particular case of the well-known solid-on-solid (SOS) model.^{31,32} SOS models and similar lattice-gas models based on the three-dimensional Ising model have been studied extensively in the literature to understand adsorption on solid substrates.²⁹⁻³⁷ But most of these works consider the wetting behavior of very thick films or the layering phase transitions at low temperatures, i.e., below the roughening temperature. The authors are not aware of any work applying the model given by Eqs. (3.3)–(3.5) to adsorption data at intermediate thickness (less than ten monolayers) above the roughening temperature, especially to those experiments mentioned above which indicate discrepancies with the Lifshitz theory of van der Waals forces.

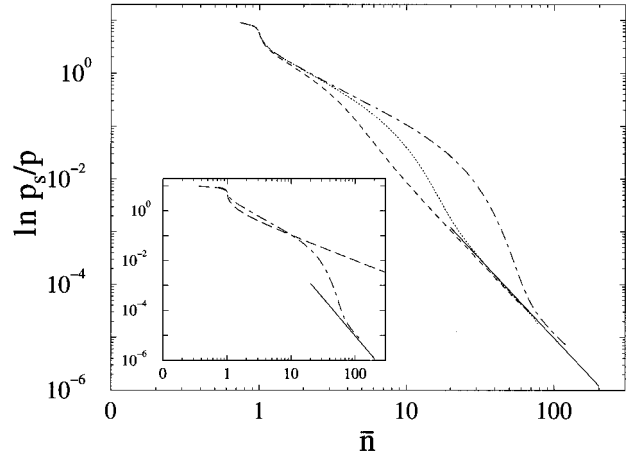


FIG. 2. Isotherms calculated self-consistently using Eq. (3.7) for $\beta\alpha = 10$, and surface tensions $\beta\gamma = 0.1$ (dashed line), $\beta\gamma = 0.01$ (dotted), and $\beta\gamma = 0.001$ (dashed-dotted). If the coverage is low (monolayer regime) or high (asymptotic scaling regime) the surface tension has no influence on the isotherm, whereas at intermediate thickness a strong dependence occurs. The FHH isotherm for the asymptotic behavior given by Eq. (2.16) is shown as a solid line. The inset shows the isotherm predicted by Brunauer, Emmett, and Teller [BET, see Eq. (2.8)] for multilayer adsorption with a final slope $s = 1$ (dashed line), and by Frenkel, Halsey, and Hill [FHH, see Eq. (2.16)] for the asymptotic behaviour approaching saturation pressure (solid line).

We can no longer perform the partition sum (2.2) in an exact manner due to the now-present interactions between neighboring film thicknesses and the restriction that $n_i \geq 0$. We therefore apply a mean-field approximation, replacing n_j in Eq. (3.3) with its mean value \bar{n} . Defining a mean-field partition sum of the film by

$$Z_{\text{MF}} = \sum_{n=0}^{\infty} e^{-\beta H(n) - \beta\gamma_{\text{MF}}(n - \bar{n})^2} \quad (3.6)$$

with an effective mean-field parameter $\gamma_{\text{MF}} = 2\gamma$, we obtain a self-consistent equation

$$\bar{n}(\mu) = \frac{1}{Z_{\text{MF}}} \sum_{n=0}^{\infty} n e^{-\beta H(n) - \beta\gamma_{\text{MF}}[n - \bar{n}(\mu)]^2} \quad (3.7)$$

for the mean thickness $\bar{n}(\mu)$. Equation (3.7) is in its simplicity our main result. The sums can be performed to any desired accuracy yielding an equation for \bar{n} , which can be solved by standard numerical procedures. The solution $\bar{n}(\mu, \beta\alpha, \beta\gamma_{\text{MF}})$ is the adsorption isotherm depending on the substrate/adsorbate parameters, $\beta\alpha$ and $\beta\gamma_{\text{MF}}$. The isotherm given by Eq. (3.7) is thus straightforward to apply to data. This is the main reason we neglect, for example, the renormalization of the adsorbent-substrate potential and the surface tension by thermal fluctuations. If discrepancies between data and theory cannot be removed via Eq. (3.7), the dependence of the parameters on the thickness \bar{n} must then be considered.

Figure 2 presents adsorption isotherms for several values of $\beta\gamma_{\text{MF}}$. The mean thickness is always enhanced compared with the FHH isotherm (2.16) shown as a solid line. Above a certain thickness the fluctuations are not relevant anymore and the thickness tends towards the FHH value. This is because the film-vapor interface can fluctuate, undisturbed by

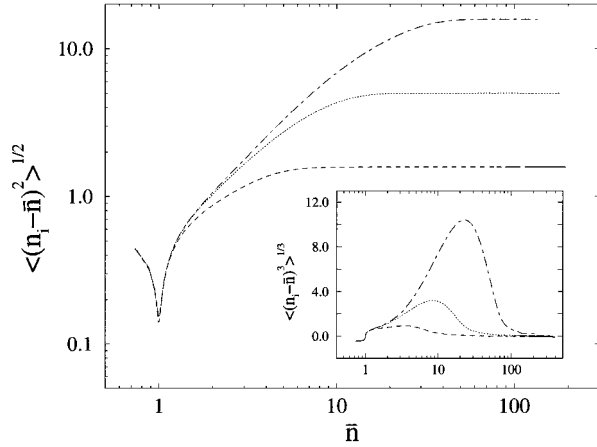


FIG. 3. Variances of the thickness for $\beta\alpha=10$, and surface tensions $\beta\gamma=0.1$ (dashed line), $\beta\gamma=0.01$ (dotted), and $\beta\gamma=0.001$ (dashed-dotted). At high coverages ($\bar{n} \gg 1$) one obtains for $\sigma_2(\bar{n}) = \{ \langle [n - \bar{n}(\mu)]^2 \rangle \}^{1/2}$ the width of a free fluid-vapor interface. This value can be used to determine the mean-field parameter γ_{MF} using Eq. (3.8). The decrease of the width at lower coverages is due to the hindrance of thermal fluctuations by the substrate. For monolayer thickness a minimum is reached indicating the existence of a saturation of the isotherm. The inset shows the variance $\sigma_3(\bar{n}) = \{ \langle [n - \bar{n}(\mu)]^3 \rangle \}^{1/3}$ for the same parameter values γ as for $\sigma_2(\bar{n})$. Positive values correspond to a dominance of fluctuations, increasing the thickness of the film.

the substrate, around its mean distance $\bar{n}(\mu)$ for films which are sufficiently thick. Since the local potential around the most probable distance \bar{n}_{FHH} is nearly symmetric, the fluctuations cannot drive the mean distance away from \bar{n}_{FHH} in such cases, yielding $\bar{n}(\mu) \approx \bar{n}_{FHH}$. We note that after completion of the first monolayer a flat “linear” regime occurs which crosses over the expected linear scaling at large $\bar{n}(\mu)$. The crossover regime itself looks like a “linear” regime, but it spans only about half a decade of $\bar{n}(\mu)$.

The inset to Fig. 2 shows an adsorption isotherm generated self-consistently by Eq. (3.7) in comparison with a BET isotherm (dashed) and a FHH isotherm (solid). Whereas the asymptotic regime can be described quite well by FHH theory with a final slope $s=3$, the shape of the isotherm near the monolayer regime is better described by BET theory with $s=1$. At intermediate thickness a crossover occurs with slope $s>3$.

To confirm our picture of a mean thickness dominated by thermal fluctuations, we calculate the variances $\sigma_2(\bar{n}) = \{ \langle [n - \bar{n}(\mu)]^2 \rangle \}^{1/2}$ and $\sigma_3(\bar{n}) = \{ \langle [n - \bar{n}(\mu)]^3 \rangle \}^{1/3}$ as a function of \bar{n} using the partition sum in Eq. (3.6) for the averages $\langle \dots \rangle$. These variances are shown in Fig. 3 as functions of the mean thickness of the film. Within the mean-field approximation, the variance of the thickness, i.e., the thickness of the film-vapor interface, is given by

$$\sigma_{int} := \sigma_2(\bar{n} \rightarrow \infty) = \frac{1}{\sqrt{2\beta\gamma_{MF}}} \quad (3.8)$$

for large $\bar{n}(\mu)$. If the mean thickness $\bar{n}(\mu)$ of the film decreases below σ_{int} , the interface fluctuations are constrained by the substrate. $\sigma_2(\bar{n})$ then decreases with decreasing distance \bar{n} until monolayer thickness is reached. Since the in-

terface is essentially fixed at monolayer height, the variance shows a minimum, and increases again in the submonolayer regime. The fluctuations of the film are primarily in one direction, i.e., away from the substrate. This clearly increases the mean thickness of the film, which can be seen in the inset to Fig. 3 where $\sigma_3(\bar{n})$ is depicted as a function of \bar{n} . This variance is positive, except in the submonolayer regime, and shows a rapid decrease to zero for large thicknesses, indicative of symmetric fluctuations around \bar{n} . If the mean thickness \bar{n} of the film decreases below σ_{int} , the interface fluctuations are constrained by the substrate and the fluctuations tend to enlarge the mean thickness above \bar{n}_{FHH} . This fluctuation-induced thickness differs significantly from the prediction of FHH theory as can be clearly seen in Fig. 2. The variance $\{ \langle (n - \bar{n})^3 \rangle \}^{1/3}$ gives a good estimate for the difference between the actual mean thickness \bar{n} and the most probable value \bar{n}_{FHH} .

Since the mean-field approximation gives only a rough sketch of the fluctuations of the interface, the relation in Eq. (3.8) may be used to define γ_{MF} instead of expressing it by the surface tension, $\gamma_{MF} = 2\gamma$. One can then employ the experimental or the capillary-wave variance of a free interface for σ_{int} in Eq. (3.8) defining γ_{MF} by $\gamma_{MF} = (2\beta\sigma_{int}^2)^{-1}$. Nevertheless, this value for γ_{MF} does not take into account the decrease of the surface tension with the layer thickness. Thus the values for γ are expected to be smaller than those given by a free liquid-vapor interface.

The asymptotic scaling regime begins at approximately $\bar{n}_\gamma = 1/\sqrt{2\beta\gamma_{MF}}$, defined by equating the mean thickness and the variance. This value is larger than the layer thicknesses studied in most of the experimental data in Refs. 1–3. The interpretation of such experimental data by means of a FHH-type theory at thicknesses less than \bar{n}_γ must therefore be carried out with extreme caution. Regions which appear “linear” need not be so, especially if the scaling is only over half a decade or so. This was already recognized by Steele,²⁶ taking into account the finite thickness of the liquid-vapor interface, and Kardar and Indekeu in their comments on the first adaptations of FHH-type theories to the case of rough substrates.⁵ Since the enhanced interfacial thickness results from thermal fluctuations of the layer thickness n_i , Steele’s explanation for the observed phenomena is quite similar to ours. Our work goes further, demonstrating that the exponent s may be either greater or less than 3, and provides a clearer picture of the physical phenomenon underlying this result.

In order to test the model and the approximations we have made, we now compare our results with the more elaborate Born-Green-Yvon (BGY) equation for a simple fluid on flat substrates.⁴⁶ This makes it possible to remove experimental uncertainties such as surface roughness and deviations from ideal van der Waals interactions. Figure 4 depicts the BGY predictions for adsorption of argon on graphite at two different temperatures ($T=120$ K, circles, and $T=80$ K, squares) along with our best fit (solid and dashed lines) to the curves via Eq. (3.7). We have used the notation $\Gamma\sigma^2 = n_0\bar{n}(\mu)$ from Ref. 46 for the excess amount of adsorption, which is proportional to the mean layer thickness $\bar{n}(\mu)$. Multilayer steps of the isotherm are evident at lower temperatures. The smoother behavior at $T=120$ K is also reproduced quite well by the self-consistent mean-field theory. We find the best-fit values to be $n_0=0.74$, $\beta\alpha=14$, and $\beta\gamma=0.78$ at $T=80$ K,

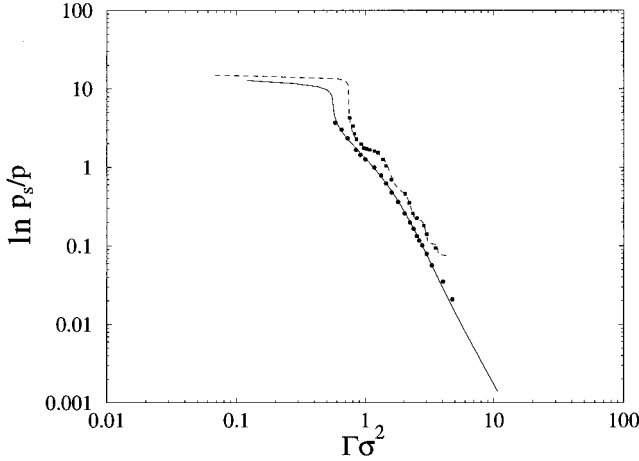


FIG. 4. The BGY results (Ref. 46) for adsorption of argon on graphite at two different temperatures ($T=120$ K, circles, and $T=80$ K, squares). The best fit of the excess amount of adsorption $\Gamma\sigma^2 = n_0\bar{n}(\mu)$ which is proportional to the mean layer thickness $\bar{n}(\mu)$ is obtained at the values $n_0=0.74$, $\beta\alpha=14$, and $\beta\gamma=0.78$ at $T=80$ K and $n_0=0.558$, $\beta\alpha=11.72$, and $\beta\gamma=0.116$ at $T=120$ K.

and $n_0=0.558$, $\beta\alpha=11.72$, and $\beta\gamma=0.116$ at $T=120$ K. Using the Lennard-Jones (LJ) parameters for argon on graphite given in Ref. 46 and assuming that the factor n_0 is related to the density n' and LJ parameter σ of liquid argon by $n_0=0.9165\sigma^2 n'^{2/3}$, we obtain the expected values $n_0=0.779$, $\beta\alpha=20.7$ at $T=80$ K, and $n_0=0.666$, $\beta\alpha=13.83$ at $T=120$ K. We do not have explicit values for γ but we do find that $\beta\gamma$ decreases with increasing temperature as expected. Also the widths of the liquid-vapor interface obtained from the fits by using Eq. (3.8) with $\gamma_{MF}=2\gamma$, 0.57 monolayers for $T=80$ K and 1.47 monolayers for $T=120$ K, are in the expected range.

Despite the good agreement of the BGY isotherms with those generated by our mean-field approach, we do find slight deviations of the respective parameters. We note, however, that the relation for n_0 involves some uncertainty and that the isotherms do not depend strongly on the parameter α . Both of these effects may contribute to deviations from the expected values. We conclude from this comparison that, although the best-fit parameters may not be exactly the same as the actual values, they will be sufficiently close. The self-consistent mean-field equation [Eq. (3.7)] meanwhile provides a straightforward method for analysis of actual adsorption data.

IV. ADSORPTION ON A ROUGH SUBSTRATE

So far we have considered only flat substrates. On a rough surface the local mean thickness \bar{n}_i is not homogeneous, but depends instead on the substrate site i . We therefore must average over all sites $\bar{n}(\mu) = (1/N)\sum_i \bar{n}_i$ in order to obtain the mean thickness $\bar{n}(\mu)$. In analogy to the FHH theory, one can calculate \bar{n}_i by minimizing the energy, Eq. (3.1), and then performing an average over all possible configurations of the substrate.^{5,6} The roughness of the substrate surface will induce undulations in the liquid-vapor interface in addition to those arising from thermal fluctuations, but we expect that this effect will only be seen in the mean thickness $\bar{n}(\mu)$ over

films thicker than \bar{n}_γ , i.e., where thermal fluctuations are essentially unconstrained by the substrate. In order to estimate the effect of the thermal fluctuations, we must consider the change of the local adsorption energy U_ν due to the roughness of the substrate. This appears to be a more important effect than the smoothing of the roughness of the film by surface tension as the film thickness increases.

To adapt the flat substrate depicted in Fig. 1 to the case of a rough substrate, the film-substrate interface at the site i is now located at h_i . We consider a substrate which exhibits self-affine roughness, so that

$$\sigma(i,j) := \sqrt{\langle (h_j - h_i)^2 \rangle} = \sigma_0 r_{ij}^H, \quad (4.1)$$

where r_{ij} is the lateral distance of the lattice sites i and j in units of the lattice spacing a , H is the roughness exponent, and σ_0 the mean square deviation at nearest-neighbor spacing. The saturation of the roughness at large distances r_{ij} is neglected, since we are interested in low or intermediate coverages. Due to the decrease of the van der Waals forces, saturation at large distances does not influence the thickness of the film in this regime. We can calculate according to (2.15) an effective mean potential

$$U_\nu^{\text{eff}} = \langle U_\nu \rangle = - \sum_{j=1}^N \frac{1}{Z} \sum_{h=-\infty}^{\infty} \sum_{z=-\infty}^h \frac{\alpha'}{[r_{ij}^2 + (z_\nu - z)^2]^3} e^{-h^2/\sigma^2(ij)} \quad (4.2)$$

by integrating over positions inside the substrate (see Fig. 1). The average $\langle \dots \rangle$ over all configurations of the substrate is performed by using a Gaussian distribution with variance $\sigma(i,j)$ given in Eq. (4.1), where i is the lattice site of the adsorbed molecule ν . Due to the homogeneity of Eq. (4.1), the effective potential U_ν^{eff} depends only on the distance z_ν of the molecule from the surface at h_i and not on the surface site i itself. The last sum in Eq. (4.2) over z might be replaced by a continuous integral which can be performed exactly, reducing the number of sums. The factor $Z = \sum_{h=-\infty}^{\infty} \exp[-h^2/\sigma^2(ij)]$ normalizes the sums in Eq. (4.2) in such a way that $U_\nu^{\text{eff}} = -\alpha/z_\nu^3$ for $\sigma_0 \rightarrow 0$, i.e., for a flat substrate, in accordance with Eq. (3.5). Numerically the sums were performed on a finite lattice and the dependence of the result on the lattice size was tested.

The inset of Fig. 5 shows this effective potential U_ν^{eff} for several values of σ_0 and $H=0$. Since we are interested only in distances up to ten monolayers, the change of the local potential U_ν due to substrate roughness is clearly a relevant effect. Using the effective potential U_ν^{eff} in the Hamiltonian (3.4), we obtain isotherms on a rough substrate shown in Fig. 5. Once more, the primary effect is an increase of the mean thickness which in turn yields a slope greater than the $s=3$ observed at large coverages.

This is surely a very rudimentary way to incorporate roughness in the mean-field approximation, because we have carried out the average in Eq. (4.2) before the self-consistent determination in Eq. (3.7) of $\bar{n}(\mu)$. It does, however, allow a mechanism for comparing theory to experimental data, which is one of the primary goals of this work. In the next

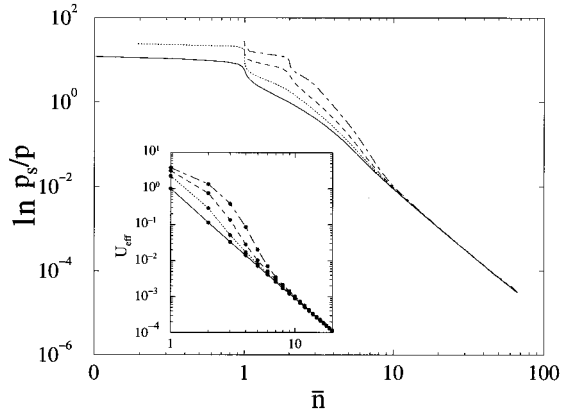


FIG. 5. Isotherms calculated self-consistently using Eq. (3.7) for $\alpha=10$ and surface tension $\beta\gamma=0.1$. The substrate roughness parameters are $H=0$ and $\sigma_0=0$ (solid line), $\sigma_0=1$ (dotted), $\sigma_0=1.5$ (dashed), and $\sigma_0=2$ (dashed-dotted). If the coverage is high (asymptotic scaling regime) the roughness σ_0 has little influence on the isotherm, whereas at small thickness an increase of the slope occurs as well as multisteped layering. The inset shows the corresponding effective interaction potential given by Eq. (4.2) used instead of Eq. (3.5) (solid line) in the Hamiltonian (3.4).

section, we provide a number of examples of comparison of our theory to actual experimental data.

V. COMPARISON WITH EXPERIMENTAL DATA

We first examine whether adsorption data recorded on flat surfaces which are not in agreement with the FHH theory might not be explained by thermal fluctuations of the film thickness. In particular, such fluctuations might be particularly important for measurements carried out at room temperature. For example, recent experimental investigations of water and cyclohexane adsorption on smooth mica¹⁰ found an exponent $s \approx 1$ and concluded that the Lifshitz theory was inadequate for these systems. In Fig. 6 we show the measurements of cyclohexane (circles) and water (squares), where we use the same notation $D=D_0\bar{n}(\mu)$ for the thickness of the adsorbed layer as in Ref. 10. The data can easily be fitted by our theory employing the Lifshitz theory for the interaction potential. The best fits are found for the values $D_0=0.545$ nm, $\beta\alpha=0.7$, and $\beta\gamma=0.304$ (solid line) and $D_0=0.142$ nm, $\beta\alpha=0.72$, and $\beta\gamma=0.01$ (dashed line). The only parameter we can compare with expected values is the thickness of the monolayer D_0 , which is given in Ref. 10 as 0.5 nm for cyclohexane and 0.15 nm for water. The widths of the liquid-vapor interface obtained from the fits by using Eq. (3.8) with $\gamma_{MF}=2\gamma$, 7.1 Å for water and 4.9 Å for cyclohexane, are, however, quite reasonable values. For example, the width of a free-standing water surface has been measured by means of x-ray reflectivity to be on the order of 3.3 Å.⁴⁷ The inset to Fig. 6 depicts the same curves with linear scale of D allowing a direct comparison with the figures in Ref. 10. We note that discrepancies of the data points result from uncertainties of the scanning of the published data plots. A fit of the data as a function of D rather $\ln D$ improves the result.

Adsorption data for alkanes on gold substrates have also been published, claiming inadequacy of the Lifshitz theory.⁹

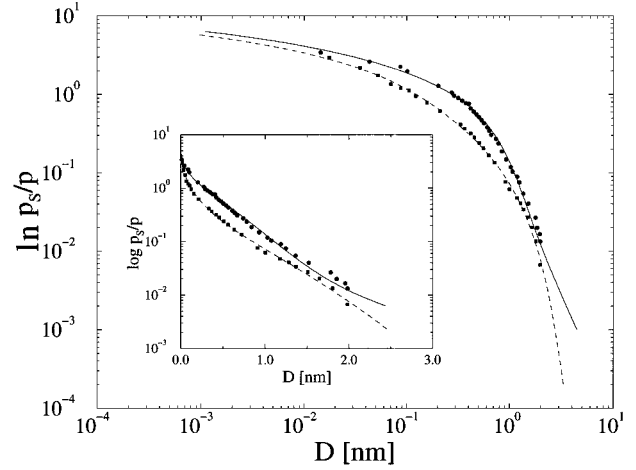


FIG. 6. Adsorption data of cyclohexane (circles) and water (squares) on mica reported by Ref. 10. The inset depicts the same curves with a linear scaling of the thickness $D=D_0\bar{n}$ of the adsorbed film showing a linear dependence of D on $\ln p_s/p$. The data can be described quite well by the self-consistency equation Eq. (3.7) and the van der Waals interaction (3.5) with $s=3$ (lines). We find the values $D_0=0.545$ nm, $\beta\alpha=0.7$, $\beta\gamma=0.304$ (solid line) and $D_0=0.142$ nm, $\beta\alpha=0.72$, $\beta\gamma=0.01$ (dashed line) for the best fit.

These data were used to argue that the interaction potential was likely to follow an inverse square law based on a linear fit of the data over half a decade in film thickness. Once again, we are able to employ Eq. (3.7) to find good agreement of the data with the van der Waals interaction in Eq. (2.13) if fluctuations of the interface are taken into account. The fit parameters in this case are not, however, as physically realistic as those obtained for the data of Ref. 10. In Fig. 7 we show the measurements for pentane (filled circles) and

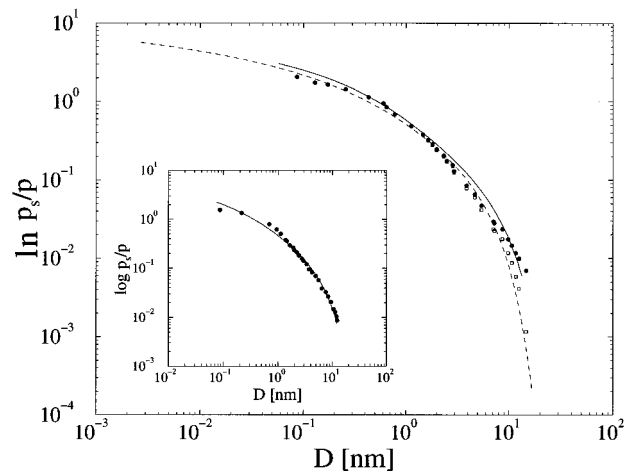


FIG. 7. Adsorption data (filled circles) of pentane and hexane (inset) on thin films reported by Ref. 9. The open squares show the change of the data points by the adjustment, i.e., 0.5% decrease, of the saturation pressure p_s . The data can be described quite well by the self-consistency equation Eq. (3.7) and the van der Waals interaction (3.5) with $s=3$ (lines). We find the values $D_0=0.61$ nm, $\beta\alpha=0.29$, $\beta\gamma=0.0025$ (pentane, solid line), $D_0=0.65$ nm, $\beta\alpha=0.21$, $\beta\gamma=0.0042$ (pentane, dashed line), and $D_0=0.59$ nm, $\beta\alpha=0.072$, $\beta\gamma=0.002$ (hexane, inset) for the best fit.

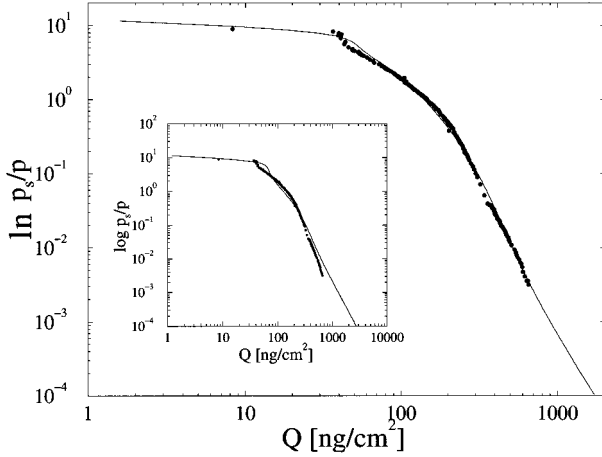


FIG. 8. Isotherm of nitrogen adsorbed on a silver substrate (Ref. 1). The data $Q = q_0 \bar{n}$ show at low pressures the covering of a monolayer and large pressures a “linear” behavior with slope $s=4.3$. The solid line is the best fit obtained for the fluid parameters $q_0 = 52.2 \text{ ng/cm}^2$, $\beta\alpha=2.22$, and $\beta\gamma=0.051$ and the roughness parameters $\sigma_0=1.8$ and $H=0.7$. The inset shows the best fit ($q_0=68.21 \text{ ng/cm}^2$, $\beta\alpha=7.6$, $\beta\gamma=0.08$) if a flat substrate with $\sigma_0=0$ and $H=0$ is assumed. The discrepancies in the vicinity of the monolayer $Q \approx 50$ are probably due to the simplicity of the assumption that the adsorption energy of the first layer is given only by the van der Waals interaction.

hexane (inset: filled circles) in comparison with the best fit (solid lines). The best-fit parameters are $D_0=0.61 \text{ nm}$, $\beta\alpha=0.29$, and $\beta\gamma=0.0025$ (pentane) and $D_0=0.59 \text{ nm}$, $\beta\alpha=0.072$, and $\beta\gamma=0.002$ (hexane). The fit of the pentane data is not particularly good, especially on account of the straight line formed by the points above $D=1 \text{ nm}$. Such linear behaviour is not observed in the hexane data depicted in the inset, which are taken from Ref. 9. The discrepancy of the shape of the curves may be due to an inaccuracy of the value taken for the saturation pressure. Decreasing p_s for pentane by only 0.5% yields new data points (Fig. 7, open squares), which can be fitted much better with only slightly changed parameters, $D_0=0.65 \text{ nm}$, $\beta\alpha=0.21$, and $\beta\gamma=0.0042$. The fit value for the width of the film-vapor interface, 7.7 monolayers, seems, however, to be unphysically large.

We next consider adsorption on rough substrates, employing Eq. (4.2) for the fits to the data. Figure 8 presents adsorption data for nitrogen on silver at 77 K (circles) which was reported in Ref. 1. We assume a linear relation $Q = q_0 \bar{n}(\mu)$ between the adsorbed mass Q measured in ng/cm^2 and the number of layers \bar{n} . The best fit assuming a flat substrate with $\sigma_0=0$ and $H=0$ is shown in the inset (solid line). The values of the isotherm are found to be $q_0=68.21$, $\beta\alpha=7.6$, and $\beta\gamma=0.08$. Neither the final slope nor the intermediate region is described well by the best fit. But assuming a rough substrate and using the parameters σ_0 and H as fit parameters as well we find the self-consistent mean-field theory in very good agreement (solid line) with the measured thickness. The parameter q_0 corresponds to a translational shift of the isotherm but does not change the shape of the curve. Of course, the remaining four fit parameters might be expected to fit the shape of nearly any isotherm. But comparing their values, $q_0=52.2 \text{ ng/cm}^2$,

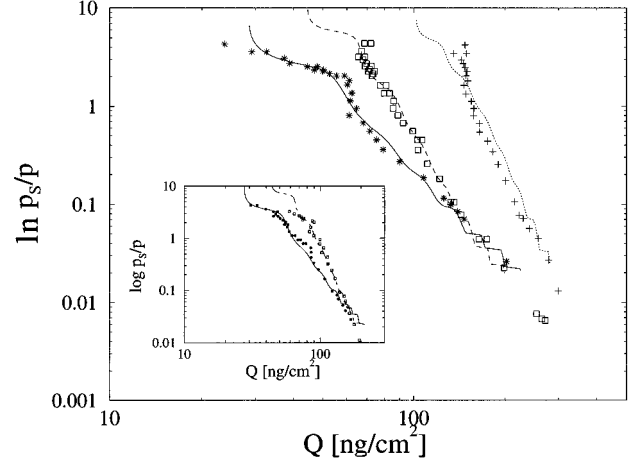


FIG. 9. Isotherm of nitrogen adsorbed on thick silver films deposited at 80 K (Ref. 3). The thickness of the silver substrate is 450 Å (stars), 1000 Å (squares), and 2000 Å (crosses). The inset shows further measurements of the same experiment reported in Ref. 2 on 750 Å (circles) and 1500 Å (squares) thick silver films. The lines are the best fits where only σ_0 and q_0 are used as fit parameters. The other values $\beta\alpha=10$, $\beta\gamma=0.67$, and $H=0.29$ are determined by the best fit for the 450 Å film only and are held fixed for the other fits. The parameters for the curves are $q_0=28.48 \text{ ng/cm}^2$, $\sigma_0=0.94$ (solid line), $q_0=22.23 \text{ ng/cm}^2$, $\sigma_0=2.23$ (dashed line), $q_0=25.47 \text{ ng/cm}^2$, $\sigma_0=3.7$ (dotted line), $q_0=27.58 \text{ ng/cm}^2$, $\sigma_0=1.08$ (inset, solid line), and $q_0=21.79 \text{ ng/cm}^2$, $\sigma_0=2.4$ (inset, dashed line).

$\beta\alpha=2.22$, $\beta\gamma=0.051$, $\sigma_0=1.8$, and $H=0.7$, for the best fit with the experimental values, $q_0=45 \pm 5 \text{ ng/cm}^2$ and $\beta\alpha=7$, we find rather reasonable agreement. This is especially true in light of the fact that all parameters can deviate from the expected experimental values somewhat, due to the approximations made in the mean-field lattice model. The parameters are, moreover, determined from different portions of the data sets. The lattice constant a , i.e., the parameter q_0 , and the adsorption energy of the first layer, i.e., $\beta\alpha$, are determined by the monolayer regime only, whereas the surface tension γ and the amplitude σ_0 are determined by the data between $Q=100$ and 1000.

We do not expect that the adsorption energy of a monolayer is given by the van de Waals force alone, but by additional contact energies. It would not be difficult, however, to introduce such terms in the Hamiltonian (3.5) for the first layer on the substrate. To avoid additional unknown fit parameters we did not, however, implement this potential improvement. We therefore expect the term $\beta\alpha$ to be different from its ideal van der Waals values. The width of the liquid-vapor interface obtained from the fit by using Eq. (3.8) with $\gamma_{\text{MF}}=2\gamma$ is 2.2 monolayers, a quite reasonable value.

We find only a very weak dependence of the isotherms on the roughness exponent H making it difficult to obtain a reliable value. Nevertheless, $H=0.7$ is within experimental error of the value reported in Ref. 1.

Adsorption data for nitrogen adsorbed on silver films deposited at 80 K are reported in Refs. 2 and 3 and are shown in Fig. 9 (for thicknesses 450, 1000, and 2000 Å; in the inset for thicknesses 750 and 1500 Å). Again, different parts of the data set determine the different parameters. Assuming that the parameters $\beta\alpha$, $\beta\gamma$, and H are the same for all samples,

we use the thinnest silver film substrate (circles, 450 Å) to fix their values ($\beta\alpha=10$ and $\beta\gamma=0.67$, i.e., $\sigma_{\text{int}}=0.61$ monolayers). The other four isotherms are fitted by varying only the roughness amplitude parameter σ_0 and the normalization factor q_0 . We emphasize that a change in q_0 yields only a shift of the curve without changing the slopes. Thus the roughness amplitude parameter σ_0 via the effective local potential U_{eff} in Eq. (4.2) is sufficient to describe the change in the slope of the isotherms. We need no further assumption on the dependence of the film thickness on the local substrate sites induced by surface tension of the film-vapor interface and roughness of the substrate.

The adsorption data are not measured at lower coverage (the monolayer regime), which makes it difficult to determine certain fit parameters. In particular, the value of $\beta\gamma$ is influenced a lot by slight changes of the data points. Nonetheless, the roughness of the 1000 Å film has been characterized by means of x-ray reflectivity, yielding $H=0.45$ and $\sigma_0 \approx 5$ Å,^{4,48} which is in fairly good agreement with the result of the fit, $H=0.29$ and 7.1 Å (taking $a=3.2$ Å). It is clear that, in order to truly test the theory, one would require not only adsorption data, but an independent determination of the surface roughness characteristics, for example, from scanning tunneling microscope measurements.

VI. SUMMARY

In this paper we studied the influence of thermal fluctuations on adsorption isotherms. A self-consistent mean-field theory of a SOS-type statistical model yields a simple but significant improvement to the standard Frenkel-Halsey-Hill theory.

We have obtained the following main results.

(1) The form of an adsorption isotherms at low thicknesses (0–10 monolayers) can be strongly influenced by thermal fluctuations. Undulations of the film-vapor interfaces are not only hindered by the substrate but also suppressed by surface tension at larger thickness of the film. Therefore a quantitative analysis of experimental data must consider not only the interaction potential of the adsorbed molecule with

the substrate alone, but also thermal fluctuations and surface tension of the adsorbed film.

(2) We find quantitative agreement between experimental data and the self-consistent mean-field theory of film thickness adsorbed by van der Waals interactions for adsorption occurring on flat surfaces. Reported discrepancies between measurements and the Lifshitz theory are partially or entirely removed by taking into account thermal fluctuations of the thickness of the adsorbed film.

(3) Recently reported data for nitrogen adsorbed on rough silver substrates have been reanalyzed. For existing adsorption data on rough substrates, it appears that the undulation of the film due to surface tension and roughness of the underlying substrate; i.e., the dependence of the local film thickness on the substrate site, is a relatively unimportant effect. More important is the change of the local interaction energy and thermal fluctuations of the thickness. The agreement of measured data and the self-consistent mean-field theory is quite reasonable in some cases, indicating that the scaling regime of asymptotic divergence is not yet reached.

(4) Although it is possible to gain some information about the roughness parameters σ_0 and H , adsorption measurements limited to less than ten monolayers are not ideally suited for such determinations.

If adsorption data can be supplemented with additional information about the substrate surface, for instance, by scanning tunneling microscopy or x-ray reflectivity, it should be possible to improve the theory and approximations therein, to eventually obtain reliable interpretations of adsorption isotherms. Further theoretical advances will require accurate measurements of substrate roughness and corresponding adsorption data.

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