Multilayer Adsorption on a Fractally Rough Surface

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Models are proposed for thick-film-coverage adsorption on a general fractal surface. The basic idea is that long-range dispersion forces dominate the thermodynamic behavior. The analysis predicts the coverage to be proportional to $[\ln(P_0/P)]^{(D-3)/3}$, where P/P_0 is the relative vapor pressure and D is the fractal dimension of the surface. Experimental examples for this behavior are presented. They are rough Ag surfaces, giving $D=2.30$.

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The characterization of surface roughness is an important problem for both basic and applied science. Traditional techniques, based on the idea of isolated deviations from planar surface geometry (e.g., a facet of an elemental solid with occasional steps and kinks), face the difficulty of identifying a small number of structural parameters that can describe the roughness for a wide variety of purposes. Typically they depend on a multitude of model-specific parameters difficult to access in practice. The concept of fractal dimensionality, in contrast, has proven very successful both in applying to a wide variety[1-3] of complex surface geometries and in advancing our understanding[4-6] of how the geometry affects the physical properties of the system.

Early fractal analyses[1] have exploited the fact that when a surface is scale invariant (self-similar or self-affine) over a range of lengths, $a_{\min}$ to $a_{\max}$, the number N_m of molecules of size a in this range required to cover the surface with a monolayer is

$$N_m = C a^{-D}, \tag{1}$$

where D is the surface fractal dimension and C is a constant. A smooth surface satisfies Eq. (1) with $D=2$ and $C \approx$ surface area. A fractal surface obeys Eq. (1) with $2<D<3$ and $C \approx$ the Hausdorff measure[6] of the surface. Other methods include electronic energy transfer,[2] small-angle x-ray and neutron scattering,[3] and pore-size distribution.[1] This paper explores how a semi-infinite solid with a fractal boundary (surface fractal) controls the thermodynamic properties of adsorbed films when the number of adsorbed molecules N is much larger than the number to form a monolayer N_m. The goal is a thermodynamic theory of fractal adsorption to replace the cumbersome implementation of Eq. (1) with a method that requires a single adsorption isotherm.[7] The two models of the adsorption process to be presented give very similar results and allow us to observe, via N_2 adsorption, fractal behavior of electron-beam evaporated Ag. To the best of our knowledge, the only other reported case of a fractal metal surface at molecular scales is small Pt particles.[8]

The starting point of our calculations is analogous to that of the Frenkel-Halsey-Hill (FHH) theory of adsorption on a flat surface.[9] The adsorbate is treated as a continuum (structureless liquid), the density and energy of which are only weakly perturbed by the substrate. In that theory, the film thickness as a function of pressure P and temperature T is predicted assuming that the film consists of a slab of liquid which wets the substrate. The difference in chemical potential between the film (μ) and bulk liquid (μ_{bulk}) is given by the difference in the van der Waals dispersion energies, $\mu - \mu_{\text{bulk}} = -\alpha z^{-3}$. Here z is the film thickness and α takes into account both the adsorbate-substrate and adsorbate-adsorbate interactions, assuming the latter to be the same as in bulk liquid. Equating the film (bulk) chemical potential to that of its coexisting vapor at pressure P (P_0), the film thickness z is given by the pressure-dependent length

$$\zeta_P \equiv \left[\frac{\alpha}{k_B T \ln(P_0/P)} \right]^{1/3}, \tag{2}$$

where k_B is Boltzmann's constant. Thus if we assume the film of thickness z to have constant number density ρ, and the volume $\Omega(z)$, the coverage at pressure P on the flat surface is

$$N = \rho\Omega(\zeta_P) = \rho\Omega(a)\zeta_P/a = N_m \zeta_P/a, \tag{3}$$

where $N_m = \rho\Omega(a)$ is the monolayer coverage for molecules of size a. Equation (3) is the classical FHH isotherm. It contains several implicit assumptions such as neglect of entropy effects, retardation, and many-body effects. In most circumstances, however, these neglects introduce only small errors (e.g., many-body effects lead only to an error in the magnitude of α [10]). Thus ζ_P is a length scale incorporating all of the basic thermodynamics and may serve as a length scale in order to probe nonplanar geometries.

To treat such nonplanar geometries, we adopt the principle of local thermodynamics, which yields the equilibrium condition for the system chemical potential μ:[11]

$$\mu = \mu_{\text{int}}(\mathbf{r}) + v(\mathbf{r}), \tag{4}$$

where μ_{int} is the chemical potential of a uniform system at the local (**r** dependent) thermodynamic condition and $v(\mathbf{r})$ is the external potential due to the substrate. Equation (4) is valid if $v(\mathbf{r})$ is slowly varying, which is the case at sufficiently large distances from the surface. If the equipotential (v) surfaces are also sufficiently flat (as discussed below), then curvature effects may be neglected in determining the film-vapor interfacial condition. Under these circumstances, this interface is an equipotential surface. One may then infer the film boundary shape corresponding to a given pressure P by comparing Eq. (4) to the corresponding film condition on a *planar* surface having the same value of v. This leads to the result that the liquid condenses in those volumes where the potential $v(\mathbf{r})$ is less than or equal to $-k_BT\ln(P_0/P)$. In our model I, we assume that v depends only on the distance z from the surface and is given by $-\alpha z^{-3}$ as in the flat-surface case. This gives a film volume of $\Omega(\zeta_P)$, where $\Omega(z)$ is the volume of points lying at a distance $\leq z$ from the surface (Fig. 1) and ζ_P is given by Eq. (2). The corresponding equipotential surfaces turn increasingly flat as z increases. For a fractal surface, $\Omega(z)$ scales as z^{-D+3} [number of particles of size z needed to cover the surface, Eq. (1), times the volume of a particle]. Normalization so that $\Omega(a)$ is the monolayer volume for molecules of size a gives $\Omega(z) = \Omega(a)(z/a)^{3-D}$. The coverage at pressure P is thus

$$N = \rho\Omega(\zeta_P) = N_m(\zeta_P/a)^{3-D}. \tag{5}$$

This is the fractal generalization of the FHH isotherm, Eq. (3). As in Eq. (3), the domain of validity is $\zeta_P > a$ because the potential $-\alpha z^{-3}$ obviously holds only for distances $z > a$. Thus for all relevant pressures, the amount adsorbed increases more slowly on a fractal surface than on a planar surface with the same number of surface sites, N_m.

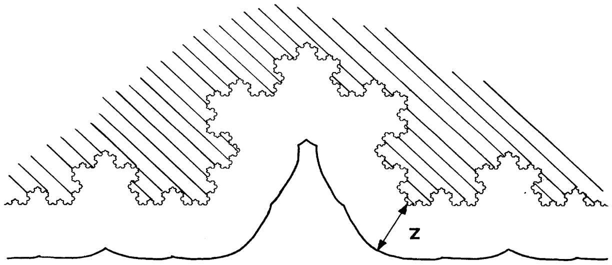

FIG. 1. Equipotential surface generated by a fractal substrate. It represents the film-vapor interface in the absence of surface tension. In the model, it consists of all points with the same (minimum) distance z from the substrate.

Improvement over the two basic approximations (potential and surface tension) should leave the power law in Eq. (5) unaffected. To check this, we turn to an approach which takes into account that the potential in a trough is lower (contributions from several nearby walls) than at the same distance near a mountain top. In this model II, the surface is replaced by a set of spherical pores mimicking troughs of various sizes (Fig. 2). Each pore is treated as isolated and surrounded by an infinite solid. This gives an upper bound to the effect of multiple walls. Proper counting of effectively overlapping pores will be done by appropriately choosing the normalization constant. In a spherical cavity of radius R, the potential energy v at distance z from the wall is adequately described by the expression[12]

$$v(z) = -8\alpha\left[\frac{R}{2Rz - z^2}\right]^3 \tag{6}$$

designed in part to give the exact behavior of $v(z)$ when $z \ll R$. We invoke the FHH *Ansatz* again to obtain the film thickness z at pressure P: $-k_BT\ln P_0/P = v(z)$. This gives

$$z(P,R) = R - (R^2 - 2\zeta_P R)^{1/2} \text{ if } \zeta_P < R/2, \tag{7a}$$

$$z(P,R) = R(\text{pore filling}) \text{ if } \zeta_P \geq R/2, \tag{7b}$$

where we write z as a function of P and R for purposes below. Equation (7) reduces to the planar limit $z = \zeta_P$ when $\zeta_P \ll R$. To calculate the total film volume, we use the fact that the number of pores with radius between R and $R + dR$ for a fractal is $BR^{-D-1}dR$, where B is a constant.[1,5] Thus the total volume of a film of thickness z' is

$$\int_0^{R_{\max}} \omega(z',R)BR^{-D-1}dR, \tag{8}$$

where $\omega(z',R) = 4\pi R^3/3$ if $R \leq z'$, and $\omega(z',R) = 4\pi[R^3 - (R-z')^3]/3$ if $R > z'$ (volume of points in a pore of radius R with distance $\leq z'$ from the wall). $R_{\max}$ is the outer cutoff of the fractal regime. The con-

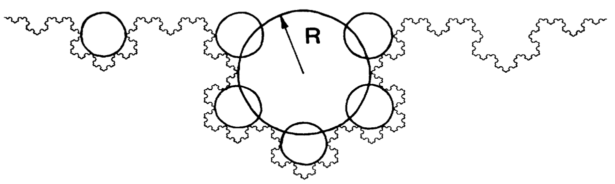

FIG. 2. Replacement of the fractal surface by a set of spherical pores of variable radius R.

stant B is determined from the condition that Eq. (8) equals the monolayer volume $\Omega(a)$ for $z'=a$. This gives

$$4\pi B/3=\Omega(a)a^{D-3}(3-D)(2-D)(1-D)D/6$$

in the limit $R_{\max}\gg a$. The coverage N at pressure P is obtained by setting z' in Eq. (8) equal to the equilibrium thickness Eq. (7):

$$N=\rho\int_0^{R_{\max}}\omega(z(P,R),R)BR^{-D-1}dR\,. \tag{9}$$

Insertion of the expressions for ω, z, and B yields

$$N=kN_m(\zeta_P/a)^{3-D}, \tag{10}$$

with

$$k=2^{(1-D)}\Gamma(D+1)\Gamma(\tfrac{3}{2})/\Gamma(D-\tfrac{1}{2})\,.$$

The gamma functions result from taking $R_{\max}/\zeta_P\to\infty$, integration by parts, and tabulated relations. Equation (10) differs from the previous result Eq. (5) by only the proportionality factor k. Thus multiple-wall effects give at most a change in prefactor, leaving the exponent unaffected. In view of the distinct approximations, it is remarkable that $1\le k\le 1.042$ in the entire range $2\le D\le 3$.

We note for comparison two recent results: Cohen, Guyer, and Machta[13] explored the problem of adsorption on a surface pockmarked with a self-similar distribution of pores. Their approximations differ from ours, as does their result.[14] Cheng, Cole, and Stella[15] computed the exact potential $v(\mathbf{r})$ for an explicit model surface which is planar at small length scales and fractal at large scales. Omitting surface tension, as was done here, they find agreement with Eq. (5) in the fractal regime and with Eq. (3) in the planar regime of film thickness.

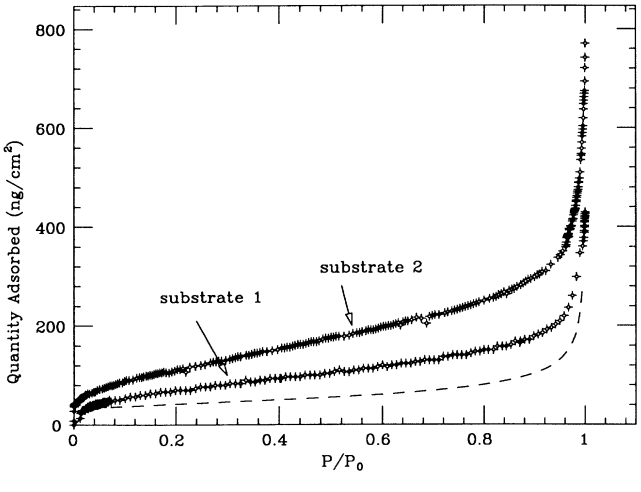

FIG. 3. Adsorption data for N_2 on two rough Ag substrates at 77 K. The substrates consist of electron-beam evaporated silver on quartz. We measure the quantity adsorbed in units of ng/cm^2 where the reference area is the macroscopic surface area of the electrode, i.e., the area of a hypothetical planar deposit. The dashed line shows the isotherm calculated for a flat surface, Eq. (3).

In Fig. 3 we present adsorption data for N_2 at 77 K on two rough Ag surfaces. The samples are the silver electrodes plated on quartz crystals normally employed in microprocessor circuits.[16] If we identify the coverage at $P/P_0\cong 0.05$ ("knee") with monolayer coverage, the experimental curves in Fig. 3 give N_m values approximately 2 and 3 times, respectively, that of a flat Ag surface. Thus from a conventional roughness viewpoint the two Ag samples have a roughness factor of 2 and 3. We now show that the isotherms suggest that the two samples have actually the same roughness (in the fractal sense), namely, a fractal dimension of $D=2.30\pm0.02$, and that the different N_m values are due to different upper limits of the fractal regime. Figure 4 exhibits that the two isotherms obey Eq. (5), or equivalently Eq. (10), over a range of $\ln(P_0/P)$ from 0.03 to 0.5 and from 0.003 to 0.5, respectively. The least-squares fit (to the linear region) results in $D=2.30$ for both samples, with a correlation coefficient of 0.997 and 0.993. The range of the fractal behavior is obtained as follows. The lower end of the pressure range where Eq. (5) holds, $\ln(P_0/P)=0.5$, corresponds to a coverage of $N=2.7N_m$ (for both samples) and thus to a layer thickness $z=2.7a$ if we assume the samples to be smooth up to that coverage. Taking $a\approx 3$ Å for N_2, we obtain $z_{\min}=8$ Å for the lower end of the fractal regime. The upper end, $z_{\max}$, is obtained from

$$\frac{z_{\max}}{z_{\min}}=\left[\frac{\ln(P_0/P_{\min})}{\ln(P_0/P_{\max})}\right]^{1/3} \tag{11}$$

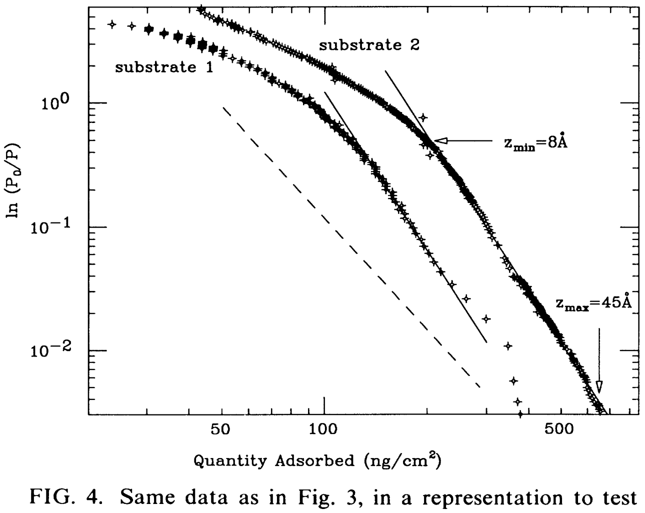

FIG. 4. Same data as in Fig. 3, in a representation to test for Eq. (5). The solid lines show the fit of Eq. (5) to the data. The dashed line corresponds to adsorption on a flat surface, Eq. (3). Note that $\ln(P_0/P)\approx(P_0-P)/P_0$ in the regime of interest ($P\to P_0$).

[recall Eq. (2)], giving $z_{\max,1}=20$ Å and $z_{\max,2}=45$ Å where the subscripts refer to the respective substrates. As the two substrates have the same $z_{\min}$ and D, a simple application of the fractal mass-radius relation[1] implies that the monolayer values should satisfy $N_{m,1}/N_{m,2}=(z_{\max,1}/z_{\max,2})^{D-2}$. This predicts $N_{m,1}/N_{m,2}=0.8$, consistent with the original value of ≈ 0.7 for this ratio. For substrate 2, the isotherm follows Eq. (5) up to the largest measured pressures. For substrate 1, the departure from Eq. (5) at large pressures is interpreted as due to nonfractal roughness above 20 Å. The departure from Eq. (5) at low coverage, for both samples, is in agreement with the remark after Eq. (5). The fact that the two samples, made by different manufacturers, give the same D value is quite remarkable. In contrast, measurements on some 30 other rough deposits (non-Ag) did not give any significant linear behavior in plots of the same type as Fig. 4.[17] More recently, scanning-tunneling-microscopy (STM) studies were carried out on a Ag surface prepared by the same manufacturer as substrate 2, and whose adsorption characteristics revealed a D value of 2.32.[18] The STM result is $D=2.30\pm0.10$ over a range of 5-50 Å (from pore-volume distributions and power spectra), in excellent agreement with the thermodynamic results presented here. Details will be published elsewhere.

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