Wetting of Fractally Rough Surfaces

Recently,[1] Pfeifer, Wu, Cole, and Krim (PWCK) studied multilayer adsorption on fractally rough surfaces, considering the fractal geometry and van der Waals forces. We show that surface-tension effects, which PWCK omit, lead to a universal divergence of the wetting layer thickness on self-similar fractals,[2] quite possibly invalidating their interpretation of adsorption isotherms. We offer an alternative interpretation that roughness of the surface is better described by self-affine fluctuations[3] with an exponent $\zeta_S \approx 0.37$.

Consider a self-similar surface with fractal dimension $d_f > 2$ between length scales l_1 and $l_2 > l_1$. The volume of voids above the surface up to a height z scales as[2] $\Omega(z) \approx l_2^{d_f} z^{3-d_f}$. The free energy of the wetting layer is given by[2,4]

$$\delta f(z) \approx l_2^{-2} \Omega(z) [u/z^{\sigma} + \mu + K/z] , \tag{1}$$

where $\sigma = 3$ (or 4) for nonretarded (retarded) van der Waals forces of amplitude u, μ is the liquid-vapor chemical potential difference, and K is the surface tension. The last term comes from the smoothening of the layer surface [its area scales as $S(z) = d\Omega(z)/dz \approx l_2^{d_f} z^{2-d_f}$]. As $\mu \to 0$, the equilibrium thickness z_e diverges: For small μ or large z ($l_1 < z_c < z_e < l_2$), $z_e \propto K\mu^{-1}$. This leading behavior is highly universal: The exponent is independent of d_f and σ. Similarly, the coverage N scales as $N \propto \mu^{-(3-d_f)}$, independent of σ.

Since PWCK omit the surface-tension term in Eq. (1), they obtain

$$z_e \propto \mu^{-1/\sigma}, \quad N \propto \mu^{-(3-d_f)/\sigma} , \tag{2}$$

valid only for films smaller than a crossover thickness z_c, such that surface tension is unimportant. As usual z_c is not precisely defined: $z_c^{(1)} = (u/K)^{1/(\sigma-1)}$ from Eq. (1), or $z_c^{(2)} = [d_f u/(d_f - 2)K]^{1/(\sigma-1)}$ from $\delta f(z_e) = 0$. For N_2 on Ag,[1] we find $z_c^{(1)} \approx 4$ Å, and assuming $d_f = 2.3$, $z_c^{(2)} \approx 12$ Å, in qualitative agreement with an estimate of Pfeifer, Kenntner, and Cole,[5] $z_c = 19$ Å. Since the observed power-law regime extends from 8 to 20 or 45 Å,[1] the interpretation in terms of a self-similar fractal with $d_f > 2$ is quite suspect.[6]

There is now emerging consensus that scanning-tunneling-microscopy pictures, with no overhangs, provide a reliable description of the substrate roughness. Thus a better characterization is that the substrate is self-affine; i.e., its height fluctuations over a distance L scale as L^{ζ_S}. (In this case, $d_f = 2$, although one can define a local fractal dimension $D_f = 3 - \zeta_S$.[3]) As shown by Andelman, Joanny, and Robbins,[7] there is a characteristic healing length ξ_H (diverging with the film thickness). For length scales less than ξ_H the surface is smooth due to surface tension, while for larger scales it follows the substrate. Incorporating the resulting surface energy, the free energy per unit area is[4]

$$\delta f(z) \approx z[u/z^{\sigma} + \mu + KA_S/z^{\tau+1}] , \tag{3}$$

where $\tau = 2(1-\zeta_S)/\zeta_S$, and A_S is related to the *amplitude* of substraight height fluctuations. [A proof of Eq. (3) from a functional renormalization-group treatment will be given elsewhere.] When the surface-tension energy in Eq. (3) dominates, the adsorption isotherms are determined by ζ_S. Indeed the experimentally observed power law is consistent with $\zeta_S \approx 0.37$. However, this value of ζ_S is too small to overcome the van der Waals attraction asymptotically. For sufficiently thick films, a crossover to van der Waals–dominated wetting is expected for $z > z_c = (KA_S/u)^{1/(\tau+1-\sigma)}$, since $\tau + 1 > \sigma$. The position of this crossover depends on microscopic features of the substrate (such as A_S), and is not universal.

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