

Pfeifer, Cole, and Krim Reply: Kardar and Indekeu¹ (KI) raise questions concerning our analysis² of N₂ multilayers on fractally rough Ag surfaces: (A) Is it legitimate to omit surface tension in that experimental analysis? (B) How does the exponent y in the adsorption isotherm $N \propto \mu^{-y}$ depend on self-affine surface roughness in a case where surface tension cannot be omitted? We have addressed these questions in detail elsewhere^{3,4} and review here why our conclusions disagree with KI. We adopt the notation of KI.

(A) For a self-similar surface with fractal dimension d_f , one may treat the competition between the substrate potential ($-u/z^3$ at a distance z from a flat surface) and the film-vapor surface tension K by taking the spherical-pore model in Ref. 2 and including the curvature energy of the film in a straightforward way. The result is³ $N \propto \mu^{-(3-d_f)/3}$ for $\mu \gg u/z_c^3$ (low coverage, van der Waals wetting) and $N \propto \mu^{-(3-d_f)}$ for $\mu \ll u/z_c^3$ (high coverage, capillary wetting). The crossover film thickness z_c depends on u , K , d_f , and the number density n of the film. For N₂/Ag and $d_f=2.3$,² one obtains $z_c=19 \text{ \AA}$ (calculated u) or $z_c=33 \text{ \AA}$ (experimental u).³ We believe this is the best available estimate of z_c : It allows for variable substrate potential and film thickness in different voids, and it is a *lower bound* for the experimental value of z_c . The experimental z_c is higher because in the model all radii of curvature of the film are negative, which overestimates the effect of surface tension; and because the Ag surface is planar at scales $> 50 \text{ \AA}$ [scanning tunneling microscopy (STM)], leaving little room for capillary wetting. Appreciable capillary wetting would give an isotherm steeper than observed at high coverage. Thus omission of surface tension is justified because the observed behavior $N \propto \mu^{-(3-d_f)/3}$ for films $\leq 45 \text{ \AA}$ is consistent with the expected z_c . This conclusion is unchanged by the fact that the Ag surface is self-affine instead of self-similar (local dimension $d_f=2.3$, global dimension 2, crossover length $b \approx 50 \text{ \AA}$ from local to global).⁴ Another treatment of the two types of wetting is to assume that the film-vapor interface has uniform distance z from the surface S and the potential at distance z from S equals $-u/z^3$. Then for arbitrary S , the film free energy is⁴

$$F(z) = n \int_a^z \left[-\frac{u}{(z')^3} + \mu \right] \frac{d\Omega(z')}{dz'} dz' + K \frac{d\Omega(z)}{dz}, \quad (1)$$

where $\Omega(z)$ is the volume of points outside the solid a distance $\leq z$ from S , and $a \approx$ monolayer thickness. For self-similar S , one has $\Omega(z) \propto z^{3-d_f}$ and minimization of (1) yields $n(-u/z_e^3 + \mu) - (d_f - 2)K/z_e = 0$ and $z_c^2 = nu/(d_f - 2)K$ for the equilibrium and crossover thicknesses z_e and z_c . Equation (1) corrects Eq. (1) of KI. Both give the same exponents y for self-similar S , but the KI equation gives incorrect prefactors for z_e and z_c .

(B) Consider a self-affine surface S with local dimension $d_f > 2$ (roughness exponent $\zeta_S = 3 - d_f$), global di-

mension 2, and crossover length b .⁴ For film thickness $z \gg b$, this requires special treatment: S in that regime scales like a flat substrate and the surface-tension contribution $\Delta(z)$ to the energy comes from *correction* to scaling of $S(d_f)$. We write $F(z) \approx L^2[nu/2z^2 + n\mu z + K \times \Delta(z)]$, where L^2 is the basal area of S and additive constants are omitted. Currently there exists three different proposals for $\Delta(z)$:

$$\Delta(z) = \zeta_S (b/z)^{1-\zeta_S}, \quad (2a)$$

$$\Delta(z) = \zeta_S [\Gamma(\zeta_S + 1)]^2 (3nu/4Kb^2)^{1-\zeta_S} (b/z)^{4(1-\zeta_S)}, \quad (2b)$$

$$\Delta(z) = \text{const} \times (b/z)^{2(1-\zeta_S)/\zeta_S}. \quad (2c)$$

Equation (2a) results from (1) and correction to scaling for $\Omega(z)$;⁴ (2b) results from a modified perturbation expansion *à la* Andelman, Joanny, and Robbins;⁵ (2c) is the expression of KI (or Lipowsky and Fisher⁶ for a film with roughness exponent ζ_S). For $z \rightarrow \infty$, minimization of $F(z)$ for (2a)-(2c) yields $y = 1/(2 - \zeta_S)$, $y = \max\{\frac{1}{3}, 1/(5 - 4\zeta_S)\}$, and $y = \max\{\frac{1}{3}, \zeta_S/(2 - \zeta_S)\}$, respectively. Thus (2a)-(2c) give different exponents and we feel it is premature to single out (2c) as superior, as KI do, before more detailed studies have been done. In fact, the exponent $y = \zeta_S/(2 - \zeta_S)$ proposed by KI from (2c), for the interpretation of the N₂/Ag data, can be ruled out experimentally because the resulting value $\zeta_S = 0.37$ disagrees with the STM value $\zeta_S = 0.7$.

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¹M. Kardar and J. O. Indekeu, preceding Comment, Phys. Rev. Lett. **65**, 662 (1990).

²P. Pfeifer, Y. J. Wu, M. W. Cole, and J. Krim, Phys. Rev. Lett. **62**, 1997 (1989).

³P. Pfeifer, J. Kennner, and M. W. Cole, in Proceedings of the Third International Conference on the Fundamentals of Adsorption, edited by A. Mersmann (American Institute of Chemical Engineers, New York, to be published).

⁴P. Pfeifer and M. W. Cole, New J. Chem. **14**, 221 (1990).

⁵D. Andelman, J.-F. Joanny, and M. O. Robbins, Europhys. Lett. **7**, 731 (1988); P. Pfeifer (unpublished).

⁶R. Lipowsky and M. E. Fisher, Phys. Rev. Lett. **56**, 472 (1986).