### Wetting and nonwetting of molecular films at zero temperature

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The wetting characteristics of classical rare gases adsorbed on smooth solid substrates at zero temperature are studied as a function of the molecule-substrate interaction. Comparisons of the relative stabilities of monolayers, bilayers, and trilayers with respect to each other and to the bulk solid phase show a succession of growth regimes with increasing substrate interaction strength relative to molecular pair interactions: nonwetting, incomplete wetting with maximum thicknesses of one layer, incomplete wetting with a mutually commensurate bilayer, and complete wetting. Their order of appearance and the values of substrate strength at crossover boundaries depend sensitively on substrate potential shape, substrate screening of interactions between adsorbate atoms, and the magnitude of the bulk solid energy. Close correspondence with experiment is obtained from Cole-Klein potentials with enhanced first-layer well depths and with substrate screening. This model has a narrow complete wetting region with boundaries at relative substrate strengths near those observed in films on graphite. The complete wetting regime is bounded on the high-strength side by incomplete wetting films consisting of mutually commensurate close-packed bilayers, and on the low-strength side by close-packed monolayers. At still weaker substrate potentials the adsorption is nonwetting. The layer densities of the incompletely wet films are found to be several percent greater than surface planes of the bulk solid, supporting the conjecture that the transition from complete to incomplete, with increasing substrate strength, is driven by structural mismatch between the film and the bulk solid. These features are consistent with observations of light molecular gases on graphite and other surfaces.

#### I. INTRODUCTION

There is a considerable amount of current interest in the wetting characteristics of molecular films adsorbed on solid substrates.<sup>1</sup> Three principal classes of wetting are observed. In "complete wetting" or "type-1 growth" the films remain uniformly flat with increasing pressure, and grow asymptotically toward infinite thickness at the saturation pressure  $P_0$  of the bulk phase. This contrasts with "incomplete wetting" or "type-2 growth," where the film is uniform only up to a finite thickness, usually one or two molecular layers, with a bulk phase forming abruptly at  $P_0$ . In extreme cases of type-2 growth, termed "nonwetting" or "type-3 growth," there is virtually no adsorption of uniform film at  $P < P_0$ , but only bulk condensation at the saturation pressure. The same types of growth are seen in chemisorbed and metallic films, where classes 1, 2, and 3 are, respectively, termed "Frank-van der Merwe," "Stranski-Krastanov," and "Volmer-Weber" growth.<sup>2</sup> Recent experiments on physisorbed molecular films $^{3-5}$  have shown that type-2 growth is predominant at low temperature. On graphite substrates at low T only Ar, Kr, and Xe exhibit type-1 behavior,<sup>3,4</sup> while on Au(111) surfaces all simple molecules studied to date form type-2 films.<sup>5</sup> It is believed that the principal factors controlling low-temperature growth are the relative strengths of the molecular-substrate and moleculemolecule interactions.<sup>1</sup> Theoretical studies, which predicted universal type-1 growth for relatively strong substrates, were based on film models of uniform density and structure.<sup>1</sup> However, recent experiments show that

the type-1 region is restricted to a narrow range of relative interaction strength, and that type-2 growth is reentrant at weaker and stronger substrate binding. It has been suggested that the reentrant type-2 regime at strong substrate binding is due to film compression, which causes a mismatch with the bulk structure.<sup>3,4</sup> The experiments have stimulated the development of improved models which relax the constant-density condition. A recent calculation based on a lattice-gas model does display reentry on strong substrates.<sup>6</sup> A study of model rare-gas films shows the possibility of reentry, but the mode of growth at low temperature is quite sensitive to the detailed range dependence of the substrate potential.<sup>7</sup>

In the present work we examined a series of film and substrate models where the forms of the potentials and their parameters are those of current approximations to physical systems. All of the models assume a smooth solid substrate. Extensive calculations explored each of the models over wide ranges of interaction parameters. The results confirm the sensitivity of growth to the detailed form and strength of the substrate interaction. For certain models we obtain reentrant wetting similar to the observed behavior. We also find that more complicated sequences may occur, having very narrow but distinct growth regimes within the main sequence. In agreement with experiment, the calculated maximum thickness of type-2 films in the reentrant strong-substrate region was typically found to be two layers. The two layers have identical structures and are mutually registered. The layer densities of the films in the strong-substrate type-2 regime are significantly different from that of the close-packed

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planes of the bulk phase, supporting the conjecture that the incomplete wetting on strong substrates is caused by substrate-potential-driven film-bulk solid lattice mismatch.

### II. EQUILIBRIUM BETWEEN FILM AND BULK AT LOW TEMPERATURE

We are concerned with the equilibrium structures of layered films at coexistence with the unconstrained bulk phase. The system chemical potential  $\mu$  is therefore fixed at the value  $\mu_0$  of the bulk at its saturated vapor pressure. If the substrate area and total particle number are also fixed, equilibrium between film and bulk corresponds to the minimum of the thermodynamic potential  $\Omega$ .<sup>8</sup> At very low temperature  $\Omega = E - N\mu$ , and hence equilibrium occurs at minimum total energy E. In order to apply the equilibrium condition it is necessary to calculate, for each set of model parameters, the structures and energies of the various possible film phases at  $\mu = \mu_0$ . The stable film phase at coexistence can then be determined by examining the total system energy as a function of the distribution of particles between bulk and film. In the example below we compare the stabilities of a monolayer and a bilayer film.

The surface densities and average energies per molecule in the monolayer and bilayer at  $\mu_0$  are denoted here by  $n_m, n_b$  and  $e_m, e_b$ , respectively. The molecular energies contain the contributions of the molecule-substrate and molecule-molecule interactions. The minimization condition yields, for the growth of the bilayer phase,

$$n_b e_b - n_b \mu_0 < n_m e_m - n_m \mu_0 . \tag{1}$$

If the bilayer is the stable phase at coexistence, then the growth of a trilayer must be unfavorable, which is indicated by the relation

$$n_b e_b - n_b \mu_0 < n_t e_t - n_t \mu_0 , \qquad (2)$$

where  $n_t$  and  $e_t$  refer to the density and average energy in the trilayer. Comparisons such as those above can be carried out for any thicknesses, but we have not extended the detailed calculations of film phases beyond trilayers. Where trilayers are found to be stable, we take it to be an indication of type-1 behavior. Justification for this criterion is presented in Sec. IV.

### III. FILM MODELS AND THEIR STABLE PHASES

In all of the calculations, we modeled the moleculemolecule interactions by Lennard-Jones 6-12 pair potentials,

$$v(r) = 4\epsilon_0 [(\sigma/r)^{12} - (\sigma/r)^6] .$$
(3)

The principal differences among the several models involve different forms of the molecule-substrate potential, although when substrate shielding effects were included, these caused changes in the effective interaction between molecules in the first layer. In the following sections we discuss each of the models in detail.

## A. Model 1: Krypton on smooth "graphite" with integrated 6-12 potentials

The parameters for v(r) were taken to be those for Kr:<sup>9</sup>  $\epsilon_0 = 201.9 k_B$  and  $\sigma = 3.57$  Å. The molecule-substrate interaction in this model is an integrated Lennard-Jones potential

$$u(z) = \alpha \left[ \frac{2}{15} (\sigma/z)^9 - (\sigma/z)^3 \right] \text{ with } \alpha = 2\pi\epsilon/3\rho_g \sigma^3 , \qquad (4)$$

where  $\rho_g$  is the density of the substrate atoms. The potential parameters are assumed to be given by the semiempirical combining laws:<sup>10</sup>

$$\epsilon = (\epsilon_0 \epsilon_g)^{1/2}, \ \sigma = (\sigma_0 + \sigma_g)/2,$$
 (5)

with the effective graphite parameters<sup>11</sup>  $\epsilon_g = 27.8 k_B$  and  $\sigma_g = 3.37$  Å. The relative strength of the substrate interaction was characterized by the ratio  $S = u_1/\mu_0$ , where  $u_1$  is the single-particle binding energy to the substrate. For the 9-3 potential,  $u_1 = -1.248\alpha$ .  $\mu_0$  is equal to the sublimation energy of the solid at T=0. For most of the calculations we set  $\mu_0 = 8.6\epsilon_0$ , corresponding to the theoretical relation for classical Lennard-Jones fcc solids,<sup>12</sup> but in model 4 we varied the ratio by 5% above and below this value to explore the sensitivity of wetting to the bulk cohesive energy. S was varied by changing the value of the "graphite" density  $\rho_g$ .

The Kr molecules were deposited on the substrate in different assumed configurations, and the average total molecular energies e due to intermolecular and moleculesubstrate interactions were calculated for each value of S. The intermolecular energies were computed by pairwise sums over the atoms in successive neighbor shells. Layer-substrate and interlayer separations were varied to find the equilibrium separations. The total energy was found to be essentially constant beyond a radius of 25 nearest-neighbor distances, but the sums were extended to twice this distance. The excellent convergence of the lattice sum is illustrated in Fig. 1.

Energies were thus obtained for various values of the film density n, and the chemical potentials calculated from the energy and its derivative,

$$\mu = e + n \frac{de}{dn} . \tag{6}$$



FIG. 1. Total energy per atom in a close-packed monolayer having Lennard-Jones 6-12 pair interactions as a function of the radius of neighbor shells included in the lattice sum. The atoms are adsorbed on a smooth attractive substrate.

Unique solutions of Eq. (6) for positive spreading pressure  $n^2 de / dn$  at  $\mu_0$  yielded the equilibrium values for e and n for each configuration. A series of such calculations was performed for selected values of S. The principal calculations were made for three film configurations: a triangular close-packed monolayer, a close-packed bilayer composed of two mutually registered layers, and a close-packed trilayer composed of three mutually registered layers. Comparisons with incommensurate and misregistered structures showed that the mutually registered configurations are more stable, consistent with experimental observations<sup>13</sup> and calculations<sup>14</sup> on specific systems.

The final stage was a comparison of the stabilities of the three film configurations relative to bulk phase, as outlined in Sec. II. The results are shown in Figs. 2 and 3. Figure 2 compares the densities of the film phases with that of the bulk over a wide range of S, extending well beyond that of classical noble gases on graphite, e.g., for Ne the estimated S equals  $1.55.^4$  All densities increase monotonically with S. Below S=1 the densities of the atomic planes of the films are smaller than that of the close-packed (111) planes of the bulk, while at higher S they are greater. Monolayer densities are the most responsive to changes in substrate binding; for example, at S=1,  $n_m$  is approximately 24% greater than that of the unconstrained monolayer in equilibrium with its twodimensional vapor. Trilayers are the least responsive to substrate binding and lie closest to the bulk density over the entire S range, while bilayers are intermediate at all S. Thus on strong substrates the density is greatest for monolayers and least for trilayers. This trend is due to the interplay between the lateral compression by the substrate attraction and the stabilization by intermolecular forces in crystalline configurations. This general result agrees with observations on Xe (Ref. 13) and Ne (Ref. 14)



FIG. 2. Densities of atomic planes of Kr monolayers, mutually commensurate bilayers, and mutually commensurate trilayers coexisting with the fcc solid at T=0. The substratemolecule interaction is assumed to be the 9-3 potential obtained by integration of 6-12 pair interactions. The S scale is the relative substrate strength  $u_1/\mu_0$ , where  $u_1$  is the single-atom adsorption energy and  $\mu_0$  is the cohesive energy of the fcc solid. Densities are compared with that of (111) planes of the solid, shown as the horizontal line at n=0.0762 Å<sup>-2</sup>.



FIG. 3. Thermodynamic energies of Kr monolayer and commensurate bilayer films in equilibrium with a bulk solid as a function of relative substrate strength. The model substrate potential and scale S are the same as in Fig. 2. The ordinate scale is the total energy per molecule in the monolayer or bilayer relative to that in the trilayer. The graph shows that below S=0.6no film is stable, indicating nonwetting, i.e., type-3 adsorption. Above this value the regime is complete wetting, i.e., type 1.

films, which show that the density of the commensurate bilayer is less than that of a coexisting monolayer on relatively strong substrates.

Figure 3 compares the stabilities of the three film configurations with coexisting bulk. We see that none of the film phases are stable below S=0.6, and that the trilayer is the stable film phase above S=0.6. Thus the wetting sequence as a function of increasing substrate strength progresses from nonwetting, i.e., a type-3 regime, to a type-1 film. The type-3 regime appears at low S in all of the model calculations, in agreement with analytic models and with experiments.<sup>1</sup> However, we find no type-2 region within the explored S range, in disagreement with experiment. This discrepancy led us to examine other models of the substrate-molecule interaction differing in the form of u(z). In models 3-5 indirect screening of v(r) was included.

# B. Model 2: Kr on smooth substrates with modified first-layer binding

This model was similar to model 1, except that the interaction between the substrate and the first film layer was changed relative to higher layers, the energies of the second and third layers being kept at their 9-3 values. It is known<sup>10</sup> that the first-layer well depths of noble gases on graphite and other solids are considerably greater than those given by Eq. (4). The empirical factor of increase is approximately 2–3, but is not known precisely for arbitrary molecule-substrate combinations. We investigated the effects of first-layer factors between 1.9 and 2.5. The separate stages of the calculations were performed as in model 1. Since model 2 is only one stage of a more complete model 3, it is discussed in the following section.

### C. Model 3: Kr on model-2 graphite with substrate screening

Molecules adsorbed on a polarizable substrate induce image dispersion forces which oppose the direct attractive interactions between molecules. This partial screening effect depends on the nature of the substrate and the molecule-substrate distance: It is estimated to be 20-30% of the direct attraction between Kr molecules in the first layer on graphite, and to have a much smaller effect on higher layers.<sup>10</sup> We introduced screening into model 2 by two alternate methods: through a factor which reduced the first-layer lateral interaction, and by the expression of McLachlan,<sup>15</sup> in the form given by Rauber *et al.*<sup>16</sup> The combined effects of screening and first-layer enhancement were explored by independent variations.

The results are summarized in Fig. 4, which presents the wetting sequences calculated for several sets of enhancement and screening factors. It can be seen that the sequence of wetting regimes and the S values at crossover from one regime to another are highly sensitive to the first-layer well depth and to the magnitude of screening. Even the order of successive growth types varies: In most sequences a type-1 regime occurs, but in others it is absent over the entire range of S. In several cases the bilayer is the stable film phase (type 2b) in the upper part of the S range; but in some, the high-S films are type 1. Two features remain the same, however. At low S the adsorption is type 3, and when this is immediately followed by partial wetting, the film is a monolayer (type 2m).



FIG. 4. Wetting sequences for Kr on model-3 substrates. The model interaction has the 9-3 form, except that first-layer binding energies are enhanced by different factors, which are given as the first number to the left of each sequence. Substrate screening by image forces is included in the top four sequences by a reduction of first-layer lateral interactions, by the factor given as the second number to the left of each sequence. In the remaining four sequences the screening is calculated from theory.

These two features persisted in all of the subsequent calculations.

### D. Model 4: Noble gases on graphite, with Cole-Klein potentials

Several major changes were made from the previous calculations. Here we abandoned pseudographite, and instead varied the relative strength of the molecule-molecule interactions through the values for the rare gases, while keeping the substrate density fixed at the normal graphite value. The empirical molecular diameters of the rare gases increase nearly linearly with the pair potential parameter  $\epsilon_0$  over the series. We constructed a model series by a linear regression fit to the measured coefficients, which is illustrated in Fig. 5. This linear scale for a model rare-gas "continuum series" permitted us to study the wetting behavior of actual gases on graphite and pseudo noble gases beyond the physical range.

Cole and Klein<sup>11,17</sup> have proposed a new analytic potential for noble gases on graphite. The new form results from an analysis of He scattering studies, which indicate that the effective pair potential between adsorbed and graphite atoms is anisotropic, as well as an extension to other rare-gas molecules. The laterally averaged potential between rare-gas molecules and the basal-plane surface of graphite is given by as

$$u(z) = \frac{4\pi\epsilon\sigma^6}{a_0d^4} \left[\frac{2}{5} \left[\frac{\sigma}{d}\right]^6 \zeta \left[10, \frac{z}{d}\right] - \zeta \left[4, \frac{z}{d}\right]\right], \quad (7)$$

where

$$\xi(n,x) = \sum_{j=0}^{\infty} (j+x)^{-n} .$$
(8)

Here a=5.24 Å is the area of the graphite-basal-plane unit cell and d=3.37 Å is the graphite planar spacing. The values  $\sigma_g = 2.84$  Å and  $\epsilon_g = 24.7k_B$  (Ref. 11) were chosen by Cole and Klein to be consistent with the above equations and the optimized parameters for He/graphite



FIG. 5. Lennard-Jones pair potential energies and molecular diameters of the noble gases. The empirical values are approximated by the linear regression line, which is used in the calculations of model-4 systems.

films determined from scattering studies.<sup>17</sup> The appropriate potentials  $\epsilon$  and diameters  $\sigma$  for specific molecules are assumed to be given by the conventional combining rules. Equations (7) and (8) show considerably deeper well depths for first-layer molecules than the 9-3 potential, and are thus in better agreement with experiment. There is also an appreciable enhancement of the interaction at second-layer distances relative to the long-range  $z^{-3}$  potential.

We calculated film stabilities with the Cole-Klein potentials for the model rare-gas series on graphite using the effective values  $\sigma_g$  and  $\epsilon_g$  estimated by Cole and Klein as input parameters.<sup>11</sup> Substrate screening was included in the form described above. The results show the type-3 and -2m regions at low S as in the previous models. A type-1 regime follows, but the sequence does not exhibit any type-2 region at high S. We therefore explored modified Cole-Klein potentials, enhancing the first-layer well depth by different factors. Complete calculations were performed for enhancement factors of 1.5, 2.0, 2.5, and 3.0. In addition, we also investigated the sensitivity of the wetting behavior to the precise value of the bulk energy, varying the ratio  $u_1/\mu_0$  by 5% above and below the theoretical ratio of 8.6, for a first-layer enhancement factor of 2.0. Discussion of the significance of these modifications, and comparisons with experimental values, are presented in Sec. IV.

Of this set of calculations, one yielded the reentrant sequence indicated by experiment. The full sequence, shown in Fig. 6, was obtained with first-layer enhancement factor of 2.5. As in the previous models the calculation predicts a type-3 regime at low S. This is followed by incomplete wetting, type 2m. The next regime at higher S is type 1: It is fairly narrow with crossover boundaries at S=1.6 and 2.2. The film densities are similar to those of the previous calculations (see the discussion of model 1 above), with regard to the trends with S: Figure 7 presents these results at selected S values.

### **IV. DISCUSSION**

The model calculations show that wetting behavior is extremely sensitive to the substrate potential, substrate screening of molecular interactions, and to the cohesive energy of the bulk solid. Each of these were studied over ranges encompassing their estimated physical forms and values in an attempt to reproduce experimental results reasonably well. The most successful set comprises a modified Cole-Klein substrate potential<sup>17</sup> with substrate screening. In order to obtain the experimental sequence of growth regimes it is necessary to modify their proposed form, deepening the substrate well for the first adsorbed layer by a substantial factor. To a certain extent, the fac-



FIG. 6. Wetting sequence of noble gases on graphite, according to the model-4 system, with empirical parameters chosen for the closest correspondence to experiment.



FIG. 7. Density of atomic planes of monolayers, bilayers, and trilayers in equilibrium with bulk solid at T=0. The model system is the same as in Fig. 6.

tor required to bring the calculation into agreement with wetting experiments is probably an artifact of the evident sensitivity of the calculation to all of the terms in the energy and their interplay. However, we find that a considerable enhancement factor must be applied to the earlier Cole-Klein potential for the heavier gases to bring the predicted single-atom binding energy into agreement with low-coverage measurements. For example, the predicted  $u_1$  for Xe is  $1530k_B$ , while experiment<sup>4</sup> gives  $2260k_B$ , a factor of 1.5 larger. Other sets of potentials and parameters might well provide equally satisfactory, or even closer, correspondence to observations. All of the models contain several simplifications, which, given the sensitivity to details, may be significant. We have already noted the sensitivity to substrate cohesive energy, which in the last calculation was assumed to be equal to  $8.6\epsilon_0$ . However, measured values for the heavy rare gases are lower by as much as 20%. We have also assumed throughout the calculation that the molecule-molecule interactions are described by Lennard-Jones pair potentials. However, improved forms have been proposed: We note that Gittes and Schick<sup>7</sup> find that wetting behavior may be significantly changed by different pair potential forms. Additional approximations include the assumption of a smooth substrate and the neglect of many-body effects in the film. The smooth-substrate assumption would seem a reasonable approximation to incommensurate films, but may not be adequate to the level required.

Nevertheless, the final model-4 calculation is qualitatively and semiquantitatively in agreement with experiment. The narrowness of the type-1 regime suggested by measurements on graphite, and confirmed by studies on gold, is an important result. Its boundaries to regimes at lower and higher S are about 30-50 % higher than the estimated experimental boundaries. At higher S the predicted growth mode is type 2b. There are no classical rare gases in this range since Ne and He have appreciable quantum corrections. However, it is worth noting that Ne/graphite films do exhibit type-2b growth. He/graphite films are particularly interesting systems, and they are discussed separately below.

Although these adsorbates exhaust the raregas/graphite series, the calculation appears to provide a

good general description of all physisorbed films. Many molecular films have been studied on graphite and other substrates, and they are all found to be type 2 or 3 at low temperature. Bienfait et al.<sup>4</sup> have analyzed their recent experiments and previous work with graphite surfaces. Among the group are water, carbon dioxide, ethylene, oxvgen, nitrogen, Ne, <sup>4</sup>He, <sup>3</sup>He, methane, <sup>18</sup> Xe, Kr, and Ar, and all except the last four form type-2 films at low temperature. None of the type-2 films have S values within the Xe, Kr, and Ar range. Type-2 behavior has also been reported for nitric oxide<sup>19</sup> and carbon tetrafluoride<sup>20</sup> on graphite, ethylene on boron nitride and carbon tetrafluoride on bromide,<sup>21</sup> carbon tetrafluoride and carbon hexafluoride on copper,<sup>22</sup> and chloromethane, ethylene, and cyclopropane on cadmium.<sup>22</sup> On Au surfaces, Ar, Kr, Xe, nitrogen, oxygen, methane, and ethane have type-2 growth below their triple points.<sup>5</sup> It is particularly interesting that even Ar, Kr, and Xe are type 2b on gold, which has appreciably stronger binding than graphite, yielding Svalues within the calculated 2b region. We are not aware of any systems which form type-1 films at low temperature, other than the heavier rare gases and possibly methane<sup>18</sup> on graphite. An additional correspondence with experiment is the prediction that incomplete wetting at low S is type 2m, and this is what is observed in most films in this range.<sup>23</sup> At still lower S, our calculations agree with earlier theories,<sup>1</sup> that sufficiently weak substrates produce type-3 systems. The theory predicts cyclic type-1-type-2 behavior on very strong substrates, but with the exception of He/graphite, there are no physical systems in this high range.

The calculated density differences between the type-2-film planes and bulk solid surfaces are consistent with experiment. Direct observations of lattice mismatches have been obtained from high-energy diffraction studies:<sup>3,4</sup> It is estimated that type-2b films have lattice parameters a few percent smaller than coexisting bulk structures.<sup>24</sup> As shown in Fig. 7 we calculate that the density excess of bilayer over bulk planes at the upper type-1 boundary is approximately 3%. It is worth noting that the film densities exceed that of bulk planes throughout the domain of stable films, down to the upper limit of nonwetting. This result is counterintuitive, for it seems to imply that the lateral stresses on bulk solid surfaces should tend to compress the surface, contrary to the physical situation. We interpret the result as being due to the qualitative difference between the effects of a smooth attractive surface and the structured substrate presented by the bulk solid, together with the particular form of the assumed pair potential. In this regard, we recall that the model-1 calculated film densities do fall below that of bulk planes near the nonwetting boundary.

Throughout our calculations we assumed that type-1 growth is indicated by the stability of trilayers relative to bulk phase. This assumption was dictated by the need to truncate the calculations to reasonable lengths. We cannot therefore rule out the possibility that limiting thicknesses of three or more layers could occur, and indeed, it is possible that the lack of a reentrant type-2 regime at large S in some of the models is simply due to our assumption that trilayer stability implies complete wetting. In these models, one might expect that examination of thicker films would reveal incomplete wetting, as continuum calculations<sup>7,25</sup> indicate. The truncation appears to be justified by experiment: With the exception of He/graphite, no type-2 films with a limiting thickness greater than two layers has been seen at low temperature. However, recent theories predict that strictly type-1 growth cannot occur except under quite stringent conditions.<sup>7,25</sup> Complete wetting of a crystalline film on an attractive substrate can only occur in special cases where the net stress tending to strain the film parallel to the surface vanishes. If the stress is small, the coexistence thickness will be large, but since the strain decays with distance from the surface more slowly than the attraction,<sup>7</sup> it must eventually raise the chemical potential of the multilaver higher than that of the bulk. This implies that even Ar, Kr, and Xe on graphite cannot grow arbitrarily thick films, although their limiting thicknesses may be greater than the 8-10 layers observed.

Our final comment concerns helium films. The evidence gathered from many studies indicate that <sup>4</sup>He (Refs. 26-28) and <sup>3</sup>He (Refs. 29 and 30) grow as type-2 films on graphite and other surfaces. The theory cannot be applied to these highly quantum systems. If <sup>4</sup>He were classical, our calculations would be consistent with graphite results, except that the limiting thickness of the experimental films on graphite is about four layers, contrasting with the predicted type 2b. This discrepancy might be attributed to quantum effects, which decrease the cohesive energy of the bulk more than the combined adhesive and cohesive energy of the film. However, a more serious problem arises from the fact that the upper layers of the film are liquidlike, with layer densities nearly equal to the bulk liquid. Therefore, structural mismatch cannot be invoked to explain the abrupt formation of the bulk phase. Nor can we suppose that superfluidity plays a role, since type-2 growth in <sup>4</sup>He extends above the  $\lambda$  point,<sup>26</sup> and <sup>3</sup>He is type 2.<sup>29,30</sup> These questions pose a challenge for theory.

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previously calculated and are in closer (but not complete) agreement with experimental heats of adsorption. Our model calculations were carried out with the values for  $\epsilon_g$  given in Ref. 11.

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