Substrate screening of the interaction between adsorbed atoms and molecules: Ne, Ar, Kr, Xe, and CH$_4$ on graphite

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This paper treats the electrodynamic screening by the substrate of the van der Waals interaction between adsorbed particles. The free-space interaction is modified by a perturbation ΔV, which describes the effect of the substrate. The McLachlan expression for ΔV is evaluated for the cases of Ne, Ar, Kr, Xe, and CH$_4$ adsorbed on graphite basal planes, and a potential energy between adsorbed molecules (atoms) is calculated. The main effect is a reduction in well depth of 15–20% from the free-space values. Experimental data are semiquantitatively consistent with these potentials. Discussion of the results and their implications is given.

I. INTRODUCTION

The Hamiltonian describing an assembly of particles adsorbed on a surface has two ingredients: the interaction of each molecule with the surface and the mutual interaction between adsorbed molecules.[1] Both are subjects of considerable interest, largely because of the intriguing properties of a quasi-two-dimensional (2D) film. This paper addresses the problem of electrodynamic screening of the van der Waals, or dispersion, part of the interaction between adsorbed particles. The role of the substrate is analogous to that of the third body in the three-body interaction between two particles embedded in a three-dimensional (3D) medium; the substrate modifies the electromagnetic fields associated with the fluctuating dipole moments of a pair of adsorbed molecules. Thus the van der Waals interaction between them is altered. As a result, the various properties of a film will change. McLachlan has computed this perturbation in the case of a continuum model of the substrate.[2] His result can be written

$$\Delta V(\rho) = \frac{4C_{S1}}{\rho^6 p^{3/2}} \left[\frac{1}{3} - \frac{L^2}{p\rho^2} \right] - \frac{C_{S2}}{\rho^6 p^3} , \qquad (1)$$

where L is the height (assumed the same) of the adatoms above an effective image plane,

$p = 1 + 4L^2/\rho^2$, and ρ is their separation.

The coefficients are[2]

$$C_{S1} = \frac{3}{\pi} \int_0^\infty \alpha^2(iE) g(iE) dE , \qquad (2)$$

$$C_{S2} = \frac{3}{\pi} \int_0^\infty \alpha^2(iE) g^2(iE) dE , \qquad (3)$$

$$g(iE) = [\epsilon(iE) - 1]/[\epsilon(iE) + 1] . \qquad (4)$$

In these expressions the functions $\alpha(iE)$ and $\epsilon(iE)$ are the polarizability of the adatoms and the dielectric function of the solid, respectively, both evaluated on the positive imaginary energy axis.[3] Values for the C coefficients for several adatom-substrate combinations are now available.[1,4,5]

In this paper the perturbation ΔV is used to calculate an effective 2D potential

$$V(\rho) = V_0(\rho) + \Delta V(\rho) \qquad (5)$$

for the cases of Ne, Ar, Kr, Xe, and CH$_4$ adsorbed on graphite. The choice of graphite is made because it satisfies the 2D assumption reasonably well, because experiment and theory have converged to yield consistent values of $\langle z \rangle$, the mean distance from the top carbon layer[6–10] (its relation to L is discussed in Sec. II), and because of considerable interest in the graphite case.

The well depths that emerge from this treatment

TABLE I. Input parameters and pair potential parameters for $V_0(\rho)$ and $V(\rho)$. All lengths are in angstrom units; D_0 and D are in kelvin.

	Ne	Ar	Kr	Xe	CH$_4$
C_{S1}[a]	1.33	17.70	37.55	84.64	37.6
C_{S2}[a]	0.70	10.49	22.65	53.05	19.8
$\langle z \rangle$	2.84[b]	3.20[c]	3.30[c]	3.35[b]	3.3[d]
L	1.155	1.515	1.615	1.665	1.60
ρ_{0m}	3.10	3.76	4.01	4.36	3.88
D_0	42	142.1	201.9	281.0	217
ρ_m	3.13	3.80	4.05	4.41	3.91
D	35.9	120	170	236	177
δ (%)	15	16	16	16	18

[a]C_{S1}, C_{S2} in units of eV—(Å)^6; noble-gas values from Refs. 1 and 4; CH$_4$ values from Ref. 5.
[b]Calculated values from Ref. 12.
[c]Experimental values from Ref. 9.
[d]Experimental values from Ref. 8.

are almost 20% smaller than those of the free-space potential V_0; experimental evidence and implications are discussed in Sec. III. It is evident that the ΔV correction must be incorporated into quantitative treatments of the film. A previous calculation[11] for ^{4}He on graphite also included a small correction due to the adatom motion perpendicular to the surface; estimates based on the atom-graphite surface interaction[12] show that the correction due to surface-normal motion is negligible for the heavier noble gases.

Similar calculations have been done by Bruch and co-workers[13] for gases on Ag(111). The results have yielded remarkable agreement with data of Webb's group over an extended region of temperature and film coverage.[14] Semiquantitative agreement has been obtained also by several groups in treating He on graphite.[11,15] The latter problem is complicated by the non-negligible effects of surface-normal vibration, periodicity in the potential, and substrate heterogeneity.

II. COMPUTATIONS OF $V(\rho)$

In evaluating ΔV an important parameter is the distance to the image plane L. We adopt the relation

$$L = \langle z \rangle - d/2 , \qquad (6)$$

where d is the interlayer spacing of graphite (3.37 Å). This assumption is believed to be approximately valid for jellium,[16] and has yielded reasonable results for noble gases on Ag(111) (Ref. 13) and He on graphite (Ref. 11). The $\langle z \rangle$ values for CH$_4$, Ar, and Kr come from neutron scattering,[8] low-energy electron diffraction (LEED),[9] and extended x-ray absorp-

tion fine-structure (EXAFS)[10] experiments. The latter two agree well with theoretical values obtained elsewhere[12]; this justifies our use of calculated values for the other systems. (See Table I for a summary.) In all cases other than He, $\langle z \rangle$ exceeds the position of the minimum of the adatom-substrate potential by less than 0.1 Å.[17]

The free-space potentials $V_0(\rho)$ are rather well known[18] in the cases of Ar, Kr, and Xe. For Ne and CH$_4$ the potentials used are of Lennard-Jones form,
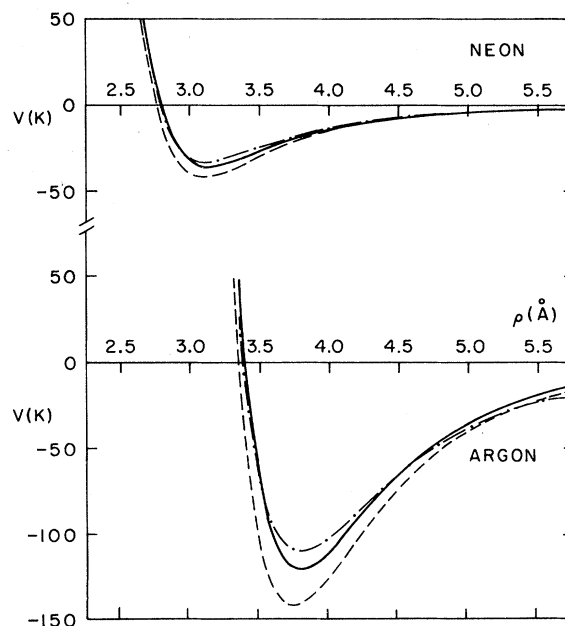

FIG. 1. Free-space potential V_0 (dashed curve), the substrate-screened potential V (solid curve), and the equivalent LJ potential V_{LJ} (dashed-dotted curve) for Ne and Ar.
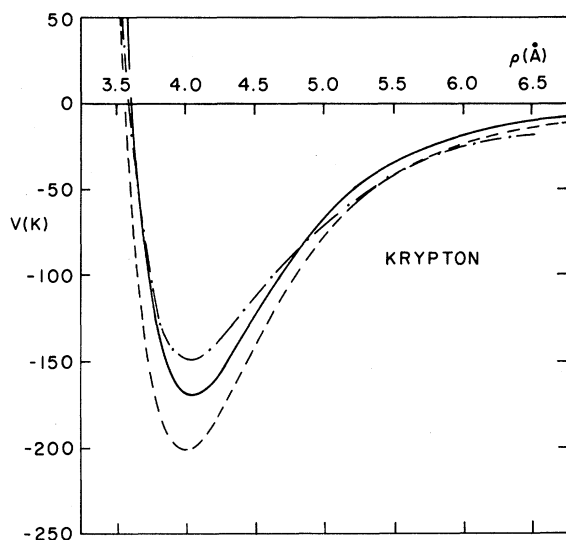
FIG. 2. Same as Fig. 1 for Kr.

FIG. 4. Same as Fig. 1 for CH$_4$.

a (12-6) for Ne using recent parameters[19] for well depth and location of minimum, and a (20-6) for methane (discussed in Sec. III). The Ne and CH$_4$ potentials are less trustworthy than those for Ar, Kr, and Xe. (See note added in proof.)

Results of the calculations are given in Figs. 1—4 and in Table I. In Table I, D and ρ_m are the well depth and the location of the potential minimum for $V(\rho)$; D_0 and ρ_{0m} are the corresponding quantities for $V_0(\rho)$; δ is the percent decrease in the well depth due to substrate screening. The principal effect of
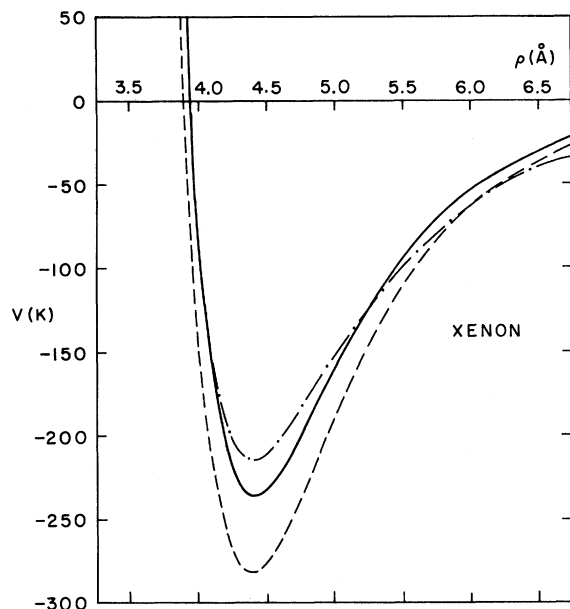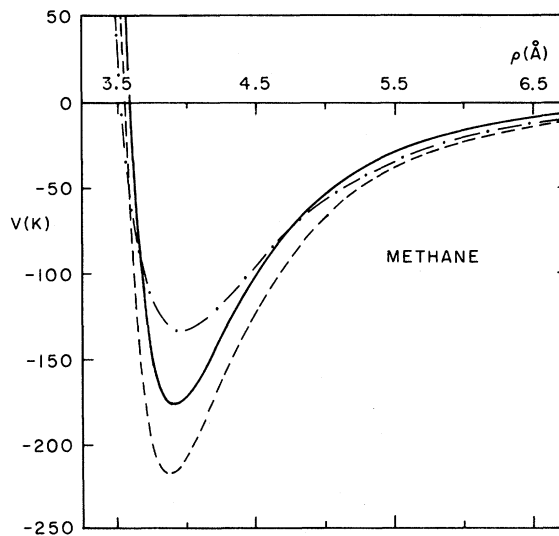

FIG. 3. Same as Fig. 1 for Xe.

the substrate-induced correction is 15—20 % reduction in the well depth. The change in the position of the minimum is always less than 0.05 Å.

III. DISCUSSION

A. Virial expansion

The most direct experimental information concerning $V(\rho)$ comes from low-coverage adsorption data. Halsey and collaborators[20] have measured adsorption isotherms for the systems studied in this paper; these data have been extensively analyzed, and many attempts have been made to determine the interaction between adsorbed molecules. If the two-dimensional (2D) film approximation is made,[21] virial coefficients can be extracted; in particular, the second virial coefficient B_{2d} can be directly related to the potential energy via

$$B_{2d} = -\pi \int_0^\infty \{\exp[V(\rho)/kT] - 1\}\rho \, d\rho \ . \qquad (7)$$

Typically, a reasonable form is chosen for $V(\rho)$, and the parameters are then chosen to fit the measured B_{2d} values. A variety of potentials have been produced in this manner. Apart from the lack of uniqueness in inverting Eq. (7), a major difficulty has been the large uncertainty in adsorbent surface area, which is needed to accurately extract B_{2d} from the data. However, a common feature of the potentials produced this way is that the presence of the graphite surface reduces the strength of the interaction by 15—20 %.[22] This feature is reproduced by the calculations described above.

One case is which a meaningful comparison can be made directly stems from the later work of Put-

nam and Fort[23] for Kr on graphite. Included in their work is a reliable determination of the surface area of their sample. Putnam[24] has recently reanalyzed his data and the Halsey Kr data and has produced an accurate $V(\rho)$ for Kr. The Kr potential shown in Fig. 3 is in striking agreement with Putnam's; the two potentials would be indistinguishable if plotted together in Fig. 3. Putnam finds a well depth of 171 K as compared to our 170 K. Briefly, Putnam's method was as follows: $V_0(\rho)$ was taken to be Barker's potential[18] and ΔV was chosen to be either of the Sinanoglu-Pitzer (SP) form $\Delta V = -C/\rho^3$ or of the McLachlan form Eq. (1). In the McLachlan case C_{S2} was set equal to zero since the second term in Eq. (1) is significantly smaller[25] than the first one; L was taken to be 2.05 Å which corresponds to $\langle z \rangle = 3.73$ Å in Eq. (6). The constants C and C_{S1} were arbitrary and were varied to fit both the Halsey and the Putnam-Fort data. Putnam finds the McLachlan form for ΔV to give a slightly better fit than the SP form. Although the best-fit value of C_{S1} appears to disagree with the Bruch-Watanabe value in Table I, this discrepancy can be explained in part by the neglect of the C_{S2} term, but mostly by a choice of L that is too large.[26] The results presented here with the use of the recently measured[9] value $\langle z \rangle = 3.3$ Å and Bruch-Watanabe values for C_{S1} and C_{S2} yield essentially the same potential as Putnam's best-fit potential.

It is expected that the noble-gas potentials are more reliable than the methane potential since the CH$_4$-CH$_4$ free-space interaction is not well known. For $V_0(\rho)$ we have chosen the (20-6) potential of Mathews and Smith,[27] which reproduces well the numerical potential obtained by inversion of experimental data. Also, the parameters C_{S1} and C_{S2} in $\Delta V(\rho)$ were calculated by an approximate method[5] whose accuracy was tested by comparing its predictions with previously determined values; the results suggest that the calculated values are accurate to within 5%. Finally, the value $\langle z \rangle = 3.3$ Å was taken from neutron scattering data.[8] A molecular dynamics calculation[28] confirms this value at low temperature, but suggests a significant increase in $\langle z \rangle$ with temperature.[29] The correction term ΔV becomes smaller with increasing L; since the extant virial coefficient data were taken at ~ 280 K, an appropriate value of L is problematical in a calculation of the virial coefficients.

B. Finite coverage calculations

Despite the uncertainties in $V(\rho)$ for methane on graphite, the results here are in clear contradiction with a conjecture of Ostlund and Berker,[30] who infer from the phase diagram of a triangular lattice-gas

model that the effective hard-core diameter of methane on graphite is 6% larger than it is in free space. Figure 4 shows that the primary effect of the substrate is to reduce the well depth; the percent increase in σ, the zero of the potential energy, is about 1%. Furthermore, this small shift in σ is largely independent of the choice of $V_0(\rho)$ or L.

In order to test the implications of our potentials, comparison can be made with either data from the low-coverage regime (via the virial expansion) or with thermodynamic properties at higher coverage. The analysis is complicated in general by the role of the substrate periodic potential. At high temperature this is a small effect because the barriers to lateral translation are only about 40 K high.[31]

Calculations of 2D phase diagrams[32–34] are usually made with the assumption that the mutual interaction between adatoms is of the Lennard-Jones (LJ) form

$$V_{\text{LJ}}(\rho) = 4\epsilon[(\sigma/\rho)^{12} - (\sigma/\rho)^6] . \tag{8}$$

To make contact with such work we must adopt criteria for choosing values of parameters ϵ and σ. Obviously, the choice is somewhat arbitrary since plausible alternative procedures exist. Our method is described and justified in the Appendix. The resulting parameters are presented in Table II. The potentials themselves are shown in Figs. 1–4 along with the 2D potentials from which they are derived. As described in the Appendix, the differences between the two potentials are consistent with similar behavior occurring when LJ potentials are fitted in 3D to viscosity and virial coefficient data. Guided by this analogy, we expect the error introduced by the LJ model to be small for temperatures of the order of the 2D critical temperature T_c^{2D}.

We may now refer to some recent 2D phase diagrams derived by Fairobent, Saam, and Sander.[34] Their calculations incorporated the weak graphite potential in a density functional theory of the adsorbate. The case of Xe is illustrated in Fig. 5. There we see the liquid-vapor coexistence curve calculated with the parameters $\sigma_0 = 4.1$ Å and $\epsilon_0 = 221$ K. The

TABLE II. Parameters for equivalent Lennard-Jones potentials.

	V_{min} (K)	ϵ (K)	σ (Å)	T_c^{2D} (K)[a]
Ne	36	33.8	2.79	
Ar	120	110	3.38	59±1
Kr	170	150	3.59	85.3±1
Xe	236	214	3.92	117±1
CH$_4$	177	136	3.53	75

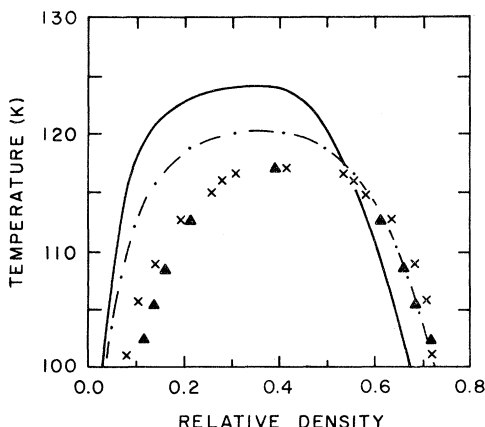[a]From Ref. 37, except for CH$_4$, which is from Ref. 35.

FIG. 5. 2D phase diagram for Xe on graphite. Data points from Ref. 35 ($\times$) and Ref. 36 ($\blacktriangle$). Solid curve, calculations of Fairobent *et al.* for $\epsilon_0 = 221$ K, $\sigma_0 = 4.1$ Å; dashed-dotted curve, revised curve calculated in this paper (Sec. III B).

critical temperature is seen to be $T_c^0 \simeq 124$ K. Our revised parameters lead to a different curve which we obtain by the following argument. A particular temperature T_0 on the curve corresponds to a reduced temperature $T^* = kT_0/\epsilon_0$. A revision of the energy parameter transforms this value to a temperature

$$T = \epsilon T^*/k = T_0 \epsilon/\epsilon_0 . \tag{9}$$

Similarly a 2D density n_0 is scaled to

$$n = n_0 (\sigma_0/\sigma)^2 . \tag{10}$$

Thus we map the old coexistence curve to a new one, shown in Fig. 5. It is seen that the revised curve agrees much better with the experimental data.[35,36] This supports the hypothesis of Fairobent *et al.* that substrate screening is at least partly responsible for the discrepancy.

Similar behavior occurs for the phase diagrams of the other noble gases. In the case of Kr our LJ well depth of 150 K yields curves intermediate between those shown in Fig. 1 of Ref. 34. It too is more consistent with the data. For Ar, the critical temperature calculated with $\epsilon_0 = 120$ K is 67 K. Our revised value $\epsilon = 110$ K yields $T_c^{2D} = 61$ K, close to the result 59 ± 1 K reported[37] by Larher and Gilquin. Finally, for ^{4}He the well-depth reduction to $\epsilon = 9.36$ K calculated by Vidali and Cole[11] improves agreement between the calculated[34] and measured[38] $\sqrt{3} \times \sqrt{3}$ ordering transition. This last case is probably fortuitous because the substrate potential is *prima facie* important and, in any case, probably underestimated in the calculation.[39] Thus there is an overall clear tendency to improve agreement between theory and experiment.

IV. SUMMARY

The potential energy between like atoms or molecules adsorbed on graphite was computed for the noble gases Ne, Ar, Kr, Xe, and for CH_4. The effect of substrate screening was seen to primarily affect the strength of the interaction, reducing the well depth by 15—20 % from the free-space values. Comparison with adsorption data both from the low-coverage regime via the virial expansion and from thermodynamic properties at higher coverage suggest that substrate screening using the McLachlan interaction should be incorporated into quantitative treatments of films.

Since the McLachlan ΔV is based on a continuum model of the substrate, the validity of ΔV when the atoms are within a few anstroms of the surface is open to question. However, the calculations presented here suggest that the McLachlan term does represent the essential features of the substrate-screening effect. Although the calculational method is semiempirical, it should be emphasized that there are no adjustable parameters in the calculations; the parameters in ΔV (viz., C_{S1}, C_{S2}, $\langle z \rangle$) are measurable or calculable. Hence apart from many-body effects (not considered here) it appears that it is now possible to predict the interaction between adsorbed molecules for many systems once the free-space interaction is known.

Note added in proof. A better choice of $V_0(\rho)$ for Ne would be the Ne potential of Brunetti *et al.*[14]; for this choice of potential the parameters ρ_{0m}, D_0, ρ_m, D, and δ in Table I for Ne are 3.12, 40.6, 3.15, 34.6, and 15, respectively.

APPENDIX

We consider the problem of choosing a LJ (12-6) potential which is approximately equivalent to the "true" potential $V(x)$, which we suppose to be known. This desired equivalence can at best be achieved over some limited range of coverage and temperature. Moreover, one must identify some specific property or properties which should be matched in this region. Given the attendant degree of arbitrariness, we have opted for simplicity in our procedure. It will emerge below that the results are qualitatively reasonable.

Our method is the following. We define two dis-

tances $x_{\pm}$ such that the true potential has half the minimum value there:

$$V(x_{\pm}) = V_{min}/2 . \tag{A1}$$

The LJ potential is then determined by requiring that it agree with the true potential at these positions,

$$V_{LJ}(x_{\pm}) = V(x_{\pm}) . \tag{A2}$$

The reasons for this choice at that (a) there will ensue an approximate balance between regions where $V_{LJ} > V$ and vice versa, and (b) the important region of the potential is that for which $V - V_{min} \simeq kT$. Since 2D critical temperatures are of order $|V_{min}|/2k$, Eqs. (A1) and (A2) assure similarity of the two potentials in the relevant regime.

Eqs. (A1) and (A2) yield

$$\sigma = x_{+}x_{-}/\bar{x} , \tag{A3}$$

$$\epsilon = |V_{min}| (\bar{x}/\sigma)^6/8 , \tag{A4}$$

$$\bar{x} \equiv (x_{+}^6 + x_{-}^6)^{1/6} . \tag{A5}$$

Section III B discusses the potentials which follow from this procedure. They are seen to differ from the true potentials by being less attractive near the minimum $(x_{-} < x < x_{+})$ and more attractive elsewhere.

In order to assess this procedure, we apply it also to 3D interactions for the systems of interest. We thus apply Eqs. (A1)–(A5) to these potentials. Not surprisingly, the same qualitative difference ensued. We may now compare the computed parameters with those fitted to gas-phase data—virial coefficients and viscosity (near room temperature). The results are encouraging. The ϵ values of Clifford et al.[40] are 1.07, 1.05, 0.98, and 0.92 times our derived values for the sequence Ar, Kr, Xe, and CH_4. The corresponding σ ratios are 1.00, 1.01, 1.01, and 1.06. The last of these (CH_4) is high perhaps because of the inability of the (12-6) interaction to mimic the unusually steep repulsion due to the constituent H atoms. It is known that a (20-6) interaction is consistent with viscosity and virial coefficient data in this case.[27] Thus 3D data confirm the plausibility of our results. We conclude that our approach is both reasonable and simple.

[1] L. W. Bruch, Surf. Sci. (in press). This reference contains a summary of information on the single atom holding potential of physical adsorption and the lateral interactions of adatoms.

[2] A. D. McLachlan, Mol. Phys. **7**, 381 (1964).

[3] These real functions are related by Kramers-Kronig transforms to the imaginary parts of α and ϵ at real frequency. See L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1969), pp. 384–391.

[4] L. W. Bruch and H. Watanabe, Surf. Sci. **65**, 619 (1977).

[5] S. Rauber, J. R. Klein, M. W. Cole, and L. W. Bruch, Surf. Sci. (in press).

[6] M. W. Cole and F. Toigo, Phys. Rev. B **23**, 3914 (1981).

[7] K. Carneiro, L. Passell, W. Thomlinson, and H. Taub, Phys. Rev. B **24**, 1170 (1980).

[8] G. Bomchil, A. Huller, T. Raymant, S. J. Roser, M. V. Smalley, R. K. Thomas, and J. W. White, Philos. Trans. R. Soc. London Sect. B **290**, 537 (1980).

[9] C. G. Shaw, S. C. Fain, M. D. Chinn, and M. F. Toney, Surf. Sci. **97**, 128 (1980).

[10] C. Bouldin and E. A. Stern, Phys. Rev. B **25**, 3462 (1982).

[11] G. Vidali and M. W. Cole, Phys. Rev. B **22**, 4661 (1980); **23**, 5649 (E) (1981).

[12] M. W. Cole and J. R. Klein, Surf. Sci. (in press).

[13] J. Unguris, L. W. Bruch, E. R. Moog, and M. B. Webb, Surf. Sci. **87**, 415 (1979); L. W. Bruch, J. Unguris, and M. B. Webb, *ibid.* **87**, 437 (1979). See also G. L. Price and J. A. Venables, Surf. Sci. **59**, 509 (1976), for Kr and Xe on graphite.

[14] L. W. Bruch and M. B. Webb, in *Interfacial Aspects of*

Phase Transformations, edited by B. Mutaftschiev (Reidel, Dordrecht, Netherlands, 1982).

[15] L. W. Bruch, Phys. Rev. B **23**, 6801 (1981); A. F. Silva-Moreira, J. Codona, and D. Goodstein, Phys. Lett. A **76**, 324 (1980).

[16] E. Zaremba and W. Kohn, Phys. Rev. B **13**, 2270 (1976).

[17] See Ref. 12. For He isotopes the shift $\langle z \rangle - z_{min} \simeq 0.2$ Å; see Refs. 6 and 7.

[18] J. A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. **21**, 657 (1971); J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. **61**, 3081 (1974).

[19] See J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976), and Table I on p. 595.

[20] J. R. Sams, Jr., G. Constabaris, and G. D. Halsey, Jr., J. Phys. Chem. **64**, 1689 (1960); G. Constabaris, J. R. Sams, Jr., and G. D. Halsey, Jr., *ibid.* **65**, 367 (1961); J. Chem. Phys. **37**, 915 (1962).

[21] W. A. Steele, Surf. Sci. **39**, 149 (1973).

[22] J. A. Barker and D. H. Everett, Trans. Faraday Soc. **58**, 1608 (1962); J. R. Sams, Jr., G. Constabaris, and G. D. Halsey, Jr., J. Chem. Phys. **36**, 1334 (1962); J. R. Sams, Jr., *ibid.* **37**, 1883 (1962); **43**, 2243 (1965); Mol. Phys. **9**, 195 (1965).

[23] F. A. Putnam and T. Fort, Jr., J. Phys. Chem. **81**, 2164 (1977).

[24] F. A. Putnam, in *Ordering in Two Dimensions,* edited by S. K. Sinha (North-Holland, Amsterdam, 1980), p. 231.

[25] In the region near the potential minimum the first term

in Eq. (1) is ~ 3.3 times larger than the second term for the potential reported here.

[26]The constant C_1 listed in Table I of Ref. 24 is related to C_{S1} in Eq. (1) by $C_1 = 24L^3 C_{S1}$.

[27]G. P. Matthews and E. B. Smith, Mol. Phys. __32__, 1719 (1976).

[28]E. S. Severin and D. J. Tildesley, Mol. Phys. __41__, 1401 (1980).

[29]Reference 28 suggests an increase in $\langle z \rangle$ of ~ 0.15 Å as temperature increases from 18.6 to 108 K.

[30]S. Ostlund and A. N. Berker, Phys. Rev. B __21__, 5410 (1980).

[31]W. A. Steele, *The Interaction of Gases with Solid Surfaces* (Pergamon, Oxford, 1974), p. 57.

[32]D. Henderson, Mol. Phys. __34__, 301 (1977).

[33]F. Hanson and J. P. McTague, J. Chem. Phys. __72__, 6363 (1980).

[34]D. K. Fairobent, W. F. Saam, and L. M. Sander, Phys. Rev. B __26__, 179 (1982).

[35]A. Thomy and X. Duval, J. Chim. Phys. __67__, 1101 (1970).

[36]J. Regnier, A. Thomy, and X. Duval, J. Chim. Phys. __74__, 926 (1977).

[37]Y. Larher and B. Gilquin, Phys. Rev. A __20__, 1599 (1979).

[38]M. Bretz, J. G. Dash, D. C. Hickernell, E. O. McLean, and O. E. Vilches, Phys. Rev. A __8__, 1589 (1973).

[39]W. E. Carlos and M. W. Cole, Surf. Sci. __91__, 339 (1980); M. W. Cole, D. R. Frankl, and D. L. Goodstein, Rev. Mod. Phys. __53__, 199 (1981).

[40]A. A. Clifford, P. Gray, and N. Platts, J. Chem. Soc. Faraday Trans. 1 __73__, 381 (1977).

[41]B. Brunetti, R. Cambi, F. Pirani, and F. Vecchiocattivi, Chem. Phys. __42__, 397 (1979).