PHYSICAL REVIEW B VOLUME 22, NUMBER 10 15 NOVEMBER 1980

Effective interaction between He atoms on a graphite surface

G. Vidali and M. W. Cole
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 3 June 1980)

Evidence is presented to show that the two-dimensional effective interaction between He atoms on graphite is less attractive than the free-space interaction V_0. The principal origin of the effect is substrate screening of the attraction. A small shift arises also from averaging the adatom motion perpendicular to the surface. The revised potential V_{eff} is shown to yield improved agreement for the specific heat in the low-coverage region where a quantum virial expansion applies.

I. INTRODUCTION

The thermodynamic properties of submonolayer He films on graphite have been studied extensively in recent years.[1-3] One of the most appealing features of this system is that it comes remarkably close to realizing a theorist's two-dimensional (2D) model. This was first argued on the basis of calculations by Hagen *et al.*[4] which showed band-structure effects to be small. Circumstantial support came from early specific-heat data[1] which approached $C \simeq Nk_B$ for temperature $T \gtrsim 3$ K. At lower T, the data agreed rather well with virial calculations[5] which assumed both the 2D model and the free-space interaction $V_0(\rho)$ between the He atoms.

Very recently, however, several experimental and theoretical developments have raised questions about the validity of these approximations. For example, the results of extensive measurements of He scattering from graphite[6,7] have indicated that equal potential-energy surfaces are more corrugated than was believed previously.[8] This is reflected in wider gaps in the adatom band structure; the resulting specific heat departs significantly from 2D behavior in the high-temperature regime, $T \gtrsim 5$ K.[9-11]

We shall be particularly interested in establishing the nature of the effective interaction between He atoms. Two factors will be taken into account here. One is that motion of the atoms in the z direction, perpendicular to the surface, must be averaged out in order to obtain a 2D interaction $V(\rho)$, where $\vec{\rho}$ is the projection on the surface of the interparticle separation $\vec{r}$.[12,13] Secondly, and more significantly, the substrate screens the attraction between adatoms.[14-17] Together these effects produce a net interaction

$$V_{\text{eff}}(\rho) = V(\rho) + \Delta V(\rho) ,$$

where ΔV is the screening correction. This potential is less attractive than the free-space interaction V_0, and yields rather different predictions for the thermodynamic properties. We find the new prediction for the specific heat to agree better with experimental data.[1,2]

Although our results for $V_{\text{eff}}(\rho)$ are quite generally applicable, our thermodynamic analysis is restricted to the regime of He at low coverage and moderately low T. By low coverage we mean sufficiently so to assure validity of a quantum virial expansion.[5] This method places a density-dependent lower limit on the temperature domain of applicability. The upper limit on temperature is $T \approx 3$ K, since at higher T the band gap starts to play an important role in determining the single-particle properties.[9-11] We do take approximate account of band-structure effects at low T by incorporating an effective-mass enhancement $m^*/m = 1.06$ (1.03) for ^{4}He (^{3}He).[9]

For convenience we parametrize each potential discussed in this paper with Lennard-Jones constants ϵ, the well depth, and σ, the distance at which it vanishes. Although this is an oversimplification, it permits us to exploit the very simple scaling behavior of two parameter potentials. We expect that our conclusions would not differ qualitatively if more realistic potentials were employed.

II. CALCULATIONS

There are two steps in our procedure. We first derive the effective interaction, taking into account z motion and substrate screening. We then compute the thermodynamic properties using the virial expansion.

A. He-He interaction

Because the atomic motion perpendicular to the graphite is very rapid compared to motion in the plane, the effective 2D interaction incorporates an average over the former.[12,13] Following Sander *et al.*,[12] we assume for simplicity a Gaussian wave function for motion in the z direction, with probability density

$$f(z)=e^{-(u/d)^2}/d\pi^{1/2}\,. \tag{1}$$

Here $u=z-z_0$ is the displacement relative to the mean position z_0. The value of d appropriate to the anisotropic 6-12 potential of Ref. 8 is 0.37 Å (0.42 Å) for ^{4}He (^{3}He). There is recent evidence from neutron scattering[18] supporting this potential, which was developed originally to fit atomic beam scattering data.[6,7] With Eq. (1), the averaged interaction at lateral separations ρ becomes

$$V(\rho)=\int\int dz_1dz_2V_0\{[\rho^2+(z_1-z_2)^2]^{1/2}\}f(z_1)f(z_2)\,, \tag{2}$$

$$V(\rho)=4\epsilon\left[\left(\frac{\sigma}{\rho}\right)^{12}G_{12}(\lambda)-\left(\frac{\sigma}{\rho}\right)^{6}G_6(\lambda)\right], \tag{3}$$

$$\lambda=\rho^2/2d^2\,. \tag{4}$$

Here we have assumed the traditional[19] Lennard-Jones 6-12 form for $V_0(r)$ and defined an integral

$$G_n(\lambda)\equiv2\left(\frac{\lambda}{\pi}\right)^{1/2}\int_0^\infty dx(1+x^2)^{-n}e^{-\lambda x^2}\,. \tag{5}$$

We need this function for $\lambda\gtrsim20$. We therefore perform an asymptotic expansion for the relevant values of n, yielding

$$G_6(\lambda)=1-\frac{3}{\lambda}+\frac{63}{4\lambda^2}-\frac{105}{\lambda^3}+\frac{6615}{\lambda^4}-\cdots\,, \tag{6}$$

$$G_{12}(\lambda)=1-\frac{6}{\lambda}+\frac{117}{2\lambda^2}-\frac{1365}{2\lambda^3}+\frac{143\,325}{16\lambda^4}-\cdots\,.$$

By halving the last term shown, one reproduces to better than 0.5% the value obtained by numerical integration of Eq. (5) for all relevant λ.

Because the amplitude d is so small compared to separations ρ of interest, the potential $V(\rho)$ does not differ substantially from the value of $V_0(r)$ evaluated at $r=\rho$. In particular, the parameters[19] $\epsilon=10.22$ K and $\sigma=2.556$ Å of V_0 are replaced by $\epsilon=10.07$ K and $\sigma=2.51$ Å.[20] The weakening of the attraction and shrinking of the repulsive core can be understood by realizing that for a given ρ, $V(\rho)$ requires as input values of $V_0(r)$ for $r\geqslant\rho$ [see Eq. (2)].

A much larger modification of the interaction arises from the substrate screening of the van der Waals interaction. This has been derived by McLachlan[14] in terms of fluctuating image dipoles in the substrate. His result can be written

$$\Delta V(\rho,L)=\frac{4C_{1s}}{\rho^6p^{3/2}}\left(\frac{1}{3}-\frac{L^2}{p\rho^2}\right)-\frac{C_{2s}}{\rho^6p^3}\,. \tag{7}$$

Here $p\equiv1+4L^2/\rho^2$ and L is the distance from the adatom plane to the continuum substrate he assumed. The coefficients $C_{1s}=3950$ K Å^6 and $C_{2s}=2150$ K Å^6 have been determined by Watanabe[21] from McLachlan's formulas[14] involving the frequency-dependent dielectric function of graphite and polarizability of He.

Several points should be noted concerning this expression. The first is that we have taken the two He atoms to lie in the same plane (parallel to the substrate), implicitly neglecting z motion. The adequacy of this approximation has been verified by evaluating the more general expression (permitting $z_1\neq z_2$) of McLachlan[14] and averaging over z motion as described above. The correction turns out to be negligible. Secondly, Eq. (6) is strictly valid only in the large-ρ limit, although it is often used more generally.[17] Finally, the value of L is uncertain since the continuum model leaves unspecified the position of the solid boundary relative to the outer graphite layer. For the jellium model of solids, it has been argued that the jellium edge lies somewhat more than half a layer spacing outward, the difference being of the order of a few tenths of an angstrom.[17,22,23] In the case of graphite, this procedure remains to be assessed. One check we may perform is to compare the prediction of Eq. (7) with a calculation for Ar by Freeman[16] using the Gordon-Kim version of the density functional method.[24,25] Figure 1 presents such a comparison for the case z

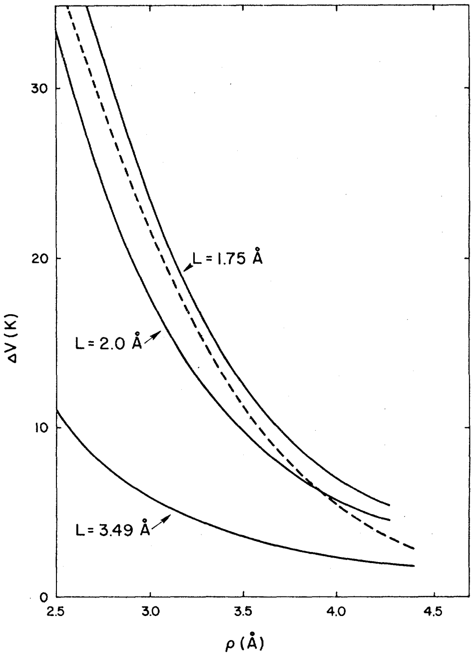

FIG. 1. Substrate screening contribution to the Ar-Ar interaction above graphite. Dashed curve is the result of Freeman (Ref. 16) at $z=3.49$ Å. Full curves are calculated from Eq. (7) for various values of L.

=3.49 Å. Quite close agreement occurs with the choice $L = 1.85$ Å, indicating that the appropriate position of the image plane is $z_i = 3.49 - 1.85 = 1.64$ Å. This agrees well with the jellium procedure, since one-half of the graphite layer spacing is 1.68 Å. Thus our best estimate for the case of He is $L = z_0 - z_i \cong (2.92 - 1.64)$ Å $\cong 1.3$ Å. Since this analysis is only suggestive, we have performed calculations using a range of L values. Figure 2 shows $V_{\text{eff}}(\rho)$ for the case $L = 1.5$ Å. Both corrections described above have been included in V_{eff}. The attraction is substantially reduced relative to $V_0(\rho)$; the well depth ϵ is 15% smaller. In contrast, σ is smaller by only 0.7% because the two contributions considered here have opposing effects on it. This trend is evident in Fig. 3 where more general values of L are considered. Note that only the effect of surface-normal motion remains in the large-L limit.

Our calculations neglect substrate phonon-mediated interactions[26] since they are (a) probably small because of the relatively strong covalent bonding of graphite, and (b) not well understood quantitatively.

B. Thermodynamic properties

We next use the quantum virial expansion to compute the specific heat C/N of N atoms adsorbed on graphite. This method has been employed previously by Siddon and Schick[5] using the free-space interaction V_0. Following their procedure, we truncate the expansion at the second term:

$$C/Nk = 1 - n\beta^2 d^2B/d\beta^2 \,, \tag{8}$$

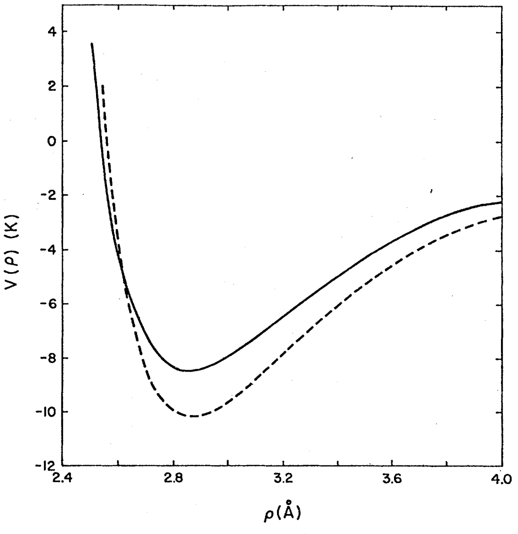

FIG. 2. Comparison between the free-space He-He interaction V_0 (dashed curve) and V_{eff} with $L = 1.5$ Å (full curve).

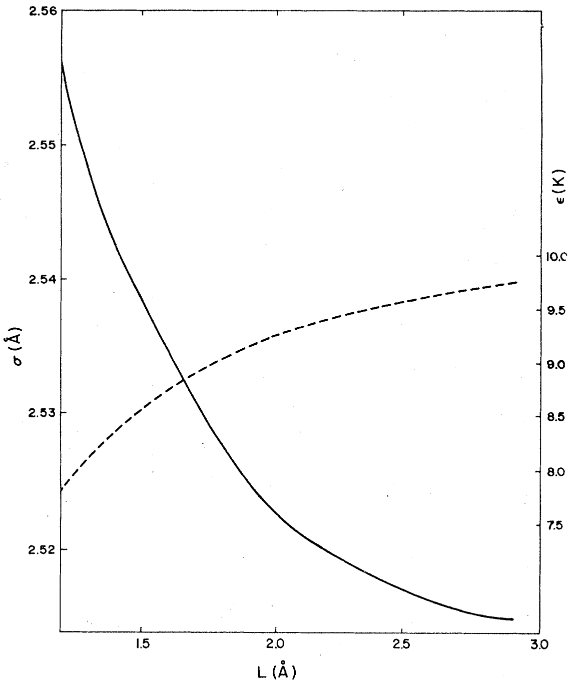

FIG. 3. He-He interaction parameters as a function of the value of L. Dashed curve is ϵ, with scale at right. Full curve is σ.

where n is the areal density, $\beta^{-1} = kT$, and B is the second virial coefficient. More generally, one would replace unity on the right-hand side by the value of C/Nk appropriate to the limit of classical, noninteracting atoms moving in the substrate's periodic potential. For $T \lesssim 2$ K, however, the band-structure effects are fairly well represented by an effective-mass correction,[9] leading to the same result (unity) for C/Nk in this limit.

The quantum law of corresponding states[27] provides the following scaling of $B(T)$ with interaction parameters:

$$(\beta/\sigma)^2 d^2B/d\beta^2 = f(\eta^*, T^*) \,, \tag{9}$$

$$T^* = kT/\epsilon \,, \tag{10}$$

TABLE I. Interaction parameters for He isotopes as a function of distance L to the continuum substrate. The band-structure enhancements $m^*/m \doteq 1.06$ (1.03) for ^{4}He (^{3}He) have been incorporated.

L (Å)	ϵ (K)	σ (Å)	η^* (^{4}He)	η^* (^{3}He)
1.2	7.82	2.556	0.2235	0.3066
1.4	8.32	2.543	0.2251	0.3089
1.5	8.53	2.539	0.2202	0.3021
1.75	8.95	2.530	0.2114	0.2901
2.0	9.24	2.523	0.2059	0.2824
2.9	9.75	2.515	0.1853	0.2543
∞	10.07	2.510	0.1801	0.2471

$$\eta^* = \hbar^2/m^*\sigma^2\epsilon\,. \tag{11}$$

The function $f(\eta^*, T^*)$ differs for fermions and bosons. Its dependence on T^* is known from the work of Siddon and Schick[5,28] for 3 (2) values of η^* for ^{4}He (^{3}He). By linear interpolation or extrapolation one can generate the values for each particular set of ϵ, σ, and m^*. These are presented in Table I for a range of L values. The procedure is then to evaluate $\beta^2 d^2B/d\beta^2$ from Eq. (9) and use it in Eq. (8).

Figures 4 and 5 show the specific-heat results for the two isotopes. The function actually plotted is chosen in order to test implicitly for the presence of higher-order terms than have been included in Eq. (8). These appear in the data for different densities as deviations from a universal curve.

In general, the new potential yields better agreement than V_0 does. Comparison in the case of ^{4}He is complicated by the role of band-structure effects for $T > 3$ K.[9-11] This may explain the high T discrepancy. Below 2 K, the points do not lie on a universal curve, corresponding to a deviation from Eq. (8).

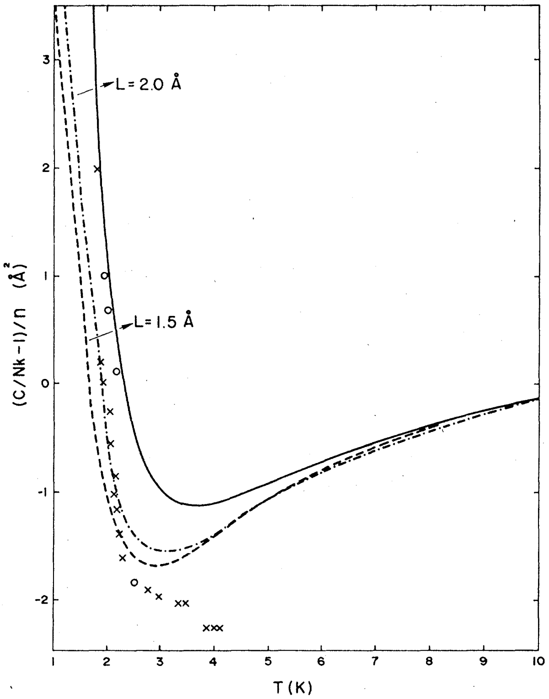

FIG. 4. $(C/Nk - 1)/n$ vs T for ^{4}He. Full curve is the result of Siddon and Schick (Ref. 5) using the free-space interaction V_0. The other curves are obtained from V_{eff}, assuming that $L = 1.5$ Å (dashed curve) or 2 Å (dash-dot). Data points are representative experimental results of Bretz *et al.* (Ref. 1) at density 0.0278 Å^{-2} (crosses), 0.042 Å^{-2} (pluses), and 0.0483 Å^{-2} (circles).

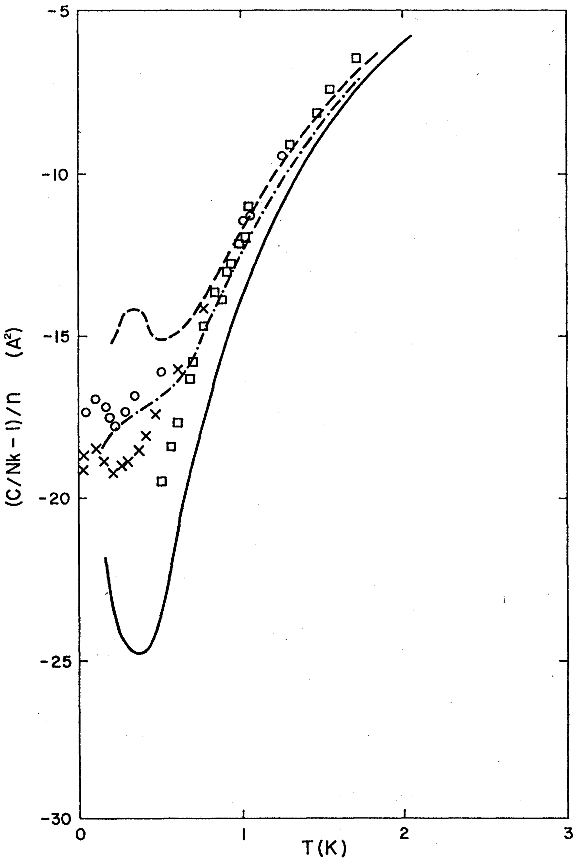

FIG. 5. Same as Fig. 4 for ^{3}He, using coverages indicated.

There is clearly improved agreement for ^{3}He when the revised potential is used. This is evident in the data for $T > 0.6$ K. Below that temperature, the deviation from Eq. (8) is again evident.

III. SUMMARY AND DISCUSSION

As shown previously,[12,13] averaging over motion perpendicular to the surface yields an interaction $V(\rho)$ which differs only slightly from V_0. In contrast, substrate screening reduces the attraction considerably (~15%). The revised potential V_{eff} yields improved agreement with the specific-heat data of Bretz *et al.*[1]

The major uncertainty in this work arises from the inadequacy of the screening term, Eq. (7). Its use for all ρ is suspect owing to the assumptions of its derivation.[14] A more realistic version of that expression is certainly a desirable, albeit formidable, goal.

ACKNOWLEDGMENTS

We are indebted to M. Schick, L. W. Bruch, H. Watanabe, D. R. Frankl, D. L. Goodstein, and A. F. Silva-Moreira for helpful discussion and communication of unpublished results. This research has been supported in part by DOE Contract No. DE-AS02-79ER10454, NSF Grant No. DMR77-22961, and by the Consiglio Nazionale delle Ricerche, Italy.

---

[1] M. Bretz, J. G. Dash, D. C. Hickernell, E. O. McLean, and O. E. Vilches, Phys. Rev. A 8, 1589 (1973).

[2] R. L. Elgin and D. L. Goodstein, Phys. Rev. A 9, 2657 (1974).

[3] For a recent review, see J. G. Dash and M. Schick, in *The Physics of Liquid and Solid Helium*, edited by K. H. Bennemann and J. B. Ketterson (Wiley, New York, 1979), Part II.

[4] D. E. Hagen, A. D. Novaco, and F. J. Milford, in *Adsorption-Desorption Phenomena* (Academic, New York, 1972), p. 99.

[5] R. L. Siddon and M. Schick, Phys. Rev. A 9, 907 (1974); 9, 1753 (1974).

[6] G. Derry, D. Wesner, W. E. Carlos, and D. R. Frankl, Surf. Sci. 87, 629 (1979).

[7] G. Boato, P. Cantini, C. Guidi, R. Tatarek, and G. P. Felcher, Phys. Rev. B 20, 3957 (1979).

[8] W. E. Carlos and M. W. Cole, Surf. Sci. 91, 339 (1980).

[9] W. E. Carlos and M. W. Cole, Phys. Rev. B 21, 3713 (1980).

[10] A. F. Silva-Moreira, J. L. Codona, and D. L. Goodstein, Phys. Lett. 76A, 324 (1980).

[11] W. E. Carlos, M. W. Cole, S. Rauber, G. Vidali, A. F. Silva-Moreira, J. L. Codona, and D. L. Goodstein, in proceedings of the International Conference on Ordering in Two Dimensions (in press).

[12] L. M. Sander, M. Bretz, and M. W. Cole, Phys. Rev. B 14, 61 (1976).

[13] A. D. Novaco, Phys. Rev. B 13, 3194 (1976).

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

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

[16] D. L. Freeman, J. Chem. Phys. 62, 4300 (1975).

[17] L. W. Bruch, J. Unguris, and M. B. Webb [Surf. Sci. 87, 437 (1979)] have incorporated this interaction in treating Xe on Ag (111); it yields a 25% reduction in the well depth.

[18] L. Passell, private communication, finds favorable agreement with the value of $z_0 = 2.92$ Å obtained by Ref. 8.

[19] J. de Boer and A. Michels, Physica (Utrecht) 5, 945 (1938); 6, 97 (1939); 6, 409 (1939).

[20] Reference 12 presents figures for various values of d.

[21] H. Watanabe, private communication. The method and input were those of Ref. 15.

[22] L. W. Bruch, P. I. Cohen, and M. B. Webb, Surf. Sci. 59, 1 (1976).

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

[24] R. G. Gordon and Y. S. Kim, J. Chem. Phys. 56, 3122 (1972).

[25] L. W. Bruch [Bull. Am. Phys. Soc. 25, 383 (1980)] has performed a similar comparison.

[26] See, e.g., M. Schick and C. E. Campbell, Phys. Rev. A 2, 1591 (1970); and K. H. Lau and W. Kohn, Surf. Sci. 65, 605 (1977).

[27] J. de Boer, Rep. Prog. Phys. 12, 305 (1949).

[28] M. Schick, private communication; and R. L. Siddon, Ph.D. thesis, University of Washington, 1974 (unpublished).