PHYSICAL REVIEW B VOLUME 33, NUMBER 7 1 APRIL 1986

Scattering of helium atoms by liquid helium

Frank O. Goodman* and Nicolas Garcia†
Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

(Received 23 September 1985)

We present results from a new He—liquid-He single-atom effective potential for scattering, obtained from an integration, over the region occupied by the liquid, of a standard Lennard-Jones 6-12 pairwise potential combined with a simple model of the pair-correlation function. The new potential is consistent with (a) the accepted internal energy (the negative of the latent heat) of liquid He, (b) the accepted long-range ($-C_3/z^3$ van der Waals) atom-surface interaction potential, and (c) the scattering (reflectivity) data of Edwards *et al.* Production of excitons (ripplons) at the surface is not necessary to interpret the data. The theory is unsymmetrized; that is, no account is taken of the fact that scattering among identical particles is being considered.

The reflectivity R (which is the square of the absolute value of the usual reflection coefficient) of ^{4}He at a ^{4}He-liquid surface (referred to hereafter as He liquid) has been studied extensively by Edwards *et al.*[1,2] The values of R, as a function of the normal component k_z of the incident wave vector $\mathbf{k}\equiv(\mathbf{K},k_z)$ of the He atom, are shown in Fig. 1. Two main properties of the data[1,2] are (i) R depends on only k_z, and (ii) there is no measurable inelastic backscattering. Point (i) implies that the problem is essentially one dimensional and, probably, that energy exchange with the surface involving exchange of parallel wave vector $\mathbf{Q}$ ($\mathbf{K}_f=\mathbf{K}_i+\mathbf{Q}$) may be neglected. Thus, the reflectivity may be a pure elastic quantum-mechanical mechanism, which is also consistent with point (ii).

Theoretical attempts[3-5] to explain the data have been made. Etxenique and Pendry[3] assumed that (a) the multiple production of ripplons together with (b) a dropping of the liquid density ρ from its bulk value, ρ_0, to its vacuum value, 0, over a distance of about 5 Å at the surface, are the main mechanisms which are responsible for the data, although their calculated reflectivities show deviations of factors of about 3 from the experimental ones. Usagawa[5] did similar calculations, in the distorted-wave Born approximation, with results quite different from those of Ref. 3. He finds a dip in $R(k_z)$, which he attributes to his truncation of the asymptotic ($z\rightarrow\infty$) single-atom (He-liquid) effective potential ($-C_3/z^3$) at $z=z_0$; we show that this interpretation of the reason for the dip is incorrect. Edwards and Fatouros[4] constructed an empirical effective potential (which we call the EF potential) for which the elastic values of R are in good agreement with the data[1,2] (Fig. 1).

We assume that no account needs to be taken of the fact that scattering among identical particles is being considered; that is, our theory is unsymmetrized. [EF (Ref. 4) found that symmetrization of their theory destroyed its agreement with experiment.] We have found a large number of He-liquid effective potentials $V(z)$ which give good fits to the data, with minima between -5 meV and $-50\ \mu$eV, and with different asymptotic behaviors $-C_3/z^3$ and $-C_4/z^4$. However, the effective potential is presumably unique and should be obtained from a He-He pairwise potential and liquid-He properties, such as a number density $\rho(z)$ and a pair correlation function, which we write as $g(r)-1$ in the usual way (p. 448 of Ref. 6), where $g(r)$ is a radial distribution function.

We propose that the total average potential energy $U(z)$ for one atom interacting with liquid He [which, as we explain below, is not the same as the single-atom effective potential for scattering, $V(z)$] be obtained by integrating a pairwise He-He potential $v(r)$ over space; that is, we define $U(z)$ by

$$U(z)=\int\int\int v(|\mathbf{r}'-\mathbf{r}|)\rho(z')g(|\mathbf{r}'-\mathbf{r}|)d^3\mathbf{r}' . \tag{1}$$

Our $U(z)$ must give the correct asymptotic ($z\rightarrow\infty$)

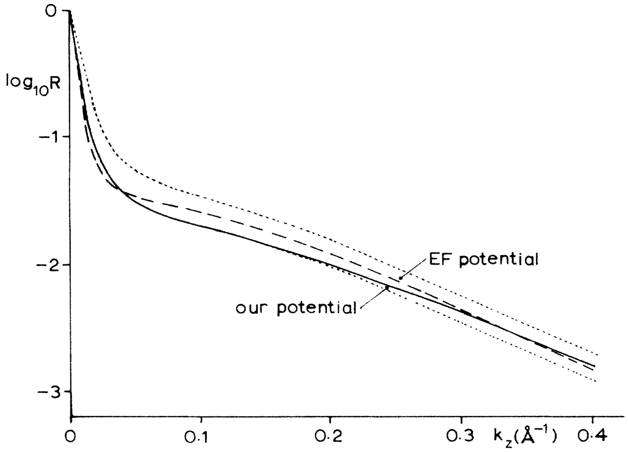

FIG. 1. Reflectivities R as functions of the normal component k_z of the incident wave vector. The dotted curves (. . . .) give the approximate limits of the reflectivity data shown in Fig. 2 of Ref. 2 (although there are no data with $R>\sim0.2$). The solid curve (——) gives results from our potential $V(z)$, and the dashed curve (— — —) gives results from the EF potential.

behavior far from the liquid,

$$\lim_{z\to\infty} z^3 U(z) = -C_3 \ , \tag{2}$$

where C_3 is the usual (nonrelativistic) van der Waals atom-surface coefficient; at the same time, the opposite asymptotic ($z \to -\infty$) behavior should give an estimate of the potential energy ($-W$) of bulk liquid He via the formula

$$U(-\infty) = 4\pi\rho_0 \int_0^\infty r^2 v(r) g(r) dr = -2W \ , \tag{3}$$

where $\rho_0 = \rho(-\infty)$ is the number density of the bulk liquid. The zero-point (correlation) energy Z may then be estimated using the result

$$W = L + Z \ , \tag{4}$$

where L is the latent heat (the negative of the internal energy) of liquid He, which is known from experiment. Also, our function $g(r)$ must obey the sum rule

$$4\pi\rho_0 \int_0^\infty r^2 [1 - g(r)] dr = 1 \ . \tag{5}$$

To model $v(r)$ consistently with (2), we choose a Lennard-Jones 6-12 potential

$$v(r) = 4D[(\sigma/r)^{12} - (\sigma/r)^6] \ , \tag{6}$$

which gives

$$C_6 = 4D\sigma^6 \tag{7}$$

for the usual van der Waals atom-atom coefficient, C_6 and C_3 being related by the standard formula

$$6C_3 = \pi\rho_0 C_6 \ . \tag{8}$$

As for $g(r)$, we adopt the approximation

$$g(r) = H(r - s) \ , \tag{9}$$

where H is the Heaviside step function and s is a length parameter. Formula (9) says that, for a He atom in the liquid, other He atoms are excluded from its spherical neighborhood of radius s and are distributed uniformly outside this neighborhood. Our $g(r)$ is compared with a $g(r)$ based on experimental x-ray scattering data in Fig. 2, and it is clear that (9) is a rather crude approximation to reality. However, it has the advantage of leading to particularly simple versions of (3) and (5), particularly when (6) and (7) are also used in (3); the results may be combined and written as follows:

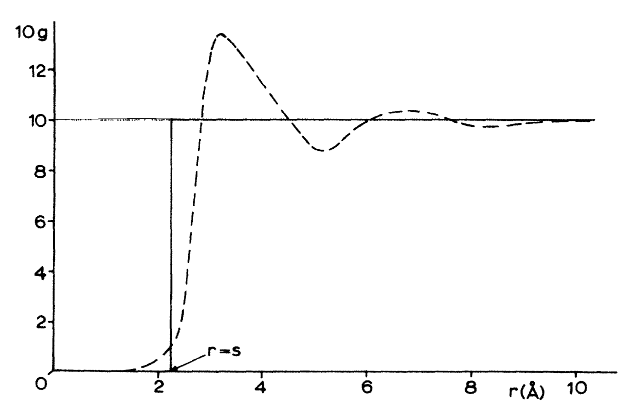

FIG. 2. Our radial distribution function (——) is compared with one (— — —) based (Ref. 10) on experimental x-ray scattering data taken at a temperature of 2.06 K (see also Sec. 2.4 of Ref. 8). The experimental curve is not drawn precisely.

$$4\pi\rho_0 s^3 = 3 \ , \tag{10}$$

$$6Ws^6/C_6 = 3 - (\sigma/s)^6 \ . \tag{11}$$

As we have stated, we obtain our total average one-atom potential energy $U(z)$ from (1), and we must assume a form $\rho(z)$ for the dependence of the liquid density on z. We assume for simplicity that ρ decreases linearly with z from ρ_0 to 0 over a distance $2q$ (Fig. 3). We do not present the analytical result for $U(z)$, as it is lengthy.

We now address the problem of obtaining a suitable effective scattering potential $V(z)$. Outside the liquid, we equate $V(z)$ to $U(z)$,

$$V(z) = U(z) \ , \quad \text{outside liquid} \ . \tag{12a}$$

Inside the liquid, it is tempting to equate $V(z)$ to $-W$, which is given from (4) as $(-L-Z)$. However, the correlation energy Z should not be included in V, and only the latent heat L should be included; that is, we write

$$V(z) = -L \ , \quad \text{inside liquid} \ , \tag{12b}$$

just as in the previous work.[3-5] Accordingly, we have the problem of how to make $V(z)$ consistent with both (12a) and (12b). We do not know how this should be done, but it seems reasonable to assume that

$$V(z) = \max(U(z), -L) \ ; \tag{13}$$

this assumption generates a discontinuity in $V'(z)$ where $U(z) = -L$ (Fig. 4), but (as we check below) this discontinuity has essentially no effect on the reflectivities.

Our procedure for fixing the several parameters is as follows. We first choose $C_6 = 872$ meV Å^6 (Ref. 7), $\rho_0 = 0.022$ Å^{-3} (Sec. 10.5 of Ref. 6), and $L = 0.62$ meV (Sec. 2.2 of Ref. 8). From (8) and (10) this choice gives immediately $s = 2.21$ Å and $C_3 = 10.0$ meV Å^3. If s is interpreted as a pairwise effective-potential scattering length for He, then our result agrees well with that (2.2 Å) quoted in Sec. 10.5 of Ref. 6. Our value of C_3, which is presumably correct, is very close to the "compromise" value (10.4 meV Å^3) chosen by EF (Ref. 4). Finally, σ and q are adjusted in order to give a good fit to the experimental reflectivity data. Such a fit is obtained with $\sigma = 2.53$ Å and $2q = 4.2$ Å. Our value of σ is close to the literature value[9] (2.56 Å), and our value of $2q$ is in

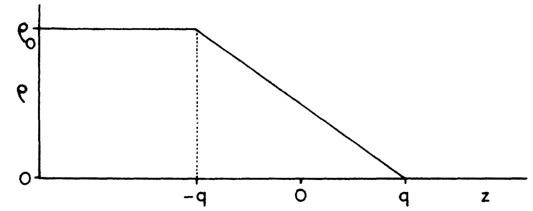

FIG. 3. The assumed dependence of the liquid density ρ on z, with $\rho_0 = 0.022$ Å^{-3} and $2q = 4.2$ Å.

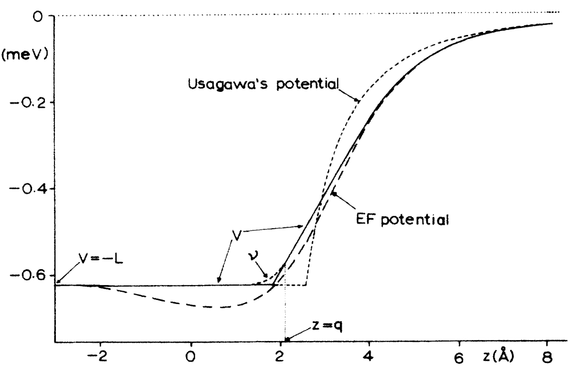

FIG. 4. Single-atom effective potentials for scattering. Our potential $V(z)$ is shown by the solid curve (——), and our potential $\nu(z)$ by the dotted curve (. . . .). The EF potential is shown by the dashed curve (— — —). The potential $\nu(z)$ joins smoothly onto $V(z)$ at $z=q=2.1$ Å. Usagawa's potential is also shown by a dotted curve (. . . .). All four potentials are asymptotic to $-L=-0.62$ meV as $z\rightarrow-\infty$.

reasonable agreement with the suggestion (~ 5 Å) in Sec. 10.5 of Ref. 6 and in Ref. 3.

Although not needed explicitly, our derived values of D, W, and Z are of interest. From (7), we get $D=0.83$ meV, reasonably close to the literature value[9] (0.88 meV). We should note, however, that the literature values[9] of σ and D give, from (7), $C_6=984$ meV Å^6, which is considerably larger than the currently accepted value;[7] thus, we are sure to get a product $D\sigma^6$ smaller than the literature product, and we are quite happy with our values of σ and D. From (4) and (11) we get $W=0.93$ meV and $Z=0.31$ meV, and both of these values are considerably smaller than those quoted in Sec. 2.4 of Ref. 8. However, calculation of W from (3), as is essentially done here, is notoriously unreliable because of the extreme sensitivity of the integral in (3) to be the exact form assumed for $v(r)$.

Our fit to the reflectivity data is shown in Fig. 1, together with the fit obtained with the EF potential. To check whether the discontinuity in $V'(z)$ affects the reflectivities, we formed another potential $\nu(z)$ by joining $U(z)$ to $-L$ by an exponential part $E(z)$, fitted smoothly to $U(z)$ arbitrarily at $z=q$; that is,

$$\nu(z)=\begin{cases}U(z), & z>q\ , & \text{(14a)}\\ E(z), & z<q\ , & \text{(14b)}\end{cases}$$

the actual form of $E(z)$ being

$$E(z)=Ce^{(z-q)/\beta}-L\ , \qquad (15)$$

with $C=48\ \mu$eV, $\beta=0.256$ Å. There is essentially no difference between the values of R obtained with $\nu(z)$ and those obtained with $V(z)$, implying that the smoothing (14) is unnecessary. We have checked that similar statements are true of Usagawa's potential.[5] Our potentials $V(z)$ and $\nu(z)$, as well as the EF potential and Usagawa's potential, are shown for comparison in Fig. 4. It is clear from Fig. 1 that the EF potential and our potential both give good fits to the experimental data (the fit with the EF potential was of course found in Ref. 2). Also, from Fig. 4, we see that our potential, particularly the smoothed from $\nu(z)$, is surprisingly similar to the EF potential (the fact that the EF potential lies below $-L$ in a region close to the surface makes essentially no difference to the reflectivities). This point is made all the more valid if it is realized that a shift of $V(z)$ along the z axis makes no difference to the reflectivities. That our potential must differ from the EF potential (at least for the larger values of z) is of course clear from the 4% difference in the chosen values of C_3. The physical reason that the results from the EF and our potentials are so much better than those from Usagawa's potential is that Usagawa's potential has far larger slopes $V'(z)$ (Fig. 4). Essentially, our integration (1) with $\rho(z)$ as in Fig. 3 "widens" our resulting potential and gives naturally smaller slopes.

It is not necessary to assume loss of energy at the liquid surface (by, for example, ripplons) to interpret the experimental data. Once the slowly moving He atom enters the liquid, it propagates in its flat-bottomed effective potential and eventually equilibrates with the liquid, by creation of multiple phonons or by some other processes, and the experiments in question give no information on these processes. That the surface does not exchange energy is consistent with the negligible number of inelastically backscattered atoms.[1,2]

In conclusion, we have shown how a single-atom effective potential for He-liquid scattering $V(z)$ may be obtained, by using (13), from the total single-atom average potential energy $U(z)$ given by (1). We have further shown that a self-consistent procedure, using this potential $V(z)$ in conjunction with the pairwise He-He potential (6) and the simple form (9) of the radial distribution function $g(r)$, gives good agreement with the scattering data[1,2] of Edwards' group, provided that the liquid-He density profile $\rho(z)$ is as suggested in Fig. 3. We can offer no good explanation of why the unsymmetrized theory works well, but can only repeat EF's suggestion[4] that the important effects take place in regions where symmetry is unimportant.

We acknowledge useful discussions with Dr. J. Garcia-Fernandez, Dr. J. Reyes, and Dr. J. M. Soler on the subject of this work. The work was supported by the Natural Sciences and Engineering Research Council of Canada under Grant No. A6282.

---

[*] Also at the Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

[†] Permanent address: Departamento de Fisica Fundamental, Universidad Autonoma de Madrid, Canto Blanco, 28049-Madrid, Spain.

[1] D. O. Edwards, P. P. Fatouros, G. G. Ihas, P. Mrozinski, S. Y. Shen, F. M. Gasparini, and C. P. Tam, Phys. Rev. Lett. **34**, 1153 (1975).

[2] V. U. Nayak, D. O. Edwards, and N. Masuhara, Phys. Rev. Lett. **50**, 990 (1983).

[3] P. M. Etxenique and J. Pendry, Phys. Rev. Lett. **37**, 561 (1976).

[4] D. O. Edwards and P. P. Fatouros, Phys. Rev. B **17**, 2147 (1978).

[5] T. Usagawa, Phys. Lett. **73A**, 339 (1979).

[6] R. K. Pathria, *Statistical Mechanics* (Pergamon, New York, 1972).

[7] A. Kumar and W. J. Meath, Mol. Phys. **54**, 823 (1985).

[8] K. R. Atkins, *Liquid Helium* (Cambridge University Press, Cambridge, England, 1959).

[9] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), Table IA.

[10] L. Goldstein and J. Reekie, Phys. Rev. **98**, 857 (1955).