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THE POTENTIAL CURVE OF THE He–α-QUARTZ SURFACE INTERACTION

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One of the fundamental problems for gas–surface interaction physics is to relate the pairwise gas atom–surface atom interaction characteristics to that of the aggregate collision complex. One method of studying the problem on a microscopic scale is to model the surface lattice structure and calculate the interaction characteristics using the Monte Carlo technique. We describe the calculation of the He–α-quartz (SiO_2) interaction potential applying this method assuming pairwise He–surface atom Lennard-Jones (12, 6) potentials. The results show that the interaction potential follows a (13.5, 3.8) shape function in the gas–surface interaction range below 8 Å, and an asymptotic dependence with $3.8 < m < 6$ for the region beyond 8 Å. This potential well shape function differs substantially from the (9, 3) function suggested by earlier work. The calculated potential curve shows a weak dependence on surface and gas temperature. The potential well depth of the gas–surface interaction shows a strong nonlinear relationship to the equilibrium internuclear distance of the He–Si pair potential applied to the calculation. We find that the empirically determined parameters for the He–Si pair potential provide resultant gas–surface potentials with well depth remarkably close to those required by the measured heat of adsorption.

1. Introduction

Energy accommodation in gas–surface interactions is a subject of interest for a broad range of applications. However, most of the research on the subject (see Trilling [1,2] and Goodman [3]) is confined to the calculation of the mean accommodation coefficient (α). Consequently these calculations produce results which have little or no dependence on the surface temperature. In fact classical formulations of the accommodation coefficient are independent of the surface temperature (Devonshire [4]). These results aparently are, in reality, basically correct. However, in a number of problems in physics we require knowledge of the details of energy distribution of the scattered gas atom. In this latter case the temperature, detailed structure of the solid, and the shape of the gas–surface interaction potential play a larger role. The continuing research reported here, involving He–SiO_2 interaction, was motivated initially by studies of the evolution of low density planetary atmospheres (Shemansky and Broadfoot [5]), in which the atmosphere is dominantly He and the surface is dominantly SiO_2. In a physical problem such as this we must examine the fundamental microscopic process of energy exchange in low-energy gas atom collisions, in order to establish the equilibrated energy distribution of a gas controlled entirely by the heterogeneous reaction. This is clearly impossible with accommodation theory that is integral in nature with no dependence on surface temperature. A computational method has been developed with application to problems of this kind in mind (Kunc and Shemansky [6]), to provide a means of determining the energy distribution of the scattered gas atoms. In these calculations of the microscopic scattering process the greater dependence of the results on the shape of the gas–surface potential curve, introduces an uncertainty because the shape functions have been established mostly on an empirical basis. The relationship of the atom–atom interaction potential to that of the gas–surface system is also a matter of substantial importance, and in this case as well, the relationship has been based simply on assumption in most cases. In this paper we report a direct calculation of the He–SiO_2 potential using the method described in ref. [6], which includes the dynamics of the surface structure in a Monte Carlo simulation of the interaction. The mean potential interaction curve is obtained through a statistical calculation using a realistic three-dimensional model of the surface structure.

The generalized Lennard-Jones (n, m) form of the physical central force potential for neutral–neutral interaction has been successful in the kinetic theory of gases [7]. Therefore this form of the potential is generally applied to physical neutral atom–surface interactions. The generalized (n, m) potential curve has the following form,

$$U(z)=\frac{mD}{n-m}\left[\left(\frac{\bar{z}}{z}\right)^n-\frac{n}{m}\left(\frac{\bar{z}}{z}\right)^m\right], \tag{1}$$

where D is the potential well-depth, z is the vertical distance above the plane of the surface, and $\bar{z}$ is the position of the potential minimum. The position at which the potential crosses zero at the inner turning point is

$$z_0=\bar{z}(n/m)^{1/(m-n)}. \tag{2}$$

If we make the assumption that the form of eq. (1) is basically correct for the gas atom–surface atom pairwise interaction, we then wish to establish the form of the gas–surface interaction in a definitive way, so that parametric dependencies can be directly determined. Generally we find that the resultant gas–surface interaction curve can be fitted to the (n, m) form for gas atom positions $z \gtrsim z_0$. The form of the apparent potential for $z \lesssim z_0$ in the calculation tends to take on complex structure because of the energy exchange reaction. Thus, at some ill-defined location in the inner turning point region, the calculated curve no longer corresponds to the interaction potential.

Through analytic fitting of the resultant potential curve, one may then produce a starting point for quantum-mechanical or semiclassical calculations of the collision system that can be related back to the atom–atom pair interaction potential. The basic disadvantage of the Monte Carlo method is the enormous demand on computation time, and we suggest that possibly a combination of theoretical techniques can be more effectively applied to gas–surface interaction calculations.

2. Monte Carlo calculation of the interaction potential

The method of calculating the interaction potential is based on the model developed by Kunc and Shemansky [6]. The model [6] was designed for the calculation of the microscopic three-dimensional scattered distribution and energy exchange in the interaction of low-energy atoms with a solid surface. The surface structure is synthesized to provide an accurate target structure for the scattering calculation. The dynamics of the surface is taken into account in the sense that the upper layer of surface atoms are non-rigid and vibrate at selected temperatures. In this case the upper layer consists of 9 upper layer sites interacting with adjacent surface atoms, requiring 60 coupled differential equations to describe the system [6]. The Monte Carlo method is adaptable to the determination of the interaction potential because details of the motion of each gas atom in its collision trajectory are traced in the calculation.

In this application the atom is launched with a given energy toward the surface with a selected vertical velocity, from the same vertical position for all trajectories. This differs from the scattering calculations described in ref. [6] in which the vertical launch point of the gas atom contained a random variable. The horizontal starting point of the gas atom is a uniform random distribution over the lattice structure. The coordinate z, the distance from the atom to the surface, has two limits, $z_{\max}$ and $z_{\min}$, which define the range of z included in the calculations. The initial position of the atom in each trajectory, $z_{\max}$, is the distance at which the atom–surface interaction potential is so weak that interaction can be neglected for $z > z_{\max}$. In the case of the helium atom–α-quartz interaction discussed below we assumed $z_{\max} = 50$ Å.

The lower limit, $z_{\min}$, is fixed by numerical analysis for a particular gas–surface complex, at some positive value close to the surface. The value of $z_{\min}$ is set for the practical purpose of limiting the computation time required for the calculation. The inner region of the potential curve in the vicinity of $z_{\min}$ is a region of high acceleration and demands rapidly increasing computation times as $z_{\min}$ is decreased. The calculated curve in the inner turning point region at some point near $z_{\min}$ loses definition as a potential as noted above. Thus, although the computational method [6] can carry the calculation of the collision complex through entrapment and adsorption events, the usefulness of applying the calculation of the aggregate potential curve to very small z is questionable.

We examine the interaction of a helium atom with the (0001) plane of α-quartz lattice (SiO_2). This lattice is hexagonal with lattice constants $a = 4.91$ Å and $b = 5.41$ Å [8]. All parameters characterizing the helium atom–α-quartz interactions are the same as those of ref. [6]. However, we have varied the potential well depth and $\bar{z}$ values of the gas atom–surface atom interaction pairs in order to obtain a measure of the dependence of the resultant potential curve on these parameters. The values of D and $\bar{z}$ used in ref. [6] are empirically determined quantities.

3. Interaction potentials

Several authors [9–11] have recently postulated the (9, 3) potential (eq. (1)):

$$U_J(z) = \frac{D_J}{2}\left[\left(\frac{\bar{z}_J}{z}\right)^9 - 3\left(\frac{\bar{z}_J}{z}\right)^3\right], \tag{3}$$

as an effective description of a neutral–surface interaction potential. Cole and Tsong [9] used the potential eq. (3) in WKB approximation for determination of the eigenvalue spectrum E_n (for $n = 0$, 1 and 2) in the He–NaF interaction and these theoretical results showed acceptable agreement with measured eigenvalues. Thus the use of the (9, 3) potential is justified strictly through comparison with experiment rather than through relating pairwise atom–atom interaction to solid structure.

The potential of the (9, 3) form was also used by Lane and Spurling [10,12] in a Monte Carlo simulation of interaction between argon atoms and a solid carbon dioxide wall. However, there was no comparison of the results of this computation with an experiment or other theoretical results.

Other forms of potentials for atom–surface interaction were proposed. One of the earliest is the Morse potential in the well-known form:

$$U_M(z) = D_M[\exp(-2\alpha z) - 2\exp(-\alpha z)], \tag{4}$$

where α is a fitting parameter.

Tsuchida [13] proposed yet another form of the atom–surface potential

$$U_T(z) = \frac{D_T}{n-3}\left[3\left(\frac{\bar{z}_T}{z}\right)^n - n\left(\frac{\bar{z}_T}{z}\right)^3\right], \tag{5}$$

in fitting theoretical calculations treating the atom–surface scattering through separation of the surface field of He above LiF and NaF crystals in Fourier components. The calculations by Tsuchida, using $n = 12$, $D_T = 10.41$ meV and $\bar{z} = 2.65$ Å, relating to the energies of the surfaces of LiF and NaF were verified by the experimental data [14,15]. The (12, 3) function found by Tsuchida to fit the numerical calculation quite accurately over the important region of the curve, evidently cannot be satisfactorily applied to the present calculation for He–α-quartz as discussed below.

Schwartz et al. [16] used two different approaches. The first was the Rydberg–Klein–Rees approach [17,18] of molecular physics based on the Bohr–Sommerfeld quantization condition for the phase integral between the turning points of the oscillator formed by the vibrational states of the atom–surface system. The second approach was based on using shifted Morse function with the energy eigenvalues the same as for Morse potential [19]. The results obtained by these two approaches were compared with the potential eq. (3) in the following modified form:

$$U_{\mathrm{JM}}(z) = \frac{3^{3/2} D_{\mathrm{JM}}}{2} \left[\left(\frac{\sigma + z_0}{z + z_0} \right)^9 - \left(\frac{\sigma + z_0}{z + z_0} \right)^3 \right], \tag{6}$$

where z_0 is a fitting parameter, typically in the 0.5–1 Å range [16]. Calculations by Schwartz et al. [16], using these two techniques, for He scattering from LiF and NaF, produced similar results. The following characteristic parameters of the potential eq. (6) were obtained: $D_{\mathrm{JM}} = 7.64$ meV and $\bar{z}_{\mathrm{JM}} = 2.16$ Å (He/NaF), $D_{\mathrm{JM}} = 8.92$ meV and $\bar{z}_{\mathrm{JM}} = 2.09$ Å (He/LiF).

The physical motivation for accepting the (9, 3) form is that, if the atom–surface interaction is derived by pairwise summation of Lennard-Jones (12, 6) interactions

$$U_{\mathrm{LJ}}(z) = D_{\mathrm{LJ}} \left[\left(\frac{\bar{z}_{\mathrm{LJ}}}{z} \right)^{12} - 2 \left(\frac{\bar{z}_{\mathrm{LJ}}}{z} \right)^{6} \right], \tag{7}$$

with substrate ions, or atoms, the (9, 3) interaction results as the average of the potential in the continuum limit for the solid [11]. In other words, the (9, 3) potential can be thought of as the surface analog of the Lennard-Jones (12, 6) interatomic interaction, which has been used extensively as a model potential in the kinetic theory of gases.

4. Results and discussion

In the present work we perform a detailed numerical analysis, using the Monte Carlo method, of helium interaction with the basal (0001) plane of α-quartz. In summary, the atom–surface interaction is determined from Monte Carlo analysis of a statistical ensemble of three-dimensional trajectories of the atom approaching the surface. The surface is represented by atoms of two

Table 1
Interaction potential ($U(z)$) of helium with the basal (0001) plane of α-quartz calculated in the present work [a)]

z (Å)	$U(z)$ (meV)						
	(A)	(B)	(C)	(D)	(E)	(F)	(G)
1.741	30.7	23.7	30.8	−4.86	23.5	−3.45	−2.01
1.790	24.3	15.6	23.8	−5.10	28.2	−2.88	−2.47
1.839	22.0	15.0	21.2	−2.87	22.6	−5.87	−2.72
1.888	13.3	20.5	12.6	−9.93−1	17.1	−4.06	−4.28
1.937	9.3	11.0	10.1	−4.11−1	12.5	−4.81	−2.09
1.986	12.0	21.8	10.8	−9.83−1	12.3	−3.94	−2.79
2.035	9.5	18.1	13.2	−5.88	15.9	−3.67	−4.91
2.084	22.7	25.6	19.1	−5.16	17.9	−3.70	−6.01
2.133	15.4	25.2	17.1	−3.19	14.3	−3.77	−6.43
2.182	18.0	19.5	16.9	−2.69	5.48	−3.60	−6.47
2.231	16.2	11.3	14.5	−3.93	−7.84−1	−5.38	−6.43
2.280	5.29	2.10	5.66	−3.61	−4.19	−6.62	−6.26
2.329	−1.05	−2.69	−1.29	−5.50	−6.01	−7.33	−6.05
2.378	−4.93	−5.76	−4.57	−4.36	−7.40	−7.60	−5.83
2.427	−6.80	−7.56	−6.81	−5.01	−8.14	−7.66	−5.56
2.476	−8.21	−8.63	−8.03	−7.46	−8.58	−7.57	−5.31
2.525	−8.96	−9.27	−8.94	−8.71	−8.73	−7.37	−5.06

2.574	−9.39	−9.57	−9.34	−9.15	−8.70	−7.10	−4.79
2.623	−9.58	−9.69	−9.56	−9.33	−8.60	−6.83	−4.53
2.721	−9.43	−9.47	−9.42	−9.21	−8.13	−6.20	−4.01
2.819	−8.92	−8.96	−8.92	−8.78	−7.50	−5.59	−3.55
3.015	−7.59	−7.64	−7.59	−7.56	−6.19	−4.49	−2.78
3.212	−6.26	−6.31	−6.26	−6.25	−4.96	−3.60	−2.20
3.506	−4.57	−4.60	−4.57	−4.59	−3.61	−2.57	−1.56
3.800	−3.38	−3.42	−3.39	−3.38	−2.66	−1.87	−1.13
4.437	−1.78	−1.80	−1.78	−1.80	−1.39	−9.75−1	−5.82−1
5.222	−8.90−1 [b]	−9.02−1	−8.90−1	−8.97−1	−6.90−1	−4.85−1	−2.88−1
6.202	−4.07−1	−4.13−1	−4.07−1	−4.17−1	−3.13−1	−2.23−1	−1.32−1
7.232	−1.92−1	−1.96−1	−1.92−1	−2.04−1	−1.46−1	−1.09−1	−6.33−2
8.311	−9.12−2	−9.32−2	−9.12−2	−1.03−1	−6.71−2	−5.46−2	−3.10−2
9.438	−3.99−2	−4.11−2	−3.99−2	−5.43−2	−2.72−2	−2.77−2	−1.49−2
11.007	−6.58−3	−7.15−3	−6.58−3	−2.31−2	−1.38−3	−1.05−2	−4.58−3
12.527	−1.27−4	−1.54−4	−1.28−4	−9.49−3	−	−3.06−3	−1.66−4
D_p (meV)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
$\bar{z}_p$ (Å)	2.98	2.98	2.98	2.98	2.86	2.69	2.47
T_S (K)	10	100	1000	100	100	100	100
T_G (K)	1500	1500	1500	300	1500	300	300

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[a] See text.

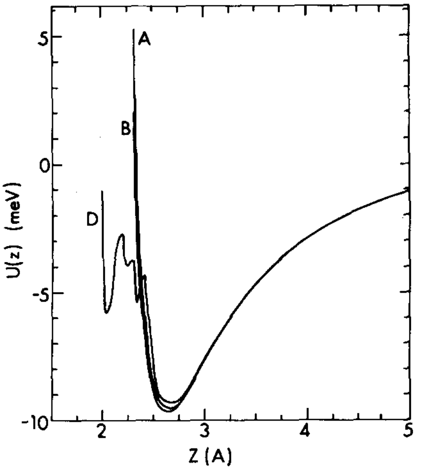
[b] $-8.90-1=-8.90\times10^{-1}$.

upper layers of the solid lattice according to crystallographic data. The incoming atom impacts the surface along a trajectory – an element of the statistical ensemble. The dynamics of the atom–surface complex is calculated from the three-dimensional Hamilton equations. The total interaction potential appearing in the Hamiltonian for the system contains two different interparticle potentials. One of these is the sum of all pairwise impacting-atom–surface-atom potentials. These potentials are Lennard-Jones (12, 6) functions [6]. The potential of a surface atom in the Hamiltonian is a sum of all pairwise potentials between the surface atom and its neighbors. The single pairwise potential in this case was assumed to be harmonic with an effective value of the force constant determined by the Debye elastic wave theory [6]. As a result of solution of the system of Hamilton equations for randomly chosen trajectories one obtains average values of such three-dimensional quantities as position, velocity, acceleration, etc., during the collision process.

The numerical results of the Monte Carlo calculation for the atom–surface interaction potential are given in table 1 for the He/α-quartz system. A Debye characteristic temperature (Θ) of 470 K was applied to the α-quartz structure. The apparent potential curve depends on a number of parameters that have not been thoroughly explored at this point because of the heavy demand on computer time. All of the calculations were carried out with a fixed value of Θ, but limited variation in gas and surface temperatures, and gas atom–surface atom LJ potential parameters, have been examined. The nature of the dependence of the calculated curve on the parameters is discussed below.

4.1. Temperature dependence

The potential curve has been calculated for surface temperatures (T_S) of 1000, 100, and 10 K, for a single He launch energy (T_G) of 1500 K. The resultant curves are very similar with divergence in shape for small values of z beginning just above the potential minimum. The differences in these curves range from a factor of 1.015 at the potential minimum, to more than 2 near the vanishing point. The dependence on surface temperature appears to be nonlinear, with the cold surface showing a shallower well depth (fig. 1, table 1). The interpretation of the effect of T_S on the apparent potential is not clear at this point because of the small computational sample. The difficulty with interpreting the differences in the inner turning point region without knowledge of a specific functional dependence is that one has no definitive means of separating momentum transfer from the apparent potential in this range of small z values. The dependence on gas atom energy, T_G, affects basically the same region of z (fig. 1, table 1), with a fractional difference in potential well depth of 1.037 for $T_G = 1500$ K relative to that for $T_G = 300$ K. The lower temperature curves ($T_G = 300$ K) show strong effects of energy exchange before the vanishing point in the inner turning point region, whereas the $T_G = 1500$ K



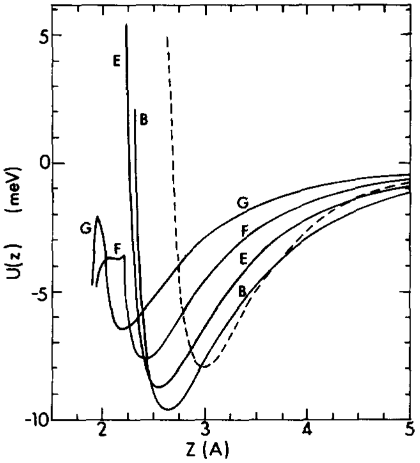


Fig. 1. Calculated apparent potential curves for He–α-quartz interaction, showing dependence on the parameters T_S and T_G. The curves labeled A, B, and D refer to the corresponding columns in table 1.

Fig. 2. Calculated apparent potential curves for He–α-quartz interaction, showing the dependence on the parameter $\bar{z}_p$. The curves labeled B, E, F, G, refer to the corresponding columns in table 1. The dashed curve is the Lennard-Jones (12, 6) He–Si interaction potential with the empirically determined parameters $D_p = 8.0$ meV and $\bar{z}_p = 2.98$ Å. Curve B is the resultant gas–surface potential curve produced from the application of the He–Si interaction curve shown in the figure.

curves show a rapidly rising function to positive potential before showing obvious effects of energy exchange.

4.2. Dependence on gas atom–surface atom pair potential

The most dramatic effect in these calculations is the dependence of the gas–surface potential well depth (D_S) on the equilibrium internuclear distance ($\bar{z}_p$) of the pair potential. Fig. 2 shows the calculated curves in which $\bar{z}_p$ is the variable quantity. The dependence of D_S on $\bar{z}_p$ is clearly quite strong, and it is remarkable that, in this instance, the empirically derived values for the pair interaction, $D_p = 8.0$ meV, $\bar{z}_p = 2.98$ Å, provide very nearly the measured heat of adsorption for He (50 K). The measured heat of adsorption can be obtained in these calculations by a relatively small change in either or both of the pair potential parameters. We estimate, for example, that the values $D_p = 8.0$ meV, $\bar{z}_p = 2.89$ Å, or $D_p = 7.3$ meV, $\bar{z} = 2.98$ Å, will provide an ~ 50 K heat of adsorption. The resultant gas–surface potential curves using these parameters then have projected values $D_S = 8.9$ meV, $\bar{z}_S = 2.53$ Å in the first case and $D_S = 8.8$ meV, $\bar{z}_S = 2.62$ Å in the second. The zero-point energy can be calculated by numerical integration of the WKB eigenvalue expression (see Shin [20,21]), The ratio of zero-point energy to the well depth ($G(v = 0)/D_e$) is in the range 0.46–0.48 for the above gas–surface potential parameters. In comparison, the quantity $G(v=0)/D_e$ is 0.49–0.50 for the 12,6 Lennard-Jones potential, using the same parameters with the Shin [21] expression or by numerical integration. On this basis the heat of adsorption is in the range 54–56 K using the potential curves calculated in the present work.

The calculated potential curves can be approximated in the $z < 8$ Å region with a single equation of the form of eq. (1). Curves for $n = 13.5$, $m = 3.8$ show a good approximation to the data in columns (A)–(D) of table 1. The longer-range interaction region ($z > 8$ Å) appears to have a more sharply defined curvature, with m confined in the range 3.8–6. The relationship of the gas–surface equilibrium distance $\bar{z}_S$ to that of the He–Si pair potential shows no dependence on the temperature parameters, and the calculated curves are related by a constant factor,

$$\bar{z}_S = 0.8826\bar{z}_p. \qquad (8)$$

The calculated gas–surface potential well depth D_S shows a strong nonlinear dependence on the He–Si pair potential internuclear equilibrium distance, $\bar{z}_p$, and a smaller ill-defined dependence on the temperature, or particle energy parameters.

The relationship between the pairwise interaction potential of the gas atom–surface atom binary collision system and that of the gas atom–surface collision system has never been established definitively. The question of exactly what mean potential function, $U(z)$, in the gas–surface interaction results from the application of a pairwise Lennard-Jones potential has thus never been determined up to this point. In principle, the application of the present method can relate the solid lattice structure and force constants to the resultant potential curve, as well as the pairwise interaction potential. The point we wish to establish at this stage is that none of the previous potential forms given by eqs. (3), (5), and (6) provide a satisfactory fit to the curve established by the Monte Carlo calculation. However, the form of eq. (1) with suitably chosen n, m can be applied to the calculated curve ($z < 8$ Å), in the region that substantially affects the interaction characteristics. The modified (9, 3) function (eq. (6)) can be forced to provide a better fit to the width of the potential function near the potential minimum but the section of the calculated curve in the $z > \bar{z}$ region is not satisfactorily reproduced. These results, in fact, are reminiscent of the result obtained by Schwartz [16] in which the constant factor in the asymptotic relation $U(z) = Cz^{-3}$ produced by eq. (6) was approximately a factor of 2 larger than expected from the theoretical calculation based on a shifted Morse hybrid potential. The basic effect of the modified (9, 3) potential is to alter the asymptotic form of the potential for the $z > \bar{z}$ region, resulting in a deviation from the $U(z) \propto z^{-3}$ dependence. For this reason we suggest that eq. (6) is fundamentally unsuitable as an approximation to the gas–surface interaction potential.

5. Summary

The He–α-quartz potential interaction curve has been calculated using a Monte Carlo method in which the surface structure is accurately modeled [6] in a simulation of the collision system. The basic assumption in the calculation was the adoption of an He–Si pairwise interaction potential of the Lennard-Jones (12, 6) form. The resultant calculated gas–surface potential curve has the basic form of eq. (1) in the range $z < 8$ Å with parameters $n = 13.5$ and $m = 3.8$, with relatively small variations around these values depending on the parameters $\bar{z}$, T_S, and T_G. In the range $z > 8$ Å the magnitude of m rises toward a value of 6. The calculated well depth, D_S, of the gas–surface potential shows a strong dependence on the equilibrium internuclear distance, $\bar{z}_p$, of the He–Si pair potential, and a weaker dependence on the energy parameters T_S and T_G. The empirically determined He–Si pair potential parameters produce a resultant gas–surface potential with a slightly larger heat of adsorption relative to measurement. Minor changes in either or both D_p and $\bar{z}_p$ bring the calculated gas–surface potential well into conformity with heat of adsorption measurements. This appears to provide some measure of confidence in the empirical method of estimating the pair potential.

The Monte Carlo method of calculating gas–surface potential interaction curves developed in this work, can serve two important areas of gas–surface interaction physics. First, one can directly relate the dependence of the potential interaction on surface characteristics such as lattice geometric structure and Debye temperature, by varying these quantities in the simultation of the collision complex. Second, the Monte Carlo calculation for the first time provides the shape of the inner turning point region of the interaction, based on the assumed Lennard-Jones pairwise function. Advances in experimental surface science technology in recent years may be capable of defining vibrational energies to sufficiently high quantum numbers and thus provide a means by which the assumed (12, 6) pairwise interaction function can be tested. We propose to examine the influence of surface lattice configuration and Debye temperature, along with the other physical parameters, in the next step of this study. A calculation of energy eigenvalues of the Monte Carlo resultant potentials using a numerical technique, with the WKB equations has been applied in order to test against experiment.

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