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INTRODUCTION

The interaction of gases with solid surfaces is a problem of considerable practical importance and has received much attention in the literature. Application of the solution of some of these problems is found in surface coatings, vacuum technology, thin-film growth, and surface contamination. In addition, new and interesting physical processes are being studied through surface scattering experiments. Our principal interest is in the study of the growth of thin, solid films on salt surfaces.

The interaction of gases with solid surfaces is characterized by a long-range attractive force combined with a short-range repulsive force (ref. 1). It is usually assumed that the total gas-surface interaction can be approximated as the sum of the gas atoms and the individual atomic constituents of the solid over the two-body interaction potentials (ref. 2). Thus, determining the interatomic potential is of fundamental importance.

In examining the literature on the binding potentials of individual atoms on salt surfaces, one is amazed by the diversity of approaches and by the wide range of final values obtained by various authors. We found no consistency in the treatment of the long-range attractive forces even though these forces are reasonably well defined from atomic spectral properties. The short-range repulsive core parameters were taken from diverse studies on gas properties and on ionic crystals with no attempt to treat all the data on a systematic basis. After a brief review of the theoretical developments in this field of research, we present a program to consistently analyze and develop a data base of physical interaction parameters for future studies of the interaction of noble metals with salt surfaces.

REVIEW OF THEORETICAL DEVELOPMENTS

Models of the interatomic potential are usually approximated with a long-range attractive-force potential varying as the inverse of the separation of the atoms raised to the sixth power. The attractive potential is usually identified with the London dispersion force (ref. 3). The short-range repulsive core potential in early models was taken as the inverse of the separation raised to the twelfth power by Lennard-Jones (refs. 1 and 2) or as an exponential by Buckingham (ref. 4). The Lennard-Jones potential

$$\phi_{LJ}(r) = \varepsilon\left[\left(\frac{R}{r}\right)^{12} - 2\left(\frac{R}{r}\right)^{6}\right]$$

has two free parameters usually taken as the equilibrium well depth ε and the mean equilibrium separation R, where r is the separation of the atoms. (A list of symbols appears after the references.) The zero potential crossing radius σ is fixed at 0.89R, independent of well depth. The constant of the London dispersion force μ is then given by $2\varepsilon R^6$. The Buckingham potential is usually written as

$$\phi_B(r) = \frac{\varepsilon}{1 - \frac{6}{\beta}}\left[\frac{6}{\beta}\exp\left(\beta - \beta\frac{r}{R}\right) - \left(\frac{R}{r}\right)^6\right]$$

where β is a parameter characterizing the repulsive force. The corresponding value of the constant of the London dispersion force is given by $\varepsilon R^6/[1 - (6/\beta)]$, which is equal to the Lennard-Jones value only for $\beta = 12$. The zero potential crossing radius is 0.89R when $\beta \approx 14.5$. Since the second virial coefficient is related to σ^3, R^3, and ε, most gases yield $\sigma \approx 0.89R$ and result in a London dispersion constant, which is 18 percent lower for the Buckingham potential than that found for the Lennard-Jones potential. The analysis of gas thermodynamic data shows more consistent results from use of the Buckingham potential (ref. 5). Early work on interatomic potentials was largely devoted to extracting potential parameters from experimental data and searching for semiempirical relations among parameters to provide some semiempirical predictive capability.

The long-range attractive forces between atoms were first analyzed by London (ref. 3). He showed that the first-order perturbation between two atoms was zero but that second-order perturbation theory gave rise to an interatomic potential related to the atomic multipole transition amplitudes, giving rise to the name dispersion forces. The r^{-6} term was related to the interaction of an induced dipole in each of the two atoms and the potential coefficient was related to the dynamic polarizabilities. He further showed that if the dipole polarizability was replaced by a single-pole term at frequency $\tilde{\omega}_1$, then the dispersion force constants could be written as

$$\mu_L = \frac{3}{2}\alpha_2\alpha_2' \frac{\tilde{\omega}_1\tilde{\omega}_1'}{\tilde{\omega}_1 + \tilde{\omega}_1'}$$

where α_2 and α_2' are the corresponding atomic static polarizabilities of the two atoms. (The unprimed and primed symbols indicate the two atoms.) Since the energy poles appear near the ionization potentials I, we have the approximation

$$\mu_L \approx \frac{3}{2}\alpha_2\alpha_2' \frac{(I)(I')}{I + I'}$$

Another approximation used in many surface physics calculations is that of Kirkwood and Müller (refs. 6 and 7):

$$\mu_{KM} = 6mc^2 \frac{\alpha_2\alpha_2'}{(\alpha_2/\chi_m) + (\alpha_2'/\chi_m')}$$

where m is the electron mass, c is the velocity of light, and χ_m and χ_m' are the magnetic susceptibilities of the two atoms. These formulas may be used to derive general relations between the force constants μ of interaction potentials for differing atomic systems (ref. 8), denoted by subscripts 1 and 2, as follows:

$$\frac{2\alpha_2\alpha_2'}{\mu_{12}} = \frac{(\alpha_2)^2}{\mu_{11}} + \frac{(\alpha_2')^2}{\mu_{22}}$$

which can be approximated as

$$\mu_{12} \approx \sqrt{\mu_{11}\mu_{22}}$$

It can be seen from this last equation that

$$\varepsilon_{12} \approx \sqrt{\varepsilon_{11}\varepsilon_{22}}$$

which follows from the Lennard-Jones potential and from the fact that $R_{12} \approx \sqrt{R_{11}R_{22}}$. The combination rules for the Lennard-Jones potential are the same as for ε_{12}, and consequently, we can derive

$$R_{12} = \frac{R_{11} + R_{22}}{2}$$

The exponential repulsive term was proposed by Zener (ref. 9), who relates the exponential decay constant to the asymptotic electronic wave functions

$$\psi = \exp\left(-\sqrt{2I/a_oe^2}\ x\right)$$

where I is the ionization potential, a_o is Bohr's radius, x is the electron radial coordinate, and e is the electron charge. Zener's results suggest that

$$\frac{\beta_{12}}{R_{12}} = \frac{1}{2}\left(\frac{\beta_{11}}{R_{11}} + \frac{\beta_{22}}{R_{22}}\right)$$

is an appropriate combination for the exponential parameter β of the Buckingham potential.

The above formalisms have been used to study physical adsorption on surfaces over the years. Studies of noble gas adsorption on salt in particular (ref. 10) relied on salt cohesive-force data (ref. 11). The London dispersion force was usually approximated through use of the Kirkwood-Müller formula, the magnetic susceptibility data of Hoare and Brindley (ref. 12), and the polarizability of Mayer (ref. 13). The repulsive core parameters were estimated from virial data for argon and studies of salt crystals (ref. 11). In addition to these forces, the electrostatic attraction caused by the induced dipole moments in the adatom was added (ref. 10). Note that static polarizability was estimated from the interatomic potential data and may or may not reflect the dispersive properties of isolated atoms. Later work used the same methodology with improved data (ref. 14).

In most applications of surface physics, the above historical development is taken as the obvious starting point for estimating surface adsorption potentials (ref. 15). Application to new adatoms for which the interaction forces are unknown usually relies on atomic spectroscopic data to estimate atomic polarizabilities (ref. 16). Although forms equivalent to the Kirkwood-Müller formula are used for dipole-quadrupole and quadrupole-quadrupole interaction terms (ref. 17), the Kirkwood-Müller formula is still used to estimate the dispersion force constant.

More recently, methods have been developed which allow calculations of interaction potentials between closed-shell atoms (refs. 18 and 19). These calculations agree satisfactorily with known noble gas interactions and provide new results for noble gas interactions with alkali and halide ions. Since we are interested in thin-film growth on salts, which requires interactions with salt ions, these interactions seem to be a natural starting point for a systematic study of potential parameters to provide a data base for estimates of physical adsorption on salts.

In the present report, we examine interatomic forces using semiempirical notions and derive relations for potential parameters in terms of basic atomic properties and repulsive core parameters. We require the formalism and the repulsive core parameters to describe diatomic interaction data, noble gas crystal data, and ionic crystal data. Such a globally consistent theory and data base should then provide a reliable basis for the estimation of potentials among many atom-atom and atom-surface systems. Because the potential parameters are related to fundamental atomic constants, the formation of a predictive capability is an inherent part of the present formalism.

INTERATOMIC POTENTIAL

The repulsive core was studied by Zener (ref. 9), who shows that the quantum analog is

$$\phi_R(r) \approx A \exp(-br) \tag{1}$$

where the exponential factor for two unlike atoms is found according to the combination rule:

$$b_{AB} = \frac{1}{2}(b_A + b_B) \tag{2}$$

for atoms A and B. The short-range forces between noble gas atoms are also calculated in the electron gas model by Waldman and Gordon (ref. 19) as well as by Gilbert and Wahl (ref. 20) using the Hartree-Fock methods. These investigations confirm the repulsive potential form given by Zener. As shown by Gordon and Kim (ref. 18), repulsion is mainly made up of the total electronic kinetic energy as a function of nuclear separation and is closely related to the product of the atomic wave functions in the overlap region as assumed by Zener. Asymptotic wave functions have been found by Handler, Smith, and Silverstone (ref. 21) to be of the form

$$\psi_i = r^{\lambda_i} \exp(-\xi_i r) \tag{3}$$

where

$$\lambda_i = \frac{Z_i - N_i + 1 - \xi_i}{\xi_i} \tag{4}$$

and Z_i is the nuclear charge and N_i is the number of electrons. Herein, ξ_i is taken as a free parameter for each atomic species. The extension of Zener's repulsive term is then

$$\phi_R(r) = A\, r^{\lambda} \exp(-br) \tag{5}$$

with

$$\lambda = \lambda_A + \lambda_B \tag{6}$$

and

$$b = \xi_A + \xi_B \tag{7}$$

The ξ_i are assumed to be closely related to the ionization potential and are to be determined.

The long-range attractive-force potential is well approximated by induced electrostatic moments caused by the perturbing presence of the second atom. At distances large enough that the electron wave functions do not significantly overlap but not so large that the signal delay times between the atoms are unimportant, the long-range force potential may be expanded as

$$\phi_L(r) = -\sum_{L,\ell} \frac{C_{L,\ell}}{r^{2L+2\ell+2}} \tag{8}$$

where the $C_{L,\ell}$ are related to the electric multipole polarizabilities (refs. 22 and 23) given by

$$C_{0,0} = (Z_A - N_A)(Z_B - N_B) \tag{9}$$

$$C_{L,0} = \frac{1}{2} \alpha_{2^L} (Z_B - N_B)^2 \tag{10}$$

$$C_{0,\ell} = \frac{1}{2}(Z_A - N_A)^2 \alpha'_{2\ell} \qquad (11)$$

where α_{2L} and $\alpha'_{2\ell}$ are static polarizabilities, Z_A and Z_B are atomic numbers, and N_A and N_B are the number of electrons in atoms A and B. These terms are equal to zero unless one of the atoms has a net charge imbalance (i.e., each expression contains a monopole term). The usual dispersion terms are given by (ref. 22)

$$C_{1,1} = \frac{3}{\pi} \int_0^\infty \alpha_2(i\omega)\alpha'_2(i\omega)\ d\omega \qquad (12a)$$

$$C_{1,2} = \frac{15}{2\pi} \int_0^\infty \alpha_2(i\omega)\alpha'_4(i\omega)\ d\omega \qquad (12b)$$

$$C_{1,3} = \frac{42}{5\pi} \int_0^\infty \alpha_2(i\omega)\alpha'_8(i\omega)\ d\omega \qquad (12c)$$

$$C_{2,2} = \frac{35}{\pi} \int_0^\infty \alpha_4(i\omega)\alpha'_4(i\omega)\ d\omega \qquad (12d)$$

where $\alpha_{2L}(i\omega)$ and $\alpha'_{2\ell}(i\omega)$ are the atomic dynamic polarizabilities. It has also been shown that a reasonable estimate of dispersion properties is given by the single frequency dispersion relation

$$\alpha_{2L}(i\omega) = \frac{\alpha_{2L}\tilde{\omega}_L^{\,2}}{\tilde{\omega}_L^{\,2} + \omega^2} \qquad (13)$$

for which equations (12a) to (12d) are approximated by

$$C_{1,1} = \frac{3}{2}\,\frac{\alpha_2\alpha'_2\tilde{\omega}_1\tilde{\omega}'_1}{\tilde{\omega}_1 + \tilde{\omega}'_1} \qquad (14a)$$

$$C_{1,2} = \frac{15}{4}\,\frac{\alpha_2\alpha'_4\tilde{\omega}_1\tilde{\omega}'_2}{\tilde{\omega}_1 + \tilde{\omega}'_2} \qquad (14b)$$

$$C_{1,3} = \frac{21}{5} \frac{\alpha_2 \alpha'_8 \tilde{\omega}_1 \tilde{\omega}'_3}{\tilde{\omega}_1 + \tilde{\omega}'_3} \qquad (14c)$$

$$C_{2,2} = \frac{35}{2} \frac{\alpha_4 \alpha'_4 \tilde{\omega}_2 \tilde{\omega}'_2}{\tilde{\omega}_2 + \tilde{\omega}'_2} \qquad (14d)$$

Hence, the attractive forces are known in terms of atomic spectral properties. We now require a formalism by which the required atomic dispersion parameters may be estimated.

Dispersion Parameters for Hydrogen

Dispersion relations for the hydrogen-like atom are exactly known (refs. 22 and 23). The static polarizability is

$$\alpha_{2^L} = \frac{2(2L + 2)!(L + 2)}{L(L + 1)(2Z_A)^{2L+2}} \qquad (15)$$

Similarly, the asymptotic limit ($\omega \to \infty$) of dynamic polarizability is given as

$$\alpha_{2^L} = \frac{L(2L)!}{(2Z_A)^{2L-1}\omega^2} \qquad (16)$$

Using equations (15) and (16) we find the lowest energy poles satisfy

$$\frac{\tilde{\omega}_2}{\tilde{\omega}_1} = \frac{3}{\sqrt{5}} \qquad (17)$$

$$\frac{\tilde{\omega}_3}{\tilde{\omega}_2} = \frac{3}{\sqrt{7}} \qquad (18)$$

As is well known, the value of $\tilde{\omega}_1$ is taken from

$$\frac{3}{4} \alpha_2^2 \tilde{\omega}_1 = C_{1,1} = 6.5 \qquad (19)$$

Through use of the above relations, the dispersion force constants shown in table I are given to within 0.2 percent for the H-H interaction calculated elsewhere (ref. 22).

Dispersion Parameters for Two-Electron Systems

The dipole spectral properties of atoms and dipole-dipole dispersion forces are well known for many atoms (refs. 23 to 25). However, we desire the means to estimate the dispersion forces on the basis of available data. The static dipole polarizability for helium is given by (refs. 26 and 27)

$$\alpha_2^{He} = 1.38 \tag{20}$$

whereas $C_{1,1} = 1.46$ (ref. 26), yielding

$$\tilde{\omega}_1^{He} = 1.02 \tag{21}$$

The remaining α_{2L} and $\tilde{\omega}_L$ are estimated from (refs. 22 and 23)

$$Z_A^{\ 2} = \frac{\alpha^H_{2L+1}}{\alpha^H_{2L}} \frac{\alpha^A_{2L}}{\alpha^A_{2L+1}} \tag{22}$$

and the frequency ratios of equations (17) and (18). Values for Li^+ and H^- are similarly obtained. The force coefficients in table I compare well with values found by Davison (ref. 23).

Dispersion Parameters for Noble Gases

The dipole polarizability for noble gas atoms has been evaluated by Starkschall and Gordon (ref. 26) and values are shown in table II. The dipole dispersion energy pole is found with equation (14a). Quadrupole and octapole polarizabilities are found in Doran (ref. 28) along with their dispersion force constants. It remains for us to estimate dispersion energy poles from the static multipole polarizabilities and their contributions to the dispersion forces. This is accomplished through use of equations (14a) to (14d). Because some inconsistencies appear for the Xe data of Doran (ref. 28), it is first necessary to observe that the spectral properties of Kr and Xe are similar before utilizing the value of the dipole energy pole of Xe.

Dispersion Parameters for Ions

The static dipole polarizabilities have been calculated from the numerical solutions of the Schrödinger equation (ref. 29) and are shown for halogen ions through chlorine and for alkali metal ions through potassium in table III along with the corresponding noble gas values. We assume that the atoms of the same isoelectronic sequence have the same value of ν, where

$$\nu = \frac{\tilde{\omega}_1}{I} \tag{23}$$

and I is the ionization potential. The parameter ν is determined from the noble gas dispersion parameter and known values of I (ref. 30). The dipole and quadrupole polarizabilities of the alkali ions are taken from Dalgarno (ref. 27). The remaining values for quadrupole polarizabilities for F^- and Cl^- are found in analogy to harmonic oscillator dispersion parameters to satisfy

$$\alpha_4 \approx 1.62 \frac{\alpha_2}{\tilde{\omega}_1} \tag{24}$$

and are assumed here for Br^- and I^- as well.

The dispersion forces have been evaluated in this paper with harmonic oscillator spectral distributions to obtain (ref. 31)

$$C_{1,3} = \frac{210}{8} \frac{\alpha_2 \tilde{\omega}_1 \alpha_2' / \tilde{\omega}_1'}{\tilde{\omega}_1 + 3\tilde{\omega}_1'} \tag{25}$$

which is to be compared with the single pole dispersion (eq. (14c))

$$C_{1,3} = \frac{21}{5} \frac{\alpha_2 \alpha_8 \tilde{\omega}_1 \tilde{\omega}_3'}{\tilde{\omega}_1 + \tilde{\omega}_3'} \tag{26}$$

Approximate values of α_8 can be found by equating (25) and (26), which results in

$$\alpha_8 \approx \frac{1.56(\tilde{\omega}_1 + \tilde{\omega}_3)\alpha_2}{\tilde{\omega}_3 \tilde{\omega}_1^2} \tag{27}$$

where the ionic values of $\tilde{\omega}_3$ are found from the corresponding noble gas values of the same isoelectronic sequence as

$$\tilde{\omega}_3' = \frac{I' \tilde{\omega}_3}{I} \tag{28}$$

The final values for the alkali and halide ions are shown in table III in comparison with the noble gas parameters.

Ionic Electric Field

As an atom comes close to an atomic ion, the Coulomb field experienced by the atom is substantially different from what it experiences from a point charge. To determine more accurately the electrostatic field we solve Poisson's equation for the ionic charge distribution as

$$\frac{1}{r}\frac{d^2}{dr^2}[r\phi(r)] = 4\pi\rho_e(r) \tag{29}$$

where $\rho_e(r)$ is the electron distribution. The electron wave functions are taken as Slater's screen wave functions (ref. 32), which are approximately applicable to ions (ref. 33). The screening factor c is given in table IV along with the corresponding principal quantum number n. The corresponding electrostatic potentials are

$$\phi_1(r) = \frac{1}{r}(cr + 1)\ \exp(-2cr) + \frac{Q}{r} \tag{30}$$

$$\phi_2(r) = \frac{1}{r}\left[\frac{(cr)^3}{24} + \frac{(cr)^2}{4} + \frac{3cr}{4} + 1\right]\ \exp(-cr) + \frac{Q}{r} \tag{31}$$

and similarly for $\phi_n(r)$, where Q is the net charge. The higher ordered potentials are approximated by scaling the 1s potentials as

$$\phi_n(r) = \frac{1}{r}\left(1 + \frac{cr}{n^2}\right)\ \exp(-2cr/n^2) + \frac{Q}{r} \tag{32}$$

The corresponding electric field strength is

$$E_n(r) = \frac{1}{r^2}\left(1 + \frac{2cr}{n^2} + \frac{2cr^2}{n^4}\right)\ \exp(-2cr/n^2) + \frac{Q}{r^2} \tag{33}$$

where $Q = 1$ for a positive ion and -1 for a negative ion. (Note that in these approximations the inner shell electrons are treated as negative point charges at the nucleus.)

General Potential Form

According to the calculations previously discussed, the general form for the interatomic potential is

$$\phi_{ij}(r) = Ar^{\lambda} \exp^{(-br)} + \frac{Q_i\phi_j(r) + Q_j\phi_i(r)}{2} - \frac{\alpha_{2_i}E_j^{\,2}(r) + \alpha_{2_j}E_i^{\,2}(r)}{2} - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} \tag{34}$$

where only A and b are as yet to be determined for each pair combination. The parameters of equation (34) are given by

$$C_6 = \frac{\alpha_{4_i}Q_j^{\,2} + \alpha_{4_j}Q_i^{\,2}}{2} + C_{1,1} \tag{35}$$

$$C_8 = C_{1,2} + C_{2,1} \tag{36}$$

$$C_{10} = C_{1,3} + C_{3,1} + C_{4,4} \tag{37}$$

The unknown potential parameters A and b may be related through the following:

$$\phi'_{ij}(R) = 0 \tag{38}$$

$$\phi_{ij}(R) = -\varepsilon \tag{39}$$

Equation (38) results in

$$A = \frac{a_{11}\exp(bR)}{bR^{\lambda} - \lambda R^{\lambda-1}} \tag{40a}$$

$$a_{11} = \frac{6C_6}{R^7} + \frac{8C_8}{R^9} + \frac{10C_{10}}{R^{11}} - \alpha_{2_i}E_j(R)E'_j(R) - \alpha_{2_j}E_i(R)E'_i(R) - \frac{Q_iE_j(R) + Q_jE_i(R)}{2} \tag{40b}$$

whereas equation (39) results in

$$A = \frac{a_{22}\exp(bR)}{R^{\lambda}} \tag{41a}$$

$$a_{22} = -\left[\frac{Q_i\phi_j(R) + Q_j\phi_i(R)}{2}\right] + \frac{\alpha_{2_i}E_j^{\,2}(R) + \alpha_{2_j}E_i^{\,2}(R)}{2} + \frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} - \varepsilon \qquad (41b)$$

It is noted here that

$$b = \frac{a_{11}}{a_{22}} + \frac{\lambda}{R} \qquad (42)$$

In the subsequent analysis, we search for values of A and b using the dispersion force and electric field parameters in tables I to IV.

Force Parameter Combination Rules

Just as the dispersion force parameters of atoms can be combined, so can the remaining force parameters referring to the core repulsion. The potential minimum occurs at the parameter value R for which the combination rule is given as

$$R_{ij} = \frac{1}{2}(R_{ii} + R_{jj}) \qquad (43)$$

Values for R_{ii} are given in table V. The core repulsion is written as

$$\phi_R(r) = A \exp(-\beta) r^{\lambda} \exp \beta[1 - (r/R)] \qquad (44)$$

so that the combination rule for β is

$$\beta_{ij} = \frac{R_{ii} + R_{jj}}{4}\left(\frac{\beta_{ii}}{R_{ii}} + \frac{\beta_{jj}}{R_{jj}}\right) \qquad (45)$$

The A_{ij} and β_{ij} are determined from an analysis of the Waldman and Gordon data (ref. 19). We solve for β_{ii} by requiring that the potential evaluated at R_{ij} gives the value $-\varepsilon_{ij}$ and the corresponding derivative of the potential is zero, thus yielding

$$\frac{\beta_{ii}}{R_{ii}} + \frac{\beta_{jj}}{R_{jj}} = \frac{2}{R_{ij}}\left(\lambda_i + \lambda_j + \frac{a_{11}R_{ij}}{a_{22}}\right) \qquad (46)$$

The Waldman and Gordon data are then divided into a group involving neutral atoms only. In the case of $i = j$, we may solve for β_{ii} directly; for $i \neq j$, values are obtained by simultaneous iteration. The least-squares error value is selected from these results. The condition that i be a neutral atom and j a positive or a negative ion allows us to solve for β_{jj} directly. The values obtained are a function of R_{ii}, and consequently we choose R_{ii} to minimize the sum of squared errors associated with all the Waldman and Gordon data. The data base is then expanded to include Herzberg's diatomic alkali-halide molecule data as compiled by Huheey (ref. 34). Again, the values of R_{ii} are adjusted to minimize the sum of the squared errors of the enlarged data set. The next step in the parameter search is to include crystal data.

NOBLE GAS SOLIDS

The many-body noble gas system is described by the first-order Hamiltonian as

$$H = \sum K_i + \frac{1}{2} \sum_{i,j} \phi_{ij}(r_{ij}) \tag{47}$$

where $\phi_{ij}(r_{ij})$ is the two-body potential and K_i is the kinetic energy operator. The cohesive energy E_{coh} is given as the sum of the zero point kinetic energy E_Z and the potential at the corresponding lattice site:

$$E_{coh} = E_Z + \sum_j \phi_{ij}(r_j) \tag{48}$$

where r_j is the distance to all the surrounding lattice sites. The zero point energy is related to the Debye temperature and is given by Glyde (ref. 35). It is customary to take the sublimation energy L_o as the separation energy from a surface kink site. If we ignore the surface energy, L_o is one-half the cohesive energy:

$$L_o \approx \frac{1}{2} E_{coh} \tag{49}$$

The experimental sublimation energy (ref. 36) and lattice spacings are used to further refine our values of β_{ii} and R_{ii} for the noble gases. The two-body potential data are shown in table VI, and final values for noble gas potentials are shown in table VII.

From the radii of the heavy noble gas atoms in table V, it is observed that R_{ii}^{-1} is proportional to $\sqrt{I}$. From the expression of Zener (ref. 9) for the repulsive potential, one can expect that β_{ii} is nearly constant for at least the heavy noble gas atoms. The final values of R and ε for the noble gas systems are shown in table VI with values for the Lennard-Jones potential, which is still used in many studies (e.g., ref. 16), and the range of results found in Waldman and Gordon (ref. 19).

IONIC CRYSTALS

The potential parameters are further refined by adding alkali-halide crystal data to the data base. Utilization of this added data is now described.

The many-body crystal Hamiltonian (eq. (47)) is written as (ref. 37)

$$H = \sum K_i + \frac{1}{2} \sum_{i,j} \phi_{ij}(r_{ij})$$

where $\phi_{ij}(r_{ij})$ is the two-body potential appropriate for the i,j pair. The cohesive energy is given by

$$E_{coh} \approx E_Z + \frac{1}{2} \sum_{i,j} \phi_{ij}(r_{ij}) \tag{50}$$

where r_{ij} are taken as the equilibrium lattice position vectors and E_Z is the zero point energy of the crystal (ref. 38). The potentials appearing in equation (50) are somewhat different from the results given by equation (34). The reason for this difference is the induction force terms do not appear in equation (50) since the electric fields at each lattice site are zero. The effective potential within the crystal at a given lattice site is thus

$$u_i = \sum_j \left[A_{ij} r^{\lambda_{ij}} \exp(-b_{ij} r_j) + \frac{1}{2} Q_i \phi_j(r_j) + \frac{1}{2} Q_j \phi_i(r_j) - \frac{C6_{ij}}{r_j^{\,6}} - \frac{C8_{ij}}{r_j^{\,8}} - \frac{C10_{ij}}{r_j^{\,10}} \right] \tag{51}$$

where the induction terms of C_6 are likewise zero.

In the usual analysis of salt crystals, the potential is calculated at a given charge site and it is assumed that the sum is independent of the site charge (refs. 11, 37, and 39 to 44). This is accomplished by neglecting the repulsive terms for like ions (refs. 37 and 41 to 44) or by assuming the repulsive terms for like ions have functional forms that are identical, for example, $\lambda_{++} = \lambda_{--} = \lambda_{+-}$ and $b_{++} = b_{--} = b_{+-}$ in equation (51) (refs. 11, 39, 40, 42, and 43). In reality, the crystals with large negative ions, such as Br^- and I^-, or with unusually small positive ions, such as Li^+, cannot be analyzed in this fashion because the negative ion repulsive cores are quite significant in determining the crystal size. For this reason, we use explicit crystal sums rather than one of the usual simplified formulas (refs. 11, 37, and 39 to 44).

The crystal lattice parameters are taken from the compilation of Fumi and Tosi (ref. 39) and the cohesive energy values are taken from the thermodynamic parameters (refs. 37, 39, 40, and 45). The atomic radii of the ions and the repulsive core parameters β_{ii} are chosen as the best fit for the crystal data and Herzberg's diatomic molecular data as compiled by Huheey (ref. 34). In this process, an adequate representation of the noble gas and ion potentials of Waldman and Gordon (ref. 19) is maintained. (See table VIII.) The crystal data and data from the present model are shown in table IX.

INTERACTIONS OF NOBLE GAS WITH CRYSTAL SURFACES

Sufficient data now exist for the study of the interaction of noble gas atoms on noble gas solids and salt crystal surfaces. The present calculations are performed without taking into account the surface distortions related to the solid-surface energy. In this way the surface energy effects may be evaluated by performing the more exact calculations.

The surface potentials for noble gas atoms on the noble gas crystal of the same element were evaluated for the three fcc surfaces (100), (110), and (111). In addition to evaluation of the potentials for the plane, two configurations were introduced on each of the planes to more accurately model a real surface. A half-plane sheet was added to study the effects of large aggregations (edge), and a kink in the edge was also introduced and studied. To complete the information needed for kinetic studies, the saddle point energy between stable points on a flat surface was also evaluated. The results are shown in table X. For comparison, the two-body potential well depths ε are also given.

It is shown in table X that the atoms of the noble gas crystal are most mobile on the close-packed (111) surface. The bonding at an edge is somewhat weak unless there is a kink site. Dimer formation at an edge is quite stable on the (111) surface. The (100) and (110) surfaces have more stable trapping sites with much less surface mobility than the (111) surface. Dimer formation on the (100) and (110) surfaces is quite stable. There is little difference between trapping at an edge and at a kink site on the (100) and (110) surfaces.

Numerous calculations of the adsorption of noble gas atoms onto alkali-halide surfaces have been made over the years, each with its own variation in the interaction potential (refs. 46 and 47). For example, table XI reveals the disparity in several of the more recently published theoretical calculations (refs. 48 and 49) for zero coverage adsorption potentials for the Ar/NaCl(100) system. Values are presented for four sites on the NaCl surface for the relaxed and unrelaxed state: a is the saddle point; b is the midpoint of the subcell edge; c is the cation; and d is the anion. Values shown in parentheses are potentials obtained from experimental heats of adsorption independent of surface heterogeneity and lateral interaction. These values are placed next to the calculated values of site c since it is the preferred site for Ar/NaCl(100). The relationship between heat of adsorption ΔH_o and the calculated potential ϕ is given by

$$-\Delta H_o = -\phi - E_Z + RT \tag{52}$$

The variation in these calculated values is basically the result of any combination of (a) the selected potential forms and parameters, (b) neglect of the ions' finite size, (c) the number of Ar and alkali-halide ion pairs summed, and (d) the state of surface relaxation. Considering the values for an unrelaxed surface and the fact that summations for most of the papers examined were in excess of 2000 pairs, the discrepancies are still quite large. It is therefore likely that the major problem is associated with the selection of the specific form for the interatomic potentials and finite size corrections to the ion charge distribution (ref. 50). Some improvement over past efforts may have been achieved for the work presented herein, since there is some overall consistency with published values (i.e., <7 percent error) in the global analysis of the paired interactions and of noble gas and alkali-halide crystal data.

Unfortunately, there is little or no modern experimental data available with which these calculations can be compared. The work of Hayakawa (ref. 46) is perhaps the most thorough experimental work available, but it was conducted under very poor experimental conditions compared with present-day surface science techniques. For example, Hayakawa's experiments appear to have been made at an ultimate pressure p of greater than 10^{-3} torr. At this pressure the surface of the alkali-halide crystals would have been completely covered by the chemical adsorption of residual gases such as CO, CO_2, H_2O, H_2, and other adsorbates. Physical adsorption of the noble gases would have occurred on top of this intermediate layer and therefore would have substantially altered the true interaction potential. Furthermore, contaminants from sample preparations such as polishing and exposure to atmosphere were not removed or even determined. In a more recent paper on Ar/NaCl(100) by Jackson and Davis (ref. 47), some effort was made to improve the quality of the (100) crystals by double heat treatment, but in every other respect the approach was similar to Hayakawa's. In table XII, the interaction potentials for an adatom of Ar on the ideal (100) surface of 16 alkali-halides are presented.

Gas surface diffraction is another area of experimental research that provides potentials that can be compared with the calculations in this work. The bound state resonance spectra that are obtained from diffraction experiments can be related to some appropriate model potential with two or more free parameters. Adjusting these parameters to fit the resonance spectra then allows a determination of either the well depth or the interaction potential. This technique is very sensitive to the model used and can generate large disparities in well depths for the same experimental data. Calculations with a continuum model by Vidali, Cole, and Klein (ref. 51) for Ar/Ar(100) and Ar/Ar(111) give values of 862.5 and 954.5 cal/mole, respectively, compared with our saddle point values of 1087.0 and 1090.0 cal/mole, respectively. Hoinkes (ref. 52) has shown that the partially summed continuum model yields well depths that are less than but near that of the saddle point for a Lennard-Jones (12-6) pair potential sum. Considering that the potential used in this work gives well depths that are 32 percent deeper than Lennard-Jones' values for Ar/Ar (see table VI), the agreement between our values and those of Vidali, Cole, and Klein would be improved had they used our interaction potential. Similarly, calculations are presented in table XIII for He on several ideal alkali-halide (100) surfaces at the three primary sites. Available well depths from scattering experiments are given in parentheses for comparison (refs. 51 to 53). As previously stated, these values are sensitive to the model used for extracting the well depth and would probably scale in the direction which substantially improves agreement if our model were used.

CONCLUDING REMARKS

The development of a theory and associated data base for the physical interaction of two atoms has been achieved. The base draws heavily on many years of study of atomic dispersions, two-body potentials, noble gas crystals, and salt crystals. The data base shows an overall consistency with crystal data to within several percent. Hence, a reliable data base for surface physics studies is herein provided.

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REFERENCES

1. Lennard-Jones, J. E.: Processes of Adsorption and Diffusion on Solid Surfaces. Trans. Faraday Soc., vol. 28, Apr. 1932, pp. 333-359.

2. Lennard-Jones, J. E.; and Dent, Beryl M.: Cohesion at a Crystal Surface. Trans. Faraday Soc., vol. XXIV, 1928, pp. 92-108.

3. London, F.: Zur Theorie und Systematik der Molekularkräfte. Z. Phys., vol. 63, no. 3-4, July 1930, pp. 245-279.

4. Buckingham, R. A.: The Quantum Theory of Atomic Polarization. I - Polarization by a Uniform Field. Proc. R. Soc. London, ser. A, vol. 160, no. 900, May 1, 1937, pp. 94-112.

5. Mason, Edward A.; and Rice, William E.: The Intermolecular Potentials of Helium and Hydrogen. J. Chem. Phys., vol. 22, no. 3, Mar. 1954, pp. 522-535.

6. Kirkwood, J. G.: Theory of Atoms With Many Electrons. Phys. Z., vol. 33, Jan. 15, 1932, pp. 57-60.

7. Müller, Alex: The van der Waals Potential and the Lattice Energy of a n-CH_2 Chain Molecule in a Paraffin Crystal. Proc. R. Soc. London, ser. A, vol. 154, no. 883, May 1, 1936, pp. 624-639.

8. Young, D. M.; and Crowell, A. D.: Physical Adsorption of Gases. Butterworths, 1962.

9. Zener, Clarence: Interchange of Translational, Rotational and Vibrational Energy in Molecular Collisions. Phys. Rev., vol. 37, Second ser., no. 5, Mar. 1, 1931, pp. 556-569.

10. Orr, W. J. C.: Calculations of Adsorption Behaviour of Argon on Alkali Halide Crystals. Trans. Faraday Soc., vol. 35, Oct. 1939, pp. 1247-1265.

11. Huggins, Maurice L.; and Mayer, Joseph E.: Interatomic Distances in Crystals of the Alkali Halides. J. Chem. Phys., vol. 1, no. 9, Sept. 1933, pp. 643-646.

12. Hoare, F. E.; and Brindley, G. W.: The Diamagnetic Susceptibilities of Salts Forming Ions With Inert Gas Configurations. III - The Alkaline Earth Halides and General Discussion. Proc. R. Soc. London, ser. A, vol. 159, no. 898, Apr. 1, 1937, pp. 395-409.

13. Mayer, Joseph E.: Dispersion and Polarizability and the van der Waals Potential in the Alkali Halides. J. Chem. Phys., vol. 1, no. 4, Apr. 1933, pp. 270-279.

14. Hayakawa, Teruo: The Adsorption of Nonpolar Gases on Alkali Halide Crystals. II. Calculations of the Adsorption Behavior of Nonpolar Gases on Cubic Sodium Chloride. Bull. Chem. Soc. Japan, vol. 30, 1957, pp. 236-243.

15. Lewis, B.; and Anderson, J. C.: Nucleation and Growth of Thin Films. Academic Press, Inc., 1978.

16. Von Harrach, Hanno Graf: Electrical Charge Effects in Thin Film Adhesion. Ph.D. Thesis, Univ. of London, Apr. 1973.

17. Olivier, J. P.; and Ross, S.: On Physical Adsorption. XVI. The Physical Interaction of H_2, D_2, CH_4, and CD_4 With Graphite. Proc. R. Soc. London, ser. A, vol. 265, no. 1323, Feb. 6, 1962, pp. 447-454.

18. Gordon, Roy G.; and Kim, Yung Sik: Theory for the Forces Between Closed-Shell Atoms and Molecules. J. Chem. Phys., vol. 56, no. 6, Mar. 15, 1972, pp. 3122-3133.

19. Waldman, Marvin; and Gordon, Roy G.: Scaled Electron Gas Approximation for Intermolecular Forces. J. Chem. Phys., vol. 71, no. 3, Aug. 1, 1979, pp. 1325-1339.

20. Gilbert, T. L.; and Wahl, Arnold C.: Single-Configuration Wavefunctions and Potential Curves for the Ground States of He_2, Ne_2, and Ar_2. J. Chem. Phys., vol. 47, no. 9, Nov. 1, 1967, pp. 3425-3438.

21. Handler, George S.; Smith, Darwin W.; and Silverstone, Harris J.: Asymptotic Behavior of Atomic Hartree-Fock Orbitals. J. Chem. Phys., vol. 78, no. 8, Oct. 15, 1980, pp. 3936-3938.

22. Chan, Y. M.; and Dalgarno, A.: The Long-Range Interaction of Atoms and Molecules. Mol. Phys., vol. 9, no. 4, Aug. 25, 1965, pp. 349-356.

23. Davison, W. D.: Variational Calculations of Long-Range Forces. Proc. Phys. Soc., vol. 87, pt. 1, no. 555, Jan. 1966, pp. 133-143.

24. Dehmer, J. L.; Inokuti, Mitio; and Saxon, R. P.: Systematics of Moments of Dipole Oscillator-Strength Distributions for Atoms of the First and Second Row. Phys. Rev. A, third ser., vol. 12, no. 1, July 1975, pp. 102-121.

25. Inokuti, M.; Dehmer, J. L.; Baer, T.; and Hanson, J. D.: Oscillator-Strength Moments, Stopping Powers, and Total Inelastic-Scattering Cross Sections of All Atoms Through Strontium. Phys. Rev. A., vol. 23, no. 1, Jan. 1981, pp. 95-109.

26. Starkschall, George; and Gordon, Roy G.: Improved Error Bounds for the Long-Range Forces Between Atoms. J. Chem. Phys., vol. 54, no. 2, Jan. 15, 1971, pp. 663-673.

27. Dalgarno, A.: Atomic Polarizabilities and Shielding Factors. Adv. in Phys., vol. 11, no. 44, Oct. 1962, pp. 281-315.

28. Doran, M. B.: The Multipole Long-Range (Van der Waals) Interaction Coefficients for Neon, Argon, Krypton and Xenon. J. Phys. B: At. & Mol. Phys., vol. 7, no. 5, Apr. 1, 1974, pp. 558-569.

29. Fraga, S.; Saxena, K. M. S.; and Lo, B. W. N.: Hartree-Fock Values of Energies, Interaction Constants, and Atomic Properties for the Groundstates of the Negative Ions, Neutral Atoms, and First Four Positive Ions From Helium to Krypton. At. Data, vol. 3, no. 4, Dec. 1971, pp. 323-361.

30. Vedeneyev, V. I.; Gurvich, L. V.; Kondrat'yev, V. N.; Medvedev, V. A.; and Frankevich, Ye. L. (Scripta Technica Ltd., transl.): Bond Energies Ionization Potentials and Electron Affinities. St Martin's Press, 1966.

31. Margenau, H.; and Kestner, N. R.: Theory of Intermolecular Forces. Pergamon Press Inc., c.1969.

32. Slater, J. C.: Atomic Shielding Constants. Phys. Rev., Second ser., vol. 36, no. 1, July 1, 1930, pp. 57-64.

33. Wilson, J. W.; Chang, C. K., Xu, Y. J.; and Kamaratos, E.: Ionic Bond Effects on the Mean Excitation Energy for Stopping Power. J. Appl. Phys., vol. 53, no. 2, Feb. 1982, pp. 828-830.

34. Huheey, James E.: Inorganic Chemistry: Principles of Structure and Reactivity, Second ed. Harper & Row, 1978.

35. Glyde, H. R.: Solid Helium. Rare Gas Solids, Volume I, M. L. Klein and J. A. Venables, eds., Academic Press Inc., c.1976, pp. 382-504.

36. Crawford, R. K.: Melting, Vaporization and Sublimation. Rare Gas Solids, Volume II, M. L. Klein and J. A. Venables, eds., Academic Press Inc., 1977, pp. 663-728.

37. Sachs, Mendel: Solid State Theory. McGraw-Hill Book Co., Inc., c.1963.

38. Duraiswamy, S.; and Haridasan, T. M.: Zero-Point Motion in Alkali Halides. Indian J. Pure & Appl. Phys., vol. 14, no. 5, 1976, pp. 337-340.

39. Fumi, F. G.; and Tosi, M. P.: Ionic Sizes and Born Repulsive Parameters in the NaCl-Type Alkali Halides - I. The Huggins-Mayer and Pauling Forms. J. Phys. & Chem. Solids, vol. 25, no. 1, Jan. 1964, pp. 31-43.

40. Ladd, M. F. C.: van der Waals Potentials and Crystal Energies of Ionic Compounds. J. Chem. Phys., vol. 60, no. 5, Mar. 1, 1974, pp. 1954-1957.

41. Woodcock, Leslie V.: Interionic Pair Potentials in the Alkali Metal Halides. J. Chem. Soc., Faraday Trans. II, vol. 8, 1974, pp. 1405-1411.

42. Michielsen, J.; Woerlee, P.; Graaf, F. V. D.; and Ketelaar, J. A. A.: Pair Potential for Alkali Metal Halides With Rock Salt Crystal Structure. J. Chem. Soc., Faraday Trans. II, vol. 10, 1975, pp. 1730-1741.

43. Szymanski, J. E.; and Matthew, J. A. D.: Empirical Interionic Potentials for Alkali Halide Molecules. Canadian J. Phys., vol. 62, no. 6, June 1984, pp. 583-589.

44. Kaur, A. J.; Bhende, W. N.; Bakhshi, P. S.; and Shanker, J.: Analysis of the Short-Range Repulsive Potential in Alkali Halides. Phys. Status Solidi (b), vol. 123, no. 1, May 1984, pp. 71-78.

45. Weast, Robert C.; Selby, Samuel M.; and Hodgman, Charles D., eds.: Handbook of Chemistry and Physics, Forty-sixth ed. Chem. Rubber Co., c.1965.

46. Hayakawa, Teruo: Adsorption of Nonpolar Gases on Alkali Halide Crystals. I. Low-Temperature Adsorption on Cubic Sodium Chloride. Bull. Chem. Soc. Japan, vol. 30, 1957, pp. 124-132.

47. Jackson, Daniel J.; and Davis, Bruce W.: Heats of Adsorption and Site-Energy Distributions for Argon and Molecular Nitrogen on Sublimated Sodium Chloride. J. Colloid & Interface Sci., vol. 47, no. 2, 1974, pp. 499-514.

48. Rogowska, J. M.: Potential Energy of Rare Gases Adatoms on Alkali Halide Crystals. J. Chem. Phys., vol. 68, no. 8, Apr. 15, 1978, pp. 3910-3917.

49. House, William A.; and Jaycock, Michael J.: Calculation of the Adsorption Interaction of Argon and Krypton on the Relaxed (100) Faces of Sodium Chloride and Potassium Chloride. J. Chem. Soc., Faraday Trans. I, vol. 7, 1975, pp. 1597-1609.

50. Wilson, John W.; Heinbockel, John H.; and Outlaw, Ronald A.: Finite Size Corrections to Madelung's Number. J. Chem. Phys., vol. 84, no. 1, Jan. 1, 1986, pp. 543-544.

51. Vidali, G.; Cole, Milton W.; and Klein, James R.: Shape of Physical Adsorption Potentials. Phys. Rev. B, vol. 28, no. 6, Sept. 15, 1983, pp. 3064-3073.

52. Hoinkes, H.: The Physical Interaction Potential of Gas Atoms With Single-Crystal Surfaces, Determined From Gas-Surface Diffraction Experiments. Rev. Mod. Phys., vol. 52, no. 4, Oct. 1980, pp. 933-970.

53. Leung, W. Y.; Larese, J. Z.; and Frankl, D. R.: Selective Adsorption of ^{4}He on the NaCl(001) Surface. Surface Sci., vol. 136, nos. 2/3, Jan. 1984, pp. 649-662.

SYMBOLS

A	atom of diatomic pair
a	lattice parameter, atomic units
a_o	Bohr's radius, 0.592×10^{-8} cm
B	atom of diatomic pair
C	screening parameter
E_Z	zero point energy of lattice, cal/mol
I	atomic ionization potential, atomic units
L_o	sublimation energy, cal/mol
n	valence shell principal quantum number
R	equilibrium separation of two-body potential, atomic units
U	potential energy of crystal, cal/mol
z	distance above surface, atomic units
α_{2^L}	multipole polarizability (2^L-pole), (atomic units)$^{2L+1}$
β	repulsive core parameter
ε	well depth, atomic units
ν	ratio of $\tilde{\omega}_1/I$
$\phi(r)$	diatomic potential energy at separation distance r, atomic units
$\tilde{\omega}_L$	pole location of the dynamic 2^L-polarizability, atomic units

TABLE I.- DISPERSION PARAMETERS AND FORCE CONSTANTS

[Values in atomic units]

Parameter	H	He^+	H^-	He	Li^+
Atomic dispersion parameters					
α_2	4.5	0.281	174	1.38	0.192
$\tilde{\omega}_1$	0.428	1.71	0.077	1.02	3.10
α_4	15.0	0.234	5 130	2.44	0.114
$\tilde{\omega}_2$	0.574	2.30	0.103	1.37	4.16
α_8	131.3	0.512	33 800	11.2	0.179
$\tilde{\omega}_3$	0.651	2.61	0.117	1.50	4.72
Hydrogen atom forces					
$C_{1,1}$	6.50	0.65	76.7	2.81	0.487
$C_{1,2}$	62.1	1.43	7 187	13.4	0.747
$C_{2,1}$	62.1	6.8	664	28.5	5.23
$C_{1,3}$	640.8	3.58	58 696	70.5	1.33
$C_{3,1}$	640.8	7.3	6 607	30.2	57.0
$C_{3,2}$	1130	28.3	117 599	259	15.1
Helium atom forces					
$C_{1,1}$	2.81	0.372	25.8	1.46	0.305
$C_{1,2}$	28.5	0.86	2 483	7.38	0.483
$C_{2,1}$	13.4	1.96	116	7.38	1.67
$C_{1,3}$	30.2	2.19	20 562	39.4	0.87
$C_{3,1}$	70.5	10.6	599	39.4	9.13
$C_{2,2}$	259	8.6	20 984	71.4	5.02

TABLE II.- NOBLE GAS DISPERSION PARAMETERS AND FORCE CONSTANTS

[Values in atomic units]

Parameter	He	Ne	Ar	Kr	Xe
α_2	1.38	2.67	11.1	16.8	27.1
$C_{1,1}$	1.46	6.48	64.8	128	295
$\tilde{\omega}_1$	1.02	1.21	0.701	0.605	0.536
α_4	2.44	6.42	48.2	78.8	128.3
$C_{1,2}$	7.38	36.9	588	1 290	2 997
$\tilde{\omega}_2$	1.37	1.09	0.504	0.455	0.403
α_8	11.2	30.4	449.7	681.4	1 105
$C_{1,3}$	39.4	292.7	9558	20 595	49 489
$\tilde{\omega}_3$	1.50	2.96	1.30	1.67	1.48

TABLE III.- DISPERSION PARAMETERS FOR CLOSED-SHELL IONS AND NOBLE GASES

[Values in atomic units]

Atom	α_2	I	ν	$\tilde{\omega}_1$	α_4	$\tilde{\omega}_2$	α_8	$\tilde{\omega}_3$
F^-	6.75	0.11	1.53	0.168	57.5	0.182	526	0.41
Ne	2.67	0.793	1.53	1.21	6.42	1.09	30.4	2.96
Na^+	1.55	1.68	1.53	2.57	1.57	2.32	3.64	6.27
Cl^-	22.0	0.10	1.22	0.122	325.9	0.126	3585	0.22
Ar	11.1	0.579	1.22	0.701	~48.2	0.504	449.7	1.30
K^+	6.38	1.13	1.22	1.38	13.6	0.97	56.9	2.54
Br^-	27.4	0.09	1.18	0.106	418	0.116	5242	0.29
Kr	16.8	0.515	1.18	0.605	78.8	0.455	681.4	1.67
Rb^+	6.75	1.02	1.18	1.204	~15	0.91	69.8	3.31
I^-	41.9	0.12	1.20	0.144	471	0.111	4287	0.40
Xe	27.1	0.446	1.20	0.536	128.3	0.403	1105	1.48
Cs^+	18.2	0.86	1.20	1.03	~49	0.77	257	2.85

TABLE IV.- ELECTROSTATIC POTENTIAL PARAMETERS ACCORDING TO SLATER'S SCREEN WAVE FUNCTIONS

Parameter	Li^+	F^-	Na^+	Cl^-	K^+	Br^-	Rb^+	I^-	Cs^+
n	1	2	2	3	3	4	4	5	5
c	2.70	4.85	6.85	5.75	7.75	5.75	7.75	5.75	7.75

TABLE V.- ATOMIC RADII AT POTENTIAL MINIMUM R AND β

Atom or ion	R, atomic units	β, atomic units
He	5.8200	14.100
Ne	6.0109	15.523
Ar	7.0632	15.104
Kr	7.5000	15.883
Xe	8.1515	15.268
Li^+	2.2130	5.097
Na^+	3.4100	8.575
K^+	4.5940	10.585
Rb^+	5.0585	13.050
F^-	4.5280	13.251
Cl^-	6.9276	15.758
Br^-	7.1397	19.692
I^-	7.7199	30.776

TABLE VI.- RADII AND WELL DEPTHS

System	Lennard-Jones values		Present values		Reference 19 values	
	R, atomic units	ε, atomic units	R, atomic units	ε, atomic units	R, atomic units	ε, atomic units
He-He	5.834	2.03×10^{-5}	5.820	2.80×10^{-5}	5.59-5.82	$3.48\text{-}3.58 \times 10^{-5}$
He-Ne	5.921	4.15×10^{-5}	5.915	5.62×10^{-5}	6.01-6.07	$4.52\text{-}5.48 \times 10^{-5}$
He-Ar	6.517	7.53×10^{-5}	6.442	1.07×10^{-4}	6.54-6.90	$6.45\text{-}11.6 \times 10^{-5}$
He-Kr	6.740	88.7×10^{-5}	6.660	1.24×10^{-4}	6.67-7.09	$7.83\text{-}16.4 \times 10^{-5}$
He-Xe	7.067	9.41×10^{-5}	6.986	1.34×10^{-4}	7.09-7.84	$7.98\text{-}17.9 \times 10^{-5}$
Ne-Ne	6.008	8.59×10^{-5}	6.011	1.13×10^{-4}	5.88-6.05	$1.12\text{-}1.35 \times 10^{-4}$
Ne-Ar	6.604	1.51×10^{-4}	6.537	2.13×10^{-4}	6.48-6.77	$1.84\text{-}2.27 \times 10^{-4}$
Ne-Kr	6.827	1.78×10^{-4}	6.755	2.45×10^{-4}	6.77-7.03	$2.20\text{-}2.36 \times 10^{-4}$
Ne-Xe	7.152	1.88×10^{-4}	7.081	2.65×10^{-4}	7.09-7.56	$2.11\text{-}2.38 \times 10^{-4}$
Ar-Ar	7.200	3.00×10^{-4}	7.063	4.39×10^{-4}	7.11-7.11	$4.50\text{-}4.61 \times 10^{-4}$
Ar-Kr	7.423	3.61×10^{-4}	7.282	5.18×10^{-4}	7.29-7.33	$5.18\text{-}5.78 \times 10^{-4}$
Ar-Xe	7.748	4.00×10^{-4}	7.607	5.77×10^{-4}	7.65-7.75	$6.01\text{-}6.68 \times 10^{-4}$
Kr-Kr	7.646	4.38×10^{-4}	7.500	6.17×10^{-4}	7.50-7.58	$6.38\text{-}7.00 \times 10^{-4}$
Kr-Xe	7.971	4.91×10^{-4}	7.826	6.95×10^{-4}	7.81-7.90	$7.25\text{-}8.37 \times 10^{-4}$
Xe-Xe	8.295	5.63×10^{-4}	8.152	7.93×10^{-4}	7.99-8.26	$8.24\text{-}11.0 \times 10^{-4}$

TABLE VII.- NOBLE GAS PAIR INTERACTION PARAMETERS AND SOLID PARAMETERS FROM PRESENT MODEL AND EXPERIMENTS

Gas type	ε, cal/mol (a)	R, atomic units (a)	a_o, atomic units (a)	a_o, atomic units (b)	E_Z, cal/mol (a)	L_o, cal/mol (a)	L_o, cal/mol (b)
Ne	70.7	6.011	8.438	8.432	149	468	473∓34
Ar	274.6	7.063	9.866	10.038	208	2010	1864∓34
Kr	386.0	7.500	10.502	10.676	160	2864	2659∓12
Xe	496.1	8.152	11.367	11.586	123	3798	3749∓58

[a] Present model.
[b] Experiments.

TABLE VIII.- DIATOMIC INTERACTION POTENTIAL PARAMETERS ε_{AB} AND r_{AB} FROM PRESENT MODEL AND LITERATURE

[All quantities are in atomic units]

A	B	ε_{AB} from present model	R_{AB} from present model	ε_{AB} from literature	R_{AB} from literature	Source
Li^+	He	1.58×10^{-3}	4.017	$1.72\text{-}2.76 \times 10^{-3}$	3.666-4.195	Reference 19
	Ne	3.02×10^{-3}	4.112	4.52×10^{-3}	3.704	Reference 19
	Ar	8.00×10^{-3}	4.638	1.13×10^{-2}	4.176	Reference 19
	Kr	10.3×10^{-3}	4.857	1.43×10^{-2}	4.365	Reference 19
	Xe	12.7×10^{-3}	5.182	1.67×10^{-2}	4.743	Reference 19
	F^-	2.85×10^{-1}	3.371	2.87×10^{-1}	2.923	Reference 34
	Cl^-	2.22×10^{-1}	4.570	2.40×10^{-1}	3.817	Reference 34
	Br^-	2.19×10^{-1}	4.676	2.30×10^{-1}	4.101	Reference 34
	I^-	2.06×10^{-1}	4.966	2.13×10^{-1}	4.520	Reference 34
Na^+	He	1.16×10^{-3}	4.615	$1.29\text{-}1.47 \times 10^{-3}$	4.441-4.573	Reference 19
	Ne	2.21×10^{-3}	4.710	2.42×10^{-3}	4.592	Reference 19
	Ar	5.86×10^{-3}	5.237	5.92×10^{-3}	5.140	Reference 19
	Kr	7.57×10^{-3}	5.455	7.43×10^{-3}	5.367	Reference 19
	Xe	9.45×10^{-3}	5.781	8.86×10^{-3}	5.764	Reference 19
	F^-	2.44×10^{-1}	3.969	2.41×10^{-1}	3.477	Reference 34
	Cl^-	1.94×10^{-1}	5.169	2.08×10^{-1}	4.462	Reference 34
	Br^-	1.93×10^{-1}	5.275	1.99×10^{-1}	4.728	Reference 34
	I^-	1.80×10^{-1}	5.565	1.87×10^{-1}	5.125	Reference 34
K^+	He	8.98×10^{-4}	5.207	8.13×10^{-4}	5.442	Reference 19
	Ne	1.72×10^{-3}	5.302	1.43×10^{-3}	5.537	Reference 19
	Ar	4.43×10^{-3}	5.829	$4.08\text{-}5.14 \times 10^{-3}$	5.442-5.896	Reference 19
	Kr	5.69×10^{-3}	6.047	5.40×10^{-3}	6.066	Reference 19
	Xe	7.11×10^{-3}	6.373	6.88×10^{-3}	6.350	Reference 19
	F^-	2.15×10^{-1}	4.561	2.16×10^{-1}	4.025	Reference 34
	Cl^-	1.73×10^{-1}	5.761	1.84×10^{-1}	5.044	Reference 34
	Br^-	1.71×10^{-1}	5.867	1.76×10^{-1}	5.331	Reference 34
	I^-	1.61×10^{-1}	6.157	1.66×10^{-1}	5.760	Reference 34

TABLE VIII.- Concluded

A	B	ε_{AB} from present model	R_{AB} from present model	ε_{AB} from literature	R_{AB} from literature	Source
Rb^+	He	8.58×10^{-4}	5.439	7.54×10^{-4}	5.726	Reference 19
	Ne	1.64×10^{-3}	5.535	1.25×10^{-3}	5.915	Reference 19
	Ar	4.21×10^{-3}	6.061	3.63×10^{-3}	6.236	Reference 19
	Kr	5.39×10^{-3}	6.279	$4.38\text{-}4.67 \times 10^{-3}$	6.312-6.406	Reference 19
	Xe	6.74×10^{-3}	6.605	6.03×10^{-3}	6.609	Reference 19
	F^-	2.08×10^{-1}	4.793	2.10×10^{-1}	4.282	Reference 34
	Cl^-	1.68×10^{-1}	5.993	1.86×10^{-1}	5.267	Reference 34
	Br^-	1.66×10^{-1}	6.099	1.72×10^{-1}	5.565	Reference 34
	I^-	1.56×10^{-1}	6.389	1.62×10^{-1}	6.004	Reference 34
F^-	Xe	7.63×10^{-3}	6.340	8.38×10^{-3}	5.820	Reference 19
Cl^-	Xe	4.02×10^{-2}	7.540	6.36×10^{-3}	6.595	Reference 19
I^-	He	2.73×10^{-4}	6.770	3.20×10^{-4}	7.578	Reference 19
	Ne	5.17×10^{-4}	6.865	3.09×10^{-4}	8.485	Reference 19
	Ar	1.55×10^{-3}	7.392	2.02×10^{-3}	7.597	Reference 19
	Kr	2.05×10^{-3}	7.610	2.94×10^{-3}	7.597	Reference 19
	Xe	2.74×10^{-3}	7.936	5.29×10^{-3}	7.276	Reference 19
Br^-	He	3.69×10^{-4}	6.480	3.57×10^{-4}	7.105	Reference 19
	Ne	6.96×10^{-4}	6.575	4.08×10^{-4}	7.861	Reference 19
	Ar	2.08×10^{-3}	7.101	2.32×10^{-3}	7.124	Reference 19
	Kr	2.76×10^{-3}	7.320	3.42×10^{-3}	7.105	Reference 19
	Xe	3.67×10^{-3}	7.646	5.84×10^{-3}	6.879	Reference 19

TABLE IX.- IONIC CRYSTAL PARAMETERS AND EXPERIMENTAL VALUES

Crystal	a, atomic units	U, kcal/mol	E_Z, kcal/mol	Experimental a, atomic units	Experimental U, kcal/mol	Source of experimental data
Li^+F^-	3.932	258	2.81	3.802	246±3	References 39,40,45
Li^+Cl^-	5.251	206	1.43	4.858	202±3	References 37,39,40,45
Li^+Br^-	5.280	205	1.51	5.193	192±4	References 37,39,40,45
Li^+I^-	5.518	187	.85	5.669	178±6	References 37,39,40,45
Na^+F^-	4.491	225	1.92	4.372	218±3	References 39,40,45
Na^+Cl^-	5.729	184	1.28	5.323	186±3	References 37,39,40,45
Na^+Br^-	5.767	181	.95	5.641	177±4	References 37,39,40,45
Na^+I^-	5.962	165	.79	6.111	166±3	References 37,39,40,45
K^+F^-	5.145	197	1.42	5.093	193±3	References 39,40,45
K^+Cl^-	6.374	162	.81	5.939	168±3	References 37,39,40,45
K^+Br^-	6.398	161	1.03	6.228	162±2	References 37,39,40,45
K^+I^-	6.623	148	.67	6.670	152±2	References 37,39,40,45
Rb^+F^-	5.343	194	1.13	5.320	184±2	References 39,40,45
Rb^+Cl^-	6.591	159	.82	6.198	163±2	References 37,39,40,45
Rb^+Br^-	6.627	157	.63	6.493	156±3	References 37,39,40,45
Rb^+I^-	6.856	143	.52	6.930	148±3	References 37,39,40,45

TABLE X.- SURFACE POTENTIALS FOR NOBLE GAS ATOMS ON NOBLE GAS CRYSTALS

[Values in parentheses are multiples of ε]

Face	Surface	Potential for Ne (ε = 70.7 cal/mol), cal/mol	Potential for Ar (ε = 274.6 cal/mol), cal/mol	Potential for Kr (ε = 386.0 cal/mol), cal/mol	Potential for Xe (ε = 496.1 cal/mol), cal/mol
(111)	Flat	316 (4.47)	1198 (4.47)	1664 (4.31)	2193 (4.42)
	Edge	475 (6.72)	1807 (6.38)	2517 (6.52)	3299 (6.65)
	Kink	547 (7.74)	2099 (7.60)	2910 (7.54)	3806 (7.67)
	Saddle	285 (4.03)	1090 (3.97)	1504 (3.90)	1998 (4.03)
(100)	Flat	372 (5.26)	1416 (5.15)	1973 (5.11)	2584 (5.21)
	Edge	533 (7.54)	2039 (7.43)	2844 (7.37)	3716 (7.49)
	Kink	547 (7.74)	2088 (7.60)	2911 (7.54)	3807 (7.67)
	Saddle	280 (3.96)	1087 (3.96)	1495 (3.87)	1987 (4.01)
(110)	Flat	452 (6.39)	1733 (6.31)	2396 (6.21)	3163 (6.38)
	Edge	533 (7.54)	2046 (7.45)	2853 (7.39)	3731 (7.52)
	Kink	547 (7.74)	2099 (7.60)	2910 (7.54)	3806 (7.67)
	Saddle	288 (4.07)	1103 (4.02)	1522 (3.94)	2029 (4.09)

TABLE XI.- SURFACE POTENTIALS FOR Ar/NaCl(100) FOR RELAXED AND UNRELAXED SURFACES

[Values in parentheses are potentials obtained from experimental isosteric heats taken from these works]

Site (a)	Relaxed state		Unrelaxed state		Source
	ϕ, cal/mol	z/a	ϕ, cal/mol	z/a	
a	2006	1.16			Reference 48
b	1790	1.22			
c	2420	1.04			
d	1481	1.32			
a	1066	1.13	1023	1.12	Reference 49
b					
c	1109	1.11	801	1.71	
d	751	1.32	780	1.28	
a			1768	1.17	Reference 46
b			1514	1.25	
c			1876 (1619)	1.17	
d			1401	1.32	
a			1119	1.19	This work
b			946	1.26	
c			1484	1.10	
d			734	1.38	
a			1098	1.18	Reference 47
b			962	1.24	
c			1096 (1749)	1.17	
d			819	1.34	

[a] Sites: a - saddle point; b - midpoint of subcell edge; c - cation; d - anion.

TABLE XII.- ZERO COVERAGE ADSORPTION POTENTIALS FOR Ar ON (100) SURFACE OF 16 ALKALI-HALIDES

Alkali-halide	Cation ϕ, cal/mol	Cation z/a	Anion ϕ, cal/mol	Anion z/a	Saddle point ϕ, cal/mol	Saddle point z/a
LiF	2270	1.438	1757	1.6	2132	1.488
LiCl	1536	1.2	644	1.413	1107	1.35
LiBr	2227	1.025	821.8	1.4	1310	1.2
LiI	5790	.838	1227	1.288	2417	1.063
NaF	1735	1.313	1518	1.4	1971	1.263
NaCl	148.4	1.1	732.8	1.375	1119	1.188
NaBr	1856	.988	763.7	1.288	1335	1.075
NaI	3766	.85	1054	1.213	2268	.95
KF	1376	1.225	1589	1.188	2033	1.063
KCl	1314	1.05	774	1.225	1342	1.013
KBr	1429	.988	799.2	1.163	1569	.925
RbF	1144	1.225	1438	1.15	1775	1.038
RbCl	1128	1.039	708.8	1.175	1279	.95
RbBr	1219	.975	737.9	1.125	1523	.863
RbI	1958	.888	903.4	1.063	2300	.775

TABLE XIII.- INTERACTION POTENTIALS FOR He ADSORBED ON SEVERAL UNRELAXED ALKALI-HALIDE SURFACES

[Well depths from scattering experiments given in parentheses for comparison]

Primary site	ϕ, cal/mol, for He adsorbed on -			Source
	LF	NaF	NaCl	
Cation	255.3	236.4	260.9	
Anion	199.4	210.8	111.7	
Saddle point	253.5	293.4	184.6	
	(185.2)	(162.2)		Reference 51
	*(197.8)	*(166.7)		Reference 52
			(163.3)	Reference 53

*Represents average of numerous experiments.

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16. Abstract

The physical forces between atoms and molecules are important in a number of processes of practical importance, including line broadening in radiative processes, gas and crystal properties, adhesion, and thin films. The components of the physical forces between noble gas atoms, alkali ions, and halogen ions are analyzed and a data base for the dispersion forces is developed from the literature based on evaluations with the harmonic oscillator dispersion model for higher order coefficients. The Zener model of the repulsive core is used in the context of the recent asymptotic wave functions of Handler and Smith; and an effective ionization potential within the Handler and Smith wave functions is defined to analyze the two-body potential data of Waldman and Gordon, the alkali-halide molecular data, and the noble gas crystal and salt crystal data. A satisfactory global fit to this molecular and crystal data is then reproduced by the model to within several percent. Surface potentials are evaluated for noble gas atoms on noble gas and salt crystal surfaces with surface tension neglected. Within this context, the noble gas surface potentials on noble gas and salt crystals are considered to be accurate to within several percent.

* GASS-SOLID INTERACTION
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