

INTERATOMIC POTENTIALS FOR CONDENSED MATTER

A.M. STONEHAM

Theoretical Physics Division, Atomic Energy Research Establishment, Harwell, Didcot, Oxon, UK

This paper forms an introduction to a discussion of interatomic forces. As such, it comments on the basic principles, and on some of the problems which underly present formulations, the ways in which future work should develop, and the classes of physical problem for which difficulties remain.

1. Introduction

Interatomic potentials provide a substitute for explicit solution of the Schrödinger equation. If one wants the total energy of a system as a function of the positions of the ionic nuclei, one approach is direct solution of the Schrödinger equation to some degree of sophistication. Any algorithm which allows one to avoid this heavy-weight approach constitutes an interatomic (or interionic) potential.

Several points are clear. First, there is no reason to expect or require the potential to be a two-body interaction, a purely radial interaction, or even (e.g. if we can have electronic degeneracy) a single-valued function. We may desire these special features (or decide to ignore tricky terms) but these hopes and fears do not limit the existence of a potential. Secondly, the potential itself may be obtained from restricted solutions of the Schrödinger equation, restricted by number of atoms, by approximations, or both. Whilst there are very few calculations starting from the Schrödinger equation which could honestly be called “*a priori*”, those potentials derived from fitting experimental data to chosen analytic forms are clearly “*empirical*” to some degree, and these two terms illustrate extreme approaches to potentials. It is worth stressing that, at present, the best empirical forms give more accurate predictions than the best *a priori* forms.

Most of the potentials described at this meeting, and indeed most listed in the two Hand-

books [1,2] are pairwise, radial, interatomic potentials intended to describe energies of rearrangement at constant volume. They may have wider validity (e.g. volume changes are described too, or small molecules are described [3]) or they may need supplementary terms (e.g. volume-dependent, or free electron gas). The most problematic, mainly in the sense that confusion can arise, are special-purpose potentials. Examples include those for the total energy as a structure is uniformly expanded without distortion (e.g. [4]) or those relating interactions of one ion with rows of others (as in the Lindhard potential describing a channelling ion), and those describing interactions between two extended defects like shear planes or between two surfaces.

2. Requirements for potentials

Much of this section will be concerned with features which should be obvious. Regrettably, many potentials have not recognized, let alone satisfied, important criteria, so that users should always be cautious.

2.1. Accuracy

Accuracy in representing experiment (or representing a Schrödinger equation solution, which is a different criterion) should not be confused with precision, i.e. the number of significant figures quoted or reproducibly calculated. The accuracy of some empirical poten-

tials is considerable when used as a means of extrapolation (see e.g. [5]). Note that quite distinct physical assumptions may be involved in changing particle (ion or electron) numbers and in simply moving ions around at constant volume. At present, direct solutions of the Schrödinger equation do not have adequate accuracy for many calculations, but have real value in suggesting the character of empirical potential needed.

2.2. Transferability

This underlies almost all use of the concept of interatomic potentials. Within a defined range of phenomena and geometries, the *same* algorithm for the total energy should hold without any special readjustment. This criterion is so important and so often misunderstood that some examples are useful.

First, suppose we wish to model a simple NaCl-structure ionic crystal. Then, as known to Born, its cohesion can be described by point-ion interactions and short-range repulsions alone. These interactions also suffice for the bulk compressibility where ions remain at fully symmetric sites. It took 40 years to realise that the shell model was needed for an adequate description for lattice dynamics and cases where sites of low symmetry mattered. Not only are ions polarisable (distortable) but the polarisability and the short-range interactions with close neighbours matter. The significant qualitative differences when there are low symmetry sites are often ignored by semiconductor and metal scientists.

Secondly, suppose an all-electron calculation is replaced by a pseudopotential calculation. Here the algorithm consists of using an electron-core interaction potential to obtain an interatomic potential. Then the same pseudopotential should describe both energy changes under volume change and under mere rearrangement at constant volume; it should also work for sites of high and of low symmetry, e.g. at surfaces and in the bulk; it should also work when there is charge transfer. However, if there is appreciable charge-transfer, it would be foolhardy not to use a self-consistent algorithm.

Thirdly, suppose a potential V_0 describes physical properties well at $T = 0$. If one wants properties at, say $T = 1000$ K, there are various options open. One common choice is to do a static lattice calculation at an expanded lattice parameter. Since this is prone to instability, it is tempting to calculate a new potential, V_{1000} , from the physical properties at the elevated temperature. Herein lies a subtle problem. V_0 and V_{1000} differ mainly because of the extra apparent ionic size due to larger thermal vibrations at the higher temperature. It is by no means clear that the same degree of thermal size change is going to be the same for an ion in a perfect crystal and for an ion near a vacancy. This type of difficulty is one reason for going from purely static models to those which include dynamics, whether explicit (as in molecular dynamics) or implicit (as in self-consistent phonons).

Fourthly, many empirical potentials are derived from bulk equilibrium data at low temperatures. These are then used and when there is massive distortion, e.g. in shock wave conditions, or with high disorder. Here transferability must be checked explicitly, e.g. by direct prediction of a range of observed quantities. There is no way to deduce the extent of transferability from general arguments alone; sometimes nature is more cooperative than anticipated [3, 5, 6].

2.3. Stability

Many published potentials are unstable, i.e. give bizarre and unphysical configurations in some circumstances. Some fail on simple tests, e.g. they do not give real vibration frequencies for perfect lattices. Others show the polarisation catastrophies or van der Waals catastrophies ($-1/r^N$ always dominates over $\exp(-ar)$ at small enough r). Thermally-expanded lattices often show both defect and bulk shear instabilities. However, it is molecular dynamics which is an especially stringent test, for even bizarre atomic geometries can arise occasionally.

2.4. Convenience

Convenience is determined by the codes with

which the potentials are to be used. Most such codes will accept shell models; some will accept bond-bending forces or simple volume-dependent forces [7]. If a potential is to be useful, it should conform to these codes or be so good that it is worthwhile rewriting the codes.

2.5. Needs

We may identify a few of the many gaps in our knowledge of potentials. First, there are classes of system like ice for which one would expect conventional approaches to work. Another example, though probably harder, concerns the transition-metal silicides, whose role in large-scale integrated circuits gives them importance. Secondly, there are the systems for which standard empirical approaches cannot be applied and where the local chemistry makes one doubt simple electron-gas methods. Examples would be C, Si, N, O or H in transition metals, or C and H in oxides. Thirdly, there are excited states, both electronic and vibrational. In particular theories like self-consistent phonons methods and molecular dynamics, and experimental studies of radiation damage or of solid-state processes like self-trapping, all involve systems far from equilibrium, in some cases with further complexities.

3. General aspects of potentials

The idea of ionic radii is universally understood in a qualitative way. Metallurgists, chemists, physicists, electrochemists, all have their favourite lists. In fact, the use of interatomic potentials is the quantitative extension of the same qualitative notions. Some aspects should carry over, e.g. one would expect certain "universal" features of potentials, and one would anticipate certain general chemical trends. Thus almost all short-range repulsions are representable as $A \exp(-r/\rho)$ with $\rho \approx \frac{1}{3} \text{\AA}$, insensitive to the system. The classical hard-sphere radius R is usually such as to make the repulsion energy of order 1 eV, so $A \approx 1340 \text{ eV}$ corresponds to $R \approx 2.4 \text{\AA}$. There is an apparent dependence of ap-

parent ionic radii on coordination N which is only loosely (if at all) related to covalency; roughly, bond lengths L in oxides and halides vary as $\alpha - \beta \ln N$ [8]. Note neither these radii nor interatomic spacings should be used as cavity radii in estimating polarisation energies (Mott and Gurney [9] page 56 et seq.)

Universal behaviour is also suggested in adsorption [10]. Suppose the Thomas-Fermi screening length for a metal substrate is a , and that a chemisorbed atom is in equilibrium at distance a^* above the substrate with binding energy E^* . Then, to a certain accuracy, there is a universal interaction form $E((a - a^*)/\lambda)/E^*$. The assumption of such a universal form has also been proposed for physisorption of rare gas atoms onto rare-gas solids [11], where the characteristic length scale is a given in terms of the ratio of the dispersion force coefficient and the well depth.

Behaviour of plane-plane interactions is more complex. Other workers [12] have analysed interactions between two halves of a crystal being separated in terms of perfect lattice phonons (low spacings) and the bulk frequency-dependent dielectric constant (large spacings). Qualitatively, this is quite effective, and indeed suggests universal behaviour for metal. For metal/non-metal interfaces, and apparently general dependence of wetting on non-metal refractive index [13] may have a common origin. However, there is no reason to believe that there is a universal surface-surface interaction scaling accurately with surface (lateral) interatomic spacing, as proposed in segregation studies by Seah [14].

More complex interplanar potentials are found, and this complexity is itself universal in some aspects. One case concerns the short-range forces between hydrophilic surfaces in water, where pronounced oscillations are observed [15] between mica surfaces. The origin is presumably the same as that discussed generally for crystallographic shear planes by Stoneham and Durham [16].

Covalency and ionicity continue to cause confusion, often unnecessarily. Since a recent review [17] covers this in detail I merely note first that, for the purposes of this meeting, charges should

usually be defined as dipole moment per unit displacement (and not as a charge within some volume) and secondly that one may often choose arbitrarily to adopt an ionic (covalent) *framework* without ignoring the physically-present covalency (ionicity). Whichever framework is chosen, the interatomic forces must properly reproduce the relatively rigid inter-bond angles characteristic of covalency. Such interactions can be parameterised in many ways, and are reviewed by Stoneham and Harding [18]. These interactions are normally short-ranged, few-body (i.e. 3-body or 4-body) terms which are defined readily only for a given coordination. One important problem is how one evaluates such terms when the coordination can change.

Many-body forces can, of course, include more complex crystal-field, Jahn–Teller and covalent (bond-bending) contributions. As an example, the crystal field energy of a transition metal ion is often conveniently expressed in terms of a symmetrised combination of displacements of the N neighbours ($N = 4$ for tetrahedral, 6 for octahedral, etc.) from an ideal geometry) i.e. tetrahedral or octahedral, etc.). It is these terms too which cause problems when there are changes in coordination (see [18]) and which can lead to multi-valued or otherwise complicated potentials.

Volume-dependent forces always cause problems, since the “volume” at a surface or dislocation is not well-defined. One important suggestion (happily independent of detailed physical models) is that of Finnis and Sinclair [7]. Here the energy is a sum of ordinary pairwise interactions and a many-body term which, for a given atom can be written $-Af(\rho)$ with A and the (non-linear) form of f independent of site, and $\rho = \sum_i \phi(\mathbf{r} - \mathbf{R}_i)$ a sum of short-range terms depending on the relative positions of nearby atoms.

4. Defects and potentials: strategies and other general aspects

Here I describe some of the aspects which are especially important when there are trapped

carriers. In particular, the use to which potentials are put is of central importance, since this determines what is an acceptable calculation.

This can be seen for instance from the two quite distinct strategies for handling defects in semiconductors. Suppose one has some code for solving the Schrödinger equation and also a conventional (e.g. valence force) potential which are to be used together to calculate lattice distortions. Strategy I (e.g. [19]) comprises

- calculation of defect forces \mathbf{F} by the electronic structure code;
- calculation of (lattice) Greens’ function \mathbf{G} , i.e. the response of the lattice to unit force;
- calculation of the relaxation $-\mathbf{G} \cdot \mathbf{F}$ and of the relaxation energy $-\frac{1}{2}\mathbf{F} \cdot \mathbf{G} \cdot \mathbf{F}$ as the sum of the strain energy and the work done by the defect forces.

Note that one term of the final energy comes explicitly from the valence-force potential. Also, since linear defect forces \mathbf{F} are involved, without higher-order terms, this strategy cannot predict the mixed-symmetry distortions seen for the negative vacancy in silicon.

Strategy II (e.g. [20]) uses the valence force potential only to relate displacements \mathbf{v} in an outer region to those (\mathbf{w}) in an inner region, e.g. nearest neighbours. One then uses the electronic structure code to evaluate the total energy for various \mathbf{w} , allowing the outer atoms to move to $\mathbf{v}(\mathbf{w})$. Here (unlike strategy I) the energy obtained is normally an upper bound, and the non-linear terms giving mixed symmetry distortions are not eliminated. Both these strategies are, of course, much simpler than ones being applied to ionic crystals (e.g. [21], which is based on the Mott–Littleton strategy, [22] which adopts a Kanzaki (or supercell) approach, and [23] which follows a strategy similar to Strategy II).

The displacements of the nearest-neighbour (\mathbf{v} above) are themselves usually symmetrised. Thus there is the “breathing” motion of the near neighbours, with A , symmetry, etc. These motions are *reaction coordinates* as a rule, and not the dynamically-independent *normal modes* of the theory of small vibrations. The distinction is far from academic, with especial importance in the study of non-radiative transitions [24]. We

note also that the generalised forces corresponding to symmetrised displacements are, by their nature, few-body forces.

References

- [1] A.M. Stoneham, *Handbook of Interatomic Potentials I: Non Metals*, AERE Report R9598 (1979, 1981).
- [2] A.M. Stoneham and R. Taylor, *Handbook of Interatomic Potentials II: Metals*, AERE Report R10205 (1982).
- [3] M. Dixon and M.J.L. Sangster, *Adv. in Phys.* 25 (1976) 247.
- [4] A.E. Carlsson, C.D. Gilatt and H. Ehrenreich, *Phil. Mag.* A41 (1980) 241.
- [5] J.H. Harding and A.M. Stoneham, *J. Phys.* C17 (1984) 1179.
- [6] M.J.L. Sangster and A.M. Stoneham, *Phys. Rev.* B26 (1982) 1026.
- [7] M. Finnis and J. Sinclair, AERE Report TP1030 (1983).
- [8] W.H. Zachariasen, *J. Less Common. Met.* 62 (1978), 1.
- [9] N.F. Mott and R.W. Gurney, *Electronic Processes in Ionic Materials* (Oxford Univ. Press, Oxford, 1948).
- [10] J.R. Smith, J. Ferrante and J.H. Rose, *Phys. Rev.* B25 (1982) 1419.
- [11] G. Vidali, M.W. Cole and J.R. Klein, *Phys. Rev.* B28 (1983) 3064.
- [12] W. Kohn and A. Yaniv, *Phys. Rev.* B20 (1979) 4948.
- [13] A.M. Stoneham, *Appl. Surf. Sci.* 14 (1983) 249.
- [14] M.O. Seah, *Proc. Roy. Soc.* A349 (1976) 535.
- [15] J. Israelachvili and R. Pashley, *Nature* 306 (1983) 249; see also *Nature* 300 (1982) 341.
- [16] A.M. Stoneham and P.J. Durham, *J. Phys. Chem. Sol.* 34 (1973) 2127.
- [17] C.R.A. Catlow and A.M. Stoneham, *J. Phys.* C16 (1983) 4321.
- [18] A.M. Stoneham and J.H. Harding, in: *Computer Simulation of Solids*, C.R.A. Catlow and W.C. Mackrodt, eds. (Springer, Berlin, 1982) p. 162.
- [19] F.P. Larkins and A.M. Stoneham, *J. Phys.* C4 (1971) 143, 154.
- [20] A.M. Mainwood, F.P. Larkins and A.M. Stoneham, *Sol. St. Electron.* 21 (1978) 1431.
- [21] J.M. Vail, *Phil. Mag.* B51 (1985) 101. See also J.M. Vail, A.H. Harker, J.H. Harding and P. Saul, *J. Phys.* C17 (1984) 3401.
- [22] A.M. Stoneham and R.H. Bartram, *Phys. Rev.* B2 (1970) 3966. See also A.M. Stoneham, *Theory of Defects in Solids* (Oxford Univ. Press, Oxford, 1975), especially chap. 8.
- [23] N. Itoh, A.M. Stoneham and A.H. Harker, *J. Phys.* C10 (1977) 4197.
- [24] A.M. Stoneham, *Rep. Prog. Phys.* 44 (1981) 1251.