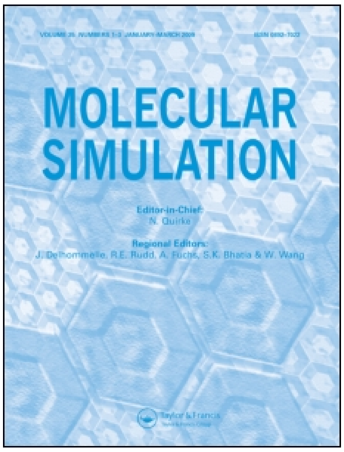

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THE PRACTICAL CALCULATION OF INTERIONIC POTENTIALS

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Most molecular simulations assume a potential model. In some cases, where one is interested only in qualitative behaviour, the details of the potential are not important provided the basic form is physically sensible. However, if one requires quantitative results, it is essential to obtain an accurate potential model. In the past, such models have been obtained by empirical fitting to suitable bulk crystal properties. Increasingly, they are now being calculated. This paper reviews the relative merits of these approaches and suggests criteria that any "good" potential should fulfill.

KEY WORDS: Interionic potentials, atomistic simulation

1. INTRODUCTION

Almost all molecular simulation calculations still rely on potentials. Despite the advent of new methods that permit a direct quantum calculation such as the Car-Parinello method [1], this is likely to continue for some time. It is simply too expensive to calculate many systems of interest from first principles. Nor is it obviously necessary; potentials have been used and are still used with great success. It is always possible to define a potential. If an energy surface exists, an algorithm that approximates it constitutes the potential. The relevant question is not whether it is possible to define potentials but whether it is always useful. In particular, when states are electronically degenerate and the potential multi-valued, it may be more sensible to attempt direct calculation.

Often, the precise form of the potential is not important provided it be physically reasonable. This is the case when we wish to simulate a physical effect that is common to a large class of systems. Here, provided it contains the basic physics, the simpler the potential the better; hence the enduring popularity of Lennard-Jones potentials. However, if we wish to explain why this material behaves in this particular way, the choice of potential is critical.

Most simulations assume that the crystal potential may be written as a sum of central-force pair potentials. That is, we write

$$\Psi = \Psi_0 + \sum_{i\neq j}^{N} \psi_{ij}(r) + \sum_{i\neq j\neq k}^{N} \psi_{ijk}(r) + \dots \tag{1}$$

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and omit everything after the second term. The first term only shifts the energy by a constant amount and its omission merely redefines the ground state. It contains the energies required to prepare the ions in the electronic states assumed by the pair-potential model (see the article of Pyper in this volume for a full discussion). Equation (1) is, in principle, exact. However, it offers no guidance as to how the various terms are to be calculated nor their functional forms . Indeed, there is a wide variety of possible forms to choose from, particularly for the many-body terms, and frequently no clear theoretical justification for their use.

In the next section we consider how the individual pair potentials $\psi_{ij}(r)$ have been obtained. We shall ignore the issue of ionic polarisation (although many of the potentials discussed are, in fact, used in shell models), deferring this matter until section three.

2. CENTRAL-FORCE PAIR POTENTIALS

The traditional method of obtaining a set of pair potentials is to choose a suitable functional form and fit the disposable parameters to experimental data. This presupposes the existence of a model of the solid that can be used to give guidance in this matter. In the case of ionic solids such a guide, of course, exists. The ionic model has been used for more than fifty years to calculate the properties of solids. This assumes that a pair potential may be written in the form

$$\psi_{ij}(r) = \frac{Z_i Z_j}{r} + \phi_{ij}(r) \qquad (2)$$

where all the long-range parts of $\psi_{ij}(r)$ are contained in the first term on the right-hand side. In the simplest version of the model, the charges Z_i are chosen to be those implied by the oxidation state of the ions. This however, begs a number of questions, as pointed out by Catlow and Stoneham [2]. In particular, there are two quite different methods of deciding the charge for an ion. One might attempt to partition the charge density of the crystal (as calculated by some suitable method or as measured from X-ray diffraction) among the ions. The problem here is that if there is any overlap charge density there is no unique way of doing this. Another way is derived from lattice dynamics. We might define the charge on an ion as the dipole moment per unit displacement. This assumes that the displacement vector is in the same direction as the internuclear vector and further assumes that the ion is rigid. There is no reason in general to suppose that this will yield a charge that corresponds to either the result of any standard method of partitioning the charge density of the crystal or the charge one might expect from simple chemical considerations. Indeed one might define ionic crystals as those where one can assume that the "chemical" charges give reasonable results for all these definitions; the errors being taken up either in the short-range part of the potential or the model of the ionic polarisability. In many cases, particularly in discussions of lattice dynamics, non-integral charges are used. This usually gives better agreement with the observed phonon spectrum, usually at the cost of poorer agreement with the cohesive energy. It is doubtful whether such schemes are useful for simulation. This frequently involves ions of different charge state to the host lattice. The use of the "chemical" charge states at least gives a clear prescription of what to do in such cases. It is far from obvious what to do if, for example, one introduces Sr^{2+} into NaCl where the charge on the sodium ions in 0.9.

This leaves the problem of how to obtain the "short-range" part of the potential $\phi_{ij}(r)$ shown in Figure 1. This diagram makes a number of points. First, the commonest way of fitting such a potential is to use elastic and dielectric data. It is important to realise that this only fixes the potential and its curvature close to the equilibrium point. Frequently we need to know the potential at quite different distances. Thus it is highly desirable to find data which we can use to check the potential at different internuclear distances. Such data may come from pressure experiments or thermal expansion measurements. Alternatively, we may assume that pair interactions remain the same for different solids and use one ion-ion interaction for a variety of different materials. This is frequently done when fitting the alkali halides.

The first thing we require, however, is a functional form. Figure 1 expresses the common case where the potential consists of a repulsive term at small internuclear

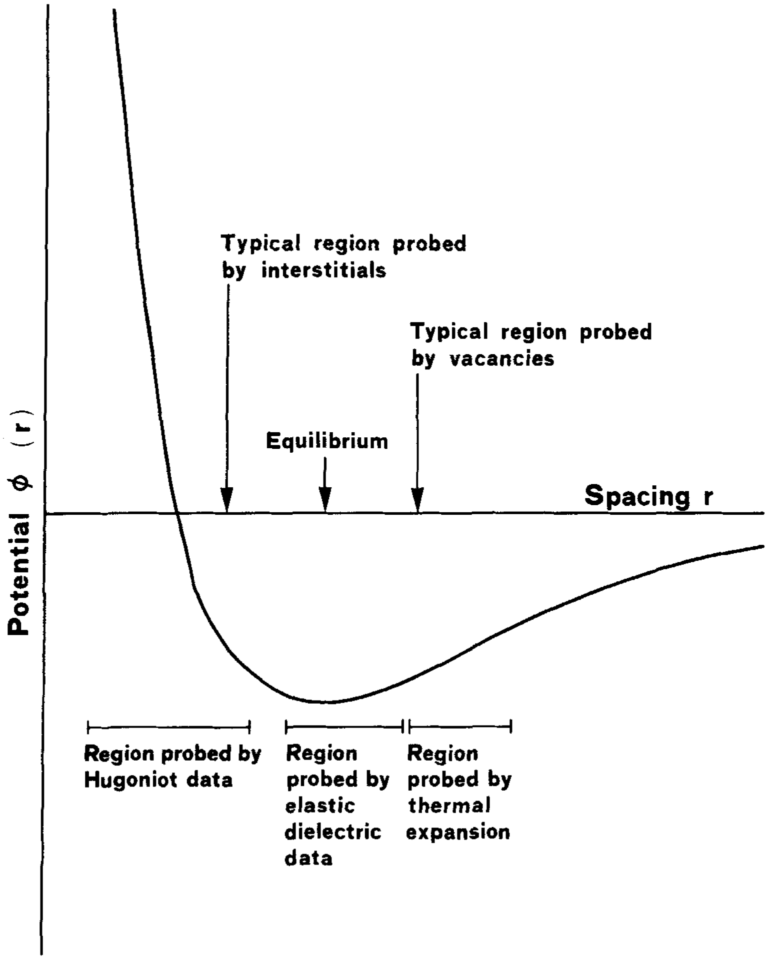

Figure 1 The short-range contribution to the interionic potential (schematic).

distances and an attractive term at longer range. It is usually assumed that the repulsive term may be represented either by a power-law or by an exponential. The attractive term is assumed to be the dispersion term which, provided the ion wavefunctions do not overlap, may be written as

$$\phi_{ij}(\text{disp}) = \sum_{n=3}^{\infty} C_{2n} r^{-2n} \tag{3}$$

A very common form is to add the first term to an exponential repulsion term to give

$$\phi_{ij}(r) = A_{ij}\exp(-r/\rho_{ij}) - C_{ij}/r^6 \tag{4}$$

This provides three disposable parameters A_{ij}, ρ_{ij} and C_{ij} that can be fitted to experiment. Despite its common use, there are serious doubts about the adequacy of equation 4. Such a form assumes that dispersion terms of the form (3) are valid at all internuclear separations. This, as we pointed out above, is incorrect. Indeed, at short internuclear separations (4) must give absurd results as it goes to $-\infty$. In many cases the simulation may not investigate these regions. However precautions may often be necessary, particularly for molecular dynamics and Monte-Carlo simulations. This is not the only problem. If the wave functions of the ions overlap, (3) should be replaced by

$$\phi_{ij}(\text{disp}) = \sum_{l=1}^{\infty}\sum_{L=1}^{\infty} \frac{\chi(l,L)\omega(l,L)}{r^{2l+2L+2}} \tag{5}$$

Details of the expressions are given in reference [3]. Each term in the series now contains a damping coefficient (the $\chi(l,L)$). For large distances, $\chi(l,L) \to 0$. However, as $r \to 0$, $\chi(l,L)\omega(l,L) \to -Ar^{2|l-L|} + Br^{2|l-L|+2} + \ldots$ Thus the dispersion goes to a finite value. Despite the unpleasant appearance of (5), all the quantities in it can be calculated.

The C_6 coefficient is best obtained from the Slater-Kirkwood approximation [4]

$$C_6(i,j) = \frac{3}{2}\frac{\alpha_i\alpha_j}{[(\alpha_i/P_i)^{1/2}+(\alpha_j/P_j)^{1/2}]} \tag{6}$$

The polarisabilities α_i may be obtained from a combination of *ab initio* quantum calculation and refactive index data [5]. The so-called "electron numbers" P_i are obtained by fitting this formula to the known results for the iso-electronic rare gas systems. A discussion is given in reference [6].

The Table shows a number of fitted dispersion coefficients compared with the

Table 1 Dispersion coefficients (units of eV Å^6)

interaction	*fitted ([7])*	*fitted ([8])*	*Slater-Kirkwood*	*Hartree-Fock ([6])*
Li^+-Li^+	-	0.029	0.047	0.045
Na^+-Na^+	-	3.096	0.949	0.906
K^+-K^+	52.0	36.23	13.66	13.63
Rb^+-Rb^+	208.8	91.86	32.98	34.84
Li^+-F^-	-	0.691	0.675	0.642
F^--F^-	26.8	23.89	13.85	11.62
Na^+-Cl^-	-	21.80	8.134	7.411
Cl^--Cl^-	165.4	193.95	107.8	95.51

calculations. The two fitted dispersion coefficients are obtained by different methods. Those of reference [7] are a simple fit to the data. Those of reference [8] are obtained by fitting the polarisabilities (see Table 4 for the fitted values) and then using the London dispersion formula. Details are given in the cited reference. Two points emerge. First, the Slater-Kirkwood approximation is indeed a reasonable approximation to the full calculation. Second, the fitted dispersion coefficients are significantly too large. This effect is enhanced if, as in reference [8], a simple formula like (4) is used. Reference [7] uses a splining scheme so that the C_6r^{-6} term is effective only at large r. These results suggest that the fitted "dispersion coefficients" may be modelling something else. Alternatively, the excessive contribution from this term may be cancelled out by a more repulsive inner part of the potential. With fitted potentials it is not possible to distinguish these alternatives. Higher order terms can be obtained from the C_6 coefficients using the approximation of Starkschall and Gordon [9]. The damping coefficients may also be calculated (see Pyper). Such calculations show that the effect of damping is already significant at interionic distances characteristic of the bulk solid.

Empirical parametrisations have been highly successful (see, for example, [10] or [11] where a number of specific cases are discussed). However, they do have their problems. One of these has already been (implicitly) discussed - because empirical parametrisation is a fitting process, it is often unclear what effects have been included. This can be a problem when one wished to investigate trends in materials. In such a case, one usually wishes to monitor the effect of a particular ionic property (ion size for example), certainly not the vagaries of a fitting process. The second problem may be simply that there is nothing suitable to fit to. In such a case one can attempt to combine potentials from other sources; this may, however, omit important terms that only arise in the specific situation at hand. A good example of this is seen in the attempt of Catlow *et al.* to predict the behaviour of spinels. The results are shown in Table 2.

The various energy terms are as follows. ΔE_L is the energy due to lattice polarisation and distortion; ΔE_{CF} is the crystal field term; $\Delta E'$ is the energy of stability of the normal spinel with respect to the inverse spinel and ΔE is the same energy but taking the effects of different coodination of the ions into account. a_0 is the lattice parameter. λ measures the extent to which the compound is a normal ($\lambda = 0$) or inverse ($\lambda = 0.5$) spinel. The u parameter appears in the crystallographic definition of the spinel structure (see Wycoff [12] for a definition) and refers to the positions of oxygen ions.

From the table, it is obvious that simply combining the potentials from other systems (which gives $\Delta E'$) fails to predict the normal-inverse transition correctly. The

Table 2 Simulation of normal and inverse spinels (see reference [11])

Oxide	a_0 (Å)	λ	ΔE_L (eV)	ΔE_{CF} (eV)	$\Delta E'$ (eV)	ΔE (eV)	u_{expt}	u_{calc}
$MnCr_2O_4$	8.436	0.0	1.23	1.64	2.87	2.27	-	0.3923
$MnAl_2O_4$	8.258	0.0	1.98	0.0	1.98	1.81	0.390	0.394
$NiCr_2O_4$	8.32	0.0	0.62	0.75	1.37	0.58	0.385	0.388
$MnFe_2O_4$	8.511	0.1	0.82	0.0	0.82	0.20	0.3846	0.3923
$NiAl_2O_4$	8.048	0.38	1.15	−0.89	0.26	−0.15	0.390	0.3867
$NiMn_2O_4$	9.403	0.5	0.39	0.09	0.48	−0.71	0.381	0.3812
$NiFe_2O_4$	8.353	0.5	0.1	−0.89	−0.79	−1.66	0.386	0.3851

effect of coordination is included by adding a further term to the potential of the form A_{ij} exp $(-\Delta r/p)$ where Δr is the difference in ion size between the octahedral and tetrahedral sites. This is assumed to be $0.06r_{oct}$. When this is inserted, much better agreement is obtained. However, the exercise has shown that simple transferability of potentials from one system to the next may be inadequate.

If one wishes to attempt calculation, a number of possibilities are available. These are discussed in depth elsewhere in this volume (see in particular the articles of Pyper and Allen) and so only a few basic comments will be made here. The electron-gas approximation is both the simplest to use and the one most obviously similar in spirit to the ionic model. Here we assume that the total electron density of the crystal is the sum of the electron densities of the individual ions. These are usually calculated by Hartree-Fock theory. The interionic interaction is obtained from this using the theory of the homogenous electron-gas to obtain the functionals for the kinetic energy and exchange terms. The correlation terms are obtained from empirical correlations and the coulomb terms are calculated directly. A large number of variants of the electron-gas approximation have emerged, depending on how one treats various terms. These are discussed by Allen. Such a method allow one to calculate the short-range repulsive part of the potential (not the dispersion terms). The accuracy is not as great as the best empirical potentials; the compensating advantages are that one knows what has gone into the approximation (an advantage when considering trends across a series) and that one is not restricted to systems where there is suitable data for fitting.

More complex (and more expensive) calculations of potentials are possible although few have as yet been done. The article of Pyper discusses progress in this field. Perhaps the most important result is the question mark set against the accuracy of the electron-gas approximation.

Finally, before turning to the question of ion polarisability, we should consider attempts to obtain many-body potentials. The first three-body term to be discussed was the Axilrod-Teller dispersion term [13]. This may be written as

$$E_{ijk} = v_{ijk}\left(\frac{3\cos\theta_{ijk}\cos\theta_{jki}\cos\theta_{kij}+1}{R_{ij}^3 R_{jk}^3 R_{ki}^3}\right) \tag{7}$$

Where θ_{ijk} denotes the angle between R_{ij} and R_{jk}. the coefficient v_{ijk} can be calculated (see reference [6]). For the systems for which this has been done (alkali halides) the effect is small.

More empirical formulations have also been tried. Catlow and co-workers have made considerable use of a bond-bending term of the form $K(\theta - \theta_0)^2$ where θ_0 is the equilibrium bond angle and θ the instantaneous bond angle. Such a term considerably improves the fitting of structural data as can be seen from Table 3. However, the lack of any theoretical justification for the expression used means that it can only be used with caution at angles significantly different from θ_0. While most potentials are approximately quadratic close to their equilibrium point, they usually depart from this behaviour quite rapidly.

3. THE SHELL MODEL

The original studies of ionic systems used simply the coulomb terms and a set of short-range forces. This assumed that the ions were unpolarisable and hence the

Table 3 Fitting of lattice data for α-quartz (see reference [11]; elastic constants are in units of 10^{11} dyne-cm^{-2})

Property	*experiment*	*2-body potential*	*3-body potential*
C_{11}	8.683	6.204	8.815
C_{13}	1.193	1.629	1.151
C_{14}	−1.8064	−1.012	−1.666
C_{33}	10.498	7.466	10.605
C_{44}	5.826	3.301	5.296
C_{66}	3.987	2.737	4.269
ε^0_{11}	4.520	5.513	4.452
ε^0_{33}	4.460	6.086	4.812
ε^∞	2.4	2.069	2.04

high-frequency dielectric constant, ε^∞, was unity. This is usually called the rigid ion model. This approximation is still frequently employed in molecular dynamics simulations to save computer time. However, such a model cannot be adequate. This can be seen from the Lyddane-Sachs-Teller relation, $\omega^2_{LO}/\omega^2_{TO} = \varepsilon^0/\varepsilon^\infty$. Clearly, if ε^∞ is necessarily unity in the rigid ion model, it cannot be expected to reproduce the optic branches of the phonon spectrum correctly. This is demonstrated in Figure 2 where the experimental phonon spectrum for NaI is shown together with the best rigid ion model fit (dashed lines) [14]. Although the behaviour of the acoustic branches is described reasonably well, the optic branches are qualitatively wrong.

To put this right, however, requires more than giving the ions a polarisability. It is also necessary to permit this polarisability to interact with the interionic forces in

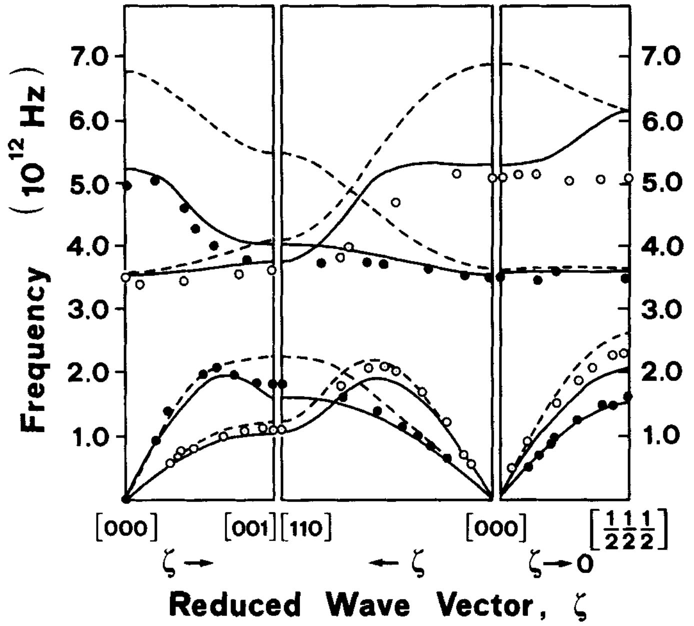

Figure 2 Comparison of rigid ion and shell models for NaI. The full line is a shell model; the dashed line rigid ion (after reference [14]).

a physically sensible manner. The simplest model that does this is the shell model. This idea, first discussed by Dick and Overhauser [15] but frequently reformulated and elaborated thereafter, models the ion as a massive core linked to a massless shell by a harmonic spring constant k. The shell is given a charge Y and so the polarisability of the ion in free space is Y^2/k. In the crystal, the coulomb forces act between all cores and shells except the core and shell of the same ion. It is usual (though not necessary within the formalism) to assume that the short-range forces act only between the shells. Within the crystal, the effective polarisability of an ion is also a function of the short-range forces of the ions surrounding it. For a rock-salt structure, the polarisability is given by $Y^2/(k + S)$ where S is the force between the ions due to the short-range potential. Physically, the shell model couples the dipole moments of the ions to the forces between the ions. It may also be looked on as a very simple form of many-body potential since the ionic polarisability, and hence the induced dipole moment, is a function of the environment. It has sometimes been assumed that the shell can be identified with the valence electrons of the ions. This suggestion is rendered doubtful by the fitted values of the parameters obtained. Table 4 shows some shell parameters for the alkali halides.

Obviously, the valence electrons cannot be positive, as suggested by the shell-charge values of reference [7]. Bilz *et al.* [16] have advanced an argument suggesting that positive shell charges are admissable even if the shells are identified with the valence electrons. They suggest that extra terms arise from the overlap of the ion wavefunctions which are large enough to produce an effective shell charge of the opposite sign. However, it must be said that no estimates of these terms have ever been obtained (nor, for that matter has any direct calculation ever been attempted of a shell parameter). It is therefore impossible to evaluate this argument. It seems better to admit that the model is purely empirical and its success is its justification.

It is, however, worth noting from the Table that the two fits give very different values for the shell parameters, and even for the polarisabilities of the small cations. It is fair to suggest that reference [8] gives the more consistent set of the two. Unless one is calculating interfaces, the sign of the shell charge does not seem to make much difference to the calculation, although potentials with large shell charges can encounter stability problems. It is possible to calculate polarisabilities directly from a Hartree-Fock calculation. Results by Fowler and Madden [17] are shown in Table 4. The fitted polarisabilities differ considerably from the calculated ones, systematically too large for the cations and too small for the anions. This suggests that the fitting

Table 4 Shell model parameters for alkali halides (calculated Hartree-Fock polarisabilities (α_{HF}) from [17] also shown)

Ion	*fitted (ref ([7])*			*fitted (ref [8])*			*calculated*
	$Y(\lvert e\rvert)$	$k(eV\text{Å}^{-2})$	$\alpha(\text{Å}^3)$	$Y(\lvert e\rvert)$	$k(eV\text{Å}^{-2})$	$\alpha(\text{Å}^3)$	$\alpha_{HF}(\text{Å}^3)$
Li^+	0.705	7.989	0.87	−0.6025	175.07	0.029	0.028
Na^+	2.128	96.44	0.66	−2.2150	284.04	0.2495	0.148
K^+	−83.55	86032	1.14	−5.9659	470.90	1.0571	0.791
Rb^+	−125.2	121460	1.81	−4.9147	216.55	1.56	–
F^-	−1.339	37.98	0.66	−1.6810	40.56	0.9743	1.58
Cl^-	−2.485	29.38	2.94	−2.6532	30.43	3.2350	4.66
Br^-	−2.705	24.66	4.15	−2.7370	23.11	4.5330	–
I^-	−4.087	39.95	5.85	−3.0332	19.03	6.7629	–

procedure is incorporating terms that are not ionic polarisabilities although it is impossible to say exactly what is being included.

Three-body potentials have been used in conjunction with the shell model by a number of authors. These assume, as users of the shell model have assumed, that the short-range forces act only between the shells. The problem here is that, since it is far from clear what the shell positions mean, it is not clear what is being done. This was not so much a problem with the two-body forces as there was a clear partition between the polarisation forces, modelled by the shells, and the short-range forces modelled by the potentials $\phi_{ij}(r)$. Since the polarisation terms are themselves many-body terms, there is no such division between the three-body forces and the shell model and it is not clear which part of the potential is modelling what. In fairness, it must be said that the three-body force models do work when they have been used to fit experimental data. However, this reinforces the point made earlier that work is needed on the question of what is a suitable functional form for such potentials.

4. TESTS FOR POTENTIALS

We have already discussed the fitting or calculation of potentials above. We must now turn to the issue of how to test the potentials we have obtained. Two main types of test may have been used (short of using them in the simulation we wish to perform). First, we may attempt to calculate the lattice thermal expansion. This may be done either using a constant pressure molecular dynamics code (if we wish to use the potential in that kind of simulation) or, more usually, within the quasi-harmonic approximation. This is particularly useful if we wish to calculate free energies of defects using the shell model. Such calculations must be done in a self-consistent manner using the potential to calculate everything. It is therefore important to see whether the potential (in particular the calculated phonon density of states) is physically reasonable at the outset. There are two ways of calculating the lattice thermal expansion. We may either calculate the Helmholtz free energy F and then use the relation

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \approx 0 \tag{8}$$

since atmospheric pressure is negligible or alternatively, as pointed out by Allen, Mackrodt and Leslie [18] we may argue as follows. From the second law of thermodynamics, temperature is defined as $(\partial E/\partial S)_V$. This, however, is far from simple to calculate. By changing variables we obtain

$$\begin{aligned}(\partial E/\partial S)_T &= (\partial E/\partial S)_V + (\partial E/\partial V)_S(\partial V/\partial S)_T \\ &= T - P(\partial V/\partial S)_T.\end{aligned} \tag{9}$$

The second term may be ignored for atmospheric pressures. $(\partial E/\partial S)_T$ may readily be calculated. An example of such a calculation is shown in Figure 3. Here the lattice thermal expansion for two different potentials for MgO is shown. It is clear that one potential is physically sensible and one is not. Such a judgement cannot be made on the basis of low-temperature properties alone.

The second method is to try to calculate properties at high pressure. One particular-

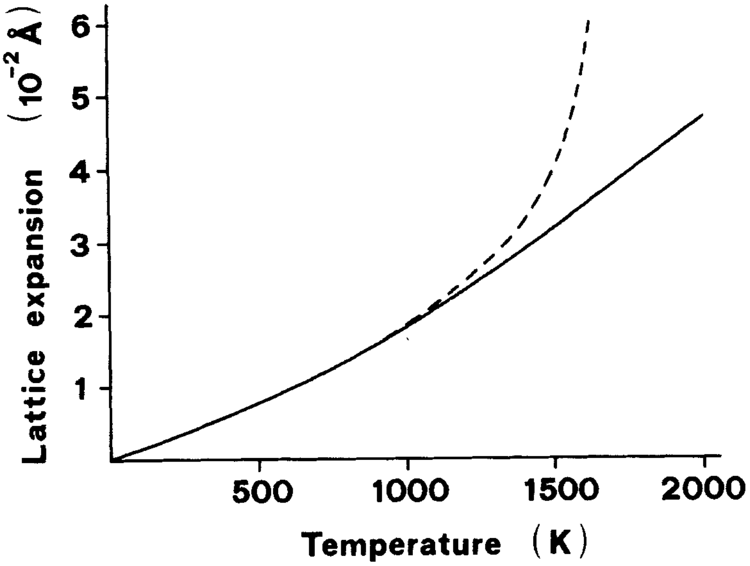

Figure 3 Prediction of the lattice expresion of MgO. The full line is an empirical potential; the dashed line an electron-gas one (after reference [18]).

ly useful source of data (when available) comes from the study of shock waves. This involves very high pressures and so allows us to check potentials at distances much shorter than those usually used for fitting. If we consider the shock to be an adiabatic process and assume that mass and energy are conserved across the shock front we may obtain the Rankine-Hugoniot relation

$$(E_1 - E_0) = \frac{1}{2}(P_1 + P_0)(V_0 - V_1) \tag{10}$$

where E, V and P are the internal energy, pressure and volume respectively and the subscripts 0 and 1 refer to the solid in front of the shock wave (i.e. in the undisturbed solid) and behind it. We shall use the Mie-Grüneisen equation of state

$$P = -\frac{d\Psi}{dV} + \gamma(V)kT/V \tag{11}$$

to calculate the pressure. Here Ψ is the static part of the internal energy and the $\gamma(V)$ the Grüneisen constant (which we can obtain from the phonon spectrum in the standard way). Figure 4 shows examples of the Hugoniot equation of state calculated sodium chloride using two different potentials. Note the phase change at about 30GPa. For this adiabatic system, the relevant thermodynamic quantity that determines the stability of phases is the enthalpy rather than the free energy. Again, it is clear that the difference in the potentials only shows up under extreme conditions.

5. POTENTIALS WITH OPEN-SHELL IONS

Most of the examples discussed to date have concerned closed shell systems. Attempts have also been made to derive potentials where one or more of the ion types are open

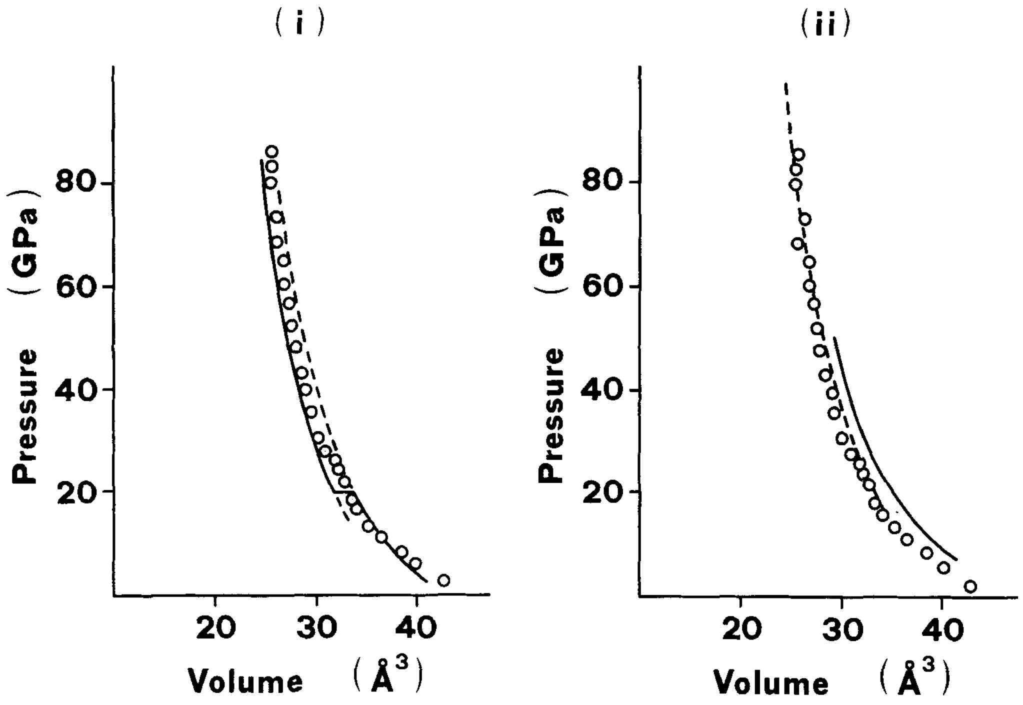

Figure 4 Prediction of the Hugoniot of NaCl for two potentials: (i) empirical; (ii) electron-gas. The full line gives the predicted stable phase. Crosses are experimental points (after reference [19]).

shell. The most obvious example is that of the transition metal oxides. The elastic and dielectric properties of MnO, CoO and NiO show no qualitative differences from those of MgO and various authors have attempted to fit potentials for the alkali halides. The results obtained are, on the face of it, perfectly reasonable (see, for example, [20]). However, as Atkinson [21] has pointed out, difficulties are encountered when we consider diffusion. Figure 5 shows the calculated and experimental migration enthalpies for a variety of oxides. It is clear that the calculations for CoO and NiO are quantitatively incorrect. The results for the others (including the half-filled shell case Mn^{2+}) are reasonable. The reason for this discrepancy cannot be due to the fact that the other ions have higher-order moments than the dipole since, although the ground state of Co^{2+} is $^5T_{1g}$, that of Ni^{2+} is $^3A_{2g}$. (Mixing with other states will produce a higher-order moment for Ni^{2+} but these states are far away in energy and the resulting moment will be small). This suggests that Jahn-Teller type terms may be responsible. The problem here is twofold. First, such terms are not expected to be much more than 0.1 eV which is not enough. Second, the migration enthalpy of Co^{2+} and Ni^{2+} in MgO is well-predicted by standard potential models [22]. The problem here seems to be that structural predictions with potentials are frequently successful, defect calculations, often with the same potentials can encounter serious problems. Something is clearly being missed out of the defect calculation, but it is not yet clear what that something is.

The other main area where open-shell ions are encountered is in the attempts to

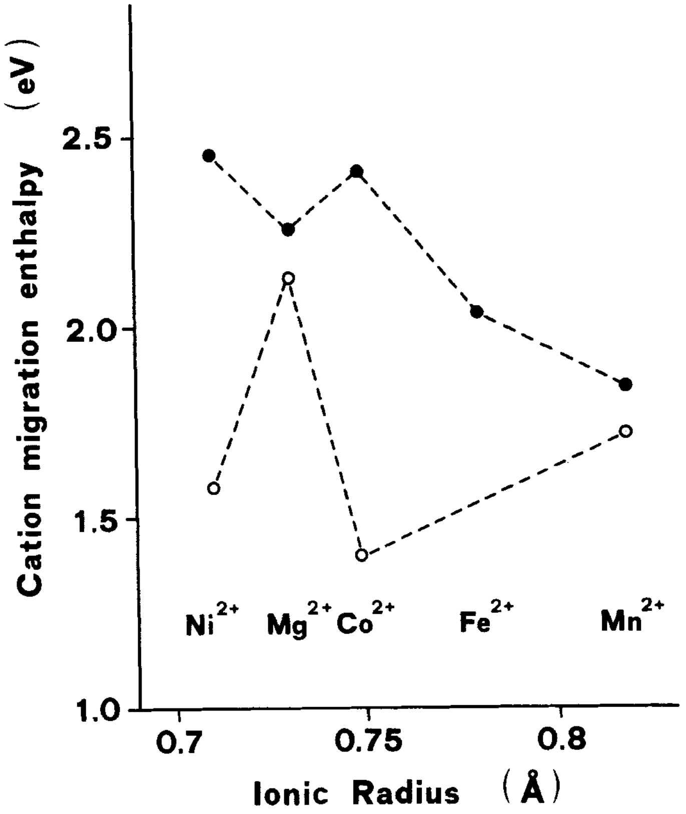

Figure 5 Migration enthalpies in transition-metal oxides. Full circles are theory; open circles experiment. (after reference [21]).

predict energies where both electronic and polarisation terms are important. Here the problem is obtaining accurate values of both terms. From the point of view of potential models, the first problem is that it is impossible to obtain potentials by fitting since, most cases involve charge states that do not appear in compounds where data are available for fitting potentials. Thus either the effect of the different ion sizes must be ignored or an attempt must be made to calculate it. Since the effect may be of the order of several tenths of a volt or more, it is rarely justifiable to ignore it. More serious is the problem that, since a potential model by its nature does not attempt to solve the Schrödinger equation, energy terms that can only be obtained from such a solution must be put in "by hand". An example of this can be seen in Table 5. The problem here is that, although the agreement with experiment is apparently respectable, the electronic terms added in by hand are so large that is is impossible to tell whether this agreement is due to good fortune in the potential model, good fortune in the rough estimates of the electronic terms or good fortune in the cancellation of errors. The only type of calculation that could resolve such doubts is one self-consistent both in the lattice polarisation and the electronic energies. Such calculations are very expensive and only a few have been attempted. Progress here is referred to elsewhere in this volume.

Table 5 Optical transition energies (eV) in alkaline earth oxides (reference [23]). (ΔE_L is the lattice polarisation term, ΔE_T the tunnelling term and ΔE_{CF} the crystal field term).

Centre	Δ_0	Δ_T	Δ_{CF}	*electronic terms (total)*	ΔE	*Experiment*
CaO V^-	2.52	0.56	0.25	0.81	1.71	1.85
CaO Li^0	2.27	0.56	0.03	0.59	1.68	1.73
CaO Na^0	2.27	0.56	0.02	0.58	1.69	1.52
CaO K^0	2.12	0.56	0.27	0.83	1.26	1.6
SrO V^-	1.87	0.48	0.14	0.62	1.25	-
SrO Li^0	2.37	0.48	−0.14	0.34	2.03	-
SrO Na^0	2.37	0.48	−0.09	0.39	1.98	1.34
SrO K^0	1.73	0.48	−0.07	0.41	1.32	1.59

6. CONCLUSIONS

In the last few years, there have been many advances in computer simulation techniques. Where we were once content to calculate internal energies, we now wish to calulate free energies as a function of temperature. We wish to study more subtle effects; the details of the diffusion process for example. Also, we wish to simulate more complex systems under more extreme conditions. The work on silicates by Catlow, Parker and others is an example. All this means that we require more of the potential model. It is not enough that it be physically reasonable, we want a good description of specific materials over a wide range of conditions. For the present it is still true that a good empirically fitted potential will perform better than one obtained by calculation. It is not obvious that this will continue to be true for that much longer. Moreover, even if one does in the end resort to fitting, one still needs guidance from theory as to a suitable functional form. The recent work on the dispersion terms suggests that most functional forms used in fitting have been too simple. Next we come to the problems of open-shell ions. Here we still have a puzzling mixture of success and failure. More work is badly needed to find out why. Finally, we come to systems where we must solve the Schrödinger equation within a distorted and polarised lattice. This challenge is already being faced but there is still much to do.

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