Many-Atom Interactions in Solids [and Discussion]

Volker Heine, I. J. Robertson, M. C. Payne, J. N. Murrell, J. C. Phillips and D. Weaire

Phil. Trans. R. Soc. Lond. A 1991 **334**, 393-405
doi: 10.1098/rsta.1991.0021

Many-atom interactions in solids

By Volker Heine, I. J. Robertson and M. C. Payne
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.

Computer simulation of complex processes in condensed matter comprises a large and broad research effort. These require good models of the interatomic interactions, valid over a wide range of circumstances. In most processes of interest, the crucial atoms are in positions far from standard bonding patterns, at least temporarily: at surfaces and defects, in clusters and in open structures like silicates, the coordination number varies widely. The difficulty of modelling interatomic interactions in such circumstances arises from the existence of strong many-atom forces, originating from the uncertainty principle and the variational principle of quantum mechanics. Some theory of many-atom interactions, and some evidence for them, will be reviewed briefly. In particular a series based on two-, three-, four-atom, etc., interactions is almost certainly not convergent in some cases. In recent years several empirical and semi-empirical, broadly similar approaches to modelling many-atom interactions have come into use, though there are few hard tests of how good they are. An alternative approach, requiring the largest computations possible, involves the Schrödinger equation for the whole simulation to a high relative accuracy.

---

1. Introduction

An understanding of bonding in condensed matter has become a matter of major interest, as witness the holding of this conference. By condensed matter we mean the usual range of ordered and disordered crystalline solids with their defects and surfaces, as well as melts, glasses and amorphous materials, and even cluster molecules. The understanding of complex processes in condensed matter is central to a broad range of physics, solid state chemistry, metallurgy and to a growing extent in ceramics and mineralogy, i.e. to much of materials science in its widest sense. For example one would like to know the nature of grain boundaries in group IV semiconductors: do they retain basically a four-fold coordination as in the perfect crystal, or a more metallic structure with higher coordination as in the melt? In metals the segregation of impurities in grain boundaries can weaken the material, even impurities such as arsenic and sulphur which form very stable compounds with metallic elements and hence might be expected to strengthen the material by glueing the grains together: Why? One of the earliest bits of science one learns at school is that metals are ductile as well as conducting heat and electricity, whereas non-metals are brittle. When one asks friends in materials science about this, one gets answers in terms of slip systems for dislocations, etc., but these answers are not relatable at the present time to the basic difference that the bonding electrons in metals are much more mobile and spread out over many atoms compared with non-metals. These examples, let alone the whole subject of surface chemistry, show how little detailed quantitative understanding we have of bonding in condensed matter.

The matter of bonding has come to the fore as computer simulation has developed

Phil. Trans. R. Soc. Lond. A (1991) **334**, 393–405
Printed in Great Britain

over the past 25 years. The point here is that a computer simulation is only as good as the model of the interatomic binding that goes into it, and that is still its Achilles heel, as it has been throughout the evolution of the subject.

It must be admitted that we are asking for a lot from interatomic potential. The foremost difficulty is that complex processes of interest usually involve atoms arranged in configurations which are very far from standard bonding geometries. Consider for example the rebonding of the broken bond at a vacancy in silicon: or an interstitial at the top of the potential barrier in diffusion. Our model of the bonding has to be correct for those geometries. These are very different situations from lattice vibrations where the bonding topology remains that of the standard coordination with only moderate deviations from equilibrium.

For the latter the ionic models and bond charge models have been very successful; but even here often only reliable within the harmonic approximation, not for third- and fourth-order anharmonicity. The second requirement is a model of the interatomic bonding applicable over a wide range of coordination number C. Consider two A atoms, together and separated, adsorbed on the surface of a different material B. We need the A–A bonding for $C = 1$ in the presence of B, and if we want to compare it with the cohesive energy of the bulk A solid the same model needs to be applicable for the much larger value $C = 4$ to 12 of the bulk A. The same point is true for studying phase transitions under pressure where materials tend to collapse to denser packing (larger C), e.g. silicates at depth in the Earth's mantle. The last example serves to illustrate a third requirement: the potential model needs to be accurate. The mantle convection sustaining geological plate tectonics is driven by density changes probably caused by phase changes as much as by thermal expansion. To make useful predictive statements about the pressures for such phase changes, the potential model has to be quite accurate in the comparison of what may be quite different structures. It all amounts to a tall order!

At one time it was hoped that the total cohesive energy of the system could be represented to considerable accuracy by a sum of pairwise interactions, supplemented by some three-atom terms for the bond bending forces but not much more. True, an atom has a constant size to a remarkable degree whatever its environment, which indicates that the short range, hard core, repulsive forces are largely pairwise in nature; but it tells us nothing about the softer cohesive interactions at larger distances.

It is not widely recognized that we have to think about many-atom bonding in condensed matter, and 1989 saw the first international conference specifically devoted to that issue (Nieminen *et al.* 1990). In metals this has been realized at the qualitative level for a long time because of the electron-gas nature of metallic electrons, as evidenced by the Cauchy anomaly among the elastic constants. But Mott & Jones (1936) in their pioneering monograph on theoretical solid state physics also treated diamond as a good example of a nearly free-electron gas, and we now know they were right (in a slightly more sophisticated sense than they realized (Heine & Jones 1969)). This is an awful warning not to be too cavalier in thinking about even the best saturated covalent materials. (Of course materials with unsaturated conjugated bonds as in benzene are similar to metals.) The issue is really whether one can write the formation energy U as a rapidly converging sum of pairwise, three-atom, four-atom, etc., interactions

$$U = I_2 + I_3 + I_4 + \dots. \tag{1.1}$$

Or must one think in terms of genuinely many-atom interactions involving simultaneously all the near neighbours of an atom, up to 12 in number for a close packed structure? In fact the series (1.1) diverges, as we show dramatically in one simple case (§3).

Section 2 outlines some simple theoretical ideas about many-atom interactions but three basic points are in order here. Firstly, we know from the Uncertainty Principle of quantum mechanics that the bonding electrons will minimize their kinetic energy by spreading themselves out in molecular orbitals extending over as many atoms as possible (though this is balanced against other terms in the total energy). Thus many-atom forces should not be unexpected and we see that they, have their origin in the essential quantum nature of electrons. Secondly in nearly-free-electron metals a large item in the total energy of the system is the Fermi kinetic energy of the electron gas which depends only on its volume per atom. Now to define the Wigner–Seitz polyhedron around an atom and hence its volume, one needs to specify all the near neighbours. This points more specifically towards many-atom interactions, with 'many' of order the coordination number C. Thirdly there is the point about diamond above. In fact it was the kinetic energy which Mott & Jones noted was equal to the free-electron value if one took the measured band width from the bottom of the occupied band to the middle of the band gap, as seen in soft X-ray spectra. In conclusion, it seems that a series like (1.1) will not be a good and rapidly convergent representation of the binding energy to cover a wide range of coordination number and bonding geometries.

Section 4 mentions some evidence for the complexity of bonding in condensed matter, including an analysis of some *ab initio* calculations designed specifically to shed light on the many-atom character. Section 5 will review briefly two quite different approaches to what one does about it in computer simulations, and draw the conclusions together.

2. Some theory relating to many-atom interactions

The origin of many-atom interactions can be seen both from nearly-free-electron model and from the tight binding or linear combination of atomic orbitals (LCAO) model, which represent two opposite extreme views of electronic structure.

The subject has been reviewed recently (Heine & Hafner 1991) so that we will not discuss the nearly-free-electron approach here at length. The basic point has already been made in §1, namely the kinetic energy is a volume force and it requires a simultaneous specification of all the near neighbours to define the volume occupied by an atom. The implications of this for the structures of bulk solids and generally the success of this approach have been well documented (Heine & Weaire 1970; Hafner 1987).

The argument applies just as much to a semiconductor such as diamond, as it does to an sp bonded metal, because the occupied band width in the semiconductor is just governed by the free-electron value. This is completely consistent with the fact that the valence electrons in diamond are not uniformly spread out in the manner of a free-electron gas but are located almost entirely in the bonds between atoms, with almost zero electron density in the large holes between the bonds. It is easiest to understand this from a simple one-dimensional example of a chain of atoms with spacing a. At the Brillouin zone boundary we have free electron waves

$$\exp(\mathrm{i}\pi x/a) \quad \text{and} \quad \exp(-\mathrm{i}\pi x/a) \tag{2.1}$$

with kinetic energy

$$E_{\text{kin}} = h^2\pi^2/(2ma^2) \tag{2.2}$$

Now as is well known, Bragg reflection results in a mixing of these two waves, giving as wave function $\sin(\pi x/a)$ [or $\cos(\pi x/a)$]. This sine wave function has charge heaped up around positions $x = (n+\frac{1}{2})\,a$ where n is integer, so that we may describe it as a p-bonding orbital between all the atoms. But the relevant point here is that the kinetic energy of the sine state is still exactly equal to the free-electron value (2.2) as before. There is nothing inconsistent with the Uncertainty Principle in this because the heaping up of charge is formed from quantum interference between waves of the same kinetic energy: it does not require any extra kinetic energy. (I am indebted to Dr J. C. Phillips for this argument.)

Unfortunately the picture of volume forces derived from the free-electron gas model does not help us much in very inhomogeneous situations of low coordination number such as at surfaces or defects. Here we must turn to the opposite model of atomic orbitals. The result is that the formation energy varies with coordination number C roughly as

$$U = -(\text{const.})\,C^{\frac{1}{2}}. \tag{2.3}$$

It may be useful to rehearse in the simplest possible way the derivation of this result (Heine 1980). Consider a structure in which all atoms are geometrically equivalent with all nearest neighbours at the same distance, and through the device of periodic boundary conditions let us deal for mathematical convenience with finite system of N atoms instead of an infinite one. We assume a single s-orbital on each atom, though this can easily be generalized to a set of three p-orbitals or five d-orbitals (for each spin direction). Let the hopping integral or bonding energy between neighbouring atoms be h (negative), and take the self-energy of the orbital E_0 on a free atom as the zero of energy. The hamiltonian matrix H_{rs} describing the motion of the electrons then consists of zeros, except where r and s are neighbouring atoms when the matrix element is equal to h. We now consider the matrix H^2 and take its trace, i.e. the sum of the diagonal elements

$$\operatorname{Tr} H^2 = \sum_r (H^2)_{rr} = \sum_r \sum_s H_{rs} H_{sr} = -NCh^2. \tag{2.4}$$

We also apply a unitary transformation to H to turn it into diagonal form H' with diagonal elements equal to the eigenvalues E_n, which gives

$$\operatorname{Tr}(H')^2 = \sum_n E_n^2 = N(W_{\text{rms}})^2. \tag{2.5}$$

The eigenvalues E_n will be spread out into a band with density of states $n(E)$ per unit energy range (figure 1), and W_{rms} in (2.5) is defined to be the root-mean-square width of this distribution. By a simple theorem the trace is unchanged by a unitary transformation so that (2.4) and (2.5) are equal, which gives

$$W_{\text{rms}} = |h|\,C^{\frac{1}{2}}. \tag{2.6}$$

As already mentioned, the result can be generalized to any band of equivalent orbitals in the simplest two-centre approximation. For example for a d-band the $|h|$ in (2.6) has to be replaced by

$$[(\mathrm{dd}\sigma)^2 + 2(\mathrm{dd}\pi)^2 + 2(\mathrm{dd}\delta)^2]^{\frac{1}{2}}, \tag{2.7}$$

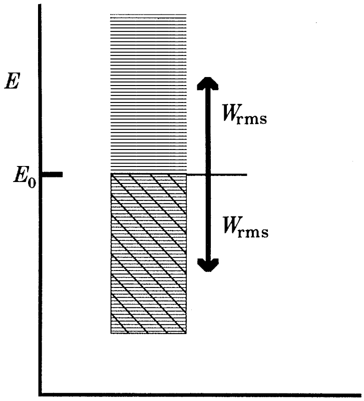

Figure 1. Electron energy levels of a system with a large number of atoms, spread into a band of root-mean-square width W_{rms}. For a half-filled band the shaded states are occupied by electrons.

where the (ddv) are the usual bonding matrix elements. The results (2.6), (2.7) are exact for any angular distribution of the neighbours about an atom.

To complete the argument we take one further, more approximate step. Let us suppose the band is half full. Then the occupied states have on average an energy about W_{rms} below the centre of the band, i.e. below the atomic level E_0. Thus the formation energy is

$$U(\text{per electron}) \approx -W_{\mathrm{rms}}, \tag{2.8}$$

which together with (2.6) then yields (2.3). The precise value in (2.8) depends of course on the detailed band shape. The argument can be extended to some other degree of band filling, say one-third or three-quarters (Woolley 1990), but becomes invalid for nearly full or nearly empty bands where the band shape dominates. Our simple treatment also breaks down for a mixed s and p band, etc., though even there the variation with C seems to apply remarkably well in the case of one set of *ab initio* calculations (§4).

3. The non-convergence of *n*-atom interactions

In §2 we saw that the binding energy is roughly proportional to $C^{\frac{1}{2}}$ and in this section we investigate whether such a function can be represented as a convergent sum of two-, three-, n-atom interactions in the manner of equation (1.1). We are considering only the (negative) contribution to the formation energy of the solid from the bonding by the electrons due to the spread of energy levels into a band as in §2. Moreover we will keep the interatomic distance and hence the h in (2.6) constant. We continue with the model of a band of s-orbitals so that the two-atom interaction should be proportional to the coordination number C. Similarly we assume that an n-atom I_n interaction will be proportional to C^{n-1}. Under these conditions we write:

$$I_n = A_n C^{n-1}. \tag{3.1}$$

This is not quite correct. If there are C neighbours, the number of contributions of pairs of neighbours, i.e. three-atom combinations, is

$$\tfrac{1}{2}C(C-1). \tag{3.2}$$

Table 1. *Coefficients* a_n *in the least squares fit in equation* (3.5), *and root-mean-square error* e_{rms} *of the fit*

(Note that the coefficients have been severely rounded for presentation.)

$n_{\max}$	2	3	4	5	6	7	8	9
a_2	1.2	2.1	2.9	3.6	4.4	5	6	7
a_3	—	−1.1	−3.8	−8.4	−15.1	−25	−39	−56
a_4	—	—	2.0	10.1	31.3	76	160	304
a_5	—	—	—	−4.3	−29.7	−119	−365	−936
a_6	—	—	—	—	10.5	92	459	1690
a_7	—	—	—	—	—	−28	−299	−1770
a_8	—	—	—	—	—	—	79	994
a_9	—	—	—	—	—	—	—	−231
e_{rms}	0.14	0.06	0.03	0.02	0.01	0.01	8.10^{-3}	6.10^{-3}

But this has C^2 as leading term so that our assumption (3.1) is approximate but sufficient for present purposes; and similarly for higher order interactions up to order $\frac{1}{2}C$.

The main purpose therefore is to test whether the form (2.3) can be expanded as follows

$$-|h|\,C^{\frac{1}{2}} = A_2\,C + A_3\,C^2 + \ldots + A_n\,C^{n-1} + \ldots . \tag{3.3}$$

It is convenient now to rewrite this in a dimensionless version in terms of the scale variable

$$z = \tfrac{1}{12}C \tag{3.4}$$

so that z runs from 0 to unity. Then (3.3) becomes

$$z^{\frac{1}{2}} = \sum_{n=2}^{n_{\max}} a_n\,z^{n-1}, \tag{3.5}$$

where $n_{\max}$ is the cut-off on the series. We have done a least-squares fit to (3.5) for $n_{\max}$ ranging from 2 to 11, with the results given in table 1. The failure of (3.5) to give a convergent series is spectacular! Since $z^{n-1} = 1$ at the end point $z = 1$ for all n, the coefficients a_n give a direct measure of the magnitude of the corresponding interaction. For $n_{\max} = 9$, we have $a_7 = -1770$! Moreover it is clear that as $n_{\max}$ is increased, the lower-order coefficients do not converge to some limiting value but continue to drift. it is noticeable that successive terms always alternate in sign throughout table 1 with each additional term trying to correct for the overshoot of the preceding one, a familiar behaviour of non-convergent series. We conclude that the function $C^{\frac{1}{2}}$ cannot be represented satisfactorily, even over a limited range, by a power series like (3.3).

Can we conclude from this that a series in n-atom interactions I_n (1.1) is similarly not convergent? At this point the argument becomes less than rigorous, but it suggests that we can so conclude at least in a practical sense. It certainly seems that we cannot hold to our cherished picture of two-atom terms dominating with some three-atom bond–bond additions and perhaps very small four-atom corrections. Look at $n_{\max} = 3$ and 4 (table 1): the three-atom term has increased three-fold in magnitude as we add a four-atom correction, which even alters the two-atom term by 39%. Also the three-atom term has become larger than the two-atom one, which cannot be right. Moreover, the value of the two-atom term is double what it was for

$n_{\max} = 2$. And when we go one step further to $n_{\max} = 5$ the coefficients already start to go haywire. Of course the function $C^{\frac{1}{2}}$ is only a crude approximation but it captures the essence of metallic bonding quite well for the theoretical reasons of §2 and the empirical experience of §§4 and 5.

There is an alternative way of analysing the bonding energy (3.3) following Pauling's ideas. The energy of an electron in a bond between two atoms is $|h|$, and since there are more bonds than electrons we can think of the latter as having an energy $-|h|$ each. In fact there are very many ways of placing the set of electrons in the available bonds, with a 'resonance' between all of these configurations and a resulting 'resonance' energy lowering E_{res}

$$-|h|^{\frac{1}{2}} = -|h| + E_{\text{res}}. \tag{3.6}$$

We can now try to expand E_{res} in two-atom, three-atom, etc., terms analogous to (3.3) which (remembering (3.4)) leads to the series

$$z^{\frac{1}{2}} = \tfrac{1}{12} + \sum_{n=2}^{n_{\max}} b_n z^{n-1} \tag{3.7}$$

instead of (3.5). We have carried out at least square fit of (3.7), which turns out just as unsatisfactory as (3.5) and table 1.

Of course a function can be expanded as a Taylor series about some chosen point, and the result made to appear (spuriously, we believe) as a series of n-atom interactions. Suppose we consider the general function $F(C)$ and that in some situation only the values C_0 and $C_0 \pm 1$ occur. A good approximation should be the linear term

$$\begin{aligned} F(C) &\approx F(C_0) + (C - C_0) F'(C_0) \\ &= [F(C_0) - C_0 F'(C_0)] + C F'(C_0) \\ &= A_1 + A_2 C. \end{aligned} \tag{3.8}$$

Hence if one sweeps the constant A_1 under the carpet, one can appear to have a two-atom interaction model. More generally, one may be able to obtain simple models to fit the bonding over a limited range of geometries, but it is probably spurious to extrapolate with them to the bonding in very different situations. And that is the task we face in the computer simulation of complex atomic processes, as emphasized in §1: these almost always involve some very non-standard arrangement of atoms.

4. Evidence for many-atom forces

The existence of volume forces in metals has been discussed since the beginning of quantum mechanics as the origin of the Cauchy anomaly in the elastic constants. The importance of such volume forces for the equilibrium volumes and crystal structures of sp-bonded elements is also well known (Heine & Weaire 1970, particularly pp. 259–282; Hafner & Heine 1983). Recently a whole conference was devoted to a discussion of many-atom forces (Nieminen *et al.* 1990). The success of the 'glue' models (see next section), which take many-atom forces specifically into account, has been impressive particularly in accounting for subtle effects such as the reconstructions of the Au surfaces.

By way of contrast, one can point to the sad history of attempts to find a satisfactory force model for Si. There has been a whole succession of models, each

Table 2. *Calculated formation energy U of various structures spanning a range of coordinated numbers*

structure	coordination	energy / (atom eV)	U / eV
atom	0	−54.95	0
line	2	−56.28	−1.33
graphite mesh	3	−56.95	−2.00
diamond	4	−57.42	−2.47
square mesh	4	−57.29	−2.34
square bilayer	5	−57.64	−2.69
simple cubic	6	−57.91	−2.96
triangular mesh	6	−57.49	−2.54
vacancy lattice	8	−58.10	−3.15
face centred cubic	12	−58.31	−3.36

fitted to experimental data plus the computed energies of a range of unstable structures covering quite a variety of bonding geometries. Yet each model failed when confronted a year or so later by the energy of some new structure. The latest chapter in this saga comes from the quantum calculation of the energies, structures and dissociation channels of the cluster molecules Si_N up to $N = 11$. The comparison between the predictions of the best empirical models with the fully quantum calculations can only be described as abysmal (Andreoni & Pastore 1990). These models are all based on n-atom expansions of type (1.1).

We would like to present here the results of some recent calculation on aluminium. These are *ab initio* quantum mechanical calculations of 10 structures with the number of nearest neighbours varying from $C = 0$ to the normal FCC structure of the bulk metal with $C = 12$. In all cases the energy was calculated keeping the nearest neighbour distance fixed, equal to the equilibrium value for the bulk metal. The results therefore focus attention directly on the variation of the energy with the coordination C. For $C = 2$ we have a linear chain of atoms. A single layer with the graphite structure has $C = 3$, while a layer with a square mesh has $C = 4$. The three-dimensional diamond structure also has $C = 4$. The $C = 5$ is obtained as a double layer, i.e. two square layers with the atoms of one over the other. $C = 6$ is achieved in two ways, one being a triangular layer and the other the simple cubic structure. A closely spaced lattice of vacancies in the FCC structure has $C = 8$. In each case all atoms are equivalent by symmetry. The calculations were carried out using a pseudopotential for aluminium (Goodwin *et al.* 1990) and the method described in §5. The chain and layer structures were modelled in a supercell with an appreciable amount of free space around them, repeatedly periodically in three dimensions. The wave functions were expanded in plane waves with a cut-off of 190 eV. A large number of k-points were sampled in the Brillouin zone using the KP scheme (Robertson & Payne 1990). The energy of an isolated atom was calculated in a supercell using the same program in an artificial spherically symmetric configuration with all six 2p spin-orbitals occupied equally, which corresponds to a 'metallic' state with $C = 0$ for comparison with the other calculations (table 2). A more detailed discussion of these results will be given elsewhere (Robertson *et al.* 1991).

The results are given in table 2 and figure 2. They are offered as a test-bed for the development of empirical potentials and study of the variation with C.

We will only give the very simplest analysis here. As a very crude approximation,

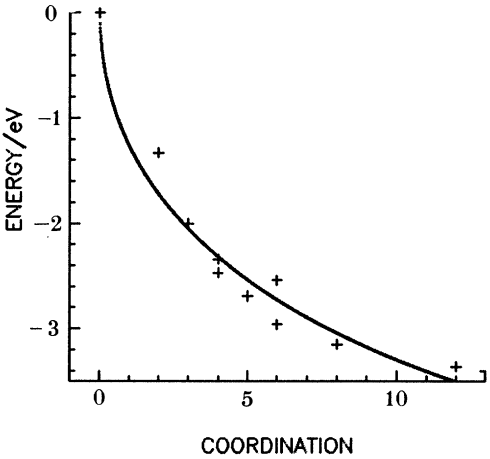

Figure 2. The formation energy U from table 2 (crosses) as a function of the coordination number C. The line is a least-squares fit of the form of equation (4.1).

we expect the formation energy $U(C)$ to consist of two parts, (i) a short range repulsion and (ii) the bonding by the electrons. The first will be proportional to C for fixed nearest neighbour distance: it is due to the coulomb repulsion of the nuclei and the exclusion principle in the overlap of the atoms. For the bonding we use (2.3). We have therefore done a least-squares fit to the energies using

$$U(C) = aC - bC^{\frac{1}{2}}, \tag{4.1}$$

where $U(C)$ is the total energy of the system per atom relative to that of the free atom ($C = 0$) defined as above.

The result of the fit is shown in figure 2 and is seen to describe the overall variation with C surprisingly well. We interpret this as general qualitative support for the picture of many atom forces painted in §2. The discussion there is only intended as a broad brush treatment, to suggest that the correct starting point is a formulation in terms of many-atom forces as in the 'glue' models mentioned in §5 rather than the series (1.1). Of course we are very conscious of the shortcomings of (4.1) as a theoretical model. It neglects the effect of second neighbours which may account for the energy differences between two pairs with the same C. We also note that (2.3) does not apply to a mixed band of s and p electrons such as we have in aluminium, and in any case ignores the shape of the band.

5. Implications for simulations

This section indicates two approaches that are being used to address the problem of many-atom interactions in computer simulations, and then add a few thoughts for the future.

The first approach consists of setting up models of the many-atom interactions, which we refer to collectively as 'glue' models. The formation energy is written

$$U = \sum_i U_e(C_i) \sum_{i \neq j}\sum \Phi(R_{ij}). \tag{5.1}$$

Here i and j denote the atoms, C_i the coordination number of atom i, and Φ is a pairwise interaction depending on the interatomic distance R_{ij}. the $U_e(C)$ is a bonding or 'glue' or 'embedding' energy depending on the coordination number C in the spirit of §§2 and 4. However we need a precise definition

$$C_i = \sum_j c(R_{ij}) \tag{5.2}$$

of the coordination number. The function $c(R)$ is normally chosen so that it is simply unity for a neighbour j at the equilibrium distance of the nearest neighbours R_{nn} in the bulk material. The function $C(R)$ is monotonically decreasing so that a neighbour closer than R_{nn} counts a little more than unity and neighbours more distant than R_{nn} count less, with $c(R)$ being cut off to zero at some suitable distance around the second neighbours. There are various versions of this basic approach. The Trieste group seems to have invented the expression 'glue model' to signify that the electron gas is a ubiquitous glue holding the structure together with a strength U_e depending on its density (Ercolessi *et al.* 1988). There and in the 'embedded atom' method (Foiles *et al.* 1986) all three functions $U_e(C)$, $c(R)$ and $\Phi(R)$ are fitted purely empirically to a variety of experimental data, whereas Finnis & Sinclair (1984) used the square-root form (2.1) for $U_e(C)$. The least empirical is the 'effective medium theory' (Jacobsen *et al.* 1987) where the embedding function $U_e(C)$ is computed quantum mechanically by inserting an atom in a free electron gas of density ρ. The ρ is determined also by the quantum calculation from the electron density contributed by neighbouring atoms. In other words in the interaction of an atom with its neighbours, the latter are replaced by a uniform electron gas whose density is determined selfconsistently.

What is common to all these glue formulations is that the embedding function U_e is usually negative with an upward curvature like (2.3) that gives the model its characteristically 'metallic' behaviour. Metals are usually stated to prefer closely packed structures, but a more apt description is to say that the ion cores swimming in a sea of electrons want to space themselves out as uniformly as possible for a given overall atomic density. This principle in three dimensions leads to the FCC structure, for example, and in two dimensions to the triangular close packed mesh. Now consider the (110) surface of gold. In its ideal (unreconstructed) state it has atoms with coordination $C_1 = 7$ in the surface layer and $C_2 = 11$ in the second layer. For the (111) surface we have $C_1 = 9$ and C_2 is already the bulk value 12. Because of the upward curvature of $U_e(C)$, we have

$$U_e(9) < \tfrac{1}{2}[U_e(7) + U_e(11)]. \tag{5.3}$$

This means that it is energetically favourable to replace pairs of atoms with $C = 7$ and 11 by atoms with $C = 9$, i.e. to replace (110) surface by 'metallic' close packed (111) surface. And indeed the observed 2 × 1 and 3 × 1 'missing row' reconstruction of the Au (110) surface has been described in terms of forming small facets of (111) surface. Of course, the detailed energetics are more complicated than equation (5.3), involving the densities of surface atoms per unit area and the bonding of the atoms at the ridges and furrows of the reconstruction. But we believe our argument captures the essence of what drives the reconstruction. The story is similar on the (100) surface where $C_1 = 8$ and $C_2 = 12$. The number of atoms per unit area is less than for the close packed (111) surface. Thus to turn (100) surface into (111) surface means taking atoms of $C = 8$ with some of $C = 12$ and replacing then by atoms with $C = 9$. An equation similar to (5.3) again suggests this may be energetically favourable and indeed the (100) surface reconstructs to give a close packed (111)-type monolayer lying on top of the (100) structure. Well, these are very hand-waving arguments but it is appealing to have some broad understandable qualitative mechanism. We refer to pp. 82–83 of Heine (1980) for some further examples based on the same curvature argument.

However, it must be admitted that none of these glue models seem to have been tested very rigorously, for example over a wide range of C or R. *Ab initio* calculations of the type discussed in §4 may have a contribution to make here, in augmenting experimental data by energy measurements in 'computer experiments'. A further shortcoming is the absence of any angular forces which certainly will not suffice for covalent semiconductors or transition metals. Of course some people would regard it as inappropriate to treat silicon starting with a glue model based on volume forces, but our arguments of §2 would suggest that to be quite sensible with the addition of angular forces. See also Heine & Hafner (1991) for a discussion of the relative magnitudes of the volume, pairwise an angular terms in silicon.

We now turn to the second approach to complicated interatomic forces in a simulation. This is to hit it with an *ab initio* quantum calculation for the whole system. With current supercomputers one can do this for a simulation of modest size (Ihm 1988; Payne *et al.* 1991). The complex process to be simulated has to be dissected into its physically significant aspects. One of these at a time has to be modelled in a supercell of typically 10 to 100 atoms, repeated periodically in three dimensions. (A surface can be simulated by including some empty space in the supercell.) Static simulations usually focus on the energy, e.g. a barrier height for diffusion, or/and on relaxing the atoms step by step to find their equilibrium positions, e.g. at a surface reconstruction. Dynamic simulations include a stepwise integration of the equations of motion for the ion cores to represent thermal agitation. In most such work the atoms are represented by pseudopotentials so that one is only solving the quantum mechanics for the valence electrons. The wave functions are expanded typically in thousands of plane waves, while the electron exchange and correlation is treated by the local density approximation within the density functional formulation of the total energy. For a review, see Ihm (1988).

Although the *ab initio* quantum calculation gives completely the interatomic forces for any arrangement of atoms, the size of system that can be simulated is somewhat limited, as already mentioned. In this connection considerable progress is being made in speeding up the numerical algorithms, based on the innovative ideas of Car & Parrinello (1985) and subsequent developments (Payne *et al.* 1991).

However, even with the next generation of supercomputers and probably several generations after that, the maximum number of atoms in the unit cell will be a restriction on the quantum simulations. More work needs to be done to find hybrid methods where *ab initio* quantum calculations give information about the interatomic forces for critical geometries furthest removed from standard bonding arrangements, and this information then gets fed into large simulations of more traditional type. One might for instance generate a data set by quantum calculation analogous to that of §4, but selected specifically to cover the relevant geometries. One is then using the fitted model to interpolate from, rather than extrapolating from the fitting configurations. At the simplest level this has already been done for example to obtain the phonon free energies of some SiC polytypes with fairly large unit cells. First some meagre experimental data on phonon frequencies in cubic SiC (the simplest polytype) were supplemented by phonon frequencies and eigenvectors at other points in the Brillouin zone from 'frozen phonon' quantum calculations. The phonon spectrum of cubic SiC was then fitted by an extended shell model. In this context having the phonon eigenvectors from quantum calculations was very important because these are difficult to obtain from experiment and the frequencies alone are known not to determine the model uniquely (Cheng *et al*. 1989). Finally the extended shell model could be applied to the whole range of polytypes because they all have locally the same tetrahedral bonding as the cubic form (Cheng *et al*. 1990). There are other examples along similar lines, for instance calculations on point defects, and modelling the interactions between organic molecules.

In conclusion, the development of reliable quantum calculations for large systems is overcoming the lack of adequate information in traditional simulations about interatomic bonding energies in unconventional geometries. On the other hand models are being developed to represent explicitly the many-atom character of interatomic forces, at least to some degree. The hope is that these can be developed further, and used to transfer the bonding information from relatively modest *ab initio* calculations to large simulations.

References

Andreoni, W. & Pastore, G. 1990 (In the press.)

Car, R. & Parrinello, M. 1985 *Phys. Rev. Lett.* **55**, 2471–2474.

Cheng, C., Kunc, K. & Heine, V. 1989 *Phys. Rev.* B **39**, 5892–5898.

Cheng, C., Heine, V. & Jones, I. L. 1990 *J. Phys. Condens. Matter* **2**, 5097–5114.

Ercolessi, F., Parrinello, M. & Tosatti, E. 1988 *Phil. Mag.* A **58**, 213–226.

Finnis, M. W. & Sinclair, J. E. 1984 *Phil. Mag.* A **50**, 45–55.

Foiles, S. M., Baskes, M. I. & Daw, M. S. 1986 *Phys. Rev.* B **33**, 7983–7991.

Goodwin, L., Needs, R. J. & Heine, V. 1990 *J. Phys. Condens. Matter* **2**, 351–366.

Hafner, J. 1987 *From hamiltonians to phase diagrams*. Berlin: Springer-Verlag.

Hafner, J. & Heine, V. 1983 *J. Phys.* F **23**, 2479–2501.

Heine, V. 1980 *Solid St. Phys.* **35**, 1–127.

Heine, V. & Jones, R. O. 1969 *J. Phys.* C **2**, 719–732.

Heine, V. & Hafner, J. 1991 In *Many-atom interactions in solids* (ed. R. Nieminen, M. J. & M. Manninen), pp. 12–33. Berlin: Springer-Verlag.

Heine, V. & Weaire, D. 1970 *Solid St. Phys.* **24**, 249–463.

Ihm, J. 1988 *Rep. Prog. Phys.* **51**, 105–142.

Jacobsen, K. W., Nørskov, J. K. & Puska, M. J. 1987 *Phys. Rev.* B **35**, 7423–7442.

Mott, N. F. & Jones, H. 1936 *The theory of the properties of metals and alloys*, p. 159. Oxford: Clarendon Press.

Nieminen, R., Puska, M. J. & Manninen, M. (eds) 1990 *Many-atom interactions in solids*. Berlin: Springer-Verlag.

Payne, M. C., Allen, D. C., Teter, M. P. & Joannopolous, J. 1991 *Rev. mod. Phys.* (In the press.)

Robertson, I. J. & Payne, M. C. 1990 *J. Phys. Condens. Matter* **2**, 9837–9852.

Robertson, I. J., Payne, M. C. & Heine, V. 1991 (Submitted.)

Woolley, R. G. 1990 *J. Phys.* B **23**, 1563–1576.

Discussion

J. N. MURRELL (*University of Sussex, U.K.*). I have for many years been working on potential energy functions for polyatomic molecules; functions that can be used both for spectroscopy and chemical kinetics (bond breaking). Only recently have I applied some of these ideas to solids and so far with any quantitative study, only to the group IV solids. On the basis of my current results I believe the prognosis from many-body expansion of the potential to be much better than suggested by the speaker. In short, I have a two-body plus three-body potential for Si which reproduces the lattice energy, lattice spacing, elastic constants, and phonon-dispersion curves with good accuracy and gives sensible energies for other bulk phases and for a graphitic structure. It may be that this potential fails for other features, e.g. surface reconstruction, and performs badly for melting, etc. With my present knowledge, however, I believe the potential is better than any other that has been published.

V. HEINE. Although I am pessimistic about the success of Professor Murrell's approach, such success would be very important and I look forward to his further results. Even partial success could be very useful, for example if it was sufficient for all likely configurations of atoms at defects in the bulk solid.

J. C. PHILLIPS (*AT&T Bell Labs, Murray Hill, U.S.A.*). Has Professor Heine extended his results to Si as well as Al?

V. HEINE. No, we have not calculated our structures for Si.

J. C. PHILLIPS. We believe that the many-atom force model of Chelikowsky at present gives the best available account of structural trends of Si clusters up to 30 atoms, although it of course does not include the Jahn–Teller distortion energies which become small for clusters containing more than 10 atoms.

D. WEAIRE (*Trinity College, Dublin, The Republic of Ireland*). Professor Heine pictured an atom in the solid state as a piece of jellium of volume defined by its Wigner–Seitz cell and hence having a *volume*-dependent energy. This defines a model, familiar enough in the case of a perfect crystal, but has it ever been used to calculate, say, dynamical properties?

V. HEINE. I do not know of any detailed work along such lines. It would be quite possible for the phonons in the perfect bulk metal and for some defects perhaps. However, the volume would not be definable this way at a surface where it would be infinite, and I have doubts about its value even at a vacancy.