Representations of the local atomic density

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Abstract. We describe two measures of the local atomic density in a monatomic crystal. A new measure (ρ_f) has the form of a function of the sum of inverse powers of the neighbour distance, and it is accurate to 2% for six simple crystalline reference structures ranging from diamond to face-centred cubic. For any periodic structure, ρ_f reproduces the global average density exactly for any uniform dilation or compression in the limit of an infinite cut-off, and to high accuracy with a smooth cut-off. We compare it with a Gaussian measure (ρ_g) of local density for large constant-volume strains of the six reference structures. The changes in ρ_f are an order of magnitude less than the shear strains for bond-length changes of <10%. However, ρ_g is even less sensitive to constant-volume strains. ρ_g is also transferable between structures, provided that a constant self-term (an on-site term) is included in the density. The measure of local density is primarily intended for atomistic simulations of inhomogeneous systems in which the atom–atom interactions or other terms describing the energy depend on the local volume.

1. Introduction

It has long been recognized that the total energy of a metal is very sensitive to the volume which atoms occupy. Over thirty years ago, the energy of simple s–p-bonded metals was treated by second-order perturbation theory, using pseudopotentials [1], and shown to be described by two terms: the first and largest was a function only of volume, $F(V)$, while the second was a pairwise sum of interatomic potentials $\phi(r_{ij}; V)$, also depending on the volume. Calculations using only the interatomic potential at constant volume are numerous in the literature, and were the state-of-the-art method of comparing the energy of different crystal structures or calculating phonon frequencies before the advent of fully self-consistent calculations which of course go beyond second order in perturbation theory. Although such pair potential calculations were often remarkably successful, the neglect of the volume-dependent terms, both in the pair potential and in $F(V)$, led to the well known inconsistency in the bulk modulus when calculated by taking the $q \to 0$ limit of the longitudinal phonon frequency as compared to direct differentiation of the full total energy with respect to volume [2–4]. The root of the problem is that the volume V which appears in perturbation theory (for example in the definition of the screening function) refers to the global volume of the system—that is, the inverse of the global mean density of conduction electrons. Yet we know physically that screening in metals is rather local (the Fermi–Thomas screening length is less than a nearest-neighbour distance), so a realistic expression for the energy of local rearrangements of atoms, which may be associated with local regions of compression or dilation, should reflect the *local* density change rather than be dependent on some mean

density defined over a macroscopic region. A similar difficulty arises in the application of the generalized pseudopotential theory of Moriarty [5, 6] for transition metals, in which terms arise which involve volume-dependent interatomic potentials, including also three- and four-body potentials.

Rosenfeld and Stott [7] demonstrated a way around this inconsistency by defining the volume dependence in a localized way. They defined a local electron density as a function of the local ion density by using a Gaussian envelope function to weight the contribution of neighbouring ions to the density. We use the same procedure and define the local atomic density (the reciprocal of the local volume V_i)

$$\rho_g^0(i) = 1/V_i = \sum_j f_g(r_{ij}) \tag{1}$$

at an atomic site i as a sum over neighbours of pairwise Gaussian functions $f_g(r_{ij})$, suitably normalized. Note that the on-site term $i = j$ is included in this summation, unlike in other formulations of the local density which are used in the effective-medium theory (EMT) [8] or embedded-atom models (EAM) [9]. In these latter formulations, the host electron density at a site is written as a sum of atomic electron densities from neighbouring sites, omitting the self-term. Furthermore, the pair potentials in these formulations are volume independent. Within the context of deriving the EMT or EAM, the density is defined in terms of superimposed atomic charge densities, and one is not justified to use a definition of local volume such as that in equation (1); nevertheless one feels that these theories should correspond to the second-order pseudopotential theory at some level.

To remove the inconsistency, the total-energy expression from second-order perturbation theory is modified to ensure that the pair potential and $F(V)$ become functions of the local atomic environment via $f_g(r_{ij})$. In practice, following Rosenfeld and Stott one would symmetrize the pair potential with respect to the local volume at each of the two atoms:

$$\phi(r_{ij}) := (\phi(r_{ij}; V_i) + \phi(r_{ij}; V_j))/2. \tag{2}$$

Besides the calculation of phonon frequencies discussed in [7], further applications would be to alloys, in which the local electron density will differ in general from that of the pure elements comprising the alloy; the volume and heat of formation are very sensitive to this difference [10].

There are, however, questions associated with this approach. Because of the functional form of $f_g(r_{ij})$, in the case of homogeneous dilations or compressions of the perfect lattice, the local density which it defines will not remain equal to the global density, even if it is constrained by normalization to be so at the equilibrium volume. Hence for volume changes, the energy predicted by such a local representation of the energy must depart from the standard result of second-order perturbation theory, leading to errors even though the model is now internally consistent. We discuss this geometric problem here. A second question, which we do not address here, is the quantitative accuracy of the resulting descriptions of the total energy.

The physical correctness of the idea of a local volume-dependent energy plus a local volume-dependent pairwise interaction is a motivation for trying to improve the description of the local volume in order to resolve the above-mentioned difficulty. A further motivation is the availability of explicit forms for $F(V)$ derived from non-local pseudopotentials by Walker and Taylor [11, 12], which only need a good definition of V for their exploitation. Since these pseudopotential models have proved very successful in the calculation of phonon spectra at constant volume, there is every reason to think that a consistent, volume-dependent formulation will be of more general use.

An alternative approach to Gaussian envelope functions for defining the local electron density is based on the observation that the following measure of local density at atom i would be exact under homogeneous density variation:

$$
\begin{aligned}
F_m^{(0)} &= (S_m^{(0)})^{3/m} \\
S_m^{(0)} &\equiv \sum_j \frac{1}{r_{ij}^m}.
\end{aligned}
\tag{3}
$$

The simplest version of this equation with $m = 3$ does not converge with increasing number of included neighbours, and would need to be cut off very sharply to be of any use. However, with higher values of m the sum converges in real space even without a cut-off. We use the superscript 0 to indicate that the functions are summed to convergence without a cut-off; this superscript will be dropped when a cut-off is implied. The essential property of this measure of density is that it scales as $1/\beta^3$ if all interatomic distances are multiplied by β, and so reproduces the mean density at all dilations. This property of $F_m^{(0)}$ does not require m to be an integer and is also satisfied by linear combinations of $F_m^{(0)}$ with different m. As a corollary to this it is satisfied in particular by $(F_m^{(0)} - F_n^{(0)})/(m - n)$ as $m \to n$ and hence by the functions $\mathrm{d}F^{(0)}/\mathrm{d}m$, a property that we shall use in this paper.

Deyirmenjian *et al* [13] recently made *ab initio* simulations of highly strained aluminium containing a lattice of vacancies. In interpreting the pattern of strain, they emphasized the importance of the tendency to conserve local volume. This feature is not captured by simple empirical models such as the Sutton–Chen potential [14], which gave qualitatively different results. Subsequently Deyirmenjian *et al* [15] applied a combination of F_6 and F_7 to describe the local atomic density and used it in a modified Sutton–Chen potential, resulting in a markedly improved description of the *ab initio* stress–strain behaviour. At that time there was no systematic attempt to optimize the choice of F_m but the combination was fitted to the density of face-centred cubic and diamond lattice structures. Unpublished calculations indicated that values of m between 5 and 7 were suitable for this purpose, and that including more than two different values was not helpful. Furthermore, the coefficients of F_6 and F_7 for example were nearly equal and opposite in sign, suggesting that a parametrization in terms of $\mathrm{d}F/\mathrm{d}m$ might be fruitful.

The main purpose of our paper is to examine a new parametrization of the local density which we denote as ρ_f, involving a linear combination of F_m and $\mathrm{d}F/\mathrm{d}m$, and to compare it with a Gaussian definition (ρ_g) over a range of crystal structures under homogeneous dilations and shears. The criterion of success for a local density expression under homogeneous strains is that the volume/atom predicted differs by less than 1–2% from the true volume/atom, even under homogeneous strains which are an order of magnitude larger than this. We suggest that in this case the resulting density function will be of use in any of the expressions for total energy which depend on the density.

The plan of the paper is as follows. In the following section we present the ρ_g- and ρ_f-formulae that we have investigated for defining the local density. In section 3 we describe how we obtained a three parameter expression for ρ_f and then how we tested the resulting expression alongside the Gaussian definition of local density over a wide range of volume-conserving shears, starting from a database of six perfect crystal structures. We also obtain the predicted local densities in the neighbourhood of a vacancy and of the (100), (110) and (111) surfaces in the face-centred cubic structure. In section 4 the overall quality of the predicted local densities is compared and discussed and we conclude with our recommendation in section 5.

2. Expressions for the local density

The quality of reproducing the true density of the lattice at all homogeneous volume expansions or compressions is referred to in what follows as *density scaling*. In order to do this a function would have to satisfy the following equation for all β:

$$\sum_j \phi(r_{ij}) = \beta^3 \sum_j \phi(\beta r_{ij}). \tag{4}$$

Consider the ρ_g-measure of local density given by equation (1). The pair function in it is given by

$$f_g(r) = \left(\frac{\alpha}{\pi}\right)^{3/2} \exp(-\alpha r^2). \tag{5}$$

This does not satisfy density scaling. Nevertheless, any correctly normalized pair function can be made to satisfy density scaling asymptotically if it decays slowly enough with distance (e.g. if α is small enough) or in the limit of high density. The inclusion of the $j = i$ term in the summation greatly accelerates the approach to density scaling at high density. To see this it suffices to consider that in the limit in which the function varies slowly on the scale of interatomic distances, the discrete summation can be represented by an integral weighted by the constant density of lattice points. The integral is independent of density by virtue of the normalization, so the result gives directly the density of lattice points. This desirable result is only of practical use if the value of α for which it becomes accurate is such that the decay length is not unphysically large on the scale of metallic screening (more than a few lattice parameters). Note that these considerations hold for any choice of pair function to define ρ, not only the Gaussian one.

For practical computations, it is necessary to apply a cut-off to the functions which are summed over lattice points. Thus the summations we consider are modified by a cut-off function $f_{co}(r)$ as follows:

$$\rho_g(i) = \sum_j f_g(r_{ij}) f_{co}(r_{ij}) \tag{6}$$

and

$$S_m(i) = \sum_{j \neq i} \frac{f_{co}(r_{ij})}{r_{ij}^m}. \tag{7}$$

We have chosen the following soft cut-off function, which goes smoothly to zero between R_l and R:

$$f_{co}(r) = \begin{cases} 1 & \text{if } 0 \leqslant r \leqslant R_l \\[2mm] 1 + \left(\exp\left[-0.6\left(\frac{2(r-R_l)}{R-R_l}\right)^{5/2}\right] - 1\right) \\ \quad \times \left(2(1 - \exp(-0.6))\right)^{-1} & \text{if } R_l \leqslant r \leqslant (R_l + R)/2 \\[2mm] \left(1 - \exp\left[-0.6\left(\frac{2(R-r)}{R-R_l}\right)^{5/2}\right]\right) \\ \quad \times \left(2(1 - \exp(-0.6))\right)^{-1} & \text{if } (R_l + R)/2 \leqslant r \leqslant R \\[2mm] 0 & \text{if } R \leqslant r. \end{cases} \tag{8}$$

We now introduce a new measure of the local density:

$$\rho_f(i) = C_1 F_m + C_2 \frac{\mathrm{d}F_m}{\mathrm{d}m} \tag{9}$$

in which

$$F_m = (S_m)^{3/m}. \tag{10}$$

We have omitted for simplicity the explicit i-dependence in $S_m(i)$ and $F_m(i)$ because in this paper we shall only be considering lattices on which all sites are equivalent. The derivative of F_m is given by

$$\frac{\mathrm{d}F_m}{\mathrm{d}m} = -(3/m^2) F_m \left[\ln(S_m) + m S_m^{(1)}/S_m \right] \tag{11}$$

where we have made the definition

$$S_m^{(1)} := \sum_{j \neq i} \frac{f_{\mathrm{co}}(r_{ij}) \ln(r_{ij})}{r_{ij}^m}. \tag{12}$$

The three parameters C_1, C_2 and m were fitted as described in the following section. Because of our introduction of a cut-off function, the sums over neighbours j need only be carried out to a radius R. The price that we have to pay is that the density scaling of F_m and its derivative is no longer exact. We shall see below the magnitude of the error which is thereby introduced. As cut-off parameters we chose first a long-range pair $(R_l, R) = (4.5, 5)$ in units of a reference nearest-neighbour distance, which we shall refer to as r_{nnref}. In addition we tested the shorter-ranged cut-off $(R_l, R) = (2.7, 3.0)$. For simplicity we denote the low and high cut-offs by lco and hco. Since we have also tested two values of α, we consider altogether six candidate measures of local density which we denote by $\rho_f(\mathrm{hco})$, $\rho_f(\mathrm{lco})$, $\rho_g(\mathrm{hco}; \alpha = 1.0)$, $\rho_g(\mathrm{hco}; \alpha = 0.5)$, $\rho_g(\mathrm{lco}; \alpha = 1.0)$ and $\rho_g(\mathrm{lco}; \alpha = 0.5)$.

3. Calculating and testing the local density

In future work one should use the same best form for the local density function $\rho(i)$ for calculations on homogeneous and inhomogeneous systems. However, because there is no absolute meaning to local density, the quality of the $\rho(i)$ as a geometrical description of local density can only be assessed in the case of perfect primitive lattices—that is, lattices of equivalent sites—in which $\rho(i)$ should reproduce as closely as possible the global mean density ρ_{exact}. As a measure in any particular case of the quality of ρ_f or ρ_g, we consider the volume deviations ΔV_f and ΔV_g respectively, where

$$\Delta V_f = \rho_{\mathrm{exact}}/\rho_f - 1 \tag{13}$$

and

$$\Delta V_g = \rho_{\mathrm{exact}}/\rho_g - 1. \tag{14}$$

This choice is of course arbitrary; the density deviations would have been just as good.

Our fitting and evaluation procedure is based on the six three-dimensional lattices which were used in the database of *ab initio* calculations set up by Robertson *et al* [16, 17], namely diamond (DIA), simple cubic (SC), the vacancy lattice (VAC), simple hexagonal (SH), body-centred cubic (BCC) and face-centred cubic (FCC). These reference structures are defined all to have the same nearest-neighbour distance, r_{nnref}, and they span the range of coordination from 4 to 12. Further details are given in table 1. Having the same nearest-neighbour

Table 1. 3D Robertson structures, together with: the unit-cell lengths a, b, c, assuming that $r_{nnref} = 1$; the exact density, ρ_{exact}; the number of atoms per unit cell, N_a; the total number of atoms within a cut-off $R = 5.0$, N_{tot}^{hco}; and the total number of atoms within a cut-off $R = 3.0$, N_{tot}^{lco}.

Structure	a	b	c	ρ_{exact}	N_a	N_{tot}^{hco}	N_{tot}^{lco}
Diamond, DIA	$4/\sqrt{3}$	$4/\sqrt{3}$	$4/\sqrt{3}$	0.649 519 05	8	356	86
Simple cubic, SC	1	1	1	1.0	1	514	122
Vacancy, VAC	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	1.060 660 17	3	570	128
Simple hexagonal, SH	1	$\sqrt{3}$	1	1.154 700 54	2	628	138
Body-centred cubic, BCC	$2/\sqrt{3}$	$2/\sqrt{3}$	$2/\sqrt{3}$	1.299 038 11	2	700	168
Face-centred cubic, FCC	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	1.414 213 56	4	766	176

distance constrains the structures to span a density range from 0.649 52 (DIA) to 1.414 21 (FCC) in units of r_{nnref}^{-3}. The natural density in metallic structures will be close to that of the FCC or BCC lattices, which have the highest densities, but the local densities will be much lower at free surfaces.

The parameter α of ρ_g was not fitted, but two values were applied, namely $\alpha = 1.0/r_{nnref}^2$ and $\alpha = 0.5/r_{nnref}^2$. Guided by the previous work in [15], a value $m = 6$ was used. The quality of the results is insensitive to variation of m from 6 to 7, so we chose the integer value for simplicity. We then fitted the parameters C_1 and C_2 to reproduce exactly the FCC and DIA densities with the cut-off functions operating. In this way we obtained the parameters

$$C_1 = 0.065\,691\,948 \qquad C_2 = -1.173\,9034 \tag{15}$$

and

$$C_1 = 0.035\,978\,179 \qquad C_2 = -1.234\,5637. \tag{16}$$

for the long- and short-ranged cut-offs respectively.

Further tests have been made with the original formulation which did not use the derivative dF/dm and therefore required four parameters rather than three, but this does not lead to any significant improvement in the quality of the fits.

Next we tested the extent to which ρ_f and ρ_g can preserve the density under strictly constant-volume homogeneous shears. The lattice vectors under a simple shear of size s along the l-direction parallel to the m-plane are given by [18]

$$\mathbf{S} = \mathbf{I} + s\mathbf{l}\mathbf{m}^{\mathrm{T}} \tag{17}$$

where the superscript T indicates the transpose.

Four shears of this type were examined here; these are now listed.

(i) The C_{44}-shear, a simple shear along the (100) direction parallel to the [001] plane,

$$\mathbf{S}_{C_{44}} = \begin{pmatrix} 1 & 0 & s \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{18}$$

(ii) The C'-shear, namely a shear along the $(1\bar{1}0)$ direction parallel to the [110] plane,

$$\mathbf{S}_{C'} = \begin{pmatrix} 1 + s/2 & s/2 & 0 \\ -s/2 & 1 - s/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{19}$$

(iii) The twinning shear, namely a shear along the $(\bar{2}11)$ direction parallel to the [111] plane,

$$\mathbf{S}_{\text{twin}} = \begin{pmatrix} 1 - 2K & -2K & -2K \\ K & 1 + K & K \\ K & K & 1 + K \end{pmatrix} \tag{20}$$

where $K = s/(3\sqrt{2})$.

(iv) The tetragonal shear for which

$$\mathbf{S}_{\text{tet}} = \begin{pmatrix} 1 + s & 0 & 0 \\ 0 & \sqrt{(1/(1+s))} & 0 \\ 0 & 0 & \sqrt{(1/(1+s))} \end{pmatrix}. \tag{21}$$

Results were obtained for a range of shears s and K from -0.5 to 0.5.

Finally we have applied the density functions to calculate the local density at neighbours of a single vacancy and the three low-index surfaces in the FCC structure. The aim here is to obtain a local density in a case for which not all of the atoms are equivalent, which is what will be needed in applications. The energy of formation of a vacancy and surface energies, calculated by using these local densities, will be the subject of future investigation.
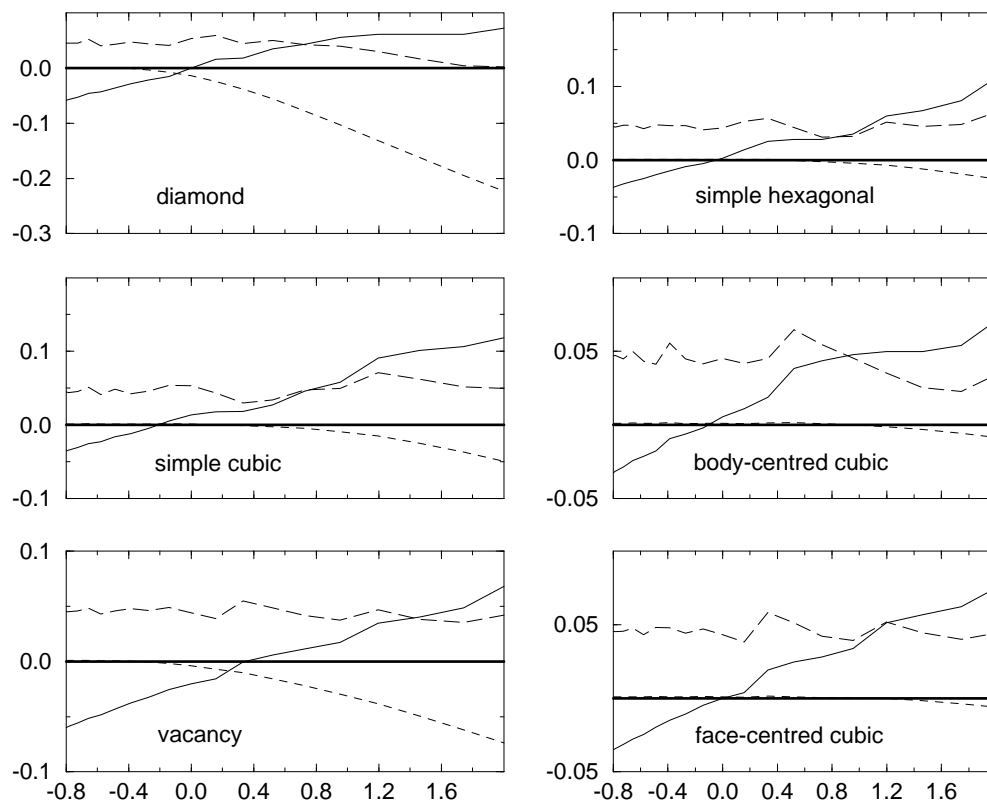

Figure 1. The variation of ΔV_f (solid line), $\Delta V_g (\alpha = 1.0)$ (short-dashed line), $\Delta V_g (\alpha = 0.5)$ (long-dashed line) with $(V - V_0)/V_0 = r_{nn}^3 - 1$ where V is the exact volume of the structure and V_0 is the exact reference volume. Here the lower cut-off $R_l = 2.7$, $R = 3.0$ is used.

4. Results and discussion

4.1. Volume changes

We first consider the results for pure volume changes. Recall that in this case, by including a cut-off function as a factor of ρ_f, we have forfeited its intrinsic ability to describe the density exactly in FCC and DIA structures at all volumes. Figure 1 shows the effect of the lower cut-off on the error in the local volume, expressed as a fraction of the exact volume per atom (equations (13) and (14)). The FCC and DIA cases are extremes in the sense of having maximum and minimum coordination, and this is reflected in the fact that the functions generally perform best in terms of volume dependence for FCC and worst for the DIA structures.

The worst error in ρ_f(hco) is for the DIA structure and amounts to about 3% at the extremes of doubling the volume or reducing it by 80%. This embraces also the BCC, SH, SC and VAC structures, for which nothing was fitted, which demonstrates a surprising degree of transferability. The density scaling with the low cut-off (figure 1) is naturally worse than with the high cut-off for the ρ_f-functions, as the truncation destroys their intrinsic density scaling. Nevertheless the error in ρ_f(lco) is still within 3% over a range of about 20% volume changes in all of the structures. The ρ_g look very different depending on their decay parameter α, as seen in figure 1. With $\alpha = 0.5$, which was by far the best representation
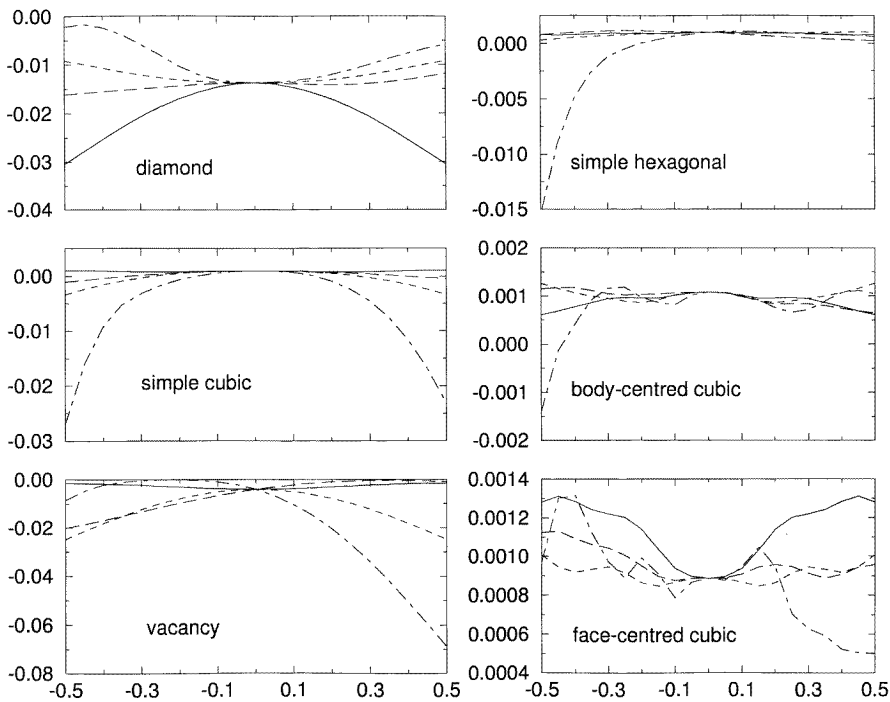

Figure 2. The variation of $\Delta V_g(\alpha = 1.0)$ with the shear strain with the lower cut-off $R_l = 2.7, R = 3.0$ for the six 3d structures from table 1 indicated in each panel. Solid line: simple shear; short-dashed line: C'-shear; long-dashed line: twinning shear; chain line: tetragonal shear.

at the high cut-off, ρ_g(lco; $\alpha = 0.5$) is now truncated abruptly, its normalization is spoiled, and it is in error by 5% at all volumes in the FCC structure. By contrast, in ρ_g(lco; $\alpha = 1$), the cut-off falls well out in the tail of the Gaussian, normalization is preserved, and it gives nearly the same results as with the high cut-off. ρ_g(lco; $\alpha = 1$) is the only one of the lco functions which does not show rapid changes in slope as a function of density, associated with shells of neighbours passing through the cut-off region. One can imagine that such changes in slope might have spurious effects on the forces in an energy minimization or molecular dynamics calculation with an energy functional involving the local densities. For this reason, the Gaussian measure with $\alpha = 1$ appears the most satisfactory of the set.

4.2. Homogeneous shear strains

Since all lattice sites remain equivalent, an ideal density function would preserve the atomic volume exactly at all strains. As in the case of volume changes, the most accurate measure is ρ_g(hco; $\alpha = 0.5$), which predicts the correct volume over the entire range of shears in all structures to better than 1%. However, ρ_g(lco; $\alpha = 1$) (figure 2) remains a good compromise; although its maximum error reaches 7% in the case of the VAC structure at 50% tetragonal strain, it is only for tetragonal strains of the VAC structure of more than 25% that the error exceeds 3%. Although there are rapid changes in the slope of ρ_g(lco; $\alpha = 1$) versus strain, they are of very small amplitude and can be eliminated completely by increasing the cut-off.
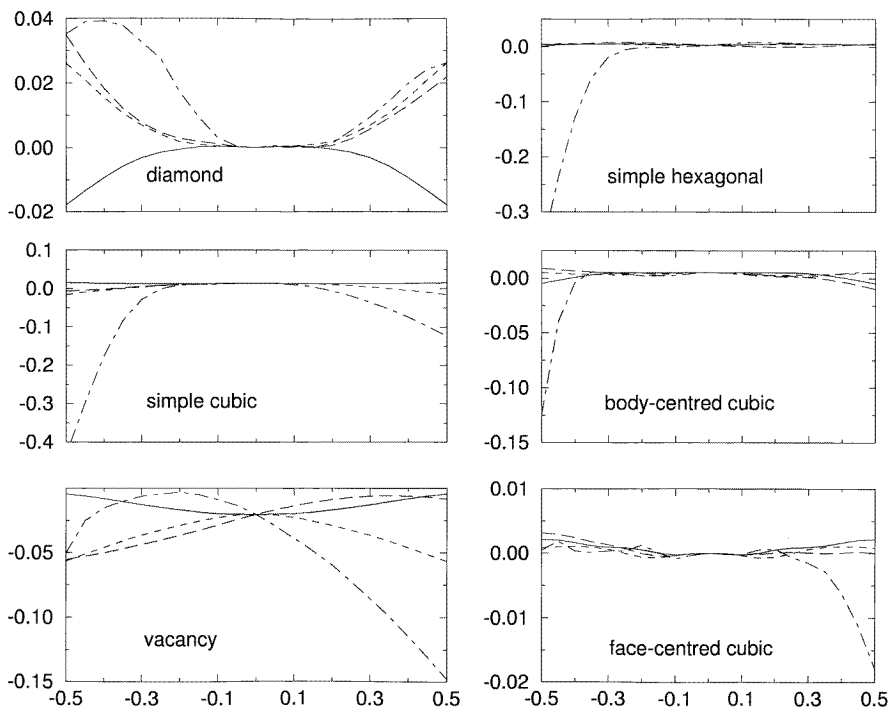

Figure 3. The variation of ΔV_f with the shear strain with the lower cut-off $R_l = 2.7$, $R = 3.0$ for the six 3D structures from table 1 indicated in each panel. Solid line: simple shear; short-dashed line: C'-shear; long-dashed line: twinning shear; chain line: tetragonal shear.

The ρ_f, by comparison to the ρ_g, do not perform so well at large strains. Again, the tetragonal strains reveal the largest errors. The higher cut-off is not a significant factor in reducing these errors. In the most extreme case, the simple cubic structure strained to -50%, the error exceeds 30% for $\rho_f(\text{hco})$ and 40% for $\rho_f(\text{lco})$ (figure 3). In the VAC structure, the error is outside 3% already at strains of 10% for the tetragonal shear.

4.3. Density near the vacancy and surfaces

Values of the density at the first ten shells of neighbours around a single vacancy in FCC have been calculated. The low cut-off falls between the eighth and ninth shells of neighbours, so $\rho_f(\text{lco})$ has reached its asymptotic bulk value by the ninth shell. However, since the reduction in density is small, we discuss only the effect at the nearest neighbours.

Although $\rho_g(\text{hco}; \alpha = 0.5)$ gives a very good bulk density, this is not a sufficient condition for adopting it. It is guaranteed that if the cut-off is large enough, by decreasing α we will approach the bulk density at *any* site near a vacancy, which would defeat the purpose of using a *local* density function. For this reason we reject the $\alpha = 0.5$ Gaussian as regards future use. For $\alpha = 1.0$, the low cut-off makes little difference to the density at the nearest neighbour to the vacancy, changing it from 95.33% to 95.24% (referred to the bulk density). These values are rather close to those given by $\rho_f(\text{lco})$ (95.5%) and $\rho_f(\text{hco})$ (95.8%). By way of comparison, simple nearest-neighbour counting at the nearest neighours of the vacancy suggests a density of $12/13 = 92.3\%$ of the bulk, which is a much more severe density deficit.

The surface results are easily interpreted in a similar way to those for the vacancy. In the limits of small α and large cut-off, the calculated density arbitrarily far from a surface will approach half the bulk value. The most satisfactory of our functions, $\rho_g(\text{lco}; \alpha = 1.0)$, predicts densities on the surface layers (100), (110) and (111) equal to 70.0%, 64.3% and 73.0% of those of the bulk respectively. For comparison, the nearest-neighbour coordinations on these surfaces are 66.6%, 58.3% and 75.0% respectively. Using the ρ_f-functions gives us surface densities as follows:

$$\rho_f(\text{lco}): 71.9\%, 65.9\%, 75.8\%$$
$$\rho_f(\text{hco}): 70.9\%, 65.1\%, 74.6\%$$

in rather good agreement with the values of $\rho_g(\text{lco}; \alpha = 1.0)$.

On the basis of these results we can expect any of the functions that we have studied except $\rho_g(\text{hco}; \alpha = 0.5)$ or $\rho_g(\text{lco}; \alpha = 0.5)$ to give rather similar corrections to vacancy formation energies or surface energies using a local volume-dependent energy function.

5. Conclusions

We have tested a new measure of the local density of atoms, ρ_f. The new measure involves three parameters and a cut-off function. The introduction of a cut-off function is necessary for numerical convergence of lattice sums within a few shells of neighbours, but it spoils the otherwise perfect density scaling of these functions, which was their prime attraction. The functions were tested on six crystal structures of coordination 4 to 12, under volume dilations over the range of -0.8 to 1.8 and under large volume-conserving shears of four types.

We also tested the Gaussian measure of local density, ρ_g, in which the width and cut-off introduce further parameters. This is a measure of density which, due to its normalization, asymptotically reproduces the bulk value for increasing Gaussian widths. We conclude

that a Gaussian ρ_g of comparable range to ρ_f is a more accurate way of calculating density provided that the on-site term is included in the lattice sum. This conclusion is only reversed for lattices of unphysically low density. The cut-off is a critical part of the function, and we find satisfactory results by truncating the functions smoothly to zero at $3r_{\text{nnref}}$, three times the nearest-neighbour distance of the reference lattice. Of the functions tested, our best choice is a Gaussian:

$$\rho_g(\text{lco}; \alpha = 1.0) = \left(\frac{1}{\pi}\right)^{3/2} r_{\text{nnref}}^{-3} \exp(-r^2/r_{\text{nnref}}^2) \tag{22}$$

which can be smoothly truncated at $3r_{\text{nnref}}$ using equation (8). With this choice of Gaussian there is little to be gained in accuracy by increasing the cut-off.

Calculations of the density at the nearest neighbours to a vacancy in a FCC structure give results which are rather insensitive to the choice of local density function, provided that it is satisfactory in the homogeneous strain tests. Between 95.2% and 95.8% of the bulk density is reached at the nearest neighbours to the vacancy, depending on which of the four acceptable functions is used. Applying these functions to surfaces, the surface densities of (100), (110) and (111) surface planes fall in the ranges 70.0–71.9%, 64.3–65.9% and 73.0–75.8% of the bulk density.

It will be of interest to investigate how the inclusion of this density variation affects defect energies within density-dependent total-energy models such as have been derived in the framework of second-order perturbation theory or the generalized pseudopotential model.

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