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Surface and bulk properties of metals modelled with Sutton–Chen potentials

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The values for surface energies, surface stresses and surface relaxation for (111), (100) and (110) faces of face-centered-cubic metals modelled by the semi-empirical many-body potentials of Sutton and Chen have been determined. The (1 \times 2) reconstruction of the (110) surface is predicted to be energetically stable for platinum and gold and not for other metals. The temperature dependence of bulk properties were investigated and values for specific heats and linear expansion coefficients are determined. Premelting behaviour on platinum, gold, silver, rhodium and iridium was investigated by carrying out molecular dynamics simulations at a number of temperatures up to the bulk melting point and monitoring surface order, surface energies and stress. The dynamics of atomic diffusion near the melting point was investigated.

1. Introduction

Atomistic simulation has proved to be a valuable tool for the investigation and understanding of microscopic processes in condensed matter. There are several methods available, molecular dynamics, Monte Carlo, energy minimisation and lattice dynamics, but they all depend on a knowledge of the interatomic potential. The advantage of computer simulation is that one knows exactly what one is measuring and the disadvantage is that the results one obtains are only as good as the potential that one obtains from.

Modelling metals poses a particular problem as one requires a potential which depends only on the nuclear positions while the bonding is caused by delocalised electrons. Following Car and Parrinello's pioneering work [1,2] it is possible to do simulations including the electrons as well as the nuclei. Such calculations are, however, time consuming and for many purposes it is more convenient to use a semi-empirical atom potential with many-body terms in it. There have been several such models proposed [3–6] including a family of potentials for face-centered-cubic metals introduced by Sutton and Chen [7]. These latter potentials may be less accurate for modelling particular metals than some of the other potentials but have several advantages. First they provide a method for analysing trends in properties in different metals; secondly they are analytic and approximate expressions for various quantities may be obtained in terms of the potential parameters; thirdly they are particularly suitable for computer modelling as they are efficient to evaluate; and finally they are longer ranged than most semi-empirical potentials, a property that may be important for the correct modelling of surface phenomena. If these potentials turn out to describe metals well, then it is likely that they will play the same role for metals as the Lennard-Jones potential has played in the description of rare gas and molecular solids and liquids, since they contain the essential physics and give at least a good qualitative description of various phenomena displayed by these systems. In fact, Sutton–Chen potentials have some similarities to the Lennard-Jones potential. They con-

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tain two terms, one attractive and one repulsive, which are characterised by a pair of exponents. There is a law of corresponding states which allows the equilibrium properties of any metals modelled by the same pair of exponents to be related by rescaling dimensions of length and energy. Dynamical properties can also be scaled, but depend on the relative atomic mass in addition to the length and energy scales.

In this paper, we report results for the properties of surfaces of metals constructed from a number of these potential modelling a range of metals. We have investigated the surface energy and relaxed structures of (111), (100), (110) and (1 × 2) reconstructed (110) surfaces at 0 K using energy minimisation. For three of the potentials, we have measured changes in the surface energy and surface stress, and looked at the extent of surface disorder and premelting phenomena at temperatures up to the bulk melting temperatures. We have also determined the energies and lattice parameters for bulk material made from three of the Sutton–Chen potentials as a function of temperature and have locate their bulk melting points approximately.

We find reasonable agreement between most properties predicted by the models and the observed quantities for the corresponding metals using the assignments of potentials to metals proposed by Sutton and Chen [7]. The melting points of rhodium, silver and iridium are approximately correct, but the models of platinum and gold melt at too low a temperature. The stability or instability of the reconstructed (110) surface of most metals is correctly predicted except for iridium and the surface relaxation of the (110), (100) and (111) surface layers agrees with observation although the detailed relaxation of the (2 × 1) reconstructed layers is not correct. Iridium is not well described by this or any other simple many-body potential as directional bonding is important.

2. The potentials

Following Finnis and Sinclair [8] the potentials have the form

\[ U = \sum_{ij} U(r_{ij}) - \sum_i \mu_i \rho_i, \tag{1} \]

where the first term represents the repulsion between atomic cores and the second term models the bonding energy due to the electrons. As the electrons are not included explicitly, the local density, \( \rho_i \), in the second term is the local density

| Table 1
Parameters used in the Sutton–Chen potentials a)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>m,n</td>
<td>(m-n)/(2m-n)</td>
<td>( e^{b)} )</td>
<td>( C_e^{b)} )</td>
<td>( a^{b)} )</td>
<td>( a_{nn}^{c)} )</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------</td>
<td>-------------</td>
<td>-------------</td>
<td>--------------</td>
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<tr>
<td>Al</td>
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<td>0.125</td>
<td>384.5</td>
<td>6307.9</td>
<td>4.05</td>
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<td>230.14</td>
<td>7919.0</td>
<td>3.92</td>
</tr>
<tr>
<td>Au</td>
<td>10.8</td>
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<td>Pt × 0.645</td>
<td>–</td>
<td>4.08</td>
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<tr>
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<td>0.23</td>
<td>64.44</td>
<td>2949.7</td>
<td>4.95</td>
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<tr>
<td>Ni</td>
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<td>0.25</td>
<td>182.29</td>
<td>7187.0</td>
<td>3.52</td>
</tr>
<tr>
<td>Cu</td>
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<td>0.25</td>
<td>Ni × 0.788</td>
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<td>3.61</td>
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<tr>
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<td>48.49</td>
<td>5250.5</td>
<td>3.89</td>
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<tr>
<td>Rh</td>
<td>12.6</td>
<td>0.33</td>
<td>57.29</td>
<td>8273</td>
<td>3.80</td>
</tr>
<tr>
<td>Ag</td>
<td>12.6</td>
<td>0.33</td>
<td>Rh × 0.515</td>
<td>–</td>
<td>4.09</td>
</tr>
</tbody>
</table>

a) These are taken from ref. [7], but energies are reexpressed as energies divided by Boltzmann’s constant \( (k_B) \). The nearest-neighbour distance at 0 K, \( a \), is given in Å. \( m \) and \( n \) are the exponents in the Sutton–Chen potentials.

b) Parameters used in eq. (3).

c) Values obtained with a cutoff in the potential at 2.5\( a_{nn} \).
of atoms. In Sutton and Chen’s potentials the local density in the second term is given by
\[ \rho_i = \sum_j \left( \frac{a}{r_{ij}} \right)^m, \]  
(2)
and the pair repulsion is also modelled by a reciprocal power so that the complete potential is
\[ U = \sum_{ij} \left( \frac{a}{r_{ij}} \right)^n C \sum_i \sqrt{\sum_j \left( \frac{a}{r_{ij}} \right)^m}. \]  
(3)

Although this is truly a many body potential, the force on each atom can be written as a sum of pairwise contributions
\[ F_i = \sum_j F_{ij}, \]  
(4)
where
\[ F_{ij} = -\frac{e}{n} \left( \frac{a}{r_{ij}} \right)^n \]
\[ - \frac{Cm}{2} \left( \rho_i^{-1/2} + \rho_j^{-1/2} \right) \left( \frac{a}{r_{ij}} \right)^m \frac{r_{ij}}{r_{ij}}. \]  
(5)

The three parameters \( e, C \) and \( a \) are not independent and are completely determined by the equilibrium lattice parameters and lattice energy of the face-centered lattice. Sutton and Chen assigned exponent pairs \((n, m)\) for modelling different metals by fitting the elastic constants as closely as possible. The ratio of the bulk elastic constant to the cohesive energy per unit volume is proportional to the product of the exponents, while the ratio of the shear to the bulk elastic constant depends mainly on the difference of the exponents. Table 1 (with numbers taken from Sutton and Chen [7]) shows properties of the metals that are modelled and the exponents used for them.

These potentials can be interpreted as being similar to the embedded atom potentials [4], but with a rather different embedding function which gives a different form to the many-body term. A difference that may be important to the description of surfaces is that the many-body term falls off more slowly with distance. At long range there is effectively an \( r^{-m} \) interaction (often \( r^{-6} \)) between atoms which models the long range van der Waals interactions between the cores.

**Technical details of the simulations**

In the calculations described in this paper, the potentials were truncated at \( 2.5a_0 \) where \( a_0 \) is the equilibrium nearest-neighbour distance at 0 K, that is between the fifth and sixth shells of neighbours. No energy shifts or long range corrections were applied. Calculations on bulk material were carried out on blocks of 512 atoms surrounded by periodic images in three dimensions. At low temperatures these calculations were initiated from portions of a perfect lattice with eight (100) layers, each containing 64 atoms. The method of constant pressure molecular dynamics was used [9] with a Berendsen barostat [10] and a Gaussian thermostat [11]. The pressure was set to zero. The minimum energy and equilibrium lattice constant for the truncated potentials were also determined.

There is always a problem in simulating surfaces with a restricted number of particles. It is usually only practicable to use approximately one thousand particles, which is much less than the number of particles in a real system. In the plane of the surface periodic boundaries can be used to mimic an infinite surface, but in the direction perpendicular to the surface one should have an infinite volume of gas above and an infinite volume of bulk material below the surface. There are two methods that are commonly used to model the bulk material, either to do a calculation on a slab with boundaries at top and bottom, or to place layers of moving atoms over a lattice of fixed atoms. In either case one is introducing a second interface into the problem which has some effect on the phonons. To check whether this affects the surface properties the best one can do is to compare calculations with different thicknesses of moving atoms to see whether surface properties are significantly affected by the second surface. In the calculations described in this paper the surfaces were modelled by placing 12 to 15 layers of 64 moving atoms over a lattice of fixed atoms. In addition a few calculations were carried out with 24 layers of moving atoms at the
highest temperature; the differences in surface energy and surface order were less than the uncertainty in these quantities. At each temperature the lattice constant of the fixed atoms was set equal to that found in a simulation of the bulk material at the same temperature. The temperature was set and maintained using a Gaussian thermostat as in the bulk calculations. Energy minimisation calculations were carried out using the same system with a slightly modified program in which atoms were moved in the direction of the forces on them until the square root of the predicted mean square displacement of the particles was less than $10^{-5}a_0$, where $a_0$ is the distance between nearest neighbours in the ideal crystal. All the calculations were carried out on a highly parallel computer, the DAP, which has an array of 4096 processors.

We define the z-axis as being along the surface normal pointing out of the metal, the x-axis to be in the surface pointing along a direction in which atoms are nearest neighbours and the y-axis to be perpendicular to both x and z.

The principal quantities monitored were the density profile in the z-direction (perpendicular to the surface), the surface energy, the surface stress and the order parameter of each layer. The order parameters used were:

$$S = \frac{1}{N^2} \sum_{i,j} \exp[k \cdot (r_i - r_j)],$$

where $k$ is the smallest Bragg vector of a single layer of atoms at the chosen surface of an ideal crystal and the summation is over all $N$ atoms $i$ and $j$ lying in the same surface layer (defined as atoms between given values of $z$). With this definition $S$ is equal to one for a perfect lattice and falls to 1/64 for a completely disordered layer of 64 atoms.

As in experimental work, some quantities are more accessible in numerical experiments than others are. In particular it is not possible to obtain values of entropies or free energies in a straightforward way from a single simulation, but values of potential and kinetic energies can readily be measured. The surface energy (as opposed to surface free energy) was calculated by determining the average energy per atom in each layer of the surface and subtracting the average energy per atom in the bulk at the same temperature. The many body energy is a property of an individual atom and so there is no ambiguity in the calculation of its contribution to the energy of atoms in a particular layer. The repulsive energy, however, is a property of pairs of atoms, and for the purposes of this calculation, was divided equally between the two atoms concerned. The surface energy, $U_{surf}$, is then given by the sum of the difference of the average energy of each layer compared to that of the same number of atoms in the bulk. There is no contribution from the kinetic energy to the surface energy.

In a crystal surface there is a difference between the surface tension, which as the surface excess free energy per unit area, and the surface stress, $g$, which is the derivative of the surface excess free energy with respect to the area [12,13]. Although the surface free energy cannot be determined from a simulation, the surface stress can be measured directly in the same way as the bulk stress or pressure tensor [9]. The $\alpha\beta$ component of the stress tensor, $\Pi$, for a homogeneous bulk phase can be written as

$$\Pi_{\alpha\beta} V = \delta_{\alpha\beta} N k T + \sum_{\text{pairs}} F_{ij,\alpha} r_{ij,\beta},$$

where $F_{ij,\alpha}$ is the $\alpha$ component of the force between the $ij$th pair of atoms separated by $r_{ij}$, $V$ is the volume considered which contains $N$ particles. In a bulk phase at equilibrium the stress is equal to the applied pressure $p_0$ but as the area, $A$, of the surface of a crystal is constrained by the bulk lattice constant, this is not necessarily true in the surface plane. The resulting excess surface stress, $g$, can be expressed as an energy per unit area and its components are given by

$$g_{\alpha\beta} A = N \delta_{\alpha\beta} (kT - p_0 V) + \sum_{\text{pairs}} F_{ij,\alpha} r_{ij,\beta}$$

$$= N \delta_{\alpha\beta} (kT - p_0 V) + \sum_{\text{atoms}} W_{i,\alpha\beta},$$

where in the last equality the virial from each pair of atoms has been divided equally between
Table 2

Bulk properties a)

<table>
<thead>
<tr>
<th></th>
<th>$U_0$ (K)</th>
<th>$U_1$ (10$^{-4}$ K$^{-1}$)</th>
<th>$U_2$ (300 K)</th>
<th>$C_p/k_B$ (10$^6$ K)</th>
<th>$c_1$ (10$^6$ K)</th>
<th>$c_2$ (10$^9$ K$^2$)</th>
<th>$\alpha$ (10$^6$ K)</th>
<th>$\gamma$</th>
<th>$\Delta H_{10k}$ (10$^4$ K)</th>
<th>$T_m$ (K)</th>
<th>$D$ (10$^{-9}$ m$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>-67840</td>
<td>2.886</td>
<td>3.16</td>
<td>-66950 (3.12)</td>
<td>13.7</td>
<td>4.8</td>
<td>16.6 (8.8)</td>
<td>4.3 + 0.3</td>
<td>1.71 + 0.02</td>
<td>1375 + 50</td>
<td>2.6</td>
</tr>
<tr>
<td>Au</td>
<td>-43760</td>
<td>2.886</td>
<td>4.90</td>
<td>-42810 (3.06)</td>
<td>3.86 ± 0.02</td>
<td>21.2</td>
<td>28.1 (14.2)</td>
<td>4.3 ± 0.3</td>
<td>1.11 ± 0.02</td>
<td>880 ± 30</td>
<td>4.5</td>
</tr>
<tr>
<td>Rh</td>
<td>-65490</td>
<td>2.926</td>
<td>2.09</td>
<td>-64590 (3.01)</td>
<td>3.05 ± 0.02</td>
<td>9.96</td>
<td>11.6 (8.2)</td>
<td>2.7 ± 0.2</td>
<td>2.80 ± 0.10</td>
<td>2180 ± 50</td>
<td>4.5</td>
</tr>
<tr>
<td>Ag</td>
<td>-33720</td>
<td>2.926</td>
<td>4.06</td>
<td>-32810 (3.05)</td>
<td>3.17 ± 0.02</td>
<td>19.3</td>
<td>25.7 (18.9)</td>
<td>2.7 ± 0.2</td>
<td>1.44 ± 0.05</td>
<td>1105 ± 30</td>
<td>-</td>
</tr>
<tr>
<td>Ir</td>
<td>-78980</td>
<td>3.237</td>
<td>0.72</td>
<td>-78002 (3.03)</td>
<td>3.28 ± 0.002</td>
<td>8.5</td>
<td>9.5 (6.4)</td>
<td>3.0 ± 0.2</td>
<td>4.4 ± 0.2</td>
<td>2950 ± 50</td>
<td>3.3</td>
</tr>
</tbody>
</table>

a) The temperature dependence of energies and lattice constants are given as coefficients in the expansion of the bulk energy per molecule $U = U_0 + U_1 T + U_2 T^2$ and the lattice constant $a = a_0 (1 + c_1 + c_2 T^2)$. Values for the molar specific heat, $C_p$, the coefficient of linear expansion $\alpha$, the Gruneisen parameter, $\gamma$, the melting point and the diffusion constant in the liquid are also shown. Experimental numbers (from ref. [11]) are given in brackets.
the atoms $i$ and $j$, to give a contribution to the local stress at atom $i$ equal to

$$W_{i,\alpha\beta} = \frac{1}{2} \sum_j F_{ij,\alpha} r_{ij,\beta}. \quad (9)$$

In the simulations the average virial contribution to the stress tensor for atoms in each layer was calculated, and the surface stress per surface unit cell found by adding the stresses for four to six successive layers. As the simulations were carried out under conditions of zero external pressure, there is no bulk stress to be subtracted. Thermal fluctuations in the instantaneous values of the stress tensor were found to be considerably larger than those in the surface energy so that the uncertainties in the values quoted for the surface stress are greater than the uncertainties in the values for surface energy.

3. Results for the temperature dependence of bulk properties

The bulk energies and lattice parameters were found to be slightly nonlinear functions of temperature in the solid and in the liquid phases. These can be fitted by second-order polynomials with coefficients given in Table 2. From these values the specific heats, $C_p$, and linear coefficients of expansion, $\alpha$, can be found at any temperature. Values at room temperature are given in Table 2. Experimental values (taken from ref. [14]) are given in brackets. The specific heats are close to the value for a classical harmonic lattice, which is $3k_B$ per atom. The small deviations from this value due to anharmonicity are of the right order of magnitude, although somewhat overestimated in most metals. A more stringent test of the accuracy of the description of the anharmonicities is the prediction of the linear coefficients of expansion. The model and experimental values shown in the table are not in exact agreement, but the trends between different metals are correctly predicted. The values predicted by the model are too large by a factor of 1.5–2. It is difficult to determine the bulk melting points of these potentials directly and the best estimates are obtained from the temperatures at which the surface becomes molten, as described in the following section. Our estimates are given in the table. The estimated values for rhodium, silver and iridium are reasonably close to experiment while those for platinum and gold are too low by a factor of 2/3. The discrepancy for the (10,8) metals, platinum and gold, is disturbing. It may be that for investigating surface phenomena these potentials should be rescaled to give the correct melting point, although this would give a bulk binding energy that is 1.5 times too large. This would give better agreement between predicted and observed latent heats (Table 2) and more acceptable surface energies.

<table>
<thead>
<tr>
<th>$U_{\text{surf}}$ (111)</th>
<th>$U_{\text{surf}}$ (100)</th>
<th>$U_{\text{surf}}$ (110)</th>
<th>$U_{\text{rec}}$ (1 × 2)</th>
<th>$g_{xx}$ (111)</th>
<th>$g_{xx}$ (100)</th>
<th>$g_{xx}$ (110)</th>
<th>$g_{yx}$ (110)</th>
</tr>
</thead>
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<tr>
<td>(J m$^{-2}$)</td>
<td>(J m$^{-2}$)</td>
<td>(J m$^{-2}$)</td>
<td>(J m$^{-2}$)</td>
<td>(J m$^{-2}$)</td>
<td>(J m$^{-2}$)</td>
<td>(J m$^{-2}$)</td>
<td>(J m$^{-2}$)</td>
</tr>
<tr>
<td>Al</td>
<td>0.47</td>
<td>0.51</td>
<td>0.576</td>
<td>0.007</td>
<td>0.94</td>
<td>0.82</td>
<td>0.82</td>
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<td>Pt</td>
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<td>2.03</td>
<td>2.04</td>
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<td>-0.010</td>
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<td>1.31</td>
<td>1.32</td>
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<tr>
<td>Pd</td>
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<td>0.296</td>
<td>0.317</td>
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<td>0.041</td>
<td>1.66</td>
<td>1.80</td>
<td>1.68</td>
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<tr>
<td>Cu</td>
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<td>1.42</td>
<td>1.32</td>
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<tr>
<td>Pd</td>
<td>0.99</td>
<td>1.10</td>
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<td>0.011</td>
<td>1.43</td>
<td>1.50</td>
<td>1.46</td>
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<tr>
<td>Rh</td>
<td>1.78</td>
<td>1.93</td>
<td>2.06</td>
<td>0.057</td>
<td>1.72</td>
<td>2.07</td>
<td>1.82</td>
</tr>
<tr>
<td>Ag</td>
<td>0.92</td>
<td>0.99</td>
<td>1.06</td>
<td>0.028</td>
<td>0.89</td>
<td>1.07</td>
<td>1.06</td>
</tr>
<tr>
<td>Ir</td>
<td>2.22</td>
<td>2.41</td>
<td>2.58</td>
<td>0.063</td>
<td>1.96</td>
<td>2.44</td>
<td>2.13</td>
</tr>
</tbody>
</table>

(a) The uncertainty in values of surface energies is about 2%.
(b) The uncertainty in values of surface stress is about 5%.
(c) $J$ m$^{-2} = N$ m$^{-1} = 10^3$ erg cm$^{-2}$. 
The final entry in the table is the diffusion constant in the liquid just above the melting point. This was determined from observations of lateral diffusion of molten surfaces as described in section 6.

4. Surface properties at 0 K

4.1. Surface energies

The results for the surface energies, stresses and relaxation of the interlayer spacing for all the metals modelled are shown in tables 3 and 4 and in figs. 1–3. Table 3 shows surface energies and stresses given in units of J/m² (= 10³ erg/cm²).

Table 4
Calculated and observed inward relaxation of the top interlayer spacing at 0 K (values are given as percentages of the actual spacing).

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Pt</th>
<th>Au</th>
<th>Pb</th>
<th>Ni</th>
<th>Cu</th>
<th>Pd</th>
<th>Rh</th>
<th>Ag</th>
<th>Ir</th>
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</thead>
<tbody>
<tr>
<td>(110)</td>
<td>18.9</td>
<td>12.1</td>
<td>12.1</td>
<td>8.8</td>
<td>7.9</td>
<td>7.9</td>
<td>5.8</td>
<td>4.3</td>
<td>4.3</td>
<td>3.2</td>
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<tr>
<td>(100)</td>
<td>7.9</td>
<td>5.1</td>
<td>5.1</td>
<td>3.6</td>
<td>2.9</td>
<td>2.9</td>
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<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>1.5 [30]</td>
<td>−0.1 [31]</td>
<td>8.9 [32]</td>
<td>2.9</td>
<td>2.3</td>
<td>1.1</td>
<td>0.5 [23]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>5.3</td>
<td>3.3</td>
<td>3.3</td>
<td>2.4</td>
<td>2.1</td>
<td>2.1</td>
<td>1.5</td>
<td>1.1</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>0 [34]</td>
<td>−1.3 [35]</td>
<td>2.1</td>
<td>2.1</td>
<td>1.5</td>
<td>1.1</td>
<td>0.9</td>
<td></td>
<td></td>
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</table>

References are given for experimental results; values without references are our calculated results.
Data presented in this way are most useful for comparison with experiment; for discussion in terms of the properties of the potentials it is more useful to use reduced units and in the figures the surface energies and stresses are shown in reduced units of \((\text{energy} / U_{\text{coh}})\) per surface unit cell, where \(U_{\text{coh}}\) is the bulk cohesive energy per atom. In reduced units any two metals modelled by the same values of \(n\) and \(m\) behave identically. In all the figures the metals are ordered according to the value of the difference of exponents, \((n - m)\), in the Sutton–Chen potential used which determines the ratio of the shear elastic constant to the bulk compressibility. Note that nickel and lead have the same value of \(n - m\) although their properties differ. The metals on the left shear more easily for a given compressibility, which means that, at least in the bulk, atoms move more easily relative to each other at constant density. These metals show greater relaxation around defects.

The first point to note about the surface energies is that, when expressed in reduced units, the values for all these metals are considerably lower than the surface energies of the corresponding face of a molecular or atomic crystal. In a molecular crystal, the order of magnitude of the surface energy can be estimated from the number of nearest neighbours. The values for a nearest-neighbour pair potential are 25, 33 and 44.7% for (111), (100) and (110) surfaces of a face-centered-cubic lattice respectively. All the values for the metals are considerably less than these. This is because the attractive part of the potential for metals is approximately proportional to the square root of the number of nearest neighbours, while in non-metals it is proportional to the number of nearest neighbours. In a Sutton–Chen metal in which the potential is cut between the first and second nearest neighbours the unrelaxed surface energy can readily be calculated and is found to be nearly proportional to \((n - m)/(2n - m)\). In our calculations the potential cutoff is larger (between fifth and sixth nearest neighbours) and the surface relaxes inwards, but as both these effects are comparatively small the trend is the same as in the nearest-neighbour model. Thus for a given \(n\), \(U_{\text{surf}}\) decreases with \(m\) (as the range of the attractive contribution decreases), while for a given \(m\), \(U_{\text{surf}}\) increases as \(n\) increases and the repulsive term becomes harder. The change due to relaxation is a small percentage of the total. For example in the (10,8) potential the (110) surface energy (in reduced units) changes from 0.14 to 0.126 while the (111) surface energy changes from 0.067 to 0.064 on relaxation.

As the average energy of each layer of particles is calculated separately we can investigate the number of layers that are significantly affected by being near the surface. Most of the surface energy is found to reside in the top layer of atoms, with about 10% in the second layer and 1% or less in the third layer.

The values obtained here for Sutton–Chen potentials are significantly lower than those obtained by Sinnott et al. [15] for “corrected effective medium potentials” and similar to those obtained for embedded atom potentials [16]. Experimentally it is difficult to obtain surface energies for individual faces, but average values quoted in the above papers suggest that our results and those of the embedded atom calculations are too low. When the experimental results are reexpressed in reduced units of energy per surface unit cell divided by bulk cohesive energy, the trends predicted by the Sutton–Chen potentials are correct for Pt, Au, Ni, Cu and Pd although Ag appears to have a lower reduced surface energy than Pd rather than a higher one as predicted here.

### 4.2. Surface stress

When the crystal lattice is cut, the resulting unrelaxed surface is stressed both in the direction perpendicular to the new plane and in the plane of the surface. The stress perpendicular to the new plane is eliminated by relaxation, but the stress in the surface cannot be eliminated as the area of the surface is fixed by the properties of the bulk lattice. In all the metals modelled here both the initial and final values of the components of the stress tensor in the plane are negative (tensile), but the values for the relaxed surfaces are considerably less than for the corresponding unrelaxed surfaces. The reason that the
initial values of the stress tensor are tensile is that the coefficient of the many body term in the effective pair potential [eq. (5)] is greater at the surface than in the bulk. Consequently the natural bond length at the surface is less than in the bulk: the surface wishes to contract. The inward relaxation of the outer layers increases the local density and so reduces the coefficient of the many body term in the pairwise force [eq. (5)] which contributes to the tensile stress. Thus the normal component of stress is reduced on inward relaxation by two effects, the shortening of the bonds between the top and second layer and a decrease in the attractive part of the force. The lateral stress in the surface is mainly due to bonds within the top layer which do not change length during relaxation. Although there is a significant decrease in the lateral tensile stress due to the increased density, overall the surface stress remains tensile. Only by increasing the density to the bulk density could the tensile stress in the surface be eliminated. The variation between different surfaces of the same metal is determined by the total number of neighbours, which determines the local density and hence the magnitude of the forces, and by the geometry of the surface which determines the way in which the forces contribute to the stress tensor. The (111) close packed face has the smallest magnitude of each pair force, but there are more pairs to contribute to the virial (eq. (8)) at each atom. For most metals the stress per surface atom is least for the close-packed face and greatest for the (110) face, although the order may change when the results are expressed in terms of energy per unit area (see table 3). The (110) surface is anisotropic and has different values for the components of stress along and perpendicular to the close-packed rows. The stress is always larger along the rows, and neither component changes much on reconstruction.

The variation of stresses between metals shown in fig. 2 is not very large, and is less easy to explain qualitatively than the surface energies. In an unrelaxed Sutton–Chen metal with nearest-neighbour interactions only the stress is proportional to \([mn/(m - 2n)]\). The values in the figure show much less variation than predicted by this expression, and are not even in the order predicted. The main reason for this is that there are large changes in surface stress as surfaces relax (e.g. 20% for Rh(1110), 25% for Rh(100), 30% for Ni(111) and over 50% for Pt(100) and (110) surfaces, so that the relationship with \(mn/(m - 2n)\) is lost.

4.3. Surface relaxation and reconstruction

The extent of the surface relaxation of the various Sutton–Chen metals is shown in table 3 and is plotted in fig. 3. Those metals with low values of \(n - m\) relax most, while ones with high \(n - m\) relax less. This agrees with the result from Sutton–Chen potentials restricted to nearest-neighbour interactions where the relaxation depends only on \(n - m\) and is approximately proportional to \(n - m\). However there is a difference between the extent of relaxation on lead surfaces compared with nickel/copper although the values of \((n - m)\) are the same for both potentials. This difference is due to the fact that the nickel/copper (9,6) potential is somewhat longer ranged than the lead (10,7) potential, which makes a difference when the second and higher shells are taken into account.

Experimental determinations [17–37] of the relaxation of interlayer spacings are available for some of the surfaces and relevant data are summarized in table 4. These values were obtained at 300 K. For all the (100) and (111) surfaces of these fcc metals the relaxation is close to zero, while the (110) surfaces of metals with a stable \((1\times1)\) structure show contractions of between 1 and 9% of the bulk spacing. No systematic trend as a function of \(n - m\) or \(C_{44}\) can be discerned. It should be emphasized that these predictions from the model potential are for 0 K. Recent measurements on Pb(110) [19] show that the relaxation of the top interlayer separation changes from \(-15.5 \pm 2.5\%\) at 29 K to \(-3 \pm 5\%\) at 485 K. This is partly due to premelting effects, but there is a significant reduction even at room temperature, which is ascribed to the greater anharmonicity of the surface than the bulk. Although we have not measured the change in interlayer spacing with temperature (thermal fluctuations in the simula-
tion make this difficult), we have evidence of anomalous surface anharmonicity in the temperature dependence of the surface stress to be described in section 5. This anharmonicity is greatest where the surface relaxation is greater (small \( n - m \)) so that any trend with \( n - m \) may be obscured. Nevertheless it appears that the model may predict too much relaxation, especially on (111) and (100) surfaces.

On all the (110) surfaces an alternation in the relaxation of interlayer spacing was seen, with a contraction of the first and third and an expansion of the second and fourth interlayer spacings. This effect is well known experimentally \([17,20-22,25-29]\) and theoretically \([38]\) and has been observed for other empirical metal potentials \([16]\). It does not occur universally on other surfaces, and we find small (approximately 0–0.2%) contractions of the second interlayer spacing on (100) and (111) surfaces of nickel, copper, palladium, rhodium, silver and iridium and expansion in aluminium, platinum, gold and lead (111). The second interlayer spacing in lead (100) is unchanged.

There has been considerable interest in the \((1 \times 2)\) “missing row” reconstruction of the (110) surface. Experimentally \([39]\), this type of reconstruction has been observed on platinum, gold and iridium, but not on other face-centered-cubic metals. At non-zero temperatures there is an entropy contribution to the relative stability of the reconstructed and normal surfaces, which we have not attempted to calculate. At \( T = 0 \) K the relative stability depends only on the change in surface energy, values of which are given in as \( U_{\text{rec}}(1 \times 2) \) in table 3. The unreconstructed surface is predicted to be more stable (i.e. with lower surface energy) for all metals except gold and platinum. The reason for this probably lies in the shorter range of the \( n_{12} \) potential compared to the other potentials. Håkkinen et al. \([40]\) have shown that nearest-neighbour potentials reconstruct if

\[
\left( \frac{\partial^2 U_{\text{surf}}}{\partial l^2} \right)_{l=9} > 0,
\]

where \( l \) is the number of nearest neighbours.

This is positive if \( E = A l - B \sqrt{l} \), the form of a nearest-neighbour Sutton–Chen potential for an ideal lattice. Håkkinen et al. also show that including next neighbours may stabilise the unreconstructed surface. The stability of the unreconstructed surfaces in these Sutton–Chen potentials must therefore be due to the longer range part of the potential, and the probable reason for the predicted instability of the platinum and gold surfaces is the shorter range of the \( r^{-8} \) form of the many body density compared to the \( r^{-6} \) or \( r^{-7} \) form of the other potentials in the Sutton–Chen family investigated here. All these many body potentials predict that the Cauchy pressure is positive and in order to obtain a negative Cauchy pressure it is necessary to include specific angle-dependent bonding. Iridium has a fairly large negative Cauchy pressure, and we are not surprised that these potentials fail to predict the correct reconstruction.

Other types of reconstruction on platinum and gold are also known \([41]\), for example a hexagonal overlayer on the (100) surface and a more close packed top layer on the (111) surface \([42]\). Although we have not investigated the stability of these reconstructions and it would be tricky to set up the right periodic boundaries to do so, the trend to have shorter interatomic spacing in the top layer is certainly contained in these potentials.

There have been several other calculations of reconstruction energies for other types of empirical potentials. Using effective medium potentials, Håkkinen and coworkers \([40]\) predict that platinum, palladium and gold reconstruct, but nickel, copper, silver and aluminium do not. Embedded atom calculations of Foiles \([43]\) predict that palladium, platinum, gold and silver reconstruct but nickel and copper do not. In several of these model intermolecular potentials, the reconstruction energy is proportional to \( C_{44}/B \). This is not true for the Sutton–Chen potentials. In table 3 the potentials are ordered in terms of this quantity and the values of the reconstruction energy do not follow the same order.

A (110) surface is unstable with respect to a \((1 \times \infty)\) reconstruction (in which a wedge with (111) faces is placed on the surface) if the ratio of
the surface energies $E(111)/E(110) < 0.816 = \sqrt{2}/3$. This is not true for any of the Sutton–Chen metals investigated in this work.

The detailed relaxation of the reconstruction (10,8) surface does not agree with experimental observations [39] on platinum and gold (see table 5). Although the vertical relaxation is modelled correctly, the pairing in the second layer and the rumpling in the third layer are in the reverse direction to that observed. The Sutton–Chen potential seems to overemphasize the advantages of bunching. This may be a general defect of empirical potentials of the many body type as results from embedded atom [43], and glue [44] potentials are similar to ours although calculations in which electrons are included give the correct sign [45].

5. Temperature dependence of surface properties

The Sutton–Chen potentials are particularly convenient for simulations at non-zero temperatures as they can be computed rapidly. We per-

Fig. 4. Order parameters (defined in text) as a function of temperature for platinum, rhodium and iridium.
Table 5
Relaxation in the 2 × 1 missing row structure in the (10,8) potential

<table>
<thead>
<tr>
<th></th>
<th>This work (%)</th>
<th>Pt $^{a)}$</th>
<th>Au $^{a)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>First interlayer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>relaxation $^{a)}$</td>
<td>-11.1</td>
<td>-19.5, -15.6, -22, -20</td>
<td></td>
</tr>
<tr>
<td>Second interlayer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>relaxation $^{a)}$</td>
<td>-3.7</td>
<td>-7.2, +2</td>
<td></td>
</tr>
<tr>
<td>Third interlayer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>relaxation $^{a)}$</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second layer pairing $^{b)}$</td>
<td>-1.6</td>
<td>2.5, 2.5, 3.4</td>
<td></td>
</tr>
<tr>
<td>Fourth layer pairing $^{b)}$</td>
<td>+1.8</td>
<td>2.0, 2.4</td>
<td></td>
</tr>
<tr>
<td>Second layer buckling $^{c)}$</td>
<td>+7.2</td>
<td>23, 27</td>
<td></td>
</tr>
<tr>
<td>Fourth layer buckling $^{c)}$</td>
<td>+1.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a)}$ Expressed as a percentage of the interlayer spacing.

$^{b)}$ Percentage change in the distance between rows. A negative number corresponds to a movement away from the position of the missing row.

$^{c)}$ Amplitude of the buckling expressed as a percentage of the interlayer spacing. A positive number corresponds to a downward movement of atoms below the missing row.

$^{d)}$ From ref. [39].

formed molecular dynamics simulations of (111), (100) and (110) faces of three of the Sutton–Chen potentials, namely those with (10,8), (12,6) and (14,6) exponents, at temperatures up to the bulk melting point. We observed the degree and nature of any surface disorder and the temperature dependence of the surface energy and stress.

The surface order was monitored in two ways, firstly, by observing the density profiles perpendicular to the surface and secondly, by monitoring the values of the order parameters defined in eq. (6) for each layer. Plots of the values of the order parameters for the top eight layers of the various surfaces are shown in fig. 4. Although a total of 15 moving layers are used in the simulations, we have only used the top 8 layers in the analysis of the results. This was to avoid the boundary effects which arise due to the interaction of lower layers with the artificially increases their order.

The most striking feature of these graphs is the abrupt nature of the change of surface order at the melting point on the (111) surface. On the (110) and (100) faces the top few layers show some disorder below the melting point, but there...
is still a well-defined temperature at which the fourth to the eighth layers (and below) become completely disordered. We identify it as the bulk melting temperature. We observed that melting is readily initiated on the (100) and (110) surfaces, but on the (111) surface superheating tends to occur, and the surface only disorders after several hundred picoseconds. Even on the more open faces there is less pre-melting disorder than was seen in simulations of multilayers of Lennard-Jones atoms [46]. In particular there is no evidence of layer-by-layer melting. On the more open (100) and (110) faces the top layer becomes 50% disordered at a few hundred degrees below the bulk melting point. The density profiles show that this generally occurs in two stages, first by promotion of atoms into an overlayer and then a general blurring of the upper layers. This is shown in fig. 5 for some rhodium surfaces. This sequence is similar to that seen on the surfaces of Lennard-Jones atoms.

There are some differences between the potentials. For example the order parameter of the top layer of the platinum/gold (111) surface has a distinctly lower value at all temperatures than the lower layers, while the difference is much less marked on the rhodium/silver and iridium surfaces. Even in platinum the top layer is by no means disordered, but the order parameter is reduced because of vibration (the same effect as seen in the Debye–Waller factor). This shows that the surface phonons are more different from the bulk phonons than in the other metals.

The temperature dependence of surface energies and surface stresses

Fig. 6 shows plots of the surface energies of three faces of platinum as a function of temperature. The reader is reminded that these quantities are energies rather than free energies. At 0 K the energy is equal to the free energy, but at higher temperatures the free energy is less than the energy due to the entropic contribution $-TS$. The energies were calculated as described before, by subtracting the mean potential energy per atom in each layer from the mean potential energy of an atom in the bulk. The surface energy arises from the top four or five layers, with layers 6–12 having mean atomic energies that were equal to the bulk energy within experimental error. At the highest temperatures the top 12 layers are molten and have the same energy as the bulk liquid rather than the bulk solid. Hence the appropriate calculation for the surface energy is to take the difference between the energy of the surface layers and the energy they would have in the bulk liquid, and this is what was used to obtain the last points. It should be noted that these represent the surface energy of the liquid state which is less than that of the solid. The results for the solid surface agree with what one might expect; the surface energy remains approximately constant until disorder begins to set in, when it increases rapidly. This increase is associated with the increase of entropy of the surface and is analogous to a latent heat of melting. The slope of the curve of surface energy versus temperature is equal to the excess specific heat of the surface which is positive, although a curve of surface free energy versus temperature would have a slope equal to minus the surface entropy and would decrease with temperature.

The results for the temperature dependence of the surface stress are more unexpected (see fig. 7). There is a large reduction in magnitude of the stress as the temperature is increased, even at temperatures well below any surface disorder.
There is no abrupt change even when the surface becomes molten. This phenomenon is not peculiar to the (10,8) potential; the changes seen on a Rh(100) surface using the (12,6) potential were very similar (2.07 at 0, 1.57 at 1500 1.40 at 2000 and 1.10 J m⁻² at 2500 K). The strong temperature dependence at low temperatures is a reflection of the anharmonicity of the surface interactions. Recall that most bulk materials expand when heated at constant pressure and show an increase in pressure when heated at constant density. This is due to the anharmonicity of the interatomic forces. The surface tensile stress arises because the surface bonds in these metals are more stretched than the bonds in the bulk. As the temperature increases the surface bonds become less stretched as their anharmonicity is greater than the anharmonicity of the bonds in the bulk material, although the surface area of each unit cell expands with temperature due to changes in the bulk equilibrium bond length. As far as we are aware there have been no measurements of the temperature dependence of the surface stress, but effective-medium calculations for copper [47] show a strong temperature dependence of the first interlayer spacing as a function of temperature which is attributed to surface anharmonicity. In fact this model shows a changeover from inward to outward relaxation for copper (110) near room temperature.

6. Dynamic properties

Molecular dynamics simulation provides a good way of investigating dynamic processes on the picosecond time scale. Where atomic diffusion occurs at liquid-like or near liquid-like rates it can be observed and measured in the simulations.

We measured the diffusion constants for atoms in slices at various depths from the surface by measuring their mean square displacement in the x, y plane. The diffusion is anisotropic, especially well below the bulk melting point where the density profile in the z direction is non-uniform.

No attempt was made to quantify the motion perpendicular to the surface. Diffusion constants for any particular layer were calculated from the mean square lateral displacement

$$\langle R^2(t) \rangle = \langle [x_i(0) - x_i(t)]^2 + [y_i(0) - y_i(t)]^2 \rangle,$$

for those atoms which remained in that specified layer. Plots of $\langle R^2(t) \rangle$ versus time were usually linear after about 4 ps, allowing us to calculate the layer diffusion constants, $D$, by fitting these plots between 4 and 25 ps with the linear function

$$\langle R^2(t) \rangle = 4Dt + C.$$

Fig. 8 shows the lateral diffusion constants for Rh as a function of layer number at two temperatures. In the original ordered surfaces the top layer is labelled 15; layer 16 contains all the atoms above the original top layer. At the higher temperature (2200 K) the metal has melted, but at 2100 K only premelting effects are present. Density profiles at some of the faces at these two temperatures are shown in fig. 5.

In the molten surfaces (lower graph) the diffusion constants are the same within the errors for layers 13 and below on all the faces. The density profiles (fig. 5c) show no residual layering at this temperature, and we may identify this value with the value for the bulk liquid. Close to the surface itself diffusion is enhanced. At the lower temperature (upper graph) the variation of diffusion constant with depth is quite different. The (111) surface shows no measurable diffusion, while the
values of the diffusion constants on the more open faces drop steeply with depth from liquid-like values in the top layer or two, to zero about four layers down. The density profiles at this temperature (figs. 5a and 5b) shows distinct residual layering although there is some blurring of the profile.

There have been measurements of surface diffusion on metals, for example Frenken et al. [48], find measurable diffusion of lead (110) at temperatures above 0.75 of the melting temperature. Within 50 degrees of the bulk melting temperature the surface diffusion is greater than that in liquid metal at the melting point. This is probably due to the lower density very close to the surface and is similar to the effect that we see in the top of the molten layer.

7. Conclusions

The aim of this work has been to investigate surface and some bulk properties of metals modelled with a particular class of empirical potentials, the Sutton–Chen family, in order to explore the degree of agreement of materials modelled with such potentials and real metals and to gain microscopic insights into surface phenomena.

It is our conclusion that, although exact numerical agreement with experimental measurements is not obtained, the qualitative results obtained from the Sutton–Chen potentials are sufficiently realistic for them to be useful for modelling face-centered-cubic metals. The unique properties of metals such as inward relaxation at the surface, surface anharmonicity and low ratios of both $U_{surf}/U_{coh}$ and $k_B T_m/U_{coh}$ (where $T_m$ is the melting point) are seen. At least some of the differences between fcc metals are successfully reproduced, for example the presence or absence of the $(1 \times 2)$ reconstruction on (110) surfaces. However, it seems that while trends in most surface properties are reproduced, the surface energies tend to be too low and the surface relaxation too high. In earlier work we showed that the change in mechanism of surface migration from platinum (by surface exchange) to rhodium (by simple migration) is also correctly predicted [49]. The mechanism of adatom migration in iridium was not correctly predicted, a failing that was ascribed to the necessity of including explicit angle-dependent forces for a metal such as iridium which has a negative Cauchy pressure. In more recent work [50] it was found on platinum/gold stepped surfaces mechanisms for diffusion which involve simultaneous movement of several atoms are found which are absent on rhodium/silver surfaces.
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References