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1989 J. Phys.: Condens. Matter 1 9765

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The effective-medium theory beyond the nearest-neighbour interaction

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Received 6 June 1989

Abstract. The effective-medium theory has been extended to include more than the nearest neighbours in the total energy calculation of a metallic system. This extension has been tested by molecular dynamics simulations of thermal expansion and melting of copper. The calculated thermal expansion coefficient, melting point, latent heat of fusion and diffusion constant of the liquid phase are in good agreement with experimental data. In the liquid phase it is necessary to go beyond the nearest-neighbour interactions.

1. Introduction

The development of atomistic models suitable for Monte Carlo and molecular dynamics simulations of metallic systems has roused great interest during the past two decades. The early pairwise models failed to describe many properties of metals arising from the electronic interaction. The electronic interaction has a many-body nature and the total energy of a metallic system cannot be calculated by simply summing interactions between pairs of atoms. The first attempt to include many-body interactions was the use of the pseudopotential theory which gives a structure-independent volume term to the total energy of the system (Harrison 1966, Ashcroft 1972). This term describes the cohesion arising from the homogeneous conduction electron gas. However, the volume-dependent term can lead to difficulties in simulations of surfaces and extended crystal defects, where the volume of the sample is ambiguous. Moreover, the sample can contain large density gradients, and the model of the homogeneous conduction electron gas becomes less suitable.

At the beginning of 1980s, a new idea on how to calculate the total energy of a metallic system was presented. The essential difference compared to the previous approach is that the electron density of the sample is allowed to vary from one lattice site to another. The main part of the cohesion at a given lattice site depends on the *local* electron density at this site. This idea was first applied to the calculation of the binding energy of impurities and adsorbates interacting with metals (Nørskov and Lang 1980, Stott and Zaremba 1980, Nørskov 1982). Later on, this approach has led to a whole new class of potentials: the 'embedded-atom method' (EAM) (Daw and Baskes 1983, 1984), the 'Finnis–Sinclair potential' (FS) (Finnis and Sinclair 1984), the 'effective-medium theory' (EMT) (Jacobsen *et al* 1987, Manninen 1986) and the 'glue model' (Ercolessi *et al* 1986). In all these models the total energy of the system

composed of N atoms can be written as

$$E_{\text{tot}} = \sum_{i=1}^N F(n_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N V(r_{ij}) \quad (1)$$

where $V(r_{ij})$ is a pair potential, n_i is a quantity describing the local density at the atomic site i and $F(n_i)$ is the corresponding energy term. The local density n_i is dependent on the distances from atom i to its neighbours, and in this way $F(n_i)$ is structure dependent and implicitly includes many-atom interactions.

The functional forms of n , F and V as well as their physical interpretations are different in each of the models mentioned above. In the semi-empirical EAM (Daw and Baskes 1984) and in the related model of Finnis and Sinclair (1984), the pair potential term is purely repulsive and interpreted as the screened Coulomb repulsion between positive ion cores. The cohesion comes from the energy function F , which describes the 'embedding energy' of atom i in a homogeneous electron gas of density n_i . The embedding energy is negative and proportional to the square root of the density n mimicking the tight-binding model. The parameters in n , F and V are determined using experimental data from the solid phase. The EAM and FS models have been used in simulations of transition metal surfaces and liquid transition metals (Foiles 1985, 1987, Ackland and Finnis 1986).

The glue model (Ercolessi *et al* 1986) is a purely empirical potential, which has been optimised to reproduce a great deal of experimental data on the solid phase of gold. In this model, n is a 'generalised coordination' and the energy function F is negative, having a minimum with $n = 12$, the coordination in an FCC lattice. The pair potential V has both a repulsive and an attractive part. The glue model has been used to simulate the structure and melting of low-index surfaces of gold (Ercolessi *et al* 1986, 1987, Carnevali *et al* 1987). It also describes well the liquid phase of gold (Iarlori *et al* 1989).

The potential derived from the EMT has been built up in a somewhat different way than the EAM and the 'glue', although the EMT can also be written in the form of equation (1). The EMT is purely theoretical but there are still many ways to do approximations in the derivation of applicable formulae (like the type of equation (1)). The 'standard' form of the total energy in the formalism of Jacobsen *et al* (1987) is

$$E_{\text{tot}} = \sum_{i=1}^N E_{\text{Ci}}(\bar{n}_i) + E_{\text{AS}} \quad (2)$$

The first term in equation (2) is a cohesive energy term which depends on the embedding energy (Puska *et al* 1981) of atom i in a homogeneous electron gas of local density \bar{n}_i . The second term is the so-called atomic sphere correction, which is explained in §2. The effective-medium theory also contains one-electron energy terms, which are important in transition metals due to partially filled d bands. It is assumed that in non-transition metals like aluminium and copper the one-electron terms can be neglected (Jacobsen *et al* 1987, Manninen 1986). The EMT model has been applied to simulations of the thermal expansion of aluminium (Stoltze *et al* 1987) and the melting of the aluminium (110) surface (Stoltze *et al* 1988).

The range of the potentials presented above is short, including generally only atoms within the nearest- (or next-nearest-) neighbour radius in the ideal lattice structure. This is an advantage for the computational efficiency, but restricts the use of the models

in some situations. For example, the nearest-neighbour formalism of EMT gives no energy for the stacking fault in the FCC lattice. Thus the processes depending on this stacking fault energy cannot be studied (Ackland *et al* 1987, Häkkinen *et al* 1989). It is also necessary to extend the EMT beyond the nearest neighbours for high-temperature dynamic simulations, where the symmetry of the ideal FCC lattice is heavily broken.

In this paper we present a way to extend the EMT beyond nearest neighbours for dynamic simulations. We have tested the extended model by molecular dynamics simulations of the thermal expansion and melting of copper. The calculated thermal expansion curve and the coefficient of thermal expansion at room temperature are in good agreement with the experimental data. The melting temperature and the coefficient of self-diffusion in the liquid state are also close to the experimental values.

2. Effective-medium theory

A detailed derivation of the energy expression (2) has been given by Jacobsen *et al* (1987) and a discussion emphasising the physical picture arising from this theory is given by Jacobsen (1988). Only the main outlines of the nearest-neighbour effective-medium approach are presented in §2.1. Section 2.2 deals with the extension of the EMT model to include more than the nearest neighbours.

2.1. The nearest-neighbour formalism

In any theory explaining the density-dependent electronic cohesion the starting point has to be the choice of the *ansatz* describing the electron density $n(\mathbf{r})$. In the EMT, this *ansatz* is

$$n(\mathbf{r}) = \sum_{i=1}^N \Delta n_i(\mathbf{r}) \quad (3)$$

which says that the total electron density is a superposition of electron densities Δn associated with each atom. In EMT Δn is estimated from the atom-induced density when it is immersed in a homogeneous electron gas. The atom embedded in a lattice site i feels a background density \bar{n}_i coming from all other atoms in the system. This background density is approximated as being uniform in the region occupied by atom i and its value is calculated as a spherical average over a neutral sphere of radius s_i centred at the lattice site i :

$$\bar{n}_i = \left\langle \sum_{j \neq i}^{\text{NN}} \Delta n_j \right\rangle_i = \frac{1}{(4/3)\pi s_i^3} \int_{s_i} \mathbf{dr} \sum_{j \neq i}^{\text{NN}} \Delta n(|\mathbf{r} - \mathbf{R}_j|) \equiv \sum_{j \neq i}^{\text{NN}} \Delta \bar{n}_j(s_i, \mathbf{R}_j) \quad (4)$$

where \mathbf{R}_j is the position vector of neighbouring atom j and NN means a nearest-neighbour sum. In a perfect lattice the sphere of radius s_i equates with the definition of a spherical Wigner–Seitz cell associated with each atom. The requirement of neutrality results in a unique correspondence between the background density \bar{n}_i of atom i and its Wigner–Seitz radius s_i . A good approximation for this relationship is an exponential dependence

$$\bar{n}(s_i) = n_0 \exp[-\eta(s_i - s_0)] \quad (5)$$

where n_0 , η and s_0 are constants. The average induced density coming from an atom at a distance r can also be approximated by an exponential relation (with constants Δn_0 , η_1 and η_2)

$$\Delta \bar{n}(s_i, r) = \Delta n_0 \exp(\eta_1 s_i - \eta_2 r). \quad (6)$$

In the ideal FCC lattice each atom has 12 nearest neighbours at a distance of βs , where $\beta = (16\pi/3)^{1/3}/\sqrt{2}$ is a geometrical factor. Equation (4) then gives for a perfect lattice

$$\bar{n}(s_i) = 12\Delta \bar{n}(s_i, r = \beta s_i) \quad (7)$$

from which $\Delta \bar{n}_0$ and the relationship between η , η_1 and η_2 can be determined: $\eta = \beta\eta_2 - \eta_1$. When the lattice does not have an ideal FCC symmetry, the neutral sphere radius s_i varies from one lattice site to another. For atom i it can be solved by replacing the right-hand side of equation (7) by the nearest-neighbour sum $\sum_{j \neq i}^{\text{NN}} \Delta \bar{n}(s_i, r_{ij})$, where r_{ij} is the distance between atoms i and j . This procedure gives an explicit r_{ij} dependence for s_i :

$$s_i = -\frac{1}{\beta\eta_2} \ln \left(\frac{1}{12} \sum_{j \neq i}^{\text{NN}} \exp(-\eta_2 r_{ij}) \right). \quad (8)$$

When s_i is inserted in equation (5) the explicit r_{ij} dependence of \bar{n}_i can be written as

$$\bar{n}_i = n_0 \left(\frac{1}{12} \sum_{j \neq i}^{\text{NN}} \exp[-\eta_2(r_{ij} - \beta s_0)] \right)^{\eta/(\eta+\eta_1)}. \quad (9)$$

The cohesive function E_C (the first term in equation (2)) is parametrised by a third-order polynomial

$$E_C(\bar{n}) = E_0 + E_2 \left(\frac{\bar{n}}{n_0} - 1 \right)^2 + E_3 \left(\frac{\bar{n}}{n_0} - 1 \right)^3. \quad (10)$$

When the symmetry of the ideal FCC lattice is broken, the overlap of the neighbouring Wigner–Seitz spheres becomes important. The energy arising from this overlap is the so-called atomic-sphere correction, which is the second term in the equation (2). For a non-transition metal the atomic-sphere correction can be approximately written in the form

$$E_{\text{AS}} = \sum_{i=1}^N \left(\alpha \bar{n}_i - \frac{1}{2} \sum_{j \neq i}^{\text{NN}} V(r_{ij}) \right) \quad (11)$$

where $V(r_{ij})$ is an explicit nearest-neighbour pair potential and α is an integral of the electrostatic potential $\Delta\phi$ over the neutral sphere of radius s :

$$\alpha = \int_s \Delta\phi(r) \, dr. \quad (12)$$

The pair potential V can be solved by demanding that the atomic-sphere correction vanishes in the ideal FCC lattice. That gives

$$V(r_{ij}) = \frac{1}{6} \alpha \bar{n}(s_i = r_{ij}/\beta) \quad (13)$$

where $\bar{n}(s_i)$ is determined from (7). The overlap energy can then be calculated as a function of atomic positions from the expression

$$E_{AS} = \alpha n_0 \sum_{i=1}^N \left[\left(\frac{1}{12} \sum_{j \neq i}^{NN} \exp[-\eta_2(r_{ij} - \beta s_0)] \right)^{\eta/(\eta+\eta_1)} - \frac{1}{12} \sum_{j \neq i}^{NN} \exp[-\eta(r_{ij}/\beta - s_0)] \right]. \quad (14)$$

The total energy of simple metal systems can now be calculated from the positions of atoms using equations (2), (9), (10) and (14). So far the parametrisation for the EMT potential has been published for aluminium and copper (Jacobsen 1988). A very appealing property of the effective-medium theory is that all parameters can be calculated from the density functional theory using the local density approximation. In practice, however, for reasons explained by Jacobsen (1988) it is more reliable to determine η_1 from experimental data.

2.2. The extension beyond nearest neighbours

In strongly distorted systems, for example in liquid metals, the nearest-neighbour sum becomes ambiguous. One way to overcome this problem is to use a Fermi-type cut-off function going to zero between the first- and second-neighbour distances of the perfect lattice. This scheme was used in the dynamical simulation of aluminium surfaces by Stoltze *et al* (1988). However, this artificial cut-off does not extend the range of the interaction in EMT and excludes applications where the long-range interactions are essential. A method for including more than the nearest neighbours in the total energy calculation was outlined in the appendix of Jacobsen *et al* (1987). We have studied this extension and tackled the problems arising from it.

The essential point in the extension of effective-medium theory is to generalise the expression for the background density (4) in the proper way. The generalisation is made by assuming that the ideal FCC lattice is space-filling, just like in the nearest-neighbour formalism (i.e. the charge densities of holes and overlaps between Wigner-Seitz spheres associated with ideal FCC lattice points equal each other). The background density is then

$$\bar{n}(s_i) = \sum_{k=1}^{\infty} N_k \Delta \bar{n}(s_i, R_k) = 12 \Delta \bar{n}(s_i, \beta s_i) + 6 \Delta \bar{n}(s_i, \sqrt{2} \beta s_i) + \dots \quad (15)$$

where N_k is the number of k th neighbours and R_k is the corresponding distance. This equation replaces (7) and defines a new $\Delta \bar{n}$. However, the same parametrisation (6) is used. By using equations (5) and (6) and by demanding the relationship $\eta = \beta \eta_2 - \eta_1$ we get for Δn_0

$$\Delta n_0 = \frac{n_0}{12 \gamma_1(s_i)} \exp(\eta s_0) \quad (16)$$

where

$$\gamma_1(s_i) = 1 + \sum_{k=2}^{\infty} \frac{N_k}{12} \exp[(1 - R_k/R_1) \beta \eta_2 s_i] = 1 + \frac{1}{2} \exp[(1 - \sqrt{2}) \beta \eta_2 s_i] + \dots \quad (17)$$

In the general case, when the summation is no longer an ideal FCC sum, the neutral ionic radius for atom i is equation (8) corrected by the factor $\gamma_1(s_i)$:

$$s_i = -\frac{1}{\beta \eta_2} \ln \left(\frac{1}{12 \gamma_1(\bar{s})} \sum_{j \neq i} \exp(-\eta_2 r_{ij}) \right) \quad (18)$$

where \bar{s} is a properly chosen average value of s_i (see below) and the background density is

$$\bar{n}_i = n_0 \left(\frac{1}{12\gamma_1(\bar{s})} \sum_{j \neq i} \exp[-\eta_2(r_{ij} - \beta s_0)] \right)^{\eta/(\eta+\eta_1)}. \quad (19)$$

The atomic-sphere correction is again obtained by demanding that in the ideal FCC lattice it must vanish. This gives

$$E_{AS} = \alpha n_0 \sum_{i=1}^N \left[\left(\frac{1}{12\gamma_1(\bar{s})} \sum_{j \neq i} \exp[-\eta_2(r_{ij} - \beta s_0)] \right)^{\eta/(\eta+\eta_1)} - \frac{1}{12\gamma_2(\bar{s})} \sum_{j \neq i} \exp[-\eta(r_{ij}/\beta - s_0)] \right] \quad (20)$$

where

$$\gamma_2(\bar{s}) = 1 + \sum_{k=2}^{\infty} \frac{N_k}{12} \exp[(1 - R_k/R_1)\eta\bar{s}] = 1 + \frac{1}{2} \exp[(1 - \sqrt{2})\eta\bar{s}] + \dots \quad (21)$$

For the molecular dynamics, the total force acting on a given atom has to be determined. For this purpose, it is useful to write the total energy (2) in the form

$$E_{\text{tot}} = \sum_{i=1}^N E_N(\bar{n}_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} V(r_{ij}) \quad (22)$$

where

$$V(r_{ij}) = -\frac{\alpha n_0}{6\gamma_2(\bar{s})} \exp[-\eta(r_{ij}/\beta - s_0)] \quad (23)$$

is the pair potential and

$$E_N(\bar{n}) = E_C(\bar{n}) + \alpha \bar{n} \quad (24)$$

is the density-dependent many-body potential. The total force acting on atom i is then

$$\mathbf{F}_i = -\nabla_i E_{\text{tot}} = -\sum_{j \neq i} [E'_N(\bar{n}_i) \bar{n}'_i(r_{ij}) + E'_N(\bar{n}_j) \bar{n}'_j(r_{ij}) + V'(r_{ij})] \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}} \quad (25)$$

where the prime in each function means a derivative with respect to the argument of the function in question. The first term is the force coming from the change in density at site i due to the movement of atom i itself. The second term is the force coming from the change in density at neighbouring sites when atom i moves. The third term is the conventional pair force.

The s_i dependence of factor γ_1 causes the theory to have a self-consistency problem. The normal way to overcome this problem would be the iterative solution of s_i and γ_1 for each atom (i.e. in (18) \bar{s} would be s_i). However, this procedure would greatly increase the amount of computation, since for each step of the molecular dynamics equations (17) and (18) would have to be solved separately for each atom. For this reason we have used a faster method: (i) determine the value of γ_1 using the neutral sphere radius s_0 , which is the Wigner-Seitz radius corresponding to the equilibrium

lattice constant at zero temperature; (ii) calculate the average value \bar{s} of s_i using $\gamma_1(s_0)$ from (18); (iii) calculate $\gamma_1(\bar{s})$, $\gamma_2(\bar{s})$ from equations (17) and (21) and use these values for each atom. In this method γ_1 and γ_2 still depend on the average value of s_i and have to be recalculated in each time step of the molecular dynamics. This also means that in expression (22) the pair potential $V(r_{ij})$ depends implicitly on the volume of the system.

The strength of the interactions between atoms falls off exponentially due to the exponential *ansatz* for the induced electron density (6). By calculating the values of exponent functions in equation (14) with different FCC lattice distances one can estimate the extent of the sum over the nearest neighbours in (15). When this is determined, the corresponding γ -factors can be calculated from equations (17) and (21).

In the constant-pressure molecular dynamics simulation the internal pressure of the system has to be calculated in each time step. This can be obtained from the potential in the usual way:

$$P = -\frac{\partial E_{\text{tot}}}{\partial \Omega} \quad (26)$$

where Ω is the volume of the system. Transforming the derivative with respect to volume into the derivative with respect to coordinates of atoms one gets

$$P = -\frac{1}{6\Omega} \sum_{i=1}^N \sum_{j \neq i} [E'_N(\bar{n}_i) \bar{n}'_i(r_{ij}) + E'_N(\bar{n}_j) \bar{n}'_j(r_{ij}) + V'(r_{ij})] r_{ij} + P_\gamma. \quad (27)$$

The first term is of the form $\sum_{i,j} \mathbf{F}_{ij} \cdot \mathbf{r}_{ij}$, which appears, in fact, in the virial theorem of the real gas (Landau and Lifshitz 1970). When the range of interactions is beyond nearest neighbours there is an extra term, P_γ , on the right-hand side of equation (27) arising from the fact that the factors γ_1 and γ_2 depend on the average equilibrium ionic radius \bar{s} and thus on the volume of the system as explained above. In the constant-pressure simulation the volume of the system is continuously fluctuating and this extra pressure term becomes important. In fact, we found that by omitting this term the equilibrium lattice constant of copper at zero temperature would be shortened by a few per cent in the extended model compared to the nearest-neighbour calculations, and the thermal expansion curve would no longer be realistic. The extra pressure P_γ is

$$P_\gamma = -\frac{1}{4\pi N \bar{s}} \sum_{i=1}^N \left(E'_N(\bar{n}_i) \bar{n}'_i(\gamma_1) \gamma'_1(\bar{s}) - \frac{\gamma'_2(\bar{s})}{2\gamma_2(\bar{s})^2} \sum_{j \neq i} V(r_{ij}) \right). \quad (28)$$

This formula is based on the notion that the volume of the system can be written as a sum of N Wigner-Seitz volumes: $\Omega = N \frac{4}{3} \pi \bar{s}^3$, thus the derivative with respect to Ω can be transformed to the derivative with respect to \bar{s} .

3. Thermal expansion and melting of copper

The effect of extending the range of EMT was tested by simulating the thermal behaviour of a copper system by molecular dynamics in the temperature range from 0 K up to the melting point at zero external pressure. We used the constant-pressure simulation method of Parrinello and Rahman (1980, 1981), which allows both volume and shape

fluctuations of the simulation cell. This kind of simulation is a critical test for the stability of the potential model.

The EMT parameters used for copper were (Jacobsen 1988)

$$\begin{array}{lll}
 E_0 = -3.56 \text{ eV} & E_2 = 1.35 \text{ eV} & E_3 = -0.237 \text{ eV} \\
 s_0 = 2.5776 a_0 & n_0 = 0.0115 a_0^{-3} & \eta = 2.50 a_0^{-1} \\
 \eta_1 = 0.25 a_0^{-1} & \eta_2 = 1.52 a_0^{-1} & \alpha = 1490 \text{ eV } a_0^3.
 \end{array} \quad (29)$$

As mentioned in the previous section, the only parameter determined from the experimental data of copper is η_1 . It is estimated from the value of a zone-boundary phonon frequency.

Two sets of simulations were carried out, one with the nearest-neighbour formalism in a cubic cell of 256 atoms and the other with the extended formalism (cut-off between third and fourth neighbours) in a cubic cell of 500 atoms. Periodic boundary conditions were employed in each dimension producing the bulk geometry. The mass parameter of the cell was chosen following the criteria of Andersen (1980), resulting in values of about 1200 amu for the 256-particle cell and 2400 amu for the 500-particle cell. The equations of motion were solved by the predictor-corrector algorithm of Nordsieck (1962) and Gear (1971) with a time step of 3.0 fs. Both sets of simulations were started from low temperatures. The system was equilibrated at each temperature during 2000 time steps (6 ps) and the thermodynamical averages were calculated during the next 2000–4000 time steps (6–12 ps). The equilibrium configuration was a starting point for the next temperature run. The temperature was raised in steps of 50–100 K between subsequent runs until the melting point was achieved.

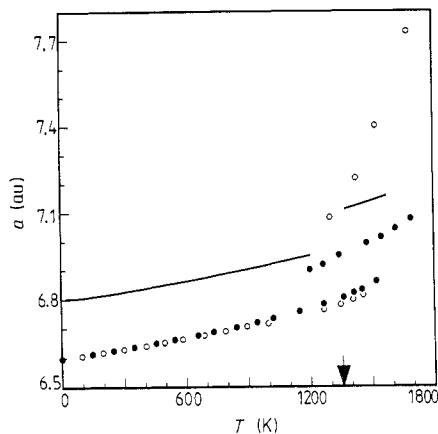


Figure 1. Lattice parameter plotted against temperature for copper. The calculated values with the extended potential are shown by full circles. The open circles show the results for the nearest-neighbour formalism. The experimental temperature dependence of the lattice constant (Fischel *et al* 1972) is shown as a full curve. The experimental curve for the liquid phase (full curve) is plotted on the basis of the measured densities of liquid copper (Weast 1985). The arrow indicates the experimental melting point of 1356 K.

The zero-pressure lattice parameter at each temperature obtained from simulations has been plotted in figure 1 together with the experimental thermal expansion curve (Weast 1985, Fischel *et al* 1972). The numerical data for the lattice parameter are given

in table 1. The lattice parameter a has been calculated from the average volume per atom \bar{v} :

$$a = (4\bar{v})^{1/3}. \quad (30)$$

In this way we can define a ‘lattice parameter’ for the liquid phase also. The nearest-neighbour EMT and the extended EMT give identical thermal expansion at low temperatures. The estimated linear coefficient of thermal expansion at room temperature is $18.1 \times 10^{-6} \text{ K}^{-1}$, which is comparable to the experimental value $(16.7\text{--}17.0) \times 10^{-6} \text{ K}^{-1}$ (Pearson 1967, Fischel *et al* 1972) and the value of $16.4 \times 10^{-6} \text{ K}^{-1}$ obtained from a quasi-harmonic calculation by Foiles and Daw (1988) using the embedded-atom method (EAM). In fact, below the Debye temperature (315 K for copper) the quantum mechanical quasiharmonic approximation is expected to describe the thermal expansion better than the classical molecular dynamics (Ashcroft and Mermin 1976). It is worth noting that the zero-temperature lattice constant differs slightly from the experimental one because it is an *output* of the effective-medium theory, *not* an input as in almost all other potentials used in molecular dynamics or Monte Carlo simulations.

Table 1. Numerical results for the zero-pressure lattice parameter a and the total internal energy per atom E at elevated temperatures in Cu. The maximum standard deviations (occurring at high temperatures) of T , a and E are about 50 K, 0.01 au and 3 meV, respectively.

	Nearest-neighbour model			Extended model		
	T (K)	a (au)	E (eV)	T (K)	a (au)	E (eV)
Solid	1	6.596	−3.560	1	6.596	−3.560
	100	6.606	−3.535	150	6.612	−3.521
	200	6.617	−3.508	250	6.624	−3.493
	300	6.628	−3.482	350	6.636	−3.466
	410	6.640	−3.453	460	6.649	−3.437
	500	6.651	−3.429	550	6.661	−3.412
	580	6.662	−3.404	660	6.676	−3.379
	690	6.676	−3.374	730	6.687	−3.357
	790	6.689	−3.343	840	6.703	−3.324
	890	6.706	−3.310	940	6.720	−3.293
	1000	6.716	−3.295	1020	6.733	−3.268
	1270	6.762	−3.211	1150	6.756	−3.226
	1350	6.779	−3.183	1270	6.782	−3.184
	1410	6.796	−3.157	1360	6.804	−3.147
	1460	6.812	−3.128	1410	6.820	−3.125
			1450	6.831	−3.109	
			1520	6.860	−3.070	
Liquid	1300	7.083	−2.920	1200	6.901	−3.069
	1430	7.219	−2.808	1260	6.919	−3.044
	1520	7.402	−2.711	1340	6.951	−3.008
	1680	7.729	−2.530	1480	6.993	−2.957
				1550	7.014	−2.931
				1620	7.043	−2.901
				1690	7.077	−2.868

Our sample melted at between 1458 and 1522 K in the nearest-neighbour simulation, the corresponding temperature range being from 1522 to 1546 K with the extended

potential. These values contain a statistical uncertainty of about 50 K. The experimental melting point of copper is 1356 K (Weast 1985). Due to the superheating the simulated melting point can be regarded as an upper limit for the true melting temperature. In molecular dynamics simulations with bulk crystals this superheating is usually quite large because, due to the finite system size and simulation time, the probability of creating thermal crystal defects is extremely small. We have found (in the case of aluminium) that the simulated melting temperature of a bulk crystal containing a vacancy is significantly lower than that of an ideal crystal (Häkkinen and Manninen 1989).

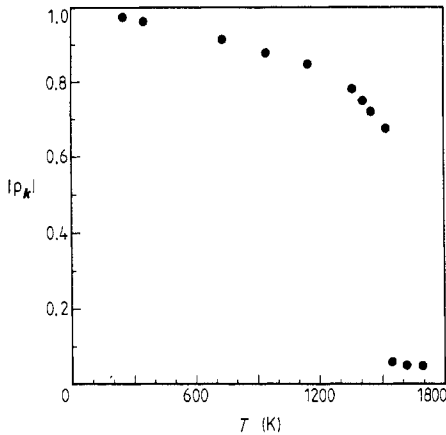


Figure 2. The mean absolute value of the order parameter, $|\rho_k|$, as a function of temperature obtained from the simulations with the extended potential.

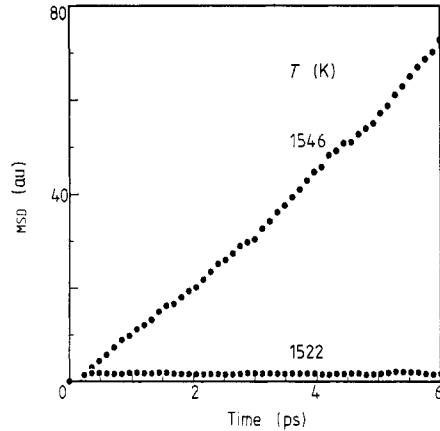


Figure 3. Mean square deviation (MSD) of atoms as a function of time at the temperatures of 1522 and 1546 K obtained from the simulations with the extended potential.

The onset of melting was observed by monitoring the order parameter of the system, the mean square deviation of atoms and the trajectory plots. At each temperature we calculated an order parameter (structure factor)

$$\rho_k = \frac{1}{N} \sum_{j=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_j) \quad (31)$$

where $\mathbf{k} = (2\pi/a)[111]$ is the shortest vector in the reciprocal lattice, \mathbf{r}_j is the position vector of atom j and a is the zero-pressure lattice constant corresponding the temperature in question. The mean absolute value $|\rho_k|$ at each temperature obtained in the simulation with the extended potential is plotted in the figure 2. The sudden fall of $|\rho_k|$ to zero is clear evidence of the complete loss of FCC structure between 1522 and 1546 K. At the same time, the mobility of the atoms is dramatically increased as seen in figure 3, which shows the mean square deviation of atoms as a function of time. The mean square deviation is defined as

$$\langle \Delta r(t)^2 \rangle = \frac{1}{N} \sum_{j=1}^N |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2. \quad (32)$$

The coefficient of self-diffusion can be estimated from the asymptotic time derivative of the mean square deviation curve:

$$\langle \Delta r(t)^2 \rangle \rightarrow 6Dt + \text{constant} \quad \text{as } t \rightarrow \infty. \quad (33)$$

The value obtained at a temperature of 1546 K is about $5.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is a typical value for a liquid phase (Butrymowicz *et al* 1977).

Another way to search for crystalline order in the sample is to calculate the pair correlation function

$$g(r) = \left\langle \frac{V}{N} \frac{n(r, r + dr)}{4\pi r^2 dr} \right\rangle \quad (34)$$

where V is the instantaneous volume of the system, $n(r, r + dr)$ is the number of neighbours in the distance range $(r, r + dr)$ and $\langle \rangle$ denotes an average over atoms and configurations in the molecular dynamics run. However, in figure 4 it is shown that the pair correlation functions just before and after melting are very similar. This is due to the large thermal motion in the crystalline phase before melting. This vibration smears out the clear peaks seen at lower temperatures. The pair correlation function at 1546 K agrees reasonably well with the experimental data of copper measured just above the melting point (Eder *et al* 1980).

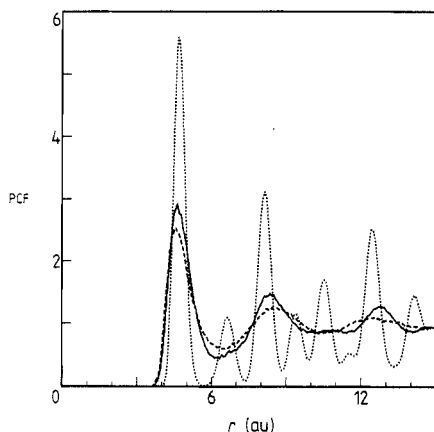


Figure 4. Pair correlation functions (PCF) obtained from the simulations with the extended potential. The full curve is the result for the solid phase at 1522 K, the broken curve is the result for the liquid phase at 1546 K and the dotted curve is the result for the solid phase at 545 K.

It is seen from figure 1 that the extended EMT potential describes the transition from solid to liquid better than the nearest-neighbour EMT formalism. The density change in melting and the coefficient of volume expansion in the liquid state are comparable to the experimental data. The nearest-neighbour formalism gives too large a density change and an unrealistically high value for the volume expansion. This is understandable because, in the liquid state, the neighbours of any given atom are very mobile, and there are large fluctuations in the density if the range of the potential is limited to a value giving the middle point of the first and second neighbours in the *ordered* phase. The large density fluctuations arising from the nearest-neighbour formalism

might also cause the slightly lower melting point compared with that obtained from the simulations using the extended potential model.

The total energy of the system is given in table 1. From the discontinuity at the melting point the heat of fusion of copper in the extended model was estimated to be 0.14 eV per atom, which is the same as the experimental value (Weast 1985). The nearest-neighbour model gives the result of 0.42 eV per atom, which is much too large.

In addition to heating, the system was also cooled down from the liquid state to find out the hysteresis process involved with the first-order phase transitions. However, due to the extremely fast cooling rate, a closed hysteresis loop was not achieved, but the sample also seemed to remain in a liquid phase at the temperatures well below the experimental melting point. With our fast cooling rate it would not be a surprise if an amorphous solid resulted (Laakkonen and Nieminen 1985).

4. Conclusion

We have presented one way of extending the range of the potential derived from the effective-medium theory. This extension was found to be necessary for dynamic simulations at high temperatures and in disordered phases. The validity of our extended model is indicated by the good results obtained from the molecular dynamics simulations of thermal expansion and melting of copper.

Acknowledgments

Discussions with M J Puska, P Stoltze and J K Nørskov are gratefully acknowledged. One of us (HH) wishes to thank the Emil Aaltonen Foundation for financial support.

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