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Abstract. Molecular dynamics studies of the temperature dependent properties of copper have been carried out. The constant pressure and constant temperature (NPT) MD method has been used together with the Finnis–Sinclair many-body potential. On the basis only of the room temperature properties the behaviour of solid and liquid copper over wide temperature range have been simulated and compared with experiment.

1. Introduction

It is well known that any pair potential is insufficient when describing most of the properties of the metallic systems. All pairwise models lead, for example, to the Cauchy relation $C_{12} = C_{44}$, contrary to experiments (e.g., for Cu $C_{12}/C_{44} \simeq 1.5$, for Au about 3.7). Pure pair interactions also imply that the surface relaxes outwards instead of inwards as is observed in experiment. From the theoretical calculation (e.g., Heine and Weaire 1970) it has been found that only few percents of a cohesive energy of a crystal are due to the pair interactions and the dominant fraction must be described by many-body interactions or by a volume dependent part.

The most important failures of the two-body models are summarised in e.g., Ercolessi *et al* 1988. There are a lot of papers analysing various models of interactions overcoming these difficulties. For more recent reviews see e.g., Finnis *et al* 1988, Vitek 1988, Ercolessi *et al* 1988. Maeda *et al* (1982) proposed a potential including an additional, phenomenological volume-dependent term. That potential has been used successfully in describing defects in metals. The method with better justification was proposed by Finnis and Sinclair (1984). Their model (hereafter denoted as FS), a kind of adaptation of the Embedded Atom Method (Daw and Baskes 1984), primarily applied to transition metals (Finnis and Sinclair 1984) and later developed for the noble metals (Ackland *et al* 1987) is used in the present study. In their approach the total energy of a metallic system is composed of a repulsive pair interaction (ion repulsion) and an attractive many-body term, so called 'gluing term', caused by conducting electrons.

There are also calculations from first principles (e.g., Heine and Weaire 1970) and very interesting MD simulations from first principles (Car and Parrinello 1985) but they require huge computing resources.

Even the relatively simple form of the FS potential requires computer numerical analysis for detailed studies. There are two alternative methods; the Monte Carlo (MC) method, in which properties of a system in question are analysed by averaging over

configurations generated in a statistical manner, and the molecular dynamics (MD) methods, in which we establish the system with the proper Hamiltonian, calculate the Hamiltonian equation of motion and calculate the time evolution of the system. Then time averages of various quantities are calculated. It can be shown that such averaging is equivalent to averaging over ensembles, provided the correct form of the Hamiltonian has been chosen. The problem lies in finding the Hamiltonian that generates the required statistical ensemble.

Andersen (1980) put forward the idea of the MD method equivalent to the NPE ensemble. This method is applied in the present study but is modified by introduction of the constant temperature technique proposed by Nosé (1984). The Andersen method has been applied to metals by e.g., Walker *et al* (1986), and to the study of the melting and freezing of argon by Chokappa and Clancy (1987a, b). In the latter case only a pair (Lennard-Jones) potential was used.

Because the aim of this paper is to study the temperature dependent properties of pure copper in the solid and liquid states, the volume change should be taken into account, so the NPT method is applied.

2. Interactions

Total energy of system U is composed of a standard pair term and a many-body term

$$U = \tfrac{1}{2} \sum_i \sum_j{}' u(R_{ij}) - \sum_i f\left(\sum_j{}' \varphi(R_{ij})\right) \tag{1}$$

where $u(R)$ is a central pair potential and f, φ are functions describing many-body interactions. Summations are carried out over all atoms. The many-body term is a version of the Embedded Atom Method (Daw and Baskes 1984) proposed by Finnis and Sinclair (1984). The extensive discussion of formula (1) is performed in Ackland *et al* (1987) and will not be repeated here.

The many-body term can be also interpreted as a local, local-configuration-dependent, pair potential. The effective potential of the interaction of atoms i and j can be approximated as (when ignoring second and higher order derivatives of f)

$$u_{\mathrm{eff}\,ij}(R_{ij}) = u(R_{ij}) - \left(f'(k_i) + f'(k_j)\right)\varphi(R_{ij}) \tag{2}$$

where

$$k_i = \left(\sum_j \varphi(R_{ij})\right). \tag{3}$$

All further calculations are classical, the quantum effects being included in the above form of the potential. It is also assumed that the potentials are temperature and structure independent. The main advantage of the FS formalism is that, in spite of the fact that potentials are more accurate and much better justified than any pair potentials, the increase in calculation time is relatively small. It should be noted that Daw and Baskes (1984) method has been also applied for liquid metals (Foiles 1985).

3. Molecular dynamics method

In order to study any temperature-dependent property (especially phase transformations) traditional NVE methods (with a constant number of particles, volume and

internal energy) are not very good. The NPT (constant number of particles, pressure and temperature) approach generates typical experimental conditions and is more suitable for studying phenomena with volume changes like melting.

The constant pressure method was derived by Andersen (1980) and later developed by Parrinello and Rahman (1980, 1981) for changes even in cell shape. The Parinello and Rahman method has been used for metallic system by Walker *et al* (1986). It was proved that the Hamiltonian in which the computational cell size L is an additional variable generates the NPH (with constant enthalpy) ensemble (to within an accuracy of $1/N$).

The Hamiltonian leads to equations of motion for particles and L. Using the correspondence between the real and scaled systems, the trajectories in the real system can be evaluated. The Andersen method has been recently criticised (Cleveland 1988), but the criticism concerns only the case with great changes in the shape of a computational cell, so does not apply to the system analysed here.

The second difficulty in the molecular dynamics studies is how to keep temperature constant. The simplest and earliest method is a momentum scaling procedure (e.g., Woodcock 1971), in which the velocities are scaled at each iteration step to maintain kinetic energy constant. But in this way any fluctuations of the total kinetic energy are suppressed. Andersen (1980) proposed the combination of MD and MC methods, in which particles velocities were randomly changed by stochastic collisions. In this method trajectories in phase space are discontinuous.

The comparison of various methods (including the 'damped force method' used by Chokappa and Clancy 1987a, b in their studies) was carried out by Brown and Clarke (1984) but later Nosé (1984) unified formulations of constant temperature methods. In his method the canonical distribution both in coordinate and momentum space is generated. He introduced in his approach, which is similar to Andersen's method of scaling coordinates, the additional degree of freedom s and the Hamiltonian contains an additional term

$$\Pi_s^2/2Q + gkT \ln s \qquad (4)$$

where k is Boltzmann's constant, Π_s the conjugate momentum, Q the pseudo-mass and $g = 3N, 3N + 1, 3N - 1$ depending on the calculation method. The second term in (4) works as a heat reservoir, s being a quantity which scales time, so the total Hamiltonian has the following form:

$$H(\boldsymbol{q}_i, \boldsymbol{p}_i, L, \Pi_L, s, \Pi_s) = \frac{1}{2mL^2s^2} \sum_i \boldsymbol{p}_i \boldsymbol{p}_i + \tfrac{1}{2} \sum_i \sum_j{}' u(L\boldsymbol{q}_{ij}) + \frac{\Pi_L^2}{2W} + pL^3$$

$$- \sum_i f\left(\sum_j{}' \varphi(L\boldsymbol{q}_{ij})\right) + \frac{\Pi_s^2}{2Q} + gkT \ln s \qquad (5)$$

where the correspondence between real (r, π, t) and scaled (q, p, τ) variables is

$$\boldsymbol{r}_i = L\boldsymbol{q}_i$$
$$\boldsymbol{\pi}_i = \boldsymbol{p}_i/Ls \qquad (6)$$
$$t = \int \frac{\mathrm{d}\tau}{s}.$$

In formula (5) Q, W are the pseudo-masses associated with s and L, respectively, Π_L, Π_s are the conjugate momenta and m the mass of particles.

Nosé proved that the logarithmic form of the term containing s is essential for generating the canonical ensemble. The Hamiltonian equations of motion in virtual variables are

$$\dot{q}_i = \partial H/\partial p_i = p_i/mL^2s^2$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} = -L\sum_j{}' \, [u'(Lq_{ij}) - \varphi'(Lq_{ij})\{f'(k_i) + f'(k_j)\}] \frac{q_{ij}}{|q_{ij}|}$$

$$\dot{s} = \partial H/\partial \Pi_s = \Pi_s/Q$$

$$\dot{\Pi}_s = -\frac{\partial H}{\partial s} = \frac{1}{s}\left[\sum_i p_i^2/mL^2s^2 - gkT\right] \tag{7}$$

$$\dot{L} = \partial H/\partial \Pi_L = \Pi_L/W$$

$$\dot{\Pi}_L = -\partial H/\partial L = \frac{1}{mL^3s^2}\sum_i p_i^2 - \frac{L}{2}\sum_i\sum_j{}' \, [u'(Lq_{ij}) - \varphi'(Lq_{ij})\{f'(k_i) + f'(k_j)\}]$$

$$\times \, (q_{ij})^2 - 3pL^2.$$

When (7) with (6) are used to generate trajectories, the time averages of any intensive quantity correspond to the system with pressure p and temperature T.

Of course the MD method cannot be applied for studying a phase transformation itself (mainly because of limited computational cell size which limits the correlation length) but can be used for determining equilibrium states at temperatures close to the critical one.

4. Potentials

The potentials from Ackland *et al* 1987 were used and copper has been chosen as a test system. The potentials were assumed to have a form (after Ackland *et al* 1987)

$$f(\varphi) = \sqrt{\varphi} \quad \text{(results from tight bonding theory of cohesion} \atop \text{and discussed fully in Ackland's paper)}$$

$$u(r) = \sum_{k=1}^{6} a_k(r_k - r)^3 H(r_k - r) \tag{8}$$

$$\varphi(r) = \sum_{k=1}^{2} A_k(R_k - r)^3 H(R_k - r)$$

where

$$H(x) = \begin{cases} 0 & x < 0 \\ 1 & x > 0. \end{cases}$$

There is no cut-off radius as usually used for the standard Lennard-Jones potential and derivatives are always continuous. This is a great advantage of the above potentials, from the point of view of numerical calculations as well as physical interpretation, over the standard Lennard-Jones potential with the cut-off radius used usually (e.g., Verlet 1967, Rahman and Clancy 1964, Chokappa 1987a, b). For calculating the values of parameters $a_1, \ldots, a_6, A_1, A_2$ the following experimental quantities were used: lattice
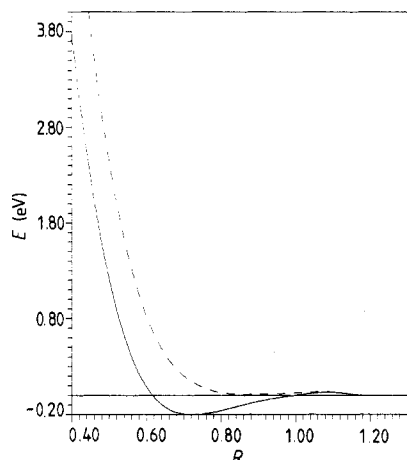
Figure 1. Pair potential (-----) and effective pair potential in ideal FCC (———) for copper.
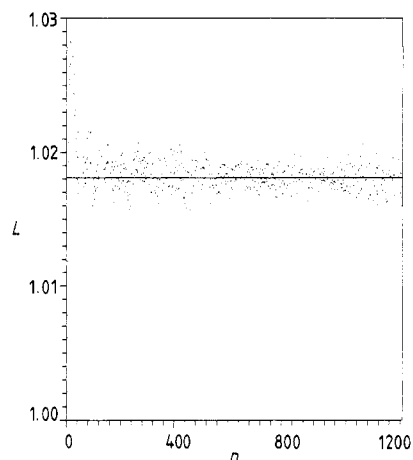

Figure 2. Dependence of L on number of iteration steps n at $T = 1200$ K.

constant, cohesive energy, elastic constants, vacancy formation energy, stacking fault energy and the pressure–volume relation. The detailed description of the method of fitting and the values of parameters can be found in Ackland *et al* (1987). They used experimental data at room temperature without using the temperature dependence of any quantity. I have not modified their parameters by using data at 0 K, mainly because not all data are available and the change in values from 0–300 K is rather small. I also prefer to use original Ackland potential and verify its applicability.

The shape of $u(r)$ is presented in figure 1 together with effective pair potential corresponding to ideal FCC structure (with no atomic displacement from lattice sites) calculated according to (2).

5. Calculations

The equations of motion were integrated using the modified 'leap-frog' algorithm. The mass of particles was equal to the mass of copper atoms, parameter W was set to 20 (in reduced units); other values were also tried but calculations are weakly influenced by this value; the wide analysis of various factors influence on MD results was carried out by Chokappa and Clancy (1987a). In the further calculations and plots the length unit equal to the lattice constant at 0 K is used. In Ackland *et al* (1987) they did not take into account kinetic contribution so one should use experimental data at 0 K. The time step used in calculation was 10^{-14} s. Trajectories of 256 (in some cases 864) copper particles were calculated using the periodic boundary conditions; in this way the behaviour of an infinite set of atoms having no surface is simulated. At any temperature the initial configuration had a pure FCC structure without any displacement from lattice sites with a random velocity distribution corresponding to the required temperature. The starting value of L was 1.

A simulation at any given temperature consisted of an 'equilibrisation' during about 1000 time steps followed by runs of 2000–20 000 time steps when time averages of various quantities were calculated. I did not find any large difference in results obtained using the Nosé method and simple scaling velocities. For reasons of numerical convenience the first equilibrisation at any temperature was conducted using only scaling of velocities;
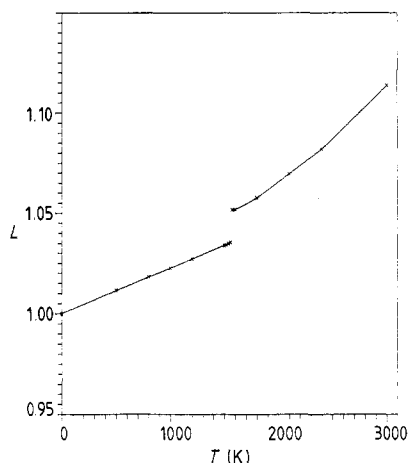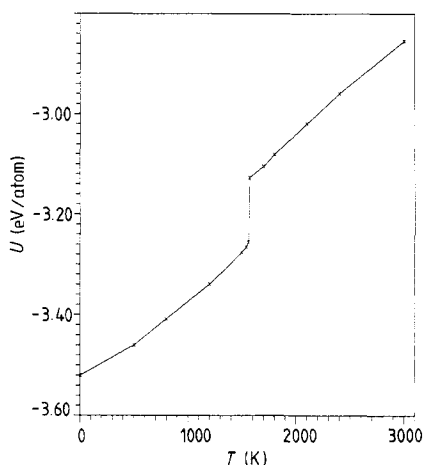
Figure 3. Dependence of L on temperature T.

Figure 4. Dependence of U on temperature T.

if the analysed system is far from equilibrium, the Nosé method results in very high temperature fluctuations. After reaching equilibrium the Nosé method was used to give the correct canonical distributions. The final results do not depend on number of particles. When comparing the simulation of 256 and 864 particles the only weak difference is in fluctuations range, whereas the increase in calculation time is considerable.

6. Results and discussion

In figure 2 the typical dependence of L on the number of iteration steps is presented. The equilibrium value of L is reached after about 20 steps and after this L oscillates around its equilibrium value.

In figure 3 the temperature dependence of L is shown and in figure 4 the temperature dependence of U. The well marked phase transition is visible at about 1565 K.

The radial distribution functions (figures 5 and 6) corresponding to selected temperatures indicate clearly (contrary to results reported by Chokappa and Clancy (1987a), who did not find any rapid changes in $g(R)$ on melting) that melting does occur. For comparison the $g(r)$ for ideal FCC is shown in figure 5(a). The melting does not correspond to the rapid changes in all peaks in the distribution function. From 0 K up to 3000 K there is a continuous broadening of the peaks but at the analysed transition peaks corresponding to the second and fifth coordination cells in FCC disappear very rapidly between 1560 and 1570 K. There is also a rapid change in volume (figure 3) and in internal energy (figure 4). The radial distribution function above 1570 K has the usual shape for liquids (e.g., Hansen and McDonald 1976). Of course for a purely random distribution of atoms g should be always equal to 1.

From figure 3 the thermal expansion coefficient for the solid phase and the liquid just after melting can be derived (for higher temperature volume is not a linear function of temperature). Also the volume change on melting and the heat of melting can be calculated. Using the Einstein relation for diffusion coefficients

$$D = \lim_{t \to \infty} \langle r^2 \rangle / 6t \tag{9}$$

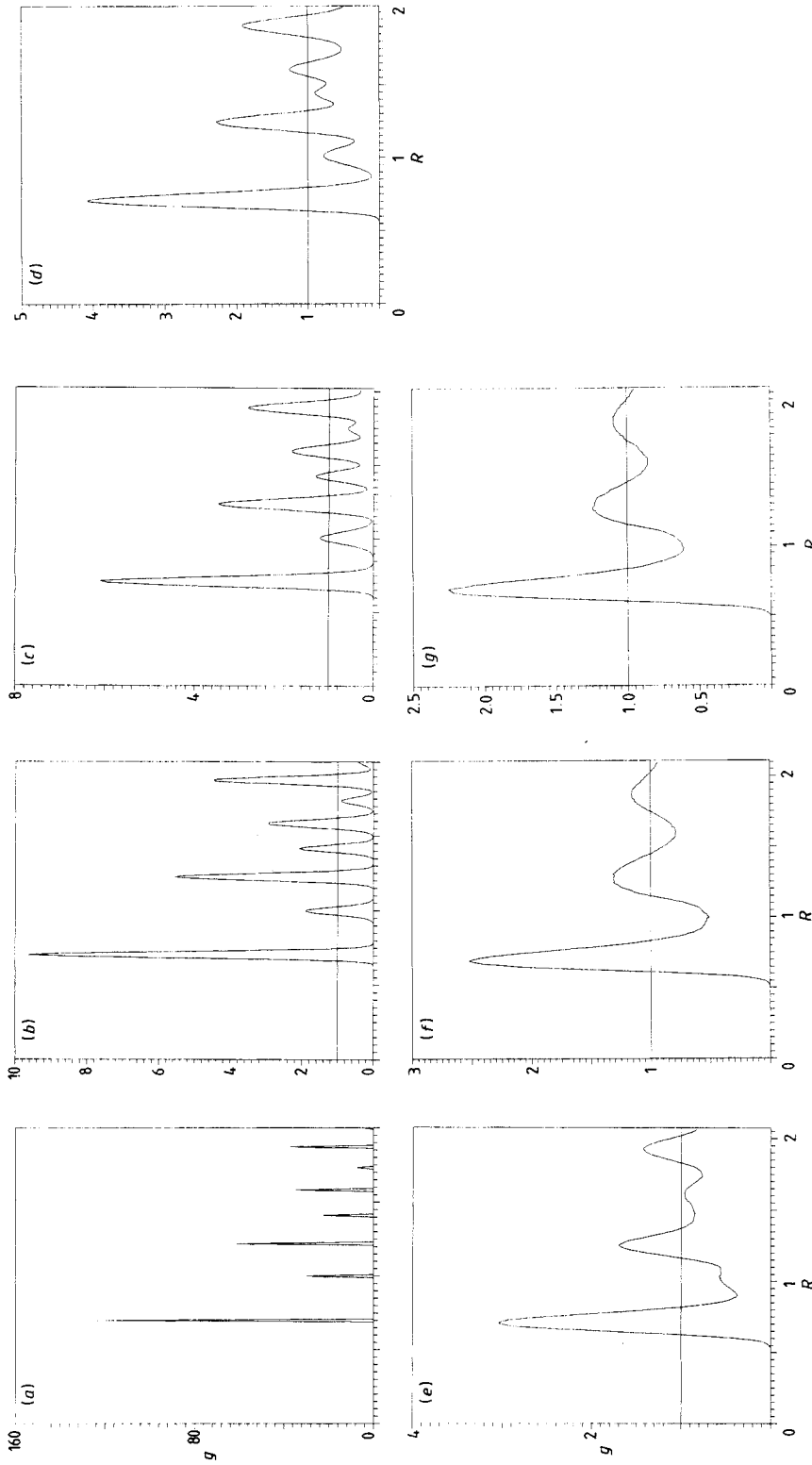the diffusion coefficients for the liquid were calculated (for the solid phase diffusion is

Figure 5. Radial distribution functions (*a*) for ideal FCC structure (*T* = 0 K) and (*b*)–(*g*) at selected temperatures (*b*) *T* = 200 K, (*c*) *T* = 500 K, (*d*) *T* = 1000 K, (*e*) *T* = 1560 K, (*f*) *T* = 1570 K, (*g*) *T* = 2100 K.
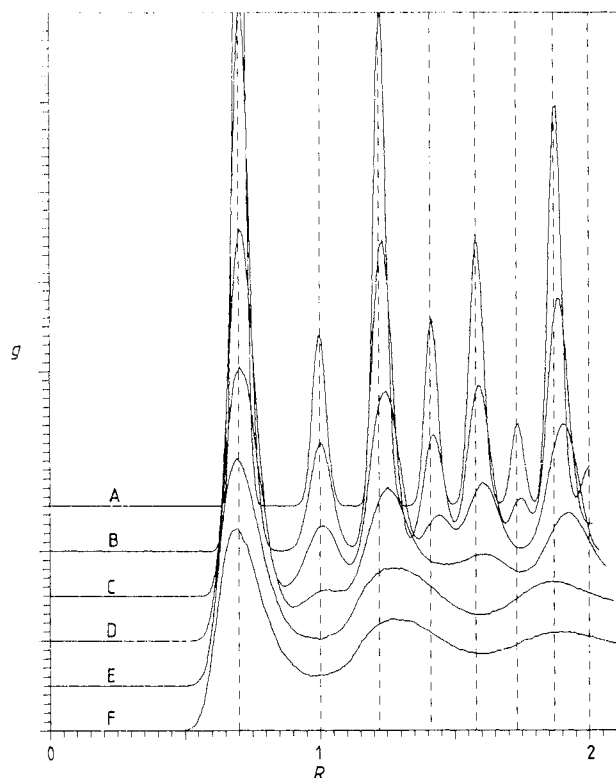
Figure 6. Collected radial distribution functions at various temperatures. The broken lines denote coordination zones for ideal FCC at 0 K. Curve A, $T = 200$ K; curve B, $T = 500$ K; curve C, $T = 1000$ K; curve D, $T = 1560$ K; curve E, $T = 1570$ K; curve F, $T = 2100$ K.

Table 1. Simulated and experimental data for copper.

Quantity		Exp.	MD
Thermal expansion (solid)	$(\times 10^{-6})$	17.0[a]	22
Thermal expansion (liquid)	$(\times 10^{-4})$	1.0[b]	1.3
Volume change on melting	(%)	4.4[b]	4.4
Melting temperature	(K)	1356[c]	1565
Heat of melting	(kJ mol^{-1})	13[c]	13
Activation energy of self diffusion in liquid	(kJ mol^{-1})	40[d]	50

[a] Brandes (1983)
[b] Faber (1972)
[c] Chase (1983)
[d] Henderson and Yang (1961) (but for another temperature range)

too slow to carry out such an analysis). From the $\ln D$ versus $1/T$ plot (figure 7) the activation energy for the diffusion in liquid was calculated. All these data are collected in table 1 together with corresponding experimental values.

The main disagreement with the experimental data is the value of the melting temperature. The model predicts a temperature about 15% too high. The same effect has been reported for argon by the molecular dynamic studies using the LJ potential (Chokappa and Clancy 1987a). It could have been caused by the lack of a surface in MD
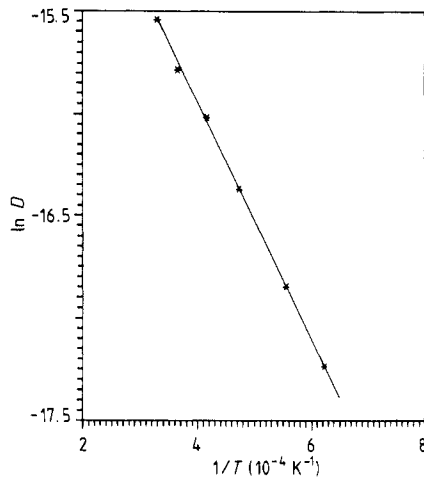
Figure 7. ln D versus $1/T$, where D is the diffusion coefficient calculated from mean square displacement.

calculations. The temperature resulting from MD studies is rather the temperature of mechanical instability of the system in question. Similar overheating results from MD studies of Ag, Au, Ni (Holender 1990a).

The fact that such overheating is due to the MD method is also justified by MD simulations of systems with a free surface (Holender 1990b). It has also been shown experimentally that under special conditions (elimination of free surface influence) metal could be overheated.

7. Summary

It can be concluded that Finnis' many-body potential combined with Andersen's molecular dynamic method gives a quite good description of the properties of copper in the solid as well as the liquid state.

It should be stressed once more that the potential parameters were derived without taking into account any temperature dependence of the physical properties and the main task of the paper was to show the applicability of the FS potential in analysing the temperature dependent behaviour of physical properties.

The present work illustrates the usefulness of the MD method for studying properties of metals. Even though used potentials are not derived from first principles, the MD method may not only explain some experimental results but also give some understanding of complex phenomena on an atomic scale (e.g., melting and thermal expansion in this study, the diffusion mechanism (Doan 1988)).

Acknowledgments

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