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Molecular-dynamics study of thermodynamical properties of liquid copper

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We have performed molecular-dynamics calculations of the heat capacities C_P and C_V, and the thermal expansion and compressibility of liquid copper up to about 3300 K, using an interaction based on an embedded-atom approach. Our calculations confirm the experimental result for some other liquid metals, that C_P is essentially independent of the temperature, while C_V decreases with temperature and extrapolates to approximately $2k_B$/atom well above the melting temperature. [S0163-1829(96)07645-X]

I. INTRODUCTION

The heat capacity C_P of liquid metallic elements, well above their melting temperature T_m, is a poorly known quantity. When C_P is at all available from experiments, it is usually known only in a small temperature range immediately above T_m, except for some metals (Hg, Li, Na, K, Rb, Cs, Pb, Ga) with low T_m. Less accurate thermophysical measurements, but up to very high temperatures ($<10\,000$ K), have been performed by several groups using the technique with rapid heating of wires through capacitor discharges. Pottlacher, Kaschnitz, and Jäger[1] report measurements of the enthalpy $H(T)$ in the liquid state over wide temperature ranges for W, Re, Ta, Mo, Nb, Fe, Co, Ni, Cu, Pb, and In. Within the experimental uncertainty, $C_P=\partial H/\partial T$ is then found to be independent of T (except for Ta). Tables of recommended data[2,3] often give C_P as independent of T, or with a shallow minimum near about $2T_m$, but in many cases without adequate experimental support. Brown and Adams[4] performed molecular-dynamics calculations on Cu, which are in many respects similar to those of the present paper. Their emphasis lies mainly on the amorphous state but they also find $H(T)$ being linear in T in the liquid phase. Related calculations by Foiles and Adams[5] on liquid Cu, Ag, Au, Ni, Pd, and Pt give the Gibbs energy near the melting temperature but no discussion of the heat capacity.

The indications of an almost temperature-independent C_P in a wide temperature range above T_m contrasts sharply with the behavior of C_P in the solid phase, and of C_V in the liquid phase. In the solid, anharmonicity causes C_P to increase steadily above the Dulong-Petit value of $3k_B$/atom. Even C_V in the solid may significantly deviate from $3k_B$/atom,[6] contrary to a widespread belief that anharmonicity does not significantly affect C_V.

For liquid Hg, Na, and K, $C_V=C_P-\beta^2VTB$ has been calculated[7] up to about $3T_m$ from experimental values for C_P, the thermal expansion coefficient β, and the bulk modulus B. It was found that C_V extrapolates to approximately $2k_B$/atom at high temperatures. Qualitatively, this can be understood as resulting from the loss of two degrees of freedom, corresponding to the potential energy of shear vibrations. A formal theoretical analysis[8] confirms this result, but no theoretical calculation seems to have been performed at high T for a real metal.

Motivated by the meager experimental and theoretical knowledge of liquid heat capacities of metals at high temperatures, this paper presents a molecular-dynamics calculation of C_P and C_V in copper.

II. THE EAM POTENTIAL FOR COPPER

The embedded-atom method (EAM) is a semiempirical model for the potential energy of metals, introduced by Daw and Baskes,[9,10] which has turned out to be particularly suitable for describing transition elements at or near the filling of the d shell. This method expresses the total energy of a system of atoms in a specific arrangement as a functional of the total electron density. Cohesion is seen as mainly originating from the energy gain in the embedding of an atom in the electron gas of the neighboring atoms. The repulsion is taken into account by a short-range pair term parametrized in a way appropriate for fitting to experimental data. Then the total energy can be written as

$$E_{\mathrm{tot}}=\sum_i F_i(\rho_{h,i})+\tfrac{1}{2}\sum_{i,j}\phi_{ij}(R_{ij}). \tag{1}$$

F_i is the embedding energy of atom i in the host electron density $\rho_{h,i}$ at the position of this atom and coming from the other atoms in the system, ϕ_{ij} is the pair interaction representing the core-core repulsion, and R_{ij} is the distance between atoms i and j.

The main assumption is now that every atom contributes a spherically averaged electron density $\rho_i^a(r)$, taken to be the single atom electron density,[11] to the total density. The host density $\rho_{h,i}$ is a superposition of the individual atomic electron densities,

$$\rho_{h,i}=\sum_{j\neq i}\rho_j^a(R_{ij}). \tag{2}$$

It remains to introduce a model for the embedding function and the pair interaction in order to construct a practical computational scheme. We have mainly used the scheme proposed by Foiles, Baskes, and Daw,[12] except for very small modifications. In this scheme, one determines the form of $F(\rho)$ by using the universal function proposed by Rose *et al.*[13] for the sublimation energy of metals as a function of the lattice constant at their equilibrium configuration (here

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fcc for Cu). In this way one can deduce the charge density at the fcc lattice sites for different lattice constants and put the value of the embedding function at this particular ρ equal to the sublimation energy of Rose *et al.* at the corresponding lattice constant.

The pair interaction term $\phi_{AB}(R)$ between two atoms A and B, separated a distance R, is assumed to be of the form of a Coulomb interaction between two effective charges:

$$\phi_{AB}(R)=Z_A(R)Z_B(R)/R. \tag{3}$$

In our monatomic case we let the effective charges have the simple parametrized form

$$Z(R)=Z_0(1+\beta R^{\nu})e^{-\alpha R}. \tag{4}$$

Z_0 is the number of outer electrons of the Cu atom, i.e., $Z_0=11$. The parameters $\alpha=1.069$ Å, $\beta=-0.283$, and $\nu=0.821$ were determined by fitting our model to the elastic constants C_{11}, C_{12}, and C_{44} and one-vacancy formation energy E_v^f, using the experimental values of Ref. 12. The difference between the input values and our fit is $<0.5\%$.

III. MOLECULAR-DYNAMICS SIMULATIONS

Our aim is to simulate liquid copper at constant pressure and at temperatures ranging from T_m to about $3T_m$. Thus we have performed a series of standard molecular-dynamics (MD) simulations using microcanonical ensembles in a box of 500 particles, while equilibrating to obtain the desired average temperatures at a constant average pressure $P\approx 0$. The series of simulations was arranged in such a way that the liquid phase is achieved by preparing a system at 2500 K, i.e., well above the melting temperature. Then the temperature is successively raised towards 3300 K or decreased towards 1400 K with steps of 200 K.

The interactions between the particles were modeled using the EAM, which yields simple and efficient expressions for the forces between the atoms[10] in spite of the many-body character of the total energy, Eq. (1). In these calculations we have cut off our interaction potential at a range of 7.5 a.u. where the forces are negligibly small.

The actual MD simulations were performed by integrating the equations of motions with a time step $\Delta t=5$ fs for an overall interval of 100 000 Δt. The simulations start with an equilibration period of 10 000 Δt where the desired temperature is achieved by *ad hoc* rescaling of the particle momenta.[14] Also during this period we find the equilibrium volume of the box by trying to obtain zero average pressure through coupling to an external bath through *ad hoc* rescaling of the particle positions.[15] After, the equilibration period follows an interval of 20 000 Δt when the temperature and the mechanical baths are uncoupled. If the average temperature or pressure deviates too much from its desired value, the equilibration procedure is started all over again.

IV. RESULTS

A. Static structure

In previous studies the liquid state has usually been explored using pair potentials. The EAM, although having been primarily developed for the solid phase, has also been successfully used in liquid simulations.[16] We therefore check the accuracy of our EAM in the liquid regime by considering the static structure factor $S(k)$, before drawing conclusions about other physical properties of our system.

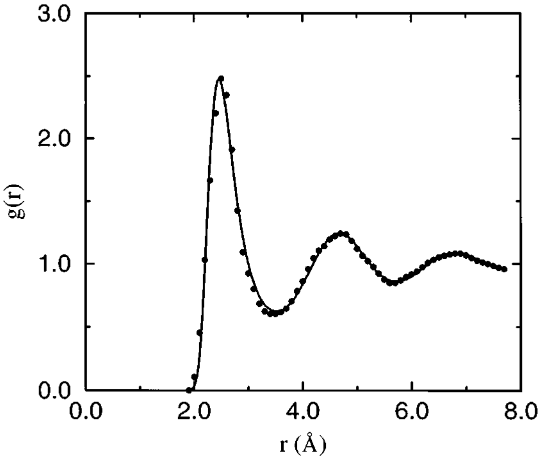

FIG. 1. Pair correlation function $g(r)$ at 1773 K. The solid line shows the simulated results and the circles are experimental values (Ref. 18).

The pair correlation function $g(r)$, which is related to $S(k)$ by

$$S(k)=1+\frac{N}{V}\int [g(r)-1]e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}, \tag{5}$$

is the quantity that is directly obtained through MD. In the experimental literature[18] $g(r)$ has been derived from $S(k)$ and tabulated for liquid Cu at three different temperatures. Figure 1 shows that our results agree very satisfactorily with the experiments.

B. Melting temperature

Due to the finite size of our system, a single melting temperature is not expected to be found. A hysteresis will be observed if we first decrease the temperature of the liquid towards solidification and then raise the temperature of the solid to obtain melting. In this work we are mainly interested in the liquid phase of copper and only briefly report on our simulated solidification. The melting temperature we get is an underestimation of what one would obtain in the thermodynamic limit. Comparison with the experimental melting temperature should still give an indication of the accuracy of our interaction potentials and simulations.

Melting is a first-order phase transition leading to discontinuities in the derivatives of the thermodynamical quantities, e.g., C_V. This is observed in our simulations at $\sim$1370 K to be compared with the experimental[2] melting temperature of 1358 K, i.e., a very satisfactory result.

C. Heat capacity at constant pressure

The enthalpy is obtained as the average

$$\langle H\rangle=\langle U\rangle+\langle P\rangle V. \tag{6}$$

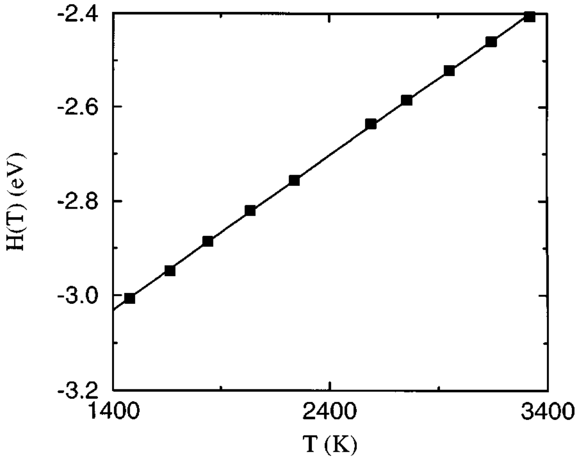

FIG. 2. Enthalpy per particle H as a function of temperature. The squares denote the simulated values. The solid line is a first-order polynomial fit, $H(\tau)=-3.491+3.813\tau$, where $\tau=k_BT$ is in units of eV.

Figure 2 shows that $H(T)$ from our calculation for Cu is linear in T. The corresponding heat capacity is $C_P=\partial H/\partial T=3.813Nk_B=31.65$ J/(K mol). The JANAF tables[2] give $C_P=32.844$ J/(K mol).

However, the experimental heat capacity also includes an electronic contribution, which for Cu should be well given by $C_{P,\mathrm{el}}\approx C_{V,\mathrm{el}}\approx\gamma_{\mathrm{el}}T\approx(2\pi^2/3)N(E_F)k_B^2T$. The electron density of states $N(E_F)$ at the Fermi level E_F of the liquid state is not known. We crudely approximate γ_{el} by its value in the solid phase[19] obtained at low T, but divided by 1.15 to account for an electron-phonon interaction[20] which is absent at high T, and take $\gamma_{\mathrm{el}}=0.6$ mJ/(mol K^2). Our molecular-dynamics calculation should be compared with the experimental $C_P-\gamma T$. Then from the JANAF tables, $C_P-\gamma T=31.6$ J/(K mol) at 2000 K, in excellent agreement with our value 31.65 J/(K mol).

D. Heat capacity at constant volume

The heat capacity at fixed volume, C_V, is obtained from fluctuations in the temperature T through the thermodynamic relation[17]

$$\frac{\langle T^2\rangle-\langle T\rangle^2}{\langle T\rangle^2}=1-\frac{3Nk_B}{2C_V}. \tag{7}$$

The result, together with a second-order polynomial fit, is shown in Fig. 3. The asymptotic approach towards $2k_B$/atom, as required by theory[8] and observed for some low-melting metals,[7] is very well reproduced. In this context, one should note that heat capacity "at constant volume" when evaluated as $C_P-\beta^2VTB$ does not refer to a fixed volume which is independent of T, but to zero incremental volume for each temperature. The difference is not always negligible, as shown, e.g., for solid W.[6]

E. Compressibility and thermal expansion

Figure 4 shows the dependence of the volume of our system on temperature at $P\approx0$. By fitting a second-order polynomial form, we can calculate the coefficient of thermal expansion $\beta_P=(1/V)(\partial V/\partial T)_P$ shown in Fig. 5.

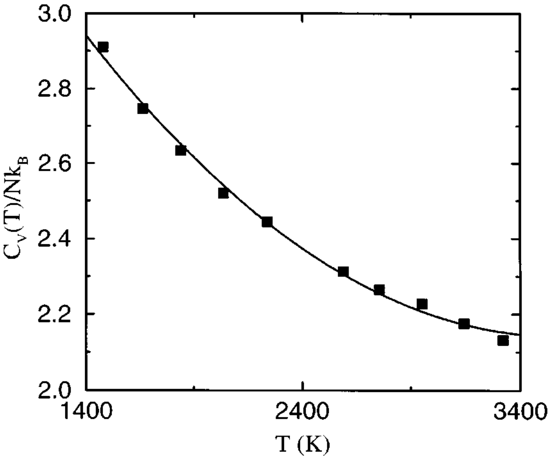

FIG. 3. Constant volume heat capacity C_V as a function of temperature. The squares denote the simulated values. The solid line is a second-order polynomial fit, $C_V(\tau)=4.306-14.08\tau+22.88\tau^2$, where $\tau=k_BT$ is in units of eV.

The thermal pressure coefficient $\gamma_V=(\partial P/\partial T)_V$ is obtained from our calculation through the fluctuation formula[17]

$$\frac{\langle PV\tau\rangle-\langle PV\rangle\langle\tau\rangle}{\langle\tau\rangle^2}=1-\frac{3V\gamma_V}{2C_V}, \tag{8}$$

where $\tau=k_BT$.

This quantity could also be calculated from the following thermodynamic relation:

$$\gamma_V=\frac{C_P-C_V}{\beta_PVT}. \tag{9}$$

Figure 6 illustrates the agreement between these two different approaches.

The isothermal compressibility $\kappa_T=-(1/V)(\partial V/\partial p)_T$ obeys the relation

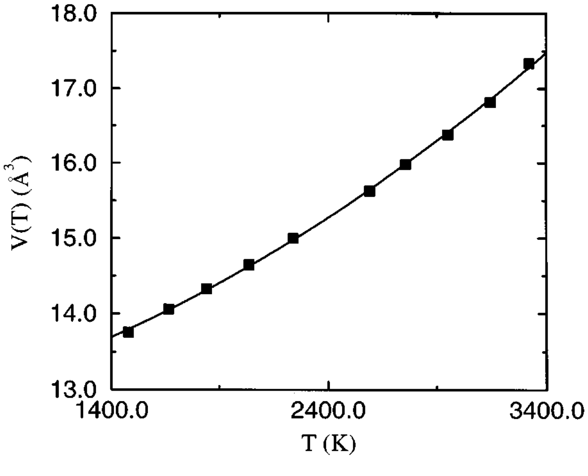

FIG. 4. Volume per particle V as a function of temperature. The squares denote the simulated values. The solid line is a second-order polynomial fit, $V(\tau)=12.51+4.787\tau+41.61\tau^2$, where $\tau=k_BT$ is in units of eV.

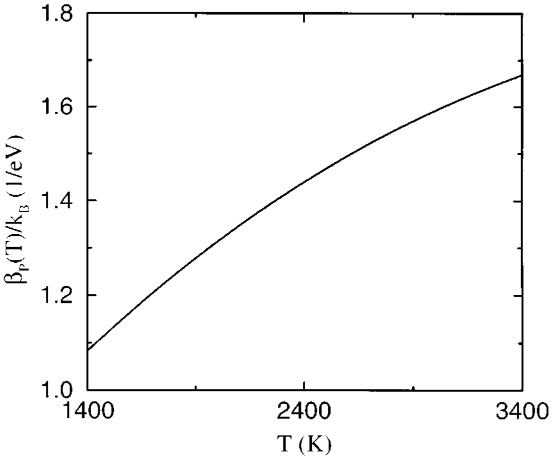

FIG. 5. The coefficient of thermal expansion β_P as a function of temperature.

$$\beta_P = \gamma_V \kappa_T. \tag{10}$$

κ_T is also related to the value of the structure factor at zero wave vector through the formula[21]

$$S(0) = \frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle^2} = \frac{N}{V} k_B T \kappa_T. \tag{11}$$

$S(0)$ is a difficult quantity to obtain since it involves, according to Eq. (5), an integration of $g(r)$ over all space. Therefore we have used the direct correlation function $c(r)$ to determine S(k). This procedure is more accurate because of the short-range nature of $c(r)$. The relations to use are[21]

$$h(r) = g(r) - 1, \tag{12}$$

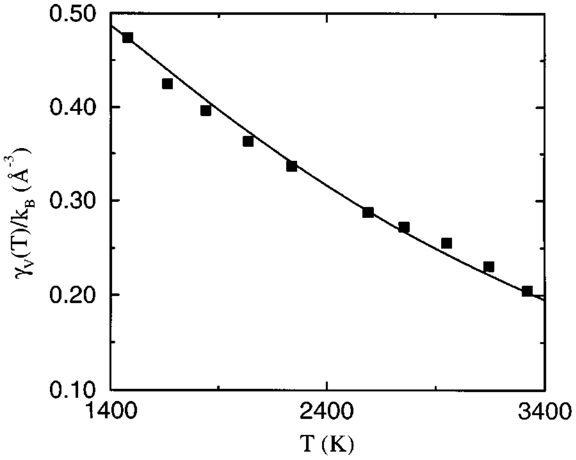

FIG. 6. The thermal pressure coefficient γ_V as a function of temperature. The squares denote the simulated values. The solid line is calculated from the thermodynamic relation (9) described in the text.

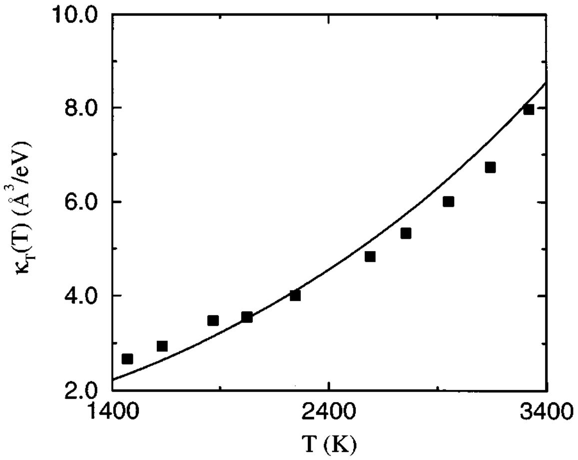

FIG. 7. The isothermal compressibility κ_T as a function of temperature. The squares denote the simulated values. The solid line is calculated from the thermodynamic relation (10) described in the text.

$$h(r) = c(r) + \frac{N}{V}\int h(|\mathbf{r}-\mathbf{r}'|)c(r')d\mathbf{r}', \tag{13}$$

$$S(k) = \left(1 - \frac{N}{V}\hat{c}(k)\right)^{-1}, \tag{14}$$

where $\hat{c}(k)$ is the Fourier space representation of the direct correlation function $c(r)$.

We solve the integral equation for $c(r)$ using the method devised by Baxter.[22,17] Figure 7 shows the agreement between the two methods to determine the compressibility, which are outlined above.

V. CONCLUSIONS

In conclusion, our theoretical calculations for Cu confirm the previous uncertain experimental finding that the heat capacity C_P of liquid Cu, like that of several other liquid metals, is essentially independent of the temperature in a wide temperature range above the melting temperature. The calculated value of C_P is in excellent agreement with experimental data (difference $<1\%$) that are available for Cu near its melting temperature. Our calculations also show that C_V of liquid Cu well above the melting temperature extrapolates towards approximately $2k_B$/atom, in agreement with a qualitative theory and with experiments for some low-melting metals. We get a pair correlation function $g(r)$ in the liquid, and a melting temperature, in good agreement with experiments. Two different simulation routes to $C_P - C_V$, one of them invoking the isothermal compressibility, the thermal expansion coefficient, and the thermal pressure coefficient, give very similar results, which lends further credibility to our results.

ACKNOWLEDGMENTS

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