Vibrational contribution to thermal transport in liquid cooper: Equilibrium molecular dynamics study

Alexander V. Evteev *, Leila Momenzadeh, Elena V. Levchenko, Irina V. Belova, Graeme E. Murch

University Centre for Mass and Thermal Transport in Engineering Materials, Priority Research Centre for Geotechnical and Materials Modelling, School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

ARTICLE INFO

ABSTRACT

The vibrational contribution to the thermal transport properties of liquid Cu is investigated in detail in the temperature range 1300–1800 K. The calculations are performed in the framework of equilibrium molecular dynamics making use of the Green–Kubo formalism and one of the most reliable embedded-atom method potentials for Cu. It is found that the temporal decay of the heat current autocorrelation function of the liquid Cu model can be described by a single exponential function, which is characterized in the studied temperature range by a constant value of the heat flux relaxation time of about 0.059 ps. The vibrational thermal conductivity of the liquid Cu model slightly decreases with temperature from about 1.1 W/(mK) at 1300 K to about 1 W/(mK) at 1800 K. Near the melting temperature it is about 30% lower than the vibrational thermal conductivity of the f.c.c Cu model. The calculated thermal diffusivity of the liquid Cu model is demonstrated to retain a constant value of about 2.7×10^{-7} m^2/s in the studied temperature range, which is about two orders of magnitude higher than the atomic diffusivity in the model at the melting temperature. The vibrational contribution to the total thermal conductivity of liquid Cu is found to slightly decrease with temperature, being estimated as about 0.7–0.5% in the temperature range of 1400–1800 K. Furthermore, the applicability of some simple theoretical treatments of vibrational thermal transport in liquid Cu is discussed.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Modern technologies continue to challenge the development of rapid thermal processing of materials. In particular, pulsed laser irradiation can offer high spatial and temporal resolution to provide fine control in the rapid cutting, welding and annealing of materials [1,2]. After delivering a large amount of energy, such rapid thermal processing results in a material's response consisting of melting of the targeted region, followed by heat dissipation into the rest of the sample and then by crystal regrowth from the undercooled melt. Therefore, knowledge of the regrowth (solidification) velocity of a material as a function of undercooling temperature is critical in the design requirements of technologies that employ rapid thermal processing.

For pure metals, experimental measurements of the solidification velocity are typically limited to temperatures close to the melting point (T_m) due to the well-known problem of avoiding crystallization at deep undercoolings [3–5]. Only a few preliminary experimental studies, using picoseconds [6,7] and femtosecond [8] lasers, have been performed to measure the solidification velocity

in pure metals (Cu and Au [6], Zn [7], and Ag [8]) at deep undercoolings. Despite difficulties in obtaining precise quantitative results in such extremely fast experiments, estimated values of the solidification velocity, about 60–100 m/s at $(0.6–0.8)T_m$, have demonstrated that the kinetic properties of the crystal–melt interface in pure metals at deep undercoolings can be effectively assessed by molecular dynamics (MD) simulations [8,9].

However, it is well known that, because of the absence of a free-electron contribution, classical MD simulations of metals are expected to underestimate the magnitude of the thermal conductivity (or thermal diffusivity), which includes in this case only the vibrational contribution [9–11]. Therefore, because of the thermal gradients caused by generation or absorption of latent heat in a local region surrounding the solid–liquid interface, one has to be sure that the heat flow in the model system occurs on a time scale that is rapid enough relative to the attachment of liquid atoms to the growing crystal [10]. Such separation of time scales has been implicitly assumed in many MD simulations of solidification kinetics [8,12–18]. Nonetheless, Monk et al. [10] demonstrated that the generation and dissipation of latent heat at the moving solid–liquid interface in the case of employing a global thermostat during free-solidification MD simulations of Ni with the embedded-atom

* Corresponding author.

method (EAM) potential developed by Foiles et al. (the so-called FBD Ni model) [19] leads to a significant underestimation (by a factor of two or even larger) of the interface mobility when compared to the isothermal result. In this context, Monk et al. [10] suggested several strategies to obtain a more accurate evaluation of the crystal–melt interface kinetics coefficient (the proportionality constant between the regrowth velocity and the interfacial undercooling) from MD simulations. Furthermore, they developed a phase field model which allows for an *a priori* estimate of the accuracy of determination of the crystal–melt interface kinetics coefficient for any given classical MD system. However, in order to properly assess the effect of heat flow on the crystal–melt interface kinetics coefficient for a free-solidification simulation employing a global thermostat, this phase field based approach requires an accurate knowledge of the thermal conductivity of the MD model considered.

In addition, it should also be noted that in a real experiment one can expect that convection can lead to an increase of heat transport ahead of the crystal–melt interface and, consequently, to an enhancement of the solidification velocity. Nonetheless, recent results of measurements of the solidification velocity as a function of undercooling for the congruently melting intermetallic $Ni_{50}Al_{50}$ alloy, both under terrestrial conditions and in reduced gravity, demonstrated that the solidification velocity of the alloy at undercoolings higher than about $0.08T_m$ is already not significantly affected by convective flow [20]. This is due to the fact that with increasing undercooling, the solidification velocity exceeds the convective flow velocity. Considering that at an undercooling of about $0.08T_m$ the solidification velocity of the intermetallic $Ni_{50}Al_{50}$ alloy was estimated to be about 0.6 m/s [20], we can safely assume that the dynamics of solidification of pure metals under terrestrial conditions with velocities of about 60–100 m/s at undercoolings (0.6–$0.8)T_m$ is expected to be primarily limited by the thermal diffusivity.

In this context, in our previous work [11] we calculated the vibrational thermal conductivity of f.c.c. Cu over a wide temperature range. The calculations were performed in the framework of equilibrium MD simulations making use of the Green–Kubo formalism [21–23] and one of the most reliable EAM potential for Cu [24]. In the present paper, we use a similar approach to evaluate the vibrational thermal conductivity of a MD model of liquid Cu with the same EAM potential over the temperature range of 1300–1800 K. The electronic contribution missing in the MD model can be estimated by subtracting the results of the MD simulations from the experimental value of thermal conductivity of real liquid Cu [25].

2. Calculation methods

The Green–Kubo formalism [21,22] is based on an equilibrium system and for an isotropic material describes the thermal conductivity, k, in terms of the time integral of the heat current autocorrelation function (HCACF), $\langle \boldsymbol{J}_q(t)\boldsymbol{J}_q(0)\rangle$ [23]:

$$k = \frac{1}{3Vk_BT^2}\lim_{t\to\infty}\int_0^t \langle \boldsymbol{J}_q(t')\boldsymbol{J}_q(0)\rangle \, dt', \tag{1}$$

where V is the volume of the system, k_B is the Boltzmann constant, T is the absolute temperature, $\boldsymbol{J}_q$ is the microscopic heat current vector and t is the time (the average $\langle\cdots\rangle$ should be taken at thermodynamic equilibrium). The microscopic heat current vector can be defined as [26]:

$$\boldsymbol{J}_q = \frac{d}{dt}\left(\sum_i e_i \boldsymbol{r}_i\right) = \sum_i e_i \boldsymbol{v}_i + \sum_i \boldsymbol{r}_i \frac{de_i}{dt}, \tag{2}$$

where the summation is over the atoms in the system, and e_i is the energy (kinetic and potential) of the i-th atom, $\boldsymbol{r}_i$ is the radius-vector of the i-th atom and $\boldsymbol{v}_i$ is the velocity vector of the i-th atom.

The first term in Eq. (2) is associated with convection whilst the second is associated with conduction. Implementation of the Green–Kubo method has no effect on the atomic dynamics and the system temperature is uniform and constant. In addition, this elegant but time consuming method allows for calculation of the temperature dependence of the thermal conductivity.

In general, the total energy of an atom i is represented in the EAM model [27] as:

$$e_i = \frac{1}{2}m_i v_i^2 + F_{\mu_i}(\bar{\rho}_i) + \frac{1}{2}\sum_{j(\neq i)}V_{\mu_i\mu_j}(r_{ij}), \tag{3}$$

where m_i is the mass of the atom, v_i is the absolute value of the velocity vector of the atom, $F_{\mu_i}(\bar{\rho}_i)$ is the embedding energy of the atom as a function of the host electron density $\bar{\rho}_i$ induced at site i by all other atoms in the system and $V_{\mu_i\mu_j}(r_{ij})$ is the pair interaction potential as a function of the distance r_{ij} between atoms i and j (μ_i and μ_j indicate whether the functional form for the species of atom i or atom j is used). The host electron density $\bar{\rho}_i$ is given by:

$$\bar{\rho}_i = \sum_{j(\neq i)}\rho_{\mu_j}(r_{ij}), \tag{4}$$

where $\rho_{\mu_j}(r_{ij})$ is the electron density induced by an atom j at the location of atom i. In particular, for a monatomic system this model involves three potential functions $F(\bar{\rho})$, $V(r)$ and $\rho(r)$ which can be treated as some fitting functions that have to be reasonably parameterized. In this work, the interactions between atoms in the MD model of liquid Cu are described by using an EAM potential developed by Mishin et al. [24]. The potential functions were obtained by fitting to experimental and first-principles data. This potential accurately reproduces the lattice parameter, cohesive energy, elastic constants, phonon frequencies, thermal expansion, lattice-defect energies, and other relevant properties of crystalline Cu. Furthermore, this potential not only accurately reproduces various properties of crystalline Cu but also gives a realistic description of the solid–liquid interface thermodynamics [28–31], even though no liquid data were included in the fitting of the potential. Moreover, the melting temperature of Cu predicted by this potential is 1327 K [28] in good agreement with the experimental value of 1357 K [32].

Considering Eqs. 2–4, the Cartesian components of the heat current vector in a system described using an EAM potential model can be represented as [11]:

$$\boldsymbol{J}_\alpha = \frac{d}{dt}\left(\sum_i e_i x_{i\alpha}\right) = \sum_i e_i v_{i\alpha} - \sum_i \Omega_i \sigma^{(p)}_{i\alpha\beta}v_{i\beta}, \tag{5}$$

where

$$\sigma^{(p)}_{i\alpha\beta}\Omega_i = \sum_{j(\neq i)}\left[\frac{\partial F_{\mu_j}(\bar{\rho}_j)}{\partial\bar{\rho}_j}\frac{\partial\rho_{\mu_i}(r_{ij})}{\partial r_{ij}} + \frac{1}{2}\frac{\partial V_{\mu_i\mu_j}(r_{ij})}{\partial r_{ij}}\right]\frac{x_{ij\alpha}x_{ij\beta}}{r_{ij}}, \tag{6}$$

Ω_i is the volume of atom i, the symbols α and β enumerate Cartesian components of vectors and tensors: $x_{i\alpha}$, $x_{i\beta}$ (or $x_{ij\beta}$) and $v_{i\alpha}$ (or $v_{i\beta}$) are the components of the vectors r_i, r_{ij} and v_i, respectively, while $\sigma^{(p)}_{i,\alpha\beta}$ denote the potential energy contribution to the components of the stress tensor of atom i.

In the present calculations, we considered the temperature range 1300–1800 K. In all MD simulations reported here, the equations of atomic motion were numerically integrated according to the well-known Verlet algorithm [33] with a time step $\Delta t = 1.5$ fs. During the simulation, the total momentum of the model system was conserved at a zero value. We started our MD simulations by heating up an initial model of a perfect f.c.c. Cu crystal at 1300 K in a cubic simulation cell of $N = 4000$ atoms with periodic boundary conditions in all three directions using NPT (isothermal–isobaric) ensemble dynamics. We used a Nosé–Hoover