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A molecular dynamics study of thermal conductivity of zirconium hydride

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Abstract

Phonon contribution to thermal conductivity of $ZrH_{1.6}$ is studied by nonequilibrium molecular dynamics (NEMD) method. Calculated thermal conductivities were compared with the values estimated from experiment results. The difference between simulated and experimental values is acceptable, considering no adjustment on potential function used in NEMD and uncertainty in estimation of the experimental value by Wiedemann–Franz relationship. The analysis of vibrational modes has been done by equilibrium molecular dynamics (EMD) method. It was pointed out that the high frequency vibration mode of hydrogen is important for heat conduction in $ZrH_{1.6}$.

Keywords: Zirconium hydride; Molecular dynamics; Thermal conductivity

1. Introduction

A metal–hydride has very high hydrogen atom density, which is equivalent to that of liquid water. The fast neutrons in nuclear reactors are efficiently moderated in the metal–hydride. Zirconium hydride is widely employed as a neutron moderator in nuclear reactors. The hydride fuel of U–Zr hydride developed by General Atomics (GA) is in use for more than 40 years in many TRIGA reactors around the world both in constant power and pulsed power operating conditions [1]. Recently, a new type of hydride fuels have been studied for transmutation of nuclear wastes [2]. Zirconium hydride is included in the hydride fuels because of its excellent stability under irradiation conditions. Thermal conductivity is one of the most important physical properties to design the reactor core materials. The zirconium hydride has a metallic nature in electrical conductivity [3]. The thermal conductivity of zirconium hydride at high temperature consists of two major contributions of electron conductivity and phonon conductivity [4,5]. In this study, the phonon conductivity was theoretically estimated by molecular dynamics (MD) method.

2. Thermal conductivity

The thermal conductivity is given by Fourier's law as

$$J_x = -\kappa\, \partial T/\partial x, \tag{1}$$

where J_x is the thermal flux; κ is the thermal conductivity; and $\partial T/\partial x$ is the gradient of the temperature along the x-axis. Experimentally, κ is typically obtained by measuring the temperature gradient that results from applying a heat current. In molecular dynamic (MD) simulations the thermal conductivity can be computed either using non-equilibrium MD (NEMD) or equilibrium MD. Since the NEMD method of computing the thermal conductivity is analogous to the experimental measurement, the NEMD method provides direct information on transport phenomena [6,7]. In this work, the heat conduction in δ-zirconium hydride by phonon was studied by the NEMD method. Fig. 1 is a schematic representation of the unit cell used to compute κ under the periodic boundary conditions. The unit cell is divided into many layers perpendicular to the x-axis. The layers are grouped into 'hot', 'cold', and 'middle' regions. The energy flows in the x direction from the hot to the cold regions through the middle region. Temperatures in the hot and cold regions are controlled by the stochastic thermostat. Heat $\Delta\varepsilon$ is added in the hot region and the same amount of heat is removed from the

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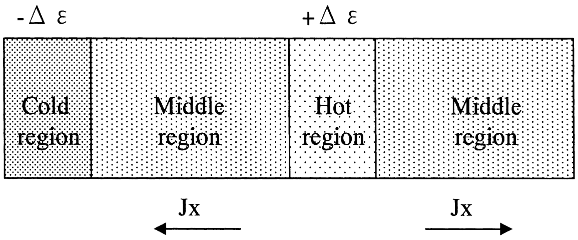

Fig. 1. Schematic representation of three-dimensional periodic simulation cell used to determine the thermal conductivity.

cold region in stationary condition. Our model system is a cubic cell ($L = 76.32$ Å) containing 42 475 atoms (16 384 zirconium atoms and 26 091 hydrogen atoms). Crystalline δ-zirconium hydride with H/Zr ratio of 1.6 is used for calculations. The δ-zirconium hydride has an f.c.c. structure, CaF_2-type, in which hydrogen atoms occupy tetrahedral positions. At room temperature the lattice parameter is 4.775. The pair potentials in zirconium hydride system are given by the following equations [8]:

$$\phi(r) = \phi_0(r) - \phi_0(r_{\text{cut}}) + (r_{\text{cut}} - r)\phi_0'(r_{\text{cut}}), \tag{2}$$

$$\phi_0(r) = -p_0(1 + (r - r_0))\exp(-\alpha(r - r_0)), \tag{3}$$

where $\phi_0'(r)$ is the first derivation of $\phi_0(r)$. The cutoff distance, r_{cut} is set to be 6.5 Å. The parameters of the pair potentials are in Table 1. These potentials accurately describe elastic properties and thermal expansion of zirconium–hydride.

The hot and cold regions consisted of four layers and each middle region consisted of 12 layers. The velocity Verlet algorithm was used with $\Delta t = 0.05$ fs, which was used in all MD calculations. In order to reach the equilibrium state, 500 000 time steps of equilibrium MD calculation were needed. After the system had been equilibrated, the thermostat was switched on and the 500 000 time steps of NEMD calculation were performed. The first 100 000 time steps were discarded to avoid transient effect. After the 100 000 time steps, the temperature gradient has converged and the value of κ is constant.

Fig. 2 shows a typical time-averaged temperature profile used to compute the thermal conductivity. The non-linear temperature profile is observed in layers near the heat source and the heat sink regions. In the intermediate region, temperature profile is fit with a linear function as shown in Fig. 2. The phonon thermal conductivities calculated by Eq. (1) are illustrated in Fig. 3. It is well known that the electron contribution to the thermal conductivity of $ZrH_{1.6}$ increases with increasing temperature [4,5]. The phonon thermal conductivity is not directly measured at high temperature. The electronic contribution κ^e to the thermal conductivity was estimated by Wiedemann–Franz relationship,

$$\kappa^e = L\sigma T, \tag{4}$$

Table 1
Parameters of pair potentials in zirconium–hydride system

	p_0 (eV)	α (Å^{-1})	r_0 (Å)
H–H	0.141	1.771	2.445
Zr–Zr	1.445	1.263	3.487
Zr–H	0.039	2.286	2.810

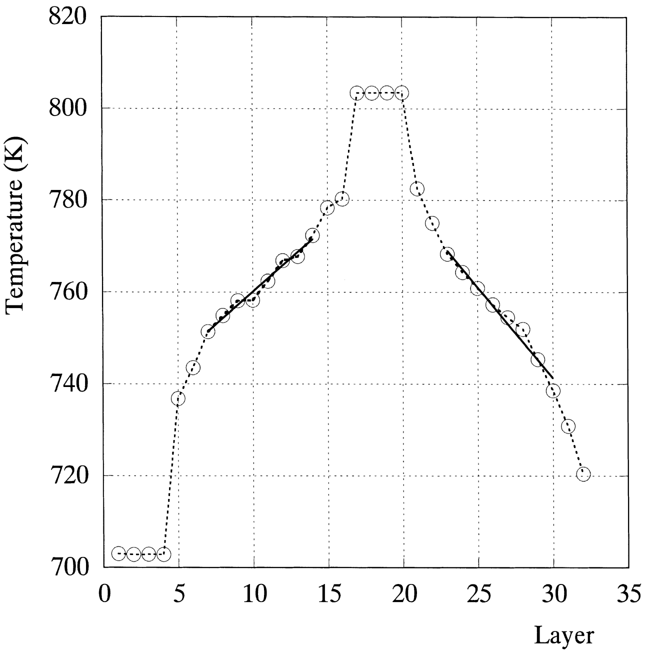

Fig. 2. Temperature profile for zirconium–hydride system at an average temperature of 750 K.

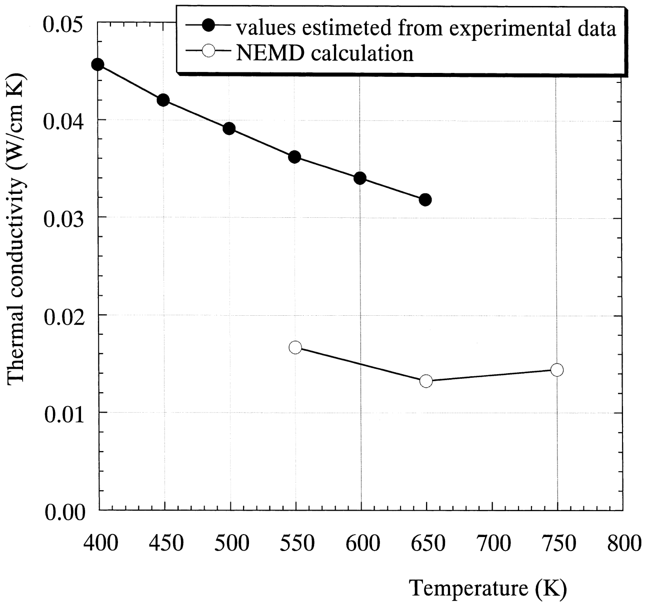

Fig. 3. Comparison of calculated phonon thermal conductivities of zirconium hydride (open circle) with values estimated from experimental values (solid circle).

where L is the Lorentz constant; T is the temperature; and σ is the electrical conductivity. Fig. 3 shows comparison of calculated values (open circle) and those estimated by experimental data [4] (solid circle). Calculated phonon thermal conductivity is different in factor 3 to the value estimated from the experiments. The difference is acceptable, considering no adjustment on literature potential function. There may also have some uncertainty in rough estimation of the electronic contribution by Wiedemann–Franz relationship.

3. Analysis of vibrational mode

The equilibrium MD (EMD) calculations have been performed to characterize the vibrational modes of the above Zr–H system at temperature of 700 K. The velocity autocorrelation function and its Fourier transform are illustrated in Figs. 4 and 5. The analysis of the vibration modes permits to separate two contributions, one low frequency mode from the vibration of host metal (Zr) and another which is related to the high frequency vibration of H.

We have also analyzed a pulse heating problem to estimate the contributions of two modes to the heat transport in the Zr–H system. A heat pulse was introduced into the center layer of the simulation cell by scaling velocities of all atoms there to those corresponding to the temperature of 2900 K. The evolution of the local temperature calculated from the kinetic energy of atoms in the heated layer is shown in Fig. 6, where the temperatures of Zr and H calculated from their kinetic energy are also shown. Fig. 7 illustrates the evolutions of temperatures of the adjacent layer to the heated layer. As seen in Figs. 6 and 7, the vibration of H and Zr atoms responses to the higher and lower frequency modulations, respectively, in the local temperature. Although this higher frequency response of H atoms does not mean directly to its higher contribution to the thermal conductivity, they seem to play more important role than Zr atoms. This was also confirmed from higher energy supply (extract) of H atoms

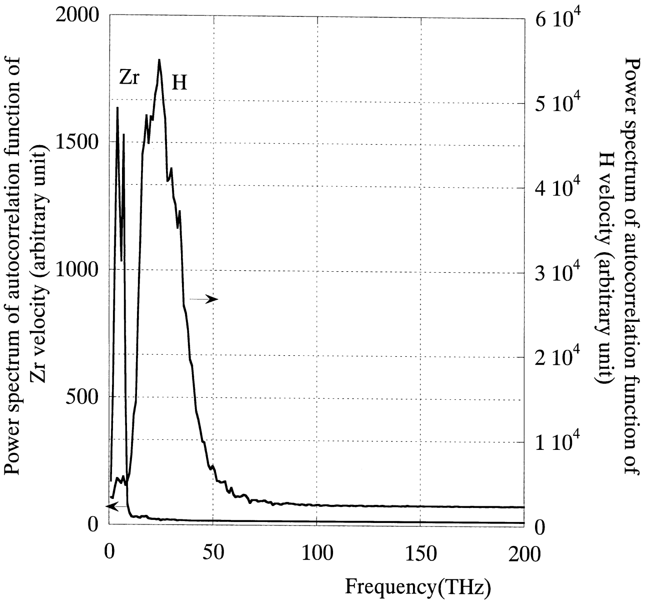

Fig. 5. Power spectra of velocity autocorrelation functions shown in Fig. 4.

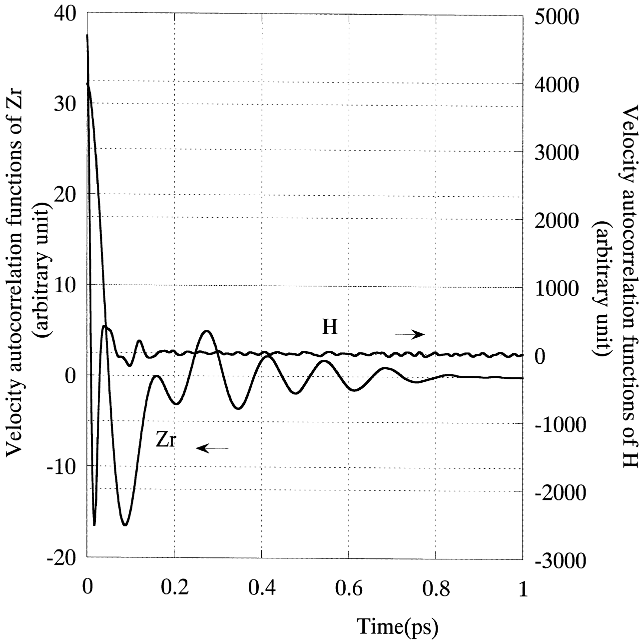

Fig. 4. Velocity autocorrelation functions of Zr and H in equilibrium condition at 700 K.

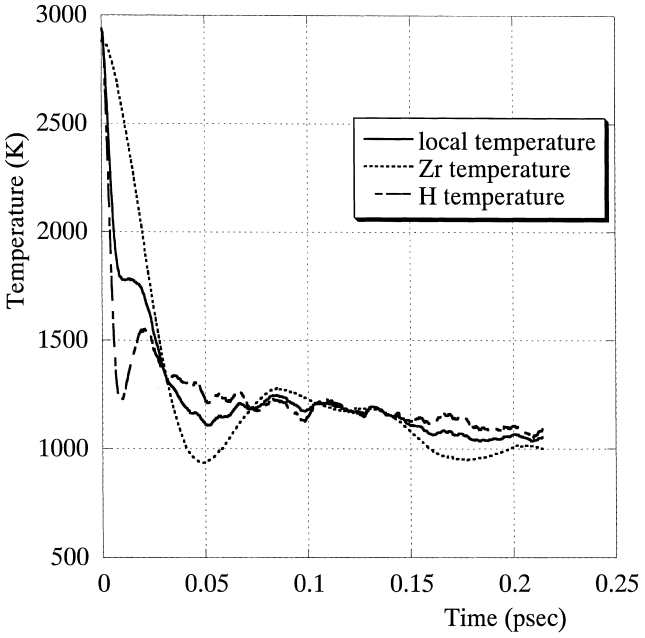

Fig. 6. Evolutions of temperatures of pulse heated layer. The temperatures of Zr and H were calculated from their kinetic energy.

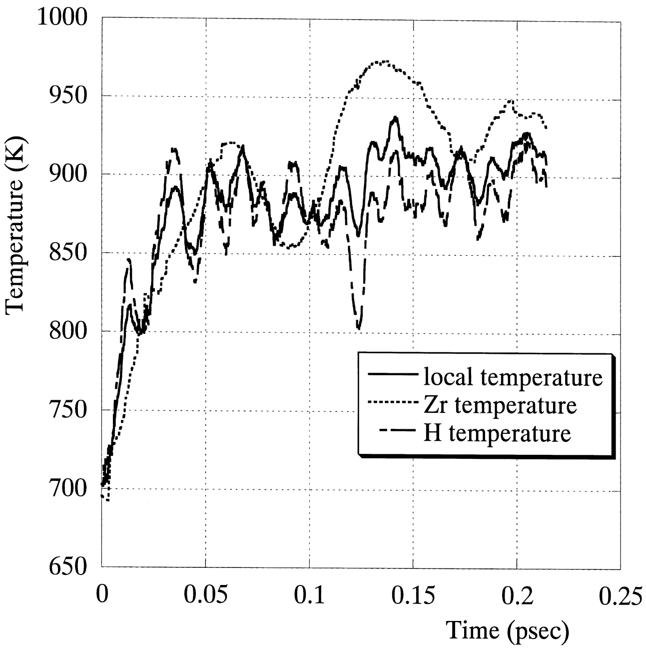

Fig. 7. Evolutions of temperatures of layer adjacent to pulse heated layer. The temperatures of Zr and H were calculated from their kinetic energy.

than of Zr atoms in the hot (cold) layers in the NEMD calculation of which results are shown in Fig. 2.

Our classical MD simulations are unable to capture any quantum effects associated with thermal conductivity. The Debye temperature of delta $ZrH_{1.6}$ is about 330 K and is well below the temperature range of the MD simulations from 550 to 750 K. On the other hand, the experimental results show the characteristic temperature of hydrogen vibration in $ZrH_{1.6}$ is 1590 K [9]. It is necessary to evaluate the quantum effect on heat conduction due to hydrogen vibration. This matter is one of the present pending questions.

4. Conclusions

We have calculated the thermal conductivity of $ZrH_{1.6}$ by NEMD in the temperature range from 550 to 750 K. To understand heat transport phenomena in the zirconium–hydrogen system, the velocity autocorrelation function and its Fourier transform were calculated by EMD at the temperature of 700 K. The pulse heating problem has been solved to estimate the two contributions of Zr vibration and H vibration to the heat conduction in the zirconium–hydrogen system. The following conclusions have been obtained from the calculation results.

1. Calculated thermal conductivities are different in factor 3 to the value estimated from the experiments. The difference is acceptable, considering no adjustment on literature potential function. There may also be some uncertainty in the estimation of the electronic contribution by Wiedemann–Franz relationship.
2. The vibration modes of particles in Zr–H system, which play a large part of heat transport, are separated to two modes, one low frequency mode from the vibration of host metal (Zr) and the other which is related to the high frequency vibration of H.
3. The analysis of the pulse heating problem shows that the vibration of H contributes mainly to the heat conduction of the Zr–H system at high temperatures above 700 K.

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