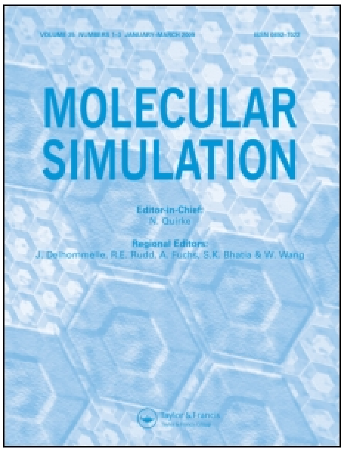

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Prediction of the intrinsic thermal conductivity of phonons in dielectric and semiconductor materials based on the density of the lattice vibration energy

Fan Qunbo[a]; Zhang Feng[a]; Wang Fuchi[a]; Zhang Huiling[a]
[a] School of Materials Science and Engineering, Beijing Institute of Technology, Beijing, People's Republic of China

To cite this Article Qunbo, Fan , Feng, Zhang , Fuchi, Wang and Huiling, Zhang(2008) 'Prediction of the intrinsic thermal conductivity of phonons in dielectric and semiconductor materials based on the density of the lattice vibration energy', Molecular Simulation, 34: 10, 1129 — 1132

To link to this Article: DOI: 10.1080/08927020802101718

URL: http://dx.doi.org/10.1080/08927020802101718

Molecular Simulation
Vol. 34, Nos. 10–15, September–December 2008, 1129–1132

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Prediction of the intrinsic thermal conductivity of phonons in dielectric and semiconductor materials based on the density of the lattice vibration energy

Fan Qunbo*, Zhang Feng, Wang Fuchi and Zhang Huiling

School of Materials Science and Engineering, Beijing Institute of Technology, Beijing, People's Republic of China

(*Received 20 December 2007; final version received 25 March 2008*)

A novel method is proposed to simulate the intrinsic thermal conductivity of the phonons in dielectric and semiconductor materials by introducing the concept of the density of the lattice vibration energy, which is a function of frequency and temperature. A quantitative relationship between the density of the lattice vibration energy and the mean free path of the phonons is established. The heat capacity and sound velocity can also be calculated by using the phonon density of states, the theoretical densities, and the elastic modulus. The thermal conductivities of some typical dielectric and semiconductor materials are then calculated, and it is found that the agreement with experimental data is good for some materials. In contrast to traditional semi-empirical methods, there is no need to input any experimental data.

Keywords: thermal conductivity of phonons; density of lattice vibration energy; mean free path of phonons

1. Introduction

In recent years there has been much research into the intrinsic thermal conductivities of phonons of dielectric and semiconductor materials. Up to now, two primary methods have been used: one is to employ the widely accepted classical formula $k = (1/3)cvl$ where c is the heat capacity per volume, v is the phonon velocity, and l is the intrinsic mean free path of phonons. The other method is based on some semi-empirical models (like Equation (1)) proposed by Klemens [1] to take many empirical parameters into account.

In Equation (1), x is a variable parameter, μ is the shear modulus, ω_D is the Debye frequency, γ^2 is the Gruneisen anharmonicity parameter, T is the absolute temperature, v is the transverse phonon velocity, and N is the number of atoms per molecular unit. Using Equation (1), Wu [2] successfully calculated the thermal conductivity of a solid solution of ZrO_2–$GdO_{1.5}$.

$$k_i = \left(\frac{3x}{2\gamma^2}\right)\left(\frac{\mu v^2}{N^{2/3}\omega_D}\right)T^{-1}. \tag{1}$$

However, it is usually difficult to determine the variable or empirical parameters. Accurate determination of the mean free path of phonons in the classical model has eluded people for years. A novel method to calculate the mean free path of phonons based on the density of the lattice vibration energy is proposed in this paper.

2. Computation details

2.1 *Heat capacity and sound velocity*

To predict the intrinsic phonon thermal conductivity, we calculated the heat capacity and sound velocity as follows. The lattice contribution to the heat capacity [3] at constant volume is given by

$$c(T) = k_B \int \frac{\left(\frac{\hbar\omega}{k_B T}\right)^2 \exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^2} g(\omega)\mathrm{d}\omega, \tag{2}$$

where $\hbar$ is Planck's constant, k_B is Boltzmann's constant, ω is the phonon frequency, and $g(\omega)$ is the phonon density of states (DOS).

The transverse phonon velocity can be expressed as

$$v = \sqrt{\frac{\mu}{\rho}}, \tag{3}$$

where ρ is the density.

2.2 *Mean free path of phonons*

The conduction of heat in dielectric and semiconductor materials may be viewed as the interaction between phonons. The mean free path associated with the phonon–phonon interaction (Umklapp process) is expected to be derived from the density of phonons ρ_p, namely the

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*Corresponding author. Email: fanqunbo@bit.edu.cn

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020802101718
http://www.informaworld.com

number of phonons per unit volume. An analogy can be drawn between gas molecules and phonons. According to the thermal conductivity theory of gas molecules, the mean free path of a molecule is inversely proportional to the density of molecules, and is independent of the thermal motions of the molecules. Correspondingly, it is suggested that the mean free path of phonons is inversely proportional to the density of phonons.

$$l \propto \frac{1}{\rho_\mathrm{p}} = \frac{V}{N}, \tag{4}$$

where V is the volume of the system studied, and N is the total number of phonons, which is obtained by

$$N = \int \bar{n} g(\omega)\mathrm{d}\omega, \tag{5}$$

where $\bar{n}$ is the average number of phonons per unit volume, defined by

$$\bar{n} = \frac{1}{\mathrm{e}^{(\hbar\omega)/(k_\mathrm{B}T)} - 1}. \tag{6}$$

By calculating the phonon spectra of dielectric and semiconductor materials, it seems that the mean free path of phonons can be obtained from Equations (4)–(6). Unfortunately, however, results calculated from Equation (6) show two deficiencies, thus making the above mentioned methodology unfeasible. On the one hand, as can be seen in Equation (6), the low frequencies near zero would cause $\bar{n}$ to be nearly infinite, thus making the overall calculation senseless. On the other hand, negative numbers of phonons due to unstable modes might cause $\bar{n}$ to be far below zero, which also renders the calculation inefficient.

So, we propose a novel method to calculate the total number of phonons by analysing the calculation of the heat capacity. Through solving Equation (2), it can be seen that low frequencies usually make only a small contribution to the energy per volume, rather than an infinitely large one. The quanta energy $\hbar\omega$ at the denominator can weaken such disadvantaged influence. Therefore, we propose Equation (7) to calculate the total number of phonons, which is a function of the frequencies of the phonons.

$$N = \int \frac{1}{\mathrm{e}^{(\hbar\omega)/(k_\mathrm{B}T)} - 1} g(\omega)\mathrm{d}\omega \approx \frac{\int \frac{\hbar\omega}{\mathrm{e}^{(\hbar\omega)/(k_\mathrm{B}T)} - 1} g(\omega)\mathrm{d}\omega}{\int \hbar\omega \mathrm{d}\omega}$$
$$= \frac{\int \bar{n}\hbar\omega g(\omega)\mathrm{d}\omega}{\int \hbar\omega \mathrm{d}\omega}. \tag{7}$$

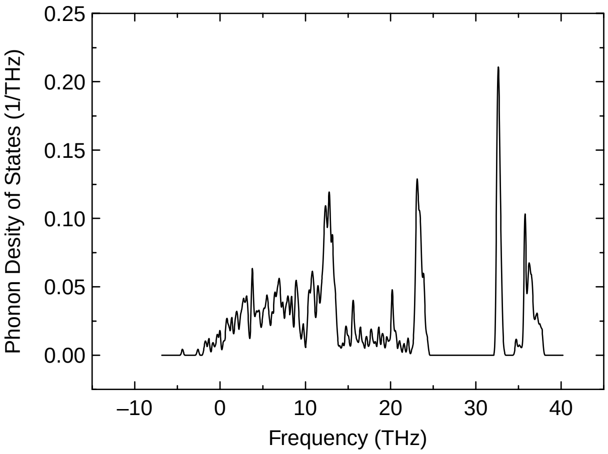


Figure 1. Phonon DOS of α-SiO_2.

Since the quanta energy $\hbar\omega$ is added to both the denominator and the numerator of Equation (7), the physical significance is still the total number of phonons. In addition, the numerator represents the vibrational energy and the denominator is supposed to be a constant if the integral range of the phonon frequency is fixed, so the numerator can be used independently to denote the total number of phonons, which is defined as the lattice vibration energy. In addition, the negative-phonon effects are successfully avoided, since the term $\bar{n}\hbar\omega$ is always a positive number.

Based on the definition of the lattice vibration energy, the density of the lattice vibration energy Π is defined as follows:

$$\Pi = \frac{\int \frac{\hbar\omega}{\mathrm{e}^{(\hbar\omega)/(k_\mathrm{B}T)} - 1} g(\omega)\mathrm{d}\omega}{V}. \tag{8}$$

Where Π is a function of temperature and frequency in eV/Å^3, reflecting the phonon energy inside the unit volume. The next step is to determine the quantitative relationship between Π and the phonon mean free path l. The related mean paths of the phonons are obtained by referencing experimental thermal conductivities, calculated heat capacities, as well as calculated sound velocity

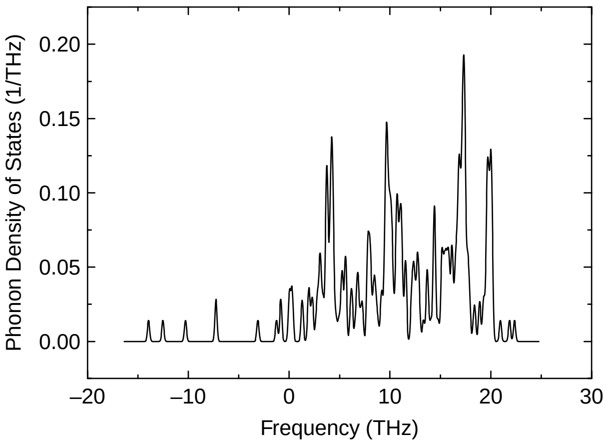
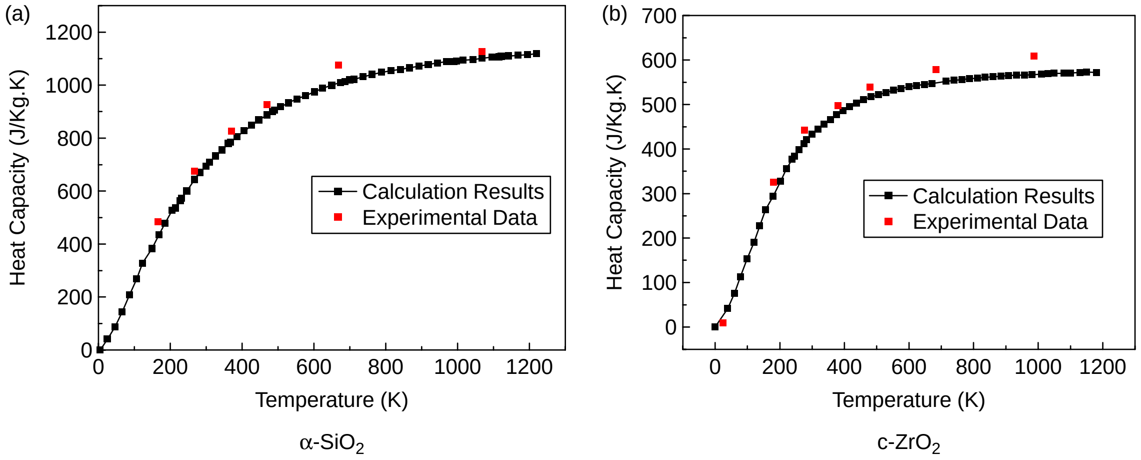


Figure 2. Phonon DOS of cubic ZrO_2.



α-SiO_2

c-ZrO_2

Figure 3. Heat capacity of α-SiO_2 and cubic c-ZrO_2.

values of many nearly perfect dielectric and semiconductor crystals on the basis of Equations (2)–(4). By solving Equation (8), the density of the lattice vibration energy Π is also easily obtained. Finally, the quantitative empirical relationship between l and Π is as follows:

$$l = 4.68 \times 10^{-21} \left(\frac{1}{\Pi} \right)^{11.32}. \qquad (9)$$

3. Results and discussion

The calculations for the phonon DOS use the total energy, plane wave pseudopotential code CASTEP [4]. Figures 1 and 2 show the phonon DOS of α-SiO_2 and cubic ZrO_2 (c-ZrO_2), respectively. Based on the phonon DOS results, the heat capacity can be calculated from Equation (2), as shown in Figure 3. The agreement with experimental data is found to be good.

Table 1 compares our results for the shear modulus of typical dielectric and semiconductor materials, Ge, Si, α-SiO_2, c-ZrO_2, La_2O_3, and $La_2Zr_2O_7$, with available experimental data [5–8]. As can be seen in Table 1, the calculations are in good agreement with the data in the literature.

According to Equation (3) and based on the shear modulus results and theoretical densities, the sound velocities of typical dielectric and semiconductor materials can be obtained (Table 2).

Equation (8) can be used to calculate the values of $1/\Pi$ for typical dielectric and semiconductor materials at 1000 K. The corresponding mean free paths of the phonons of these materials are then obtained by solving Equation (9) (Table 3). It should be noted that the mean free path of ZrO_2 is 1.203 Å, which is far below the lattice constant of the ZrO_2 unit cell (4.916 Å) [9]. It has been widely accepted that the dimension of the unit cell limits the mean free path of the phonons, resulting in a lower limit to the thermal conductivity. So, the mean free path of the phonons of ZrO_2 at 1000 K is adjusted to 4.916 Å. The thermal conductivities can then be calculated on the basis of the heat capacity, sound velocity, and phonon mean free path (Table 4). A comparison between the calculated and experimental thermal conductivities shows that the calculated values of Si, α-SiO_2, and $La_2Zr_2O_7$ are reasonably good. Although there were some differences between the calculations and experiments for Ge and c-ZrO_2, these were probably caused by the calculation of the phonon DOS, or phonon scatter effects due to various defects in the crystals. It is still a first-step methodology to calculate the intrinsic phonon thermal conductivity of perfect-crystal dielectric and semiconductor materials

Table 1. Shear modulus of typical dielectric and semiconductor materials.

	Calculations (GPa)	Experimental data (GPa)
Ge	67.66	67 [5]
Si	79.75	63 [6]
α-SiO_2	30.15	32 [7]
c-ZrO_2	157.11	105 [5]
La_2O_3	105.26	89 [5]
$La_2Zr_2O_7$	73.83	67 [8]

Table 2. Sound velocity results of typical dielectric and semiconductor materials.

	Theoretical density (10^3 kg/m^3)	Sound velocity (m/s)
Ge	5.905	3385.1
Si	2.346	5831.0
α-SiO_2	2.578	3523.4
c-ZrO_2	6.107	5072.0
La_2O_3	8.092	3606.6
$La_2Zr_2O_7$	6.054	3492.3

Table 3. Calculated mean free path of phonons of typical materials.

	1/Π	l(Å)
Ge	91.509	47.631
Si	97.722	78.834
α-SiO_2	73.761	9.114
c-ZrO_2	56.650	1.203
La_2O_3	68.932	5.422
$La_2Zr_2O_7$	73.378	8.757

Table 4. Comparison of thermal conductivities determined from experiments and simulations.

	K_{cald} (W/mK)	K_{exp} (W/mK)
Ge	16.994	37.2 [10]
Si	30.611	31.38 [10]
α-SiO_2	2.622	3.138 [10]
c-ZrO_2	2.106	3.5 [10]
La_2O_3	1.293	–
$La_2Zr_2O_7$	2.704	2.1 [11]

through theoretical calculation without the need to input any experimental data.

4. Conclusions

By introducing the concept of the density of the lattice vibration energy for the first time, we have established a quantitative relationship between the mean free path of phonons and the density of the lattice vibration energy. This can be coupled with the heat capacity and sound velocity to predict the intrinsic thermal conductivities of the phonons of some typical dielectric and semiconductor materials. The methodology proposed in this paper seems to be more reliable than the traditional empirical or semi-empirical formulas, since the variable parameters are successfully avoided.

Acknowledgements

The authors gratefully acknowledge support from the Commission of Science Technology and Industry for National Defense (Grant 9140A12020306BQ01) and from the Excellent Young Teacher Foundation of Beijing Institute of Technology (Contract 1040012040101).

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