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Heat capacity per unit volume

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Abstract

In the thermal design of micro-electro-mechanical systems, micro-electronics, etc., it is necessary to solve thermal conduction equation at various boundary conditions. In such an analysis the values of thermophysical properties in a thin film on a substrate, a superlattice, an interfacial region, etc. which have usually width with a nanometer scale are required. Among the thermophysical properties, heat capacity per unit volume in a small-scale region is difficult to measure and then, we need to estimate it in an appropriate way. In this paper, I propose that the heat capacity per unit volume at room temperature lies around 2×10^6 J m^{-3} K^{-1} over a variety of materials, contrary to the thermal conductivity which markedly depends on a material and the state of a material, especially whether it is ordered or disordered. Then, we can use the above heat capacity per unit volume for a small-scale region in a practical purpose.

Keywords: Debye heat capacity; Design of device; Interface; Molar heat capacity; Thermal conductivity; Thermal diffusivity

Recently, we are able to control or manipulate atoms or molecules to organize a functional material. The study on thermal characteristics in such a material is a challenging subject. To consider thermal characteristics, phonon or electron mean free path plays an important role, since it lies in a few tens of nanometers at room temperature. Then, we should pay attention to thermophysical properties in a small-scale region, such as a thin film on a substrate, a superlattice, an interfacial region, etc. whose widths are comparable to phonon or electron mean free path. Generally, a small-scale region has specific structure which depends on the neighboring materials, the material preparation, etc. For instance, in epitaxial superlattices, disorder of atomic arrangement results in interfacial region with about a few nanometers; in a metal film on a substrate, the microscopic structure changes gradually from the bottom surface at the substrate side to the upper free surface since the crystal size of such a metal film becomes large as being away from the substrate surface [1]. In the thermal design of micro-electro-mechanical systems, micro-electronics, etc. it is necessary to know thermal conductivity, heat capacity and thermal diffusivity in a small-scale region. In the present paper, I focus my attention to heat capacity in such a region. Usually it is difficult to measure heat capacity in a small-scale region which is embedded in bulk materials.

Heat capacity does not depend on materials as expected from the Dulong and Petit law at room temperature [2]. Furthermore, it is well known that molar heat capacity can be well expressed by the Debye model for a variety of solid materials [2]. In the low temperature region the molar heat capacity is proportional to T^3, where T is temperature in units of K. In the intermediate temperature region the molar heat capacity exhibits sigmoidal behavior. At the high temperature the molar heat capacity saturates and finally becomes the constant, $3R$, where R is the gas constant. The saturated value $3R$ has been known as the Dulong and Petit heat capacity. Then, above Debye temperature Θ_D molar heat capacity of solid materials is approximately given by $3R$ [2]. But, in the thermal design of micro-electro-mechanical systems, micro-electronics, etc., in condensed matters heat capacity per unit volume near room temperature is required because we need to solve the thermal conduction equation such as

$$\lambda \frac{\partial^2 T}{\partial x^2} = \rho \tilde{C}_p \frac{\partial T}{\partial t}, \tag{1}$$

where λ is thermal conductivity in the x-direction, ρ the density and $\tilde{C}_p$ is specific heat capacity. Heat capacity in unit volume c_p is given by

$$c_p = \rho \tilde{C}_p. \tag{2}$$

In the present paper, I will list the data of heat capacity per unit volume together with thermal conductivity and thermal diffusivity for a variety of materials. Furthermore, I will discuss the

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Table 1
Molar heat capacity, heat capacity per unit volume, thermal conductivity and thermal diffusivity for a variety of condensed materials [3,4]

Substance	C_p (J mol^{-1} K^{-1})	c_p (10^6 J m^{-3} K^{-1})	λ (10^2 J m^{-1} K^{-1} s^{-1})	a (10^{-4} m^2 s^{-1})
Ag	25.5	2.49	4.27	1.72
Al	24.4	2.44	2.37	0.97
Au	25.5	2.47	3.15	1.27
Bi				
Crystal (‖)	25.5	1.19	0.053	0.044
Crystal (⊥)			0.092	0.077
Polycrystal			0.079	0.066
C				
Diamond I	6.16	1.80	9.00	5.00
Diamond IIa			23.1	12.8
Diamond IIb			13.5	7.50
Co	24.8	3.73	0.99	0.27
Cr	23.2	3.20	0.90	0.28
Cu	24.5	3.44	3.98	1.16
Fe	25.0	3.53	0.80	0.23
Gd	37.0	1.85	0.093	0.050
Ge	23.4	1.73	0.60	0.35
In	26.7	1.70	0.82	0.48
Mn	26.3	3.56	0.078	0.022
Mo	23.8	2.54	1.38	0.54
Na	28.2	1.19	1.32	1.11
Ni	25.8	3.91	0.91	0.23
Pb	26.4	1.45	0.35	0.24
Pd	25.5	2.88	0.76	0.26
Pt	25.7	2.83	0.71	0.25
S	23.7	1.53	0.0027	0.0018
Sb	25.2	1.38	0.24	0.176
Si	20.0	1.66	1.48	0.89
Sm	28.3	1.42	0.133	0.094
Ti	25.0	2.35	0.22	0.093
U	27.8	2.23	0.28	0.124
W	24.8	2.60	1.78	0.68
Zn	25.4	2.77	1.21	0.44
Brass (Cu 70, Zn 30)	–	3.26	1.19	0.37
Al_2O_3				
Crystal	79.9	3.20	0.46	0.144
Polycrystal	79.0	3.16	0.36	0.114
BeO	25.4	3.09	2.7	0.88
MgO	37.2	3.34	0.60	0.18
SiO_2				
Crystal (‖)	44.3	1.94	0.104	0.054
Crystal (⊥)			0.062	0.032
Glass	44.6	1.63	0.0138	0.0084
Glass (Pyrex 7740)	–	1.60	0.0110	0.0069
NaCl	50.8	1.88	0.064	0.034
Polyethylene (M21000)	–	1.50	0.002	0.00147
Polyvinylchloride (M1000)	–	1.31	0.0016	0.00122
Polystyrene ($d = 1.03 \times 10^3$ kg m^{-3})	–	1.26	0.0012	0.00095
Nylon 6 ($d = 1.15 \times 10^3$ kg m^{-3})	–	1.75	0.0025	0.00143

reason why heat capacity per unit volume at room temperature has a concentrated value at room temperature independent of materials and also the state of materials.

1. Heat capacity per unit volume at room temperature

In Table 1, molar heat capacity and thermal conductivity are listed for various materials [3,4], together with heat capacity per unit volume calculated from molar heat capacity and thermal diffusivity obtained from heat capacity per unit volume and thermal conductivity. The above molar heat capacities are close to $3R$(=24.9 J mol^{-1} K^{-1}) for a simple substance and behave in the same tendency for compounds. First of all, in Table 1 it should be pointed out that the heat capacities per unit volume lie within a confined region of $1–4 \times 10^6$ J m^{-3} K^{-1}. In Table 1, the mean of the heat capacities per unit volume is $2.3 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$ and the standard deviation is $0.6 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$. On the other hand, the thermal conductivities lie from 0.12 to $2310\,\mathrm{J\,m^{-1}\,K^{-1}\,s^{-1}}$, that is, they spread over five-digit figure.

Furthermore, heat capacity per unit volume of the materials composed of the same element is approximately the same independent of the states of the material. Namely as seen in Table 1 among diamonds with different qualities the heat capacity per unit volume is the same; in Al_2O_3 it does not depend on whether the state is crystal or polycrystal; in addition in SiO_2 there is no significant difference between the heat capacities per unit volume of the crystal and glass state. On the other hand, the thermal conductivity markedly depends on the states of these materials. More in detail to the estimation for heat capacity per unit volume of compounds Neumann and Kopp law [6] seems to be applied. For brass composed of 70% of Cu and 30% of Zn, that is, the ratio of the number of atoms per unit volume is 0.7:0.3, the heat capacity per unit volume of brass is $3.26 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$ as seen in Table 1. From the heat capacities per unit volume of Cu and Zn in Table 1, it is estimated to be $3.24 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$ ($(=3.44 \times 0.7 + 2.77 \times 0.3) \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$). This is due to the fact that the heat capacity per unit volume is proportional to the number of atoms per unit volume as shown in Eq. (3) later on. The coincidence of the measured and the estimated values is satisfactory. This fact indicates that Neumann and Kopp law can be applied rationally to the estimation of heat capacity per unit volume of compounds.

Then, in the thermal design of micro-electro-mechanical systems, micro-electronics, etc. if there are no data for a new solid material or an unknown state, we can assume tentatively that the heat capacity per unit volume is approximately $2 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$ since from Table 1 the heat capacities per unit volume are scattered statistically as given by $(2.3 \pm 0.6) \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$. If we know the heat capacity per unit volume of a bulk crystal, this value is able to apply to the disordered state of the material. Furthermore, if we know the elements of a constituent of the material, we can apply Neumann and Kopp law to the estimation.

2. Discussion

First, I will extend the Dulong and Petit concept to heat capacity per unit volume. When we employ the number of atoms per unit volume, N, heat capacity per unit volume at high temperature is given by

$$c_p = 3Nk, \tag{3}$$

where k is Boltzmann's constant. The values are listed in Table 2 for typical materials together with the Debye temperature Θ_D. They do not always coincide with those shown in Table 1 at room temperature. From Table 2, we can draw the result that the coincidence is well for Zn and NaCl, but heat capacity per unit volume is considerably reduced for diamond, Al_2O_3 and MgO. This might be due to the fact that when the Debye temperature is close to room temperature the heat capacity per unit volume is nearly saturated in the heat capacity curve, on the other hand when the Debye temperature is far higher than room temperature it lies at the middle of the sigmoidal heat capacity curve.

Based upon the Debye model, I will further consider the reason why heat capacity per unit volume at room temperature lies around a confined value. Under the Debye approximation, heat capacity per unit volume at constant volume is given by [2]

$$c_v = 9Nk\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_m} \frac{e^x x^4\,dx}{(e^x - 1)^2} \tag{4}$$

where x and x_m are defined as

$$x = \frac{\hbar\omega}{kT} \tag{5}$$

and

$$x_m = \frac{\hbar\omega_m}{kT} = \frac{\Theta_D}{T}, \tag{6}$$

respectively. ω_m is the cut-off angular frequency on the acoustic phonon dispersion curve. Here it is assumed that the acoustic phonon dispersion curve has constant slope such that

$$\omega = v_0 q, \tag{7}$$

where v_0 is sound velocity and q is wave vector of acoustic phonon. Next I consider further the reduction of the heat capacity per unit volume within the framework of the above Debye approximation. The Eq. (4) can be applied to any materials under the assumption of Eq. (7), that is, the relation of $c_v/3Nk$ versus T/Θ_D gives a single curve notwithstanding materials. For solid materials there is no significant difference between c_v and c_p, then, I will apply Eq. (4) to the following estimation of heat capacity per unit volume at constant pressure. Based upon the relation of $c_p/3Nk$ versus T/Θ_D, c_p for an individual material at room temperature (300 K in Table 2) can be derived from Θ_D as

Table 2
Debye temperature Θ_D [4,5], atomic density N [5], $3Nk$, $300/\Theta_D$ and heat capacity per unit volume at room temperature estimated from the relation of $c_p/3Nk$ vs. T/Θ_D

Substance	Debye temperature (Θ_D) (K)	N ($10^{30}\,\mathrm{m^{-3}}$)	$3Nk$ ($10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$)	$300/\Theta_D$	c_p(r.t.) ($10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$)
C (diamond)	2230	0.176	7.29	0.13	1.14
Si	640	0.0502	2.06	0.47	1.65
Zn	310	0.0656	2.72	0.97	2.60
Al_2O_3	899	0.120	5.00	0.33	3.30
MgO	946	0.0541	4.48	0.32	2.88
SiO_2	470	0.0662	2.74	0.64	2.43
NaCl	321	0.0447	1.85	0.93	1.75

given in Table 2. The values of heat capacity per unit volume at room temperature, c_p(r.t.), in Table 2 can be interpreted as follows. When the atomic density N is sparse, the elastic constant (or sound velocity) might be relatively small since the distance between the neighboring atoms is long. As a result, the Debye temperature is comparatively low and therefore, the estimated heat capacity per unit volume c_p(r.t.) based upon the relation of $c_v/3Nk$ versus T/Θ_D is close to the saturated value $3Nk$. On the other hand, when the atomic density N is dense, the elastic constant (or sound velocity) might be large since the distance between the neighboring atoms is short. As a result, the Debye temperature is high and therefore, the estimated heat capacity per unit volume c_p(r.t.) derived from the same way is lower than the saturated value $3Nk$. Thus, the estimated values for c_p(r.t.) agree fairly well with the values in Table 1 even under the assumption of Eq. (7). Resultantly heat capacities per unit volume at room temperature settle at the values around $2 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$. Summing up, when the Debye temperature is close to room temperature the heat capacity per unit volume is near the saturated value in the heat capacity curve and on the other hand when the Debye temperature is far higher than room temperature the heat capacity per unit volume is lower than the saturated value; (2) at room temperature the heat capacity per unit volume for solid materials with high Debye temperature is reduced and as a result over a variety of solid materials the heat capacity unit volume lies around $2 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$ as given in Table 1. On solving thermal conduction equation in a small-scale region we can use this heat capacity per unit volume in the practical purpose.

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