Journal of Thermal Analysis and Calorimetry, Vol. 57 (1999) 765-771

THERMAL CONDUCTIVITIES OF MOLECULAR MATERIALS

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Abstract

Heat conduction is one of the most fundamental properties of a material. Knowledge of its magnitude and temperature dependence can be important in determining use limitations of a material. Experimental studies of heat conduction in molecular systems are summarized, with emphasis on N_2 and CBr_4, and placed in the context of our understanding of heat conduction mechanisms in solids.

Keywords: molecular solids, thermal conductivity

Introduction

Thermal conductivity can play an important role in the application of materials, from heat dissipation in thermoelectrics [1] to conduction of heat into a material from its environment, potentially determining use limitations of a material. The heat flux is quantified by the thermal conductivity, κ, which can vary over many orders of magnitude from one material to another, and as a function of temperature and pressure within a given material. Although we usually discuss κ, with SI units of $W\ K^{-1}\ m^{-1}$, as if it were a scalar, thermal conductivity is a second-rank tensor, reflecting potential anisotropy of heat flux within a material.

The relationship between thermal conductivity and heat capacity, C_p, is given by:

$$\kappa = DC_p\rho \tag{1}$$

where D is the thermal diffusivity and ρ is the density. For molecular solids, the topic of the present discussion, models of thermal conductivity are much less well established than models of heat capacity. Furthermore, experimental accuracy of heat capacity determinations, typically ±0.5% or even better, is much better than for thermal conductivity, which is about ±10% at best, and even order of magnitude uncertainty in many cases.

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimentally, thermal conductivity can be determined in several different ways. If large single crystals are available, thermal conductivity can be measured directly by its defining equation:

$$\kappa = \dot{q}/A(\mathrm{d}x/\mathrm{d}T) \tag{2}$$

where power, $\dot{q}$, is passed through a crystal of cross sectional area A under steady state conditions, and the temperature gradient, $\mathrm{d}T/\mathrm{d}x$, is determined directly.

Of course, single crystals are not always available, and other methods can be used. For example, in the transient hot wire method, a heat pulse is applied to a wire embedded in a sample and then the temperature is followed as a function of time using the wire as a thermometer. This method has been used to investigate a number of molecular solids at high pressure [2].

In the 3–ω method, a wire also serves as heater/thermometer, and temperature oscillations are measured at the third harmonic of the heater frequency. This method is especially useful for determination of thermal conductivity of insulators, and it reduces potential errors due to black-body radiation [3].

In the modulated radial heat flow method, a periodic heat pulse is applied to the outside of a cylindrical sample and the thermal diffusivity is determined by measurement of the amplitude of the temperature increase into the sample, and/or the phase lag between it and the heater pulse. Apparatus using this method for determination of thermal properties of low thermal diffusivity powders at low temperatures using fast Fourier transformation of the data has been described recently [4].

The generally accepted model for thermal conductivity of simple, crystalline, insulating solids can be considered in terms of heat carried by acoustic phonons. By analogy with the kinetic theory of gases, the phononic thermal conduction can be expressed as:

$$\kappa = C\nu\lambda \tag{3}$$

where C is the heat capacity per unit volume, ν is the speed of sound and λ is the phonon mean free path. At very high temperatures (much above the Debye temperature, θ_D), the heat capacity is relatively independent of temperature and the thermal conductivity is governed by the temperature dependence of the phonon mean free path, which increases as the temperature increases due to increased probability of phonon-phonon collisions (so called ‘Umklapp’ processes to indicate that they turn back the heat flux) which cause resistance to heat flow. As the temperature decreases, the mean free path becomes longer until it is limited by the distance between defects or impurities, or, if the crystal is nearly perfect, by the boundaries of the crystal. Eventually, the mean free path reaches a maximum value, but by this point the heat capacity has a strong temperature-dependence and drives $\kappa\rightarrow 0$ as $T\rightarrow 0$ K. This is shown schematically in Fig. 1.

For amorphous materials, the mean free path is short at all temperatures due to the lack of periodicity, and therefore the thermal conductivity is much reduced relative to a corresponding crystal, and $\mathrm{d}\kappa/\mathrm{d}T$ is positive at all temperatures (Fig. 1).

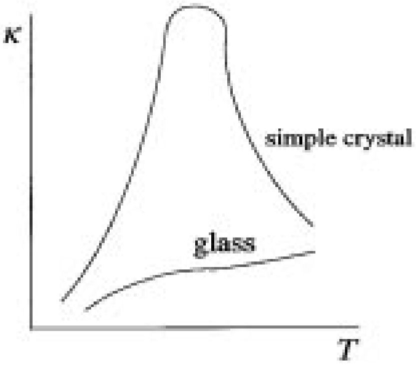

Fig. 1 A schematic view of the temperature-dependence of the thermal conductivity of a simple crystal and its corresponding amorphous (glass) phase

Rather than a phononic model, thermal conductivity in glasses has been considered as a random walk of localized oscillators [5].

Thermal conductivity has been used to explain matters as diverse as quality of popping corn: the cellulose of higher-quality kernels is more crystalline, giving it a higher thermal conductivity, and concomitant higher heat transfer, and good mechanical strength allowing for build-up of higher pressure of water vapour before popping open [6].

In this paper, we consider heat conduction in a few molecular systems, and especially the role of dynamical disorder. The topic has been reviewed relatively recently [7]. We concentrate on systems in which optic modes dominate the heat capacity (e.g. large molecules with relatively low-lying intramolecular degrees of freedom), keeping in mind that a perfect harmonic solid has no mechanism for resistance to heat flow, i.e., $\kappa=\infty$, and the most insight can be gained by consideration of mechanisms of thermal resistance.

Inclusion compounds

In 1981, it was reported that the thermal conductivity of a clathrate hydrate was very much less than that of ice, and with the opposite sign of the temperature dependence [8]. A clathrate hydrate is an inclusion compound, in which the host lattice is composed of water molecules, and guest species reside in the cages. They are known to be crystalline structures [9] and yet, as is apparent from the discussion above, from the perspective of its thermal conductivity, the clathrate hydrate seemed more like an amorphous material. We extended measurements to lower temperatures (much less than θ_D), and proposed the concept of interaction between the vibrational-rattling of the guest species in the cage with the heat-carrying acoustic modes [10]. An ideal test of this concept would be to measure the thermal conductivity of a clathrate hydrate with and without its guests. Unfortunately, the empty host lattice structure is not stable, collapsing to ice Ih.

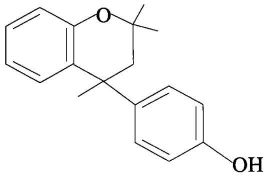

Fig. 2 The molecular structure of Dianin's compound

However, there are a few other inclusion compounds that form the same structure both with and without guests. One is Dianin's compound; its molecular structure is shown in Fig. 2. The host molecules form hexamers held together by hydrogen bonding through the phenolic oxygens, giving cages 11 Å high and 6.3 Å at the widest spot. Each cage can hold, for example, two ethanol molecules or one CCl_4 molecule [11]. Thermal conductivity measurements show that ethanol guests, which are dynamically disordered, give more thermal resistance than CCl_4 guests, which only librate slightly and therefore do not increase the thermal resistivity beyond what is observed in the empty host lattice [12, 13]. Measurements of thermal conductivity of another inclusion compound, hexakisphenylthiobenzene, with CBr_4 guests, show [14] thermal conductivity similar to Dianin's compound and clathrate hydrates, low and with $d\kappa/dT>0$, again, presumably, due to low-lying optic modes associated with dynamical disorder of the guests and/or host lattice. The data for all these inclusion compounds have been found to fit well in terms of the 'universal' model of thermal conductivity of glasses [14], showing how interaction between the heat-carrying acoustic modes and optic modes associated with dynamical disorder can shorten the mean free path to the same range as in a glass. The interaction between optic and acoustic modes has been put on a firmer theoretical basis by recent results from lattice dynamical simulations [15].

Solid nitrogen

Solid nitrogen is an interesting system to examine for its thermal conductivity because it exhibits two solid phases, one ordered and one disordered.

In its α phase, which exists below 35.6 K, the nitrogen molecules are ordered on a cubic lattice, and the thermal conductivity exhibits the 'normal' behaviour of a simple insulator (as shown schematically in Fig. 1) with a peak at about 4 K [16]. The thermal conductivity is understood in terms of normal resistance mechanisms, viz. grain boundaries, point defects, dislocations and phonon-phonon (Umklapp) processes.

The higher temperature phase of nitrogen, β-N_2, has a hexagonal close packed structure in which the N_2 molecules are dynamically disordered while remaining in place on their lattice sites. The thermal conductivity in this phase is less than in the α phase, with the additional resistance associated with orientational fluctuations of the N_2 molecules on their lattice sites [17]. The thermal conductivity of β-N_2 is almost independent of temperature, and certainly less steep than α-N_2 where $d\kappa/dT<0$ above 4 K.

Carbon tetrabromide

CBr_4 has four solid phases, as shown in Fig. 3 [18]. In phase I, the structure is face-centred cubic, and the CBr_4 molecules are dynamically disordered. The structure of phase II is monoclinic, and there has been some discussion as to whether this phase is fully ordered or not; we return to this point later. Phase III appears to be orientationally disordered, and phase IV is cubic and ordered.

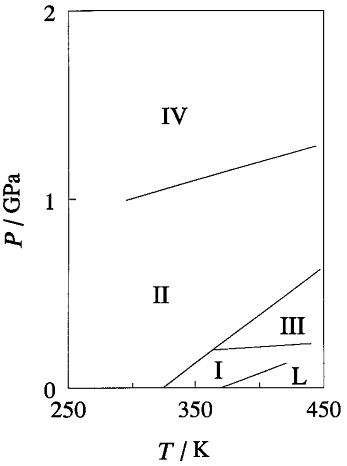

Fig. 3 The phase diagram of CBr_4 [18]

The thermal conductivity of CBr_4 has been measured as a function of temperature and pressure [18]. In phase I, the thermal conductivity is found to be nearly the same as for phase III and for the liquid, and the data have been fit satisfactorily to a model that included two scattering processes: Umklapp scattering and structural disorder. In phase IV, which is ordered, the dominant thermal resistance mechanism is phonon-phonon scattering.

In phase II, the thermal conductivity was fit to both Umklapp processes and structural disorder as:

$$\kappa^{-1} = R_{sd} + AT \tag{4}$$

where R_{sd} is the resistance due to structural disorder and AT represents the Umklapp contribution. Phase II of CBr_4 is structurally ordered, but recent heat capacity measurements show that the rigid CBr_4 molecules are fully rotationally-vibrationally excited at temperatures as low as 45 K [19]. How can structural disorder (from κ measurements) be reconciled with an ordered structure?

An answer could come from the realization that the thermal conductivity data for CBr_4 were determined under isobaric conditions, but the models for thermal conductivity are generally isochoric. In many materials this would not make much difference, but molecular solids are rather compressible so it is worth investigating futher.

Fortunately, the required data (molar volume [20], compressibility [21], thermal expansion [22]) are available for CBr_4-II to convert κ_p to κ_v. The resulting temperature-dependence of the thermal conductivity is shown in Fig. 4.

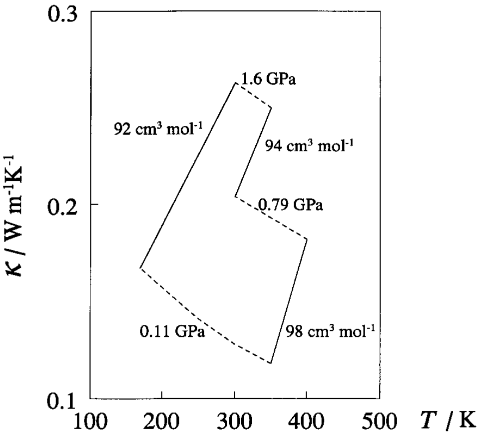

Fig. 4 Thermal conductivity of CBr_4 in phase II as a function of temperature. Solid lines indicate isochoric data (the volumes are indicated) and dashed lines indicate isobaric data (the pressures are indicated)

The most dramatic finding in Fig. 4 is that $d\kappa_v/dT>0$, despite the fact that CBr_4-II is an ordered structure and the temperature is far above θ_D(≈60 K for CBr_4) [19]. Nevertheless, as indicated already, its heat capacity shows evidence of significant molecular motion in phase II, and this is supported by NMR [23] and NQR [24] results. The structural disorder model of thermal conductivity (Eq. (4)), only increases thermal resistivity and cannot lead to $d\kappa/dT>0$, as observed in the isochoric data. However, a mechanism for achieving a positive thermal conductivity temperature coefficient is given by the resonance scattering model [10]: if the optic modes associate with libration of the CBr_4 molecules are in the same energy range as heat-carrying acoustic modes, and the interaction between them interrupts the heat flow, this would cause lower thermal conductivity as the temperature increases, as described earlier for the inclusion compounds. Determination of the dispersion relations in CBr_4 would provide a test of this proposal.

Conclusions

Thermal conductivity is an important property of materials, and there is a need for more high-accuracy data, especially in molecular systems where we are only now beginning to understand the role of optical modes in thermal resistance mechanisms. The prevalence of low-frequency optical modes in molecular materials and other soft matter could make optic-acoustic interactions the norm for such systems, in contrast with our present models in which the role of optic modes in heat conduction has been largely ignored.

Our work on thermal conductivity has formed the basis for the PhD theses of M. Zakrzewski, D. Michalski and V. Murashov, and I am grateful to them for their contributions. This work was funded by the Natural Sciences and Engineering Research Council of Canada, and the Killam Trusts.

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