CHIN. PHYS. LETT. Vol. 37, No. 10 (2020) 104401 **Express Letter**

A Ubiquitous Thermal Conductivity Formula for Liquids, Polymer Glass, and Amorphous Solids

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The microscopic mechanism of thermal transport in liquids and amorphous solids has been an outstanding problem for a long time. There have been several approaches to explain the thermal conductivities in these systems, for example, Bridgman's formula for simple liquids, the concept of the minimum thermal conductivity for amorphous solids, and the thermal resistance network model for amorphous polymers. Here, we present a ubiquitous formula to calculate the thermal conductivities of liquids and amorphous solids in a unified way, and compare it with previous ones. The calculated thermal conductivities using this formula without fitting parameters are in excellent agreement with the experimental data. Our formula not only provides a detailed microscopic mechanism of heat transfer in these systems, but also resolves the discrepancies between existing formulae and experimental data.

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Thermal conductivity is a fundamental physical quantity describing a material's capability of heat conduction. It is a macroscopic quantity reflecting the statistical properties of heat carriers such as phonons, electrons, or molecules at microscopic level. It has been a challenge to describe this macroscopic quantity in terms of only fundamental parameters specifying material characteristics. Although many works have been devoted to this problem, a unified formula for calculating the thermal conductivities of all these systems is still lacking, as the heat carriers are different in different states of matters.

In this Letter, we first discuss the existing (different) formulae of thermal conductivity for various states at high temperatures, exemplified by gases, liquids, crystals, amorphous solids, and polymers. Then we present a unified formula for thermal conductivity of these material forms using only fundamental structural components.

The thermal conductivity formulae proposed for different forms of materials are listed in Table 1. The $\kappa_{\rm G}$ is derived from the kinetic theory of gases (KTG),[1] where ϵ is a pure number, η is the viscosity, and C_v is the heat capacity at constant volume. Bridgman[2] proposed in 1923 an empirical formula $\kappa_{\rm L}$ to calculate the thermal conductivity of liquids, where $n_{\rm mole} = \rho/m_{\rm mole}$ is the number density of molecules, ρ the mass density, and $m_{\rm mole} = M_{\rm mole}/N_{\rm A}$ the mass of molecules. $k_{\rm B}$ is the Boltzmann constant, $v_{\rm s}$ the sound velocity, $N_{\rm A}$ the Avogadro constant, and $3k_{\rm B}$ the heat capacity per molecule. For $\kappa_{\rm L}$, Bridgman[2] assumed that the neighboring molecules form a simple cubic lattice. This model works well for liquids (such as methanol, carbon tetrachloride, chloroform, and water) and breaks down for liquids with complicated polyatomic molecules (such as liquid alkane). Later on, another formula of thermal conductivity of liquid was proposed by Eyring *et al.*[3] by taking into account the parts of gas-like and solid-like thermal conduction in liquids,[4] namely, combining $\kappa_{\rm G}$ and $\kappa_{\rm C}$ together.

In non-metallic crystalline solids, heat carriers are phonons — the collective excitation of lattice vibrations.[5] By treating phonons as gas-like, the thermal conductivity is given by the kinematic formula $\kappa_{\rm C}$ in Table 1,[5–7] where C is the phonon heat capacity, Λ the mean free path (MFP), and $\bar{v}_{\rm s} = \frac{1}{3}(v_{\rm sl} + 2v_{\rm st})$ the average sound velocity where $v_{\rm sl}$ and $v_{\rm st}$ are longitudinal and transverse sound velocities, respectively.

The derivation of thermal conductivities in amorphous solids is much less rigorous because of the ill-defined phonons due to the lack of lattice periodicity.

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Kittel[8] employed κ_C to calculate the thermal conductivity of amorphous solids by assuming a nearly constant MFP (Λ_0) which is close to the size of unit cell. However, Kittel's attempt was not successful in amorphous polymers, because Λ_0 in polymers should be less than 1 Å to recover experimental data.[9] This value is much shorter than the bond length of molecules.

Cahill and Pohl[10–12] extended this idea and proposed the concept of the minimum thermal conductivity (MTC) based on Einstein's theory.[13] Einstein[13] postulated the heat transfer as a random walk of energy elements between neighboring localized oscillators with 26 atomic neighbors. Cahill and Pohl[10–12] modified Einstein's theory by assuming a cluster of atoms as a vibrational "entity" where the size of cluster is one half of the phonon wavelength. At high temperatures, the MTC is reduced into a simple form of κ_A, where $n_{atom} = \rho/m_{atom}$ is the number density of atoms, and $m_{atom} = M_{atom}/N_A$ is the average mass of atoms. The κ_A works well for many inorganic amorphous solids such as vitreous silica (v-SiO_2), whose atomic structure can be described by the continuous random network (CRN) model.[14] However, it significantly overestimates thermal conductivities of amorphous solids such as amorphous selenium (a-Se) composed of crown ring Se_8 molecules and polymeric chains of Se. Such molecular solids are not described by the CRN model.

Very recently, a thermal resistance network (TRN) model was proposed by us to calculate the thermal conductivity of polymers whose structures can be described by the random coil model,[15] see κ_P in Table 1, where R_{inter} is the thermal resistance across contact points between molecular chains, i.e., the interchain resistance. L is the length of molecular chains, $n_{mole}L = \rho L/m_{mole} = \rho l_{unit}/m_{unit}$. Note that l_{unit} and m_{unit} are length and mass of repeating unit, respectively.

Table 1. The heat carriers and the formulae for calculating thermal conductivity in different states of materials.

	Heat carrier	Thermal conductivity	Ref.
Gas	Molecule	$\kappa_G = \epsilon\eta C_v$	[1]
Liquid	Vibration of molecule	$\kappa_L = 3k_B v_s n_{mole}^{2/3}$	[2,4]
Crystal	Phonon	$\kappa_C = \frac{1}{3}C\bar{v}_s\Lambda$	[5–7]
Amorphous solid	Vibration of atom/molecule	$\kappa_A = 1.2k_B\bar{v}_s n_{atom}^{2/3}$	[10–13]
Polymer	Vibration of molecule	$\kappa_P = (n_{mole}L)^{1/2}\frac{1}{R_{inter}}$	[15]

It is worth pointing out that κ_L of liquids and κ_A of amorphous solids are analogous because they are proportional to $n_{mole}^{2/3}$ and $n_{atom}^{2/3}$, respectively, and include the sound velocity. One may ask: is there any common physical mechanism between them? Indeed, κ_L and κ_A can be rewritten as $\kappa_L \propto Cv_s n_{mole}^{-1/3}$ and $\kappa_A \propto C\bar{v}_s n_{atom}^{-1/3}$, respectively, where $C \sim k_B n_{mole}$, and $\sim k_B n_{atom}$ at high temperatures. These two forms are basically the same as κ_C except a dimensionless prefactor 3 in κ_L and 1.2 in κ_A, when choosing the MFP Λ to be on the same order of magnitude of $n_{mole}^{-1/3}$ and $n_{atom}^{-1/3}$.

Further comparison of κ_P with κ_L and κ_A makes it clear that the number density dependence of thermal conductivity in polymers $n_{mole}^{1/2}$ is different from that in κ_L and κ_A and the sound velocity dependence vanishes. We note that the actual value of $\frac{(Ln_{mole}^{-1/3})^{1/2}}{R_{inter}}$ is of the same order of magnitude of $k_B v_s$ because L and $n_{mole}^{-1/3}$ are typically a few Angstroms and the thermal resistance R_{inter} is between 0.65–1.6 $\times 10^{10}$ K/W from fitting results.[15] Therefore, $\frac{(Ln_{mole}^{-1/3})^{1/2}}{R_{inter}} \approx 10^{-20}$ Wm/K is very close to the value of $k_B v_s$.

Based on the above analysis, we conjecture that κ_L, κ_A, and κ_P might be expressed as a single formula. The difference for different materials lies only in a prefactor. In the following, we shall derive such a formula from the fundamental heat carriers in these materials.

We adopt Einstein's idea[13] that thermal transport is a random walk of heat through the coupling between vibrational modes.[16] Einstein[13] considered that the random walk occurs between an atom and its surrounding neighbors. The difference from our theory is: we postulate that molecules or clusters of atoms work as individual fundamental units in which the atomic arrangements are ordered or nearly ordered that maintaining short-range order. Then the random walk of heat through the network formed by these fundamental units plays a key role for the overall thermal conductivity.

Our hypothesis is based on the fact that both liquids and amorphous solids possess short-range order only.[17] The size of fundamental units usually ranges from several Angstroms to several nanometers as demonstrated by x-ray diffraction measurements.[17] It should be emphasized that such a length scale of fundamental units is too small to define a local temperature distribution. It is natural that the thermal equilibrium in each fundamental unit is achieved very fast compared with overall one, not affecting the overall thermal resistance above room temperature. Thus, the thermal transport between neighboring fundamental units are governed by the interaction at the contact, for example, via weak van der Waals (VDW) interaction, H-bond, chemical bond, etc, where these units are regarded as phase uncorrelated oscillators.

In complex network systems, heat conduction gen-

erally depends on the degree of networks (the average coordination number surrounding a constituent element).[18,19] We can regard fundamental units as nodes and the contact between fundamental units as links among nodes in analogy to the nodes-links-blobs model for complex network systems.[20] In this regard, the number of links per unit length along the direction of heat current is the cubic root of the number density of links. Then we can write the universal formula of thermal conductivity which is valid for a wide range of complex disordered systems, at high temperatures as

$$\kappa = \left(\frac{Z}{3\Xi}\tilde{n}\right)^{1/3} h, \tag{1}$$

where Z is the degree of network (the average coordination numbers), 3 is the dimension, Ξ is the number of nodes (fundamental units) sharing one link, and $\tilde{n}$ is the number density of nodes (fundamental units). h is the heat conductance between blobs, which means the average energy flow across links per unit time per temperature drop. Its unit is $\mathrm{J{\cdot}K^{-1}{\cdot}s^{-1}}$. The heat conductance can be written as

$$h = \frac{1}{\gamma}\frac{C_{\mathrm{per}} v_{\mathrm{s}}}{\delta}, \tag{2}$$

where γ is the proportion of inter-molecular heat transfer, C_{per} is the heat capacity per particle whose high-temperature limit is $(\frac{3}{2} + \frac{D_{\mathrm{v}}}{2})k_{\mathrm{B}}$ with 3 in the numerator corresponding to the translational degree of freedom and D_{v} the average vibrational degree of freedom of particle. The value of D_{v} should be from 0 to 3. δ is the length of link, namely, the distance between neighboring atoms or functional groups (such as $\mathrm{-CH_3}$ in paraffin or polymers) at contact points.

Here we apply Eqs. (1) and (2) to calculate thermal conductivity of liquids and amorphous solids with different fundamental units in different network structures. Substances are categorized into three types according to the characteristics of fundamental units, instead of the matter state. The illustrations in Fig. 1 show different types of networks with different fundamental units. In liquids and amorphous solids made of simple molecules, such as alkane and paraffin, the fundamental units are individual molecules. In inorganic amorphous solids with covalent bonded atoms such as v-$\mathrm{SiO_2}$, the fundamental unit is a dense cluster of atoms as marked by blue circles in Fig. 1(b). In polymers made of macromolecules, fundamental units are drawn by purple ellipse in Fig. 1(c), namely, the chain segments between adjacent contact points of different chains. The average segment length is defined by ξ. The fast thermal equilibrium achieved in individual small fundamental unit is indubitable for all cases above room temperature. Thus, the thermal transport can be described as a random walk from one fundamental unit to its touching neighbor units. At low temperatures, these two processes should be considered simultaneously. In this Letter, we focus only on high-temperature regime, where the equipartition theorem is valid and quantum effects are negligible. Low-temperature cases will be considered elsewhere.

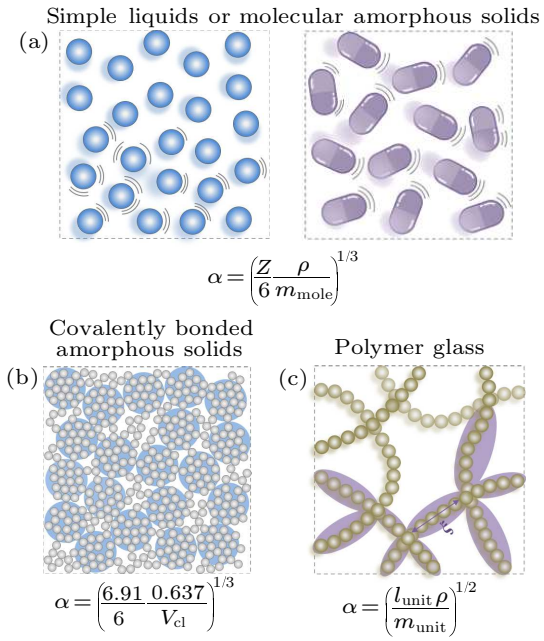

Fig. 1. The schematic illustration of different types of fundamental units transferring heat in liquids and amorphous solids and the prefactor α in Eq. (3). (a) The fundamental unit for liquid or molecular amorphous solid is individual molecule. (b) The fundamental unit for covalent amorphous solid is dense cluster (shaded areas in blue). V_{cl} is the volume of atomic cluster. (c) The fundamental unit for polymer is a chain segment (shaded areas in purple).

Table 2. Selections of fundamental units and corresponding parameters for different types of materials.

Material type	Fundamental unit	$\tilde{n}$	Typical size of fundamental unit	Ξ	γ	D_{v}	δ
Molecular liquids and solids	Nearly-spherical molecules	$= n_{\mathrm{mole}}$	$a \times a \times a$	2	1	1–3	$= a \approx n_{\mathrm{mole}}^{-1/3}$
Molecular liquids and solids	Capsule-like molecules	$= n_{\mathrm{mole}}$	$L \times a \times a$	2	1	1	$\approx a < n_{\mathrm{mole}}^{-1/3}$
Molecular liquids and solids	Disk-like molecules	$= n_{\mathrm{mole}}$	$L \times L \times a$	2	1	1	$\approx a < n_{\mathrm{mole}}^{-1/3}$
Covalently bonded amorphous solids	Atomic clusters	$\ll n_{\mathrm{atom}}$	$\zeta \times \zeta \times \zeta$	2	1	2	$\approx b < n_{\mathrm{atom}}^{-1/3}$
Polymer liquids and solids	Chain segments	$\gg n_{\mathrm{mole}}$	$\xi \times a \times a$	4	1/2	1	$= a' \ll n_{\mathrm{mole}}^{-1/3}$

By properly taking the parameters for different fundamental units, Eq. (1) reduces to

$$\kappa = \alpha \frac{1}{\delta}\left(\frac{3}{2} + \frac{D_{\rm v}}{2}\right) k_{\rm B} v_{\rm s}, \tag{3}$$

where the prefactor α differs from state to state as presented in Fig. 1. Its physical meaning is given in the Supplementary Information. The fundamental units for different types of liquids and amorphous solids are summarized in Table 2. The parameters Ξ, γ, $D_{\rm v}$, and δ are also presented (see details in Supplementary Information).

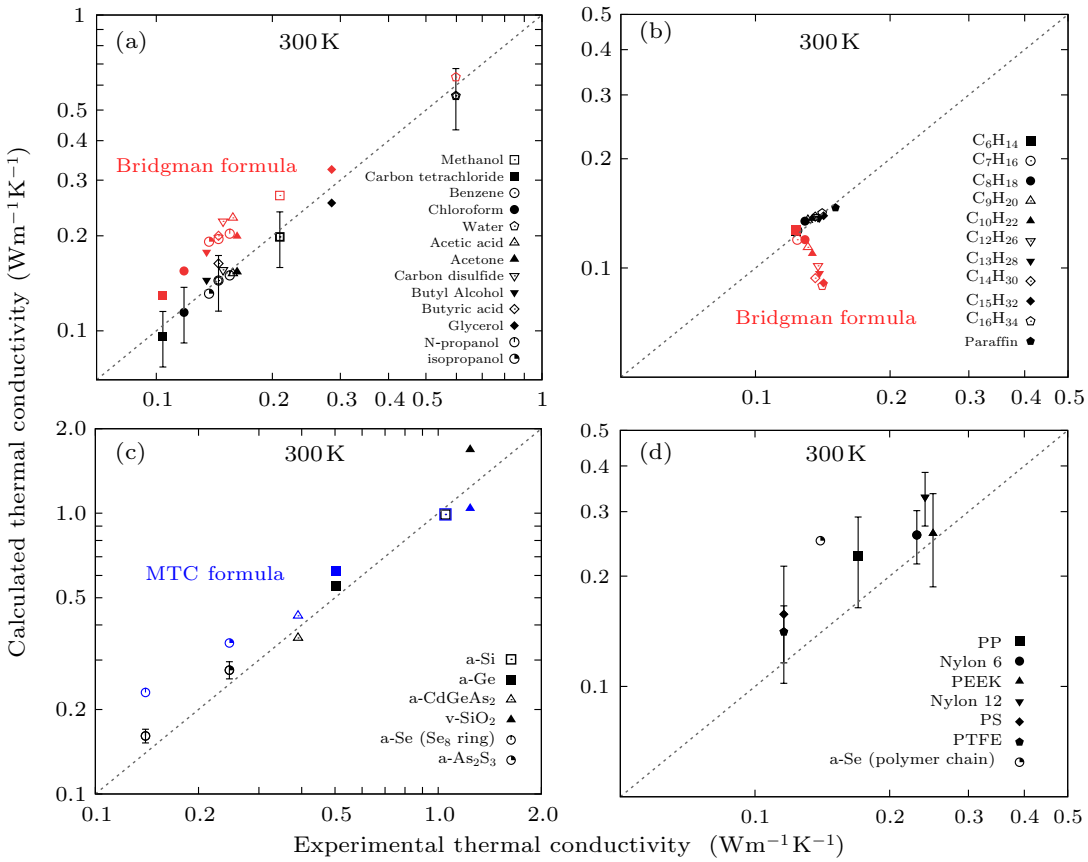

Fig. 2. Comparison of calculated thermal conductivities from Eq. (3) with experimental ones. The diagonal (dotted) line is given to guide for eyes. Symbol lies on this line means calculated thermal conductivity has the same value with experimental one. (a) Calculated thermal conductivities (black symbols) of thirteen different liquids at 300 K versus the experimental values. $D_{\rm v}$ is chosen to be 1–3 for nearly spherical molecules (methanol, carbon tetrachloride, benzene, chloroform, and water) and $D_{\rm v} = 1$ for non-spherical molecules. The experimental data of thermal conductivities are taken from Refs. [2,21]. Thermal conductivities calculated from the Bridgman formula (red symbols) are also given for comparison. (b) Calculated thermal conductivities (black symbols) of ten different alkane liquids and paraffin at 300 K versus the observed values when $D_{\rm v} = 1$. The calculated values of Z are listed in Supplementary Information. The experimental thermal conductivities are taken from Ref. [21]. Thermal conductivity calculated according to the Bridgman formula (red symbols) are also given for comparison. (c) Calculated thermal conductivities (black symbols) for six different inorganic amorphous solids at 300 K versus the observed values when $D_{\rm v} = 2$ except for a-As_2S_3 and a-Se, in which case we take As_2S_3 and Se_8 molecules as fundamental units with $5 < Z < 7$ and $D_{\rm v} = 1$. The experimental thermal conductivities are taken from Ref. [11]. Thermal conductivity calculated using the MTC formula (blue symbols) are also given for comparison.[11] (d) Calculated thermal conductivities (black symbols) for six polymers and a-Se composed of 100% polymeric chains at 300 K versus the experimental values when $D_{\rm v} = 1$. The experimental data are taken from Ref. [22].

We shall point out that the number density of fundamental units is the key parameter in determining the thermal conductivity, as can be seen from Eq. (1). When the fundamental unit is the entire small molecule, $\tilde{n}$ can be replace by $n_{\rm mole}$. When the molecules are large as in polymers, $\tilde{n}$ should be much larger than $n_{\rm mole}$ by choosing chain segments as fundamental units which contain tens of atoms. Similarly, $\tilde{n}$ should be the number density of atomic clusters which contains tens of atoms in covalently bonded amorphous solids. It needs to be cautious when applying Eq. (3) to polymer glasses consisting of extremely long chains, as it is assumed that fundamental units (polymer segments) reach to the thermal equilibrium within the time scale $\tau_{\rm C}$, faster than the time-scale $\tau_{\rm V}$ of the heat conductance between those units. Namely, the situation $\tau_{\rm C}/\tau_{\rm V} < 1$ gives the criterion for the applicability of Eq. (3) to polymer glass. Since the

polymer segments execute coherent vibrations at finite temperatures, its characteristic time scale is considered to be connected with the strength of covalent bonding in polymer chain, while the time scale $\tau_{\rm V}$ is governed by the strength of VDW force. The ratio can be estimated from the strengths of covalent bonding in polymer chains and VDW coupling between chain segments, which is around 100. This means that Eq. (3) is applicable for polymer glasses consisting of polymer segments within around 100 times of periodic unit of polymer chains.

Our formula is in excellent agreement with the experimental data when $1 \leq D_{\rm v} \leq 3$ for all substances. We further find that $D_{\rm v}$ is reduced to 1 when the shape of molecules is capsule-like or disk-like. This is due to the shape effect on the liquid relaxation process. In covalently bonded amorphous solids, the value of $D_{\rm v}$ is found to be 2. Possible explanation is the strongly distorted atomic structure at the edge of fundamental unit where the internal stress shifts from negative value to positive one.[23]

Another major difference of our model from the Bridgman's formula or the MTC one is the intermolecular/interatomic separation δ. The Bridgman's formula uses $n_{\rm mole}^{-1/3}$ as the intermolecular separation. This is valid only for simple liquids with spherical-like molecules because $a \approx n_{\rm mole}^{-1/3}$, where a is approximately equal to the length scale of the occupying space of molecules/atoms. When the molecule is non-spherical, for example, Se_8 is disk-like and acetone is capsule-like, the intermolecular separation is not the distance between the centers of adjacent molecules. The distance should be the separation between contact atoms or functional groups. Therefore, the value of δ is approximately a which is obviously much smaller than $n_{\rm mole}^{-1/3}$. In covalently bonded amorphous solids, it is convenient to chose δ to be the bond length, b, which is smaller than $n_{\rm atom}^{-1/3}$. When the molecule is extremely long in polymer, δ is the average value of the size of atoms or functional groups at the contact points, a'.

In Fig. 2, we compare the calculated thermal conductivities from our formula with experimental values for various liquids, molecular solids, inorganic amorphous solids, and polymers. The symbols given by black are calculated results obtained from Eq. (3), and the diagonal (dotted) lines are used to guide eyes to judge the agreement between calculated and experimental thermal conductivities. It shows that our formula agrees very well with the experimental data. For more comprehensive analysis, please refer to the Supplementary Information.

Equation (3) holds in the temperature regime that fundamental units execute incoherent/independent vibrations respectively. This situation is achieved at high temperatures where the measured thermal conductivities are saturated or show weak temperature dependence. This temperature regime has been universally observed for a wide range of complex disordered materials. We note that Eq. (3) recovers the weak temperature dependence of κ via the temperature dependences of macroscopic parameters included in Eq. (3) such as mass density, distance between neighboring fundamental units, and sound velocity.

We shall emphasize here that thermal conductivities are highly dependent on the detailed atomic/molecular structure of fundamental unit. We further point out that the mechanism of thermal conductivity of liquids and non-crystalline solids has the same origin. For heat transport, liquids should behave as amorphous solids rather than as fluids, when the oscillation period $1/\omega$ of atoms in liquids is much shorter than their structure relaxation time τ, namely, $\omega\tau > 1$.[24–26]

In summary, by introducing the concept of the fundamental units characterizing the types of complex disordered systems such as liquids, amorphous solids, and amorphous polymers, we have proposed a ubiquitous formula for thermal conductivity that applicable for both liquids and amorphous solids. With properly defined fundamental units, we have demonstrated that the thermal conductivity is dominated by the thermal resistance between neighboring fundamental units. This is because the fundamental units reach thermal equilibrium much faster than the heat transfer between units.

Our formula of Eq. (1) not only provides a deeper physical understanding compared with the existing well-accepted empirical/theoretical ones, but also resolves the discrepancies between these formulae and experiment measurements.

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Supplementary Information for "A ubiquitous thermal conductivity formula for liquids, polymer glass and amorphous solids"

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SA. Fundamental units transferring heat in molecular liquids and amorphous molecular solids

In liquids and amorphous solids made of weakly coupled molecules, the fundamental units characterizing thermal conduction are individual molecules, whose atomic arrangement can be described by relatively close packing with voids in liquids and random packing in solid.

Molecular Liquids

The kinetic theory of gases (KTG) fails to explain the thermal transport in liquids because the molecules are neither localized around fixed equilibrium positions like in solids nor move freely like gases. Tranchenko and Brazhkin [1] have demonstrated that the thermodynamical properties of simple liquids are determined by the vibrational contributions as in solids in all range of liquid relaxation times [2, 3]. In other words, the characteristic time of thermal transport is shorter than the duration between two events of jump of certain atom accompanied by large scale rearrangement of its surrounding atoms. The surrounding atoms can be seen as temporary touching neighbours. We have evaluated the coordination number of touching neighbours for several typical liquids by the Monte Carlo simulation. The simulation details are given in section SD and the results are shown in Table S1.

Using the simulated Z, we further calculated the thermal conductivities by Eq. (1) with $\tilde{n} = \rho/m_{\rm mole}$, $\Xi = 2$, and $\gamma = 1$, and it is reduced to Eq. (3) with $\alpha = \left(\frac{Z}{6}\frac{\rho}{m_{\rm mole}}\right)^{\frac{1}{3}}$. $\delta = a$ should be used for most molecules, where a is the Van der Waals diameter of molecule. The only exception is benzene because of its ring structure. The calculated thermal conductivities using parameters in Table. S1 are shown in Fig. 2(a) and (b) in comparison with the experimentally measured data. Figure 2(a) gives the thermal conductivities of various liquids, whose aspect ratio is $L/a < 2$, including methanol, carbon tetrachloride, benzene, chloroform, water, acetic acid, acetone, carbon disulfide, butyl alcohol, butyric acid, glycerol, N-propanal, and isopropanol. The calculated values are in excellent agreement with the experimental values by choosing D_v to be 1∼3 for nearly spherical molecules ($L/a \sim 1$) and $D_v = 1$ for non-spherical molecules ($L/a > 1$). For alkanes whose aspect ratio is $L/a > 2$, we find that the calculated thermal conductivities perfectly match the experimental values by choosing $D_v = 1$ as shown in Fig. 2(b). The reduction of D_v for liquids with long molecules originates from the higher possibility of thermal transport along the longitudinal axis of molecules while it is hard to transport along the transverse axis. This feature can be understood as an analogy of reptation of molecules [4].

We now revisit the Bridgman's formula. In his original paper, Bridgman considered six nearest neighbours forming a simple lattice structure. Adopting this structure, it is easy to reproduce the Bridgman's formula from Eq. (3) by taking $Z = 6$, $\gamma = 1$, $D_v = 3$, $\tilde{n} = n_{\rm mole}$, and $\delta = n_{\rm mole}^{-\frac{1}{3}}$. We shall point out that the Bridgman's formula is applicable only when the molecules are nearly-spherical. For nearly-spherical molecules (such as methanol, carbon tetrachloride, chloroform, and water), the calculated values of Z are between 4.4∼5.3 as shown in Table. S1. This results in $0.90 < \left(\frac{Z}{6}\right)^{\frac{1}{3}} < 0.96$. We further compare a with $n_{\rm mole}^{-\frac{1}{3}}$ by taking methanol and carbon tetrachloride as examples. We find that the values $n_{\rm mole}^{-\frac{1}{3}} = 4.07$Å for methanol and 5.43Å for carbon tetrachloride are very close to their diameters 4.2Å and 5.6Å, respectively. Therefore, $a \approx n_{\rm mole}^{-\frac{1}{3}}$ is valid in liquids with nearly spherical molecules.

The Bridgman's formula breaks down for non-spherical molecules. This discrepancy comes from the enhancement of Z with increasing L and the significant difference between a and $n_{\rm mole}^{-\frac{1}{3}}$. For example, $n_{\rm mole}^{-\frac{1}{3}} = 7.88$Å for $C_{16}H_{34}$ is much larger than its diameter 4Å. We further compare the thermal conductivities between isomers by taking N-propanal and isopropanol as an example. They have exactly the same chemical composition, C_3H_7OH. The observed thermal conductivities of N-propanal and isopropanol are 0.155 $\rm Wm^{-1}K^{-1}$ and 0.137 $\rm Wm^{-1}K^{-1}$, respectively. Their relative difference is 13%. The calculated results from our formula Eq. (1) are 0.150 $\rm Wm^{-1}K^{-1}$ and 0.131 $\rm Wm^{-1}K^{-1}$ by taking $D_v = 1$.

TABLE S1. Mass density, molecular length, molecular diameter, molar mass, and sound velocity of typical liquids used in the calculations [5, 6]. Z is calculated by Monte Carlo simulation except for water which is taken from Ref. [7].

Liquids	ρ	L	a	$M_{\rm mole}$	v_s	Z
	(g/cm^3)	(Å)	(Å)	(g/mol)	(m/s)	
Methanol (CH_3OH)	0.787	-	4.2	32.04	1076	4.59
Carbon tetrachloride (CCl_4)	1.594	-	5.6	153.8	926	4.59
Benzene (C_6H_6)	0.876	-	5.4	78.11	1321	4.45
Chloroform ($CHCl_3$)	1.479	-	5.2	119.37	979	4.40
Water (H_2O)	0.998	-	2.8	18.015	1482	4.7,5.3
Acetic acid (CH_3COOH)	1.045	4.99	4.0	60.05	1150	4.03
Acetone (CH_3COCH_3)	0.784	6.54	4.0	58.08	1190	4.84
Carbon disulfide (CS_2)	1.263	4.94	4.0	76.15	1158	3.26
Butyl alcohol ($C_4H_{10}O$)	0.810	7.26	4.0	74.12	1222	4.62
Butyric acid ($C_4H_8O_2$)	0.959	7.26	4.0	88.11	1380	4.63
Glycerol ($C_3H_8O_3$)	1.261	6.71	4.0	92.09	1920	5.13
N-propanol (C_3H_7OH)	0.805	5.99	4.0	60.1	1220	4.20
isopropanol (C_3H_7OH)	0.785	5.27	4.0	60.1	1170	3.27
C_6H_{14}	0.659	10.35	4.0	86.18	1113	5.85
C_7H_{16}	0.680	11.62	4.0	100.2	1131	6.33
C_8H_{18}	0.699	12.89	4.0	114.23	1213	6.78
C_9H_{20}	0.718	14.16	4.0	128.25	1226	7.33
$C_{10}H_{22}$	0.726	15.43	4.0	142.28	1252	7.75
$C_{12}H_{26}$	0.750	17.97	4.0	170.33	1279	8.74
$C_{13}H_{28}$	0.756	19.24	4.0	184.36	1278	9.19
$C_{14}H_{30}$	0.763	20.51	4.0	198.39	1294	9.68
$C_{15}H_{32}$	0.768	21.78	4.0	212.41	1307	10.16
$C_{16}H_{34}$	0.770	23.05	4.0	226.44	1338	10.54

The relative difference from our calculation is also 13% which is in excellent agreement with experimental data. The main difference comes from the decrease of the value of Z as shown in Table. S1. In contrast, the Bridgman's formula gives larger values of 0.203 Wm^{-1}K^{-1} and 0.192 Wm^{-1}K^{-1}. The relative difference is only 5.7%. Therefore, our formula Eq. (1) captures well the underlying chemical structural effect on thermal transport in liquids.

Molecular amorphous Solids

The thermal conductivity of amorphous solids composed of small molecules are considered in a similar way as liquids. In contrast to liquids, the molecules in solids vibrate at equilibrium positions and the neighbouring molecules are fixed. Then the thermal conductivity is evaluated by Eq. (3) with $\alpha = \left(\frac{Z}{6}\frac{\rho}{m_{\rm mole}}\right)^{\frac{1}{3}}$, which is close to the case of molecular liquids. The only difference is to replace v_s by $\bar{v}_s$ because there are additional two transverse modes in solids.

TABLE S2. Mass density, molar mass of molecule, diameter of atom, and sound velocity of three molecular amorphous solids used in the calculations [9]. Calculated Z of paraffin is shown. The values of Z of a-Se and a-As_2S_3 are unknown because of their irregular structures.

Molecular	ρ	$M_{\rm mole}$	a	v_{sl}	v_{st}	Z
amorphous solids	(g/cm^3)	(g/mol)	(Å)	(m/s)	(m/s)	
Paraffin ($C_{18}H_{38}$)	0.777	254.5	4.0	1400	-	11.43
a-Se (Se_8 ring)	4.30	631.7	3.80	2060	1060	-
a-As_2S_3	3.20	246.05	3.60∼3.70	2650	1440	-

We consider paraffin, amorphous octaselenium (a-Se), and amorphous As_2S_3 (a-As_2S_3) as examples where their parameters are given in Table. S2. It has been experimentally confirmed, e.g., from the optical spectroscopy measurements, that a-Se are composed of polymeric chains and crown ring Se_8 molecules[10]. Since it is difficult to control this ratio in sample preparations of a-Se, we estimate κ for two extreme cases for a-Se, one is composed of 100% of Se_8 molecules (in this section) and the other is 100% polymeric chains (in section SC). The calculated results for these extreme cases are given in Fig. 2 (c) and (d). We see that there exists discrepancy with the observed data of κ. This is due to that it is difficult to prepare the actual samples of two extreme cases, in addition to the difficulty to identify the detailed microscopic structures in a-Se.

Paraffin is long molecule whose Z is calculated to be 11.43. The molecular structures of a-Se, which takes crown-shaped disk-like structure, and a-As_2S_3 are too irregular to calculate their value of Z by our simple Monte Carlo simulations. Therefore, we show the results for $5 < Z < 7$ which is a typical range due to random close packing model [8]. Fig. 2(c) shows that the calculated thermal conductivities in comparison with experimental data when $D_v = 1$. The calculated thermal conductivity of a-Se (a-As_2S_3) is 0.152-0.170 (0.257-0.296) Wm^{-1}K^{-1} which is close to the experimental data 0.140 Wm^{-1}K^{-1} (0.246 Wm^{-1}K^{-1}). As for comparison, the minimum thermal conductivity (MTC) formula gives an overestimated value of 0.230 Wm^{-1}K^{-1} (0.345Wm^{-1}K^{-1}). Therefore, we should conclude that the MTC formula is inappropriate to calculate the thermal conductivity of molecular amorphous solids, while our formula gives the correct value.

SB. Fundamental units in covalent-bonded amorphous solids

In amorphous solids such as amorphous Si (a-Si), amorphous Ge (a-Ge), amorphous $CdGeAs_2$ (a-$CdGeAs_2$), and vitreous silica (v-SiO_2) in which atoms are covalently bonded. We should stress that atomic clusters with local order should be chosen as fundamental units. In order to reach thermal equilibrium, it should take shorter time than the heat transfer between neighbouring clusters. Such ordered clusters have been experimentally observed through radial distribution

TABLE S3. Mass density, average molar mass of atom, bond length, diameter of cluster, and sound velocity of four amorphous covalently bonded solids used in the calculations [9].

Covalently bonded amorphous solids	ρ (g/cm^3)	$M_{\rm atom}$ (g/mol)	b (Å)	ζ	v_{sl} (m/s)	v_{st} (m/s)
a-Si	2.33	28.09	2.33	4b	7360	4370
a-Ge	5.32	72.64	2.41	4b	4350	2630
v-SiO_2	2.21	20.03	1.63	7Å	5980	3740
a-$CdGeAs_2$	5.72	83.72	2.50	4b	3030	1860

function (RDF) by X-ray diffraction where the RDF shows sharp peaks when the distance from a center atom is smaller than $2b$, where b is the length of the covalent bond. We assume that the average size of fundamental units is approximately $4b$. This is consistent with the observed size of crystalline domain, for example, 7 Å for amorphous silica [11].

We assume that the amorphous solids are formed by random close packing of spherical clusters, whose volume is $V_{cl} = \frac{4\pi}{3}(\frac{\zeta}{2})^3$ where ζ is the diameter of cluster. According to the theory of random close packing, the average coordination number $Z = 6.91$ [8] and the filling factor $V_{cl}\tilde{n} = 0.637$ [12]. Therefore, the thermal conductivity can be evaluated by choosing $\Xi = 2$ and $\gamma = 1$, which leads to Eq. (3) with $\alpha = \left(\frac{6.91}{6}\frac{0.637}{V_{cl}}\right)^{\frac{1}{3}}$. If we rewrite the mass density of solid as $\frac{N_{cl}}{V_{cl}} m_{\rm atom} = \rho$ where N_{cl} is the number of atoms in each cluster. The numerical simulations showed that $N_{cl} = 14.2 + 1$ [13] which means 1 atom with 14.2 neighbouring atoms. One can easily reproduce the MTC formula as $\kappa \approx 0.474(3/2 + D_v/2)k_B\bar{v}_s n_{\rm atom}^{\frac{2}{3}}$ by choosing $D_v \approx 2$. We calculated the thermal conductivities of a-Si, a-Ge, a-$CdGeAs_2$, and v-SiO_2 with the parameters given in Table. S3. The calculated values are in good agreement with the measured ones as shown in Fig. 2(c) when D_v is chosen to be 2.

SC. Macromolecular chain segments as fundamental units in polymer solids and polymer liquids

Polymers solids and polymer melts consist of macromolecules with extremely long length, i. e. $L \gg a$. Therefore, it is inappropriate to consider an entire chain as one fundamental unit. It has been pointed out that there are three processes when a heat current flow through polymers [14, 15]: inter-chain heat transfer and intra-chain heat transfer at contact points and thermal transport inside each segment between two adjacent contact points. It is obvious that thermal equilibrium of each fundamental unit is faster than inter-chain heat transfer because of the large intrinsic thermal conductivity of a single molecular chain [16, 17]. Therefore, $\tilde{n} = \frac{L}{\xi} n_{\rm mole}$, $\Xi = 4$ and $Z = 6$ as shown in Fig. 1(c). Zhou et al. [14] have evaluated that $\xi = 4\sqrt{\frac{m_{\rm unit}}{l_{\rm unit}\rho}}$ where $m_{\rm unit}$ and $l_{\rm unit}$ are the mass and length of repeating units, respectively. Moreover, in isotropic polymers, $\frac{1}{h} = (1-\gamma)R_{\rm intra} + \gamma R_{\rm inter} \approx \frac{R_{\rm inter}}{2}$ because $\gamma \approx (1-\gamma) \approx 1/2$ where $R_{\rm intra}$ is the intra-chain thermal resistance which is negligible compared to $R_{\rm inter}$ [14]. Therefore, the average value of h can be obtained as $2\frac{C_{per}\bar{v}_s}{\delta}$. Eq. (1) is then reduced to Eq. (3) with $\alpha = \left(\frac{l_{\rm unit}\rho}{m_{\rm unit}}\right)^{1/2}$ as given in Fig. 1(c). It is easy to reproduce $\kappa_{\rm P}$ by using $\frac{l_{\rm unit}\rho}{m_{\rm unit}} = \frac{L\rho}{M_{\rm mole}} = Ln_{\rm mole}$. The value of δ is determined by the size of functional groups, noted as a', such as -CH_3, -F, -OH, =CO etc. We have performed molecular-dynamic (MD) simulation in Ref. [14] to clarify the impact of the intermolecular separation δ on the inter-chain thermal resistance. The MD simulations have demonstrated that the inter-chain thermal resistance severely depends on the intermolecular separation δ. Here we evaluate the actual value of δ from van der Walls diameter of functional groups. This estimation is reasonable, while the accurate determination of δ deserves further investigation. Figure 2(d) shows the calculated thermal conductivity of several typical polymers in comparison with the experimental data, where $D_v = 1$ and other parameters are listed in Table. II.

TABLE S4. Mass density, length and molar mass of repeating unit, size of functional groups, and sound velocity of a-Se and six polymers: polypropylene (PP), Nylon 6, poly(ether ether ketone) (PEEK), Nylon-12, polystryrene (PS), and polytetrafluoroethylene (PTFE) [6, 14, 18, 19].

Polymers	ρ (g/cm^3)	$l_{\rm unit}$ (Å)	$m_{\rm unit} \times N_A$ (g/mol)	a' (Å)	v_{sl} (m/s)	v_{st} (m/s)
PP	0.85	2.17	42.1	4.0-7.1	3420	1750
Nylon 6	0.65	8.6	113.2	4.0-5.6	3470	1610
PEEK	1.26	10	288.3	3.0-5.4	3000	1500
Nylon 12	1.02	16	198	4.0-5.6	3380	1630
PS	1.05	3.32	104	4.0-8.4	2870	1480
PTFE	2.0	1.3	50.01	2.8-4.0	1350	550
a-Se (polymer chain)	4.3	1.88	78.96	3.80	2060	1060

SD. Monte Carlo simulations

In order to evaluate the coordination number of molecules in liquid, the molecules are simplified into either spheres or cylinders with hemisphere at two ends, see Fig. S1. The positions of molecules are random, thus we adopted the Monte Carlo method to generate an equivalent liquid structure. We first evaluate the number $N_{\rm MC}$ of particles generated in a given box, $N_{\rm MC} = (\ell^3 \times \rho)/m_{\rm mole}$. The size of the simulation box, ℓ, is chosen to be 10 nm. Then the position of particles is randomly generated and recorded. Once a new particle is generated, the distance to the previously generated particles in the box will be calculated. If the distance is smaller than the van der Waals diameter given in Table. S1, it will be recorded as a contact point. After all particles has been generated, the total

contact number N_{contact} is obtained. The average coordination number is then evaluated from $Z = 2 \times N_{\text{contact}}/N_{\text{MC}}$.

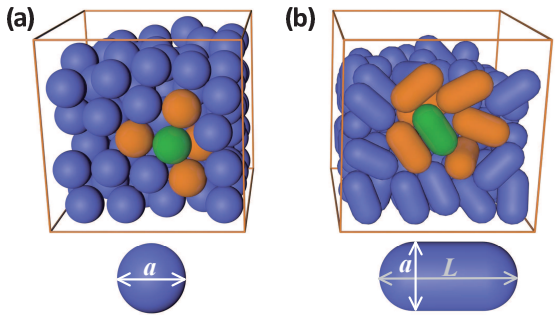

FIG. S1. (Color online) Random close packing of (a) spherical molecules and (b) capsule-like molecules which consists of a cylinder and two hemispherical ends. The diameter of sphere and the diameter of cylinder are noted as a. The length of capsule is L. Touching neighbours (in orange) of a certain molecule marked in green are shown.

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