A Unified Theory of Thermal Conductivity of Liquids and Amorphous Solids

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The thermal transport mechanisms in both liquids and amorphous solids remain unclear due to the lack of successful theories. Several models have been proposed to explain the thermal conductivity, for example, the Bridgman’s model for liquids with simple molecules, the minimum thermal conductivity model for amorphous solids, and the thermal resistance network model for polymers. In this paper, we propose a unified theory to calculate the thermal conductivity of liquids, organic and inorganic amorphous solids simultaneously. The atomic/molecular arrangement of liquids and amorphous solids is considered by including the coordination number of touching neighbours. The theoretical calculations are in excellent agreement with the experimental data without using any fitting parameters. The chemical structure effect on thermal conductivity can be included in our model. All above three existing models are proved to be special cases of our theory. We find that the unification of thermal transport in liquids and amorphous solids originates from the similar atomic/molecular structures which possess short-range order but no long-range order.

I. INTRODUCTION

The thermal conductivity of substance is a fundamental physical property which has been widely studied for a long time. The thermal conductivity of gases has been derived from the kinetic theory of gases (KTG) [1]:

$$\kappa_{\text{gas}} = \epsilon \eta C_v,$$

(1)

where $\epsilon$ is a pure number, $\eta$ is the viscosity, and $C_v$ is the heat capacity at constant volume. In an analogy way, the thermal conductivity of non-metallic crystalline substances is written as [2-4]:

$$\kappa_{\text{crystal}} = \frac{1}{3} C \bar{v}_s \Lambda,$$

(2)

where $C$ is the phonon heat capacity, $\bar{v}_s$ is the average sound velocity, and $\Lambda$ is the mean free path (MFP). Phonons which are the quasiparticles of collective excitation of lattice vibrations [4] are the heat carriers.

In contrast to gases and crystals, there is very few successful theories of thermal transport in liquids and amorphous solids. Eq. (1) is not applicable in liquids because of the disconnection between thermal conductivity and viscosity [5] although both gases and liquids are fluids. In 1923, Bridgman [6] proposed an empirical model to calculate the thermal conductivity of liquids:

$$\kappa_{\text{liquid}} = 3k_B \bar{v}_s n_{\text{mole}}^{2/3},$$

(3)

where $n_{\text{mole}} = (\rho/m_{\text{mole}})$ is the number density of molecules, $\rho$ is the mass density and $m_{\text{mole}}$ ($M_{\text{mole}} = m_{\text{mole}}N_A$) is the mass (molar mass) of molecules. $k_B$ is the Boltzmann constant, $\bar{v}_s$ is the sound velocity, and $N_A$ is the Avogadro constant. $3k_B$ is the heat capacity per molecule. In Eq. (3), Bridgman assumed that the neighbouring molecules form a simple cubic lattice. This model works well for simple liquids (such as methanol, carbon tetrachloride, chloroform, and water) and breaks down for liquids with complicated polyatomic molecules (such as liquid alkane). Later, a similar expression was also obtained by Eyring et al. [7] from another approach. Another rough estimation of $\kappa_{\text{liquid}}$ is simply combining Eq. (1) and Eq. (2) together [8].

The thermal conductivity of amorphous solids ($\kappa_{\text{amor}}$) is even mysterious because of the absence of well-defined phonons due to the lack of periodic lattice. In 1949, Kittel [9] extended Eq. (2) to calculate $\kappa_{\text{amor}}$ by assuming a nearly constant MFP ($\Lambda_0$) which is close to the size of unit cell. However, we must pointed out that Kittel’s attempt is not successful especially in amorphous polymers. Because $\Lambda_0$ in polymers should be less than 1 Å if Eq. (2) works [10]. This value is much shorter than the bond length of molecules. In 1989, Cahill and Pohl proposed a minimum thermal conductivity (MTC) model [11-13] based on the Einstein’s model. In Einstein’s original paper [14], a random walk of energy between neighbouring uncoupled oscillators with 26 atomic neighbours were considered. Cahill and Pohl modified Einstein’s model by considering a cluster of atoms as vibrational entity where the size of cluster is one half of the phonon wavelength. At high temperature limit, the MTC model gives

$$\kappa_{\text{amor}} = 1.2k_B \bar{v}_s n_{\text{atom}}^{2/3},$$

(4)

where all vibrational modes are thermally excited. $n_{\text{atom}} = (\rho/m_{\text{atom}})$ is the number density of atoms. $m_{\text{atom}}$ ($M_{\text{atom}} = m_{\text{atom}}N_A$) is the mass (molar mass) of atoms. $k_B$ is the Boltzmann constant, $\bar{v}_s$ is the sound velocity, and $N_A$ is the Avogadro constant. $3k_B$ is the heat capacity per molecule. In Eq. (3), Bridgman assumed that the neighbouring molecules form a simple cubic lattice. This model works well for simple liquids (such as methanol, carbon tetrachloride, chloroform, and water) and breaks down for liquids with complicated polyatomic molecules (such as liquid alkane). Later, a similar expression was also obtained by Eyring et al. [7] from another approach. Another rough estimation of $\kappa_{\text{liquid}}$ is simply combining Eq. (1) and Eq. (2) together [8].

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$m_{\text{atom}}N_A$ is the average mass (molar mass) of atoms. $\bar{v}_s = \frac{1}{3}(v_{sl} + 2v_{sd})$ where $v_{sl}$ and $v_{sd}$ are longitudinal and transverse sound velocities, respectively. Eq. (1) works well for many inorganic solids such as vitreous silica, whose atomic structure can be described by the continuous random network (CRN) model [15]. However, Eq. (1) significantly overestimates of thermal conductivity of amorphous solids such as selenium (Se$_8$) which is a typical molecular solid. Such molecular solids should not be described by the CRN model.

It is interesting to see that Eq. (3) of liquids and Eq. (4) of amorphous solids are very similar because they are proportional to $n^{2/3}$ mole and $n^{2/3}$ atom, respectively, and the sound velocity. If such similarity is not an coincident, what is the connection between them? If we rewrite Eq. (3) and Eq. (4) to be $\kappa_{\text{liquid}} \propto C_v n^{2/3}$ mole and $\kappa_{\text{amor}} \propto C_v n^{2/3}$ atom, respectively, where $k_B n^{2/3}$ mole $\sim C$ and $k_B n^{2/3}$ atom $\sim C$ at high temperature. Comparing them to Eq. (2), the only difference is the dimensionless prefactor: 3 in Eq. (3) and 1.2 in Eq. (4), when the MFP is chosen to be on the same order of magnitude of $n^{-1/2}$ mole and $n^{-1/2}$ atom. The key problems are what is the origin of the frefacors and how to calculate them.

Very recently, a thermal resistance network (TRN) model was proposed to calculate the thermal conductivity of polymers ($\kappa_{\text{polymer}}$) whose structures can be described by the random coil model [16].

$$\kappa_{\text{polymer}} = (n_{\text{mole}}L)^{1/3} \frac{1}{R_{\text{inter}}}, \quad (5)$$

where $R_{\text{inter}}$ is the thermal resistance across contact points between molecules, i. e. the inter-chain resistance. $L$ is the length of molecules, $n_{\text{mole}}L = \rho L/m_n_{\text{mole}} = \rho_{\text{unit}}/m_{\text{unit}}$. $l_{\text{unit}}$ and $m_{\text{unit}}$ are the length and mass of repeating unit, respectively. This formula shows excellent agreement with the experimental measured values of thermal conductivity in both polymer solids and polymer melts. The widely used empirical temperature-dependence and pressure-dependence of thermal conductivity of polymers have also been successfully reproduced from Eq. (5).

Comparing Eq. (5) to Eqs. (3) and (4), we find that the number density dependence of thermal conductivity in polymers $n^{-1/3}$ mole is different from that in Eqs. (3) and (4) and the sound velocity dependence vanishes. We further notice that the value of $\frac{(L n_{\text{mole}})^{1/3}}{R_{\text{inter}}}$ seems to be of the same order of magnitude of $k_B v_s$. Because $L$ and $n_{\text{mole}}^{1/3}$ are typically a few Angstroms, $R_{\text{inter}}$ is between 0.65-1.6 $\times 10^{10}$ K/W due to fitting results [16]. Therefore, $\frac{(L n_{\text{mole}})^{1/3}}{R_{\text{inter}}} \sim 10^{-20}$ Wm/K is very close to the value of $k_B v_s$ with $v_s \sim 10^3$ m/s and $k_B = 1.38 \times 10^{-23}$ J/K.

Based on above analysis, there seems to be some universality among Eqs. (2)-(5). Actually, Kittel [9] has pointed out that their formula should be applicable for both liquids and solids. However, no justification has been made. In this paper, we are inspired to search for the possible universal formula of thermal conductivity of liquids and amorphous solids. The microscopic structures of substances should be considered. More important, this formula must be compatible with Eqs. (2)-(5).

II. MODEL

We adopt the spirit of the Einstein’s model [14] by considering the thermal transport process to be a random walk of heat which is carried by the coupling of vibrational modes [17]. The Einstein’s model considered the random walk between a atom and its neighbors. The difference between our model and the Einstein’s model is: we hypothesize that molecules or clusters of atoms should be considered as individual entities in which the atomic arrangements are ordered or nearly ordered. Then the random walk through the network fromed by these entities and the thermal transport inside entities determine the overall thermal conductivity simultaneously. Our hypothesis is based on the fact that both liquids and amorphous solids possess short-range order but no long-range order [13].

The sizes of entities are usually several Angstroms to several nanometers according to the X-ray diffraction measurements in both liquids and amorphous solids [18]. Such sizes of entities are too small to define the local temperature distribution inside it, we assume that the thermal equilibrium inside each entity is too fast to affect the overall thermal resistance above room temperature. We further assume that the thermal transport between neighbouring entities are determined by the contact atoms, which can be regarded as uncoupled oscillators, via van der Waals interaction etc. This assumption also comes from the Einstein’s model [14].

In the terminology of network science, we propose that the thermal conductivity depends on the degree of network where entities are nodes. The contact between entities can be regarded as links among nodes. Then we write the universal formula of thermal conductivity as:

$$\kappa = \left( \frac{Z}{3\Xi} \tilde{n} \right)^{\frac{1}{2}} h, \quad (6)$$

where $Z$ is the degree of network which means the average coordination number of neighbours. $3$ is the space dimensionality. $\Xi$ is the number of entities which share one link, and $\tilde{n}$ is the number density of entity/nodes. $h$ is the heat transfer capability of each link. It means the average energy flow across links per unit time per temperature drop with unit JK$^{-1}$s$^{-1}$. It can be written as $h = \frac{1}{2} C_{\text{per}} v_s^2 \bar{v}_s$ where $\gamma$ is the possibility of inter-molecular heat transfer, $C_{\text{per}}$ is the per particle heat capacity whose high-temperature limit is $D_v k_B$ with $D_v$ the average vibrational degree of freedom of particle. The value of $D_v$ should be 2 to 3. $\delta$ is the distance between the neighbouring atoms or touching functional group (such as -CH$_3$) at contact points, or the length of link.
FIG. 1. (Color online) Schematic diagrams of thermal transport in four different types of networks with different entities/nodes: (a) liquids or solids with nearly-spherical small molecules, (b) liquids or solids with non-spherical small molecules, (c) inorganic amorphous solids with atomic clusters, (d) polymers with macromolecules. The entities of atomic clusters and polymers are marked by blue circles and purple ellipses in (c) and (d), respectively. ξ is the average length of the polymer segments between two contact points. Typical heat trajectories through networks are also shown by red arrows as examples.

III. RESULTS AND DISCUSSIONS

In this section, we will study the thermal conductivity of liquids and amorphous solids with different entities and different network structures. Substances are categorized into three types according to the property of entities, instead of the matter state. Figure 1 shows different types of networks with different entities and typical random walk trajectories. In liquids and amorphous solids made of small molecules, such as alkane and paraffin, the entities are individual molecules as shown in Figs. 1 (a) and 1 (b). In inorganic amorphous solids with covalent bonded atoms such as vitreous silica, the vibrational entity is a cluster of atoms as shown in Fig. 1 (c). In polymers made of macromolecules, the molecular chains are too large to be considered as one entity. We thus divide them into a series of segments between adjacent contact points as shown in Fig. 1 (d). The average segment length is noted as ξ. The fast thermal equilibrium inside individual small entity is indubitable for all cases above room temperature. Thus the thermal transport can be described as a random walk from one entity to its touching neighbours. At low temperature, these two processes should be considered simultaneously. In this paper, only high temperature cases are considered and the low temperature cases will be considered in our future works.

A. Individual small molecules as entities: molecular liquids and amorphous molecular solids

In liquids and amorphous solids made of small molecules, the entities characterizing for thermal conduction are individual molecules, whose arrangement can be described by relatively close packing with voids in liquids and close packing in solid.

Molecular Liquids

The KTG failed to explain the thermal transport in liquids because the molecules are neither localized around fixed equilibrium positions permanently like solids nor move freely like gases. Tranchenko and Brazhkin [19] have proved that the thermodynamical properties of simple liquids are determined by the vibrational contributions as in solids of all range of liquid relaxation times [20][21]. 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 evaluated the coordination number of touching neighbours for several typical liquids by the Monte Carlo simulation. The simulation results are listed in Table. I and the simulation details are given in the Appendix. Using the simulated $Z$, we further calculated the thermal conductivities by Eq. (6) with $	ilde{a} = \rho/m_{\text{mole}}, Z = 2$, and $\gamma = 1$, namely,

$$\kappa = \left( \frac{Z}{6 m_{\text{mole}}} \right)^{\frac{1}{2}} \frac{D_0 k_B v_s}{\delta} \frac{1}{\sigma}$$

for liquids. (7)

$\delta = a$ 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. We find $\delta = a/2$ should be used for benzene. The calculated thermal conductivities using parameters in Table. II are shown in Fig. 3 and Fig. 4.
in comparison with the experimentally measured data. The thermal conductivity of various liquids, whose aspect ratio is $L/a < 2$, including benzene, acetic acid, acetone, carbon disulfide, butyl alcohol, butyric acid, glycerol, N-propanal, and isopropanol are given in Fig. 3. The calculated values are in excellent agreement with the measured values by choosing $D_v$ to be 2~3 for nearly spherical molecules ($L/a \sim 1$) and $D_v = 2$ 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 measured values by choosing $D_v = 2$ as shown in Fig. 4. The reduction of $D_v$ for liquids with long molecules originates from the higher possibility of jumping along the longitudinal axis of molecules while it is hard to jump along the transverse axis. This feature can be understood as an analogy of reptation of polymers.

We now revisit the Bridgman’s model. In Bridgman’s original paper, he considered six nearest neighbours forming a simple lattice structure. Adopting this structure, it is easy to reproduce Bridgman’s formula (Eq. (3)) from Eq. (7) by taking $Z = 6, \gamma = 1, D_v = 3, n = n_{\text{mole}},$ and $\delta = n_{\text{mole}}^{-\frac{1}{2}}$. We 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. 1. This results in 0.90 < $(\frac{Z^3}{\gamma}) < 0.96$. We further compare $a$ with $n_{\text{mole}}$ by taking methanol and carbon tetrachloride as examples. We find that the values $n_{\text{mole}}^{-\frac{1}{2}} = 4.07$ Å for methanol and 5.43 Å for carbon tetrachloride are very close to their diameters 4.2 Å and 5.6 Å, respectively. Therefore, $a \approx n_{\text{mole}}^{-\frac{1}{2}}$ is valid in liquids with nearly spherical molecules. However, Bridgman’s formula breaks down for polyatomic molecules which are non-spherical. We find the reasons are the enhancement of $Z$ with increasing $L$ and the significant difference between $a$ and $n_{\text{mole}}^{-\frac{1}{2}}$. For example, $n_{\text{mole}}^{-\frac{1}{2}} = 7.88$ Å for C16H34 is much larger than its diameter 4 Å.

We further compare the thermal conductivity between isomers by taking N-propanal and isopropanol as an example. They have exactly the same chemical composition, C3H7OH. The measured thermal conductivities of N-propanal and isopropanol are 0.155 Wm$^{-1}$K$^{-1}$ and 0.137 Wm$^{-1}$K$^{-1}$, respectively. Their relative difference is 13%. The calculated results from our model are 0.150 Wm$^{-1}$K$^{-1}$ and 0.131 Wm$^{-1}$K$^{-1}$ by choosing $D_v = 2$. The relative difference from our calculation is also 13% which is in excellent agreement with experiment. The main difference comes from the decrease of the value of $Z$ as shown in Table. 1. In contrast, the Bridgman’s formula gives larger values of 0.203 Wm$^{-1}$K$^{-1}$ and 0.192 Wm$^{-1}$K$^{-1}$.

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 around permanent equilibrium positions and the neighbouring molecules are fixed. Molecules cannot be rearranged. Then the thermal conductivity is similar to Eq. (7):

$$\kappa = \left(\frac{Z}{6} \frac{\rho}{M_{\text{mole}}}\right)^{\frac{1}{2}} \frac{D_v k_B T}{a}, \text{for molecular solids.}$$

\[(8)\]
TABLE I. Mass density, length of molecule, diameter of molecule, molar mass, and sound velocity of typical liquids used in the calculations [28–29]. Z is calculated by Monte Carlo simulation except for water which is taken from Ref. [30].

| Liquids                  | $\rho$ (g/cm$^3$) | $L$ (Å) | $\alpha$ (Å) | $M_{\text{mole}}$ (g/mol) | $v_s$ (m/s) | $Z$ |
|--------------------------|-------------------|---------|---------------|-----------------------------|---------|-----|
| Methanol (CH$_3$OH)      | 0.787             | 4.2     | 32.04         | 1076                        | 4.59    |     |
| Carbon tetrachloride (CCl$_4$) | 1.594         | 5.6     | 153.8         | 926                         | 4.59    |     |
| Benzene (C$_6$H$_6$)     | 0.876             | 5.3     | 71.81         | 1321                        | 4.45    |     |
| Chloroform (CHCl$_3$)    | 1.479             | 5.1     | 119.37        | 979                         | 4.40    |     |
| Water (H$_2$O)           | 0.998             | 2.8     | 18.015        | 1482                        | 4.75,5  |     |
| Acetic acid (CH$_3$COOH) | 1.045             | 4.9     | 60.05         | 1150                        | 4.03    |     |
| Acetone (CH$_3$COCH$_3$) | 0.784             | 6.5     | 58.08         | 1190                        | 4.84    |     |
| Carbon disulfide (CS$_2$) | 1.263            | 4.9     | 76.15         | 1158                        | 3.26    |     |
| Butyl alcohol (C$_4$H$_9$OH) | 0.810         | 7.2     | 74.12         | 1222                        | 4.62    |     |
| Butyric acid (C$_4$H$_8$O$_2$) | 0.959         | 7.6     | 88.11         | 1380                        | 4.63    |     |
| Glycerol (C$_3$H$_8$O$_3$)| 1.261             | 6.7     | 92.09         | 1920                        | 5.13    |     |
| N-propanol (C$_3$H$_7$OH) | 0.805             | 5.9     | 60.11         | 1220                        | 4.20    |     |
| iso-propanol (C$_3$H$_7$OH) | 0.785          | 5.2     | 60.12         | 1170                        | 3.27    |     |
| C$_6$H$_4$               | 0.659             | 10.3    | 86.18         | 1113                        | 5.85    |     |
| C$_7$H$_8$               | 0.680             | 11.6    | 100.22        | 1311                        | 6.33    |     |
| C$_8$H$_8$               | 0.699             | 12.8    | 114.23        | 1213                        | 6.78    |     |
| C$_9$H$_8$               | 0.718             | 14.1    | 128.25        | 1226                        | 7.33    |     |
| C$_{10}$H$_{12}$         | 0.726             | 15.4    | 142.28        | 1252                        | 7.75    |     |
| C$_{12}$H$_{16}$         | 0.750             | 17.9    | 170.33        | 1279                        | 8.74    |     |
| C$_{13}$H$_{18}$         | 0.756             | 19.2    | 184.36        | 1278                        | 9.19    |     |
| C$_{14}$H$_{18}$         | 0.763             | 20.5    | 198.39        | 1294                        | 9.68    |     |
| C$_{15}$H$_{20}$         | 0.768             | 21.7    | 212.41        | 1307                        | 10.16   |     |
| C$_{16}$H$_{18}$         | 0.770             | 23.0    | 226.44        | 1338                        | 10.54   |     |

The only difference is replacing $v_s$ by $\bar{v}_s$ because there are additional two transverse modes in solids. We study paraffin, octaselenium (Se$_8$), and As$_2$S$_3$ as examples where their parameters are given in Table II. Paraffin is long molecule whose $Z$ is calculated to be 11.43. The molecular structures of Se$_8$, which is disk-like, and As$_2$S$_3$ are too irregular to calculate their value of $Z$ by using 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 [13]. Fig. 2 shows that the calculated thermal conductivities in comparison with experimental data when $D_v = 2$. The calculated thermal conductivity of Se$_8$ (As$_2$S$_3$) 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 a comparison, the MTC model in Eq. (4) gives an overestimated value of 0.230 Wm$^{-1}$K$^{-1}$ (0.345Wm$^{-1}$K$^{-1}$). Therefore, we pointed out that the MTC model is not able to calculate the thermal conductivity of paraffin and our model successfully gives the correct value.

TABLE II. Mass density, molar mass of atom, diameter of atom, and sound velocity of three molecular amorphous solids used in the calculations [12]. Calculated $Z$ of paraffin is shown. The values of $Z$ of Se$_8$ and As$_2$S$_3$ are unknown because of their irregular structures.

| Molecular solids | $\rho$ (g/cm$^3$) | $M_{\text{atom}}$ (g/mol) | $b$ (Å) | $\zeta$ | $v_{sd}$ (m/s) | $v_{st}$ (m/s) | $Z$ |
|------------------|-------------------|----------------------------|---------|--------|---------------|---------------|-----|
| Paraffin (C$_{18}$H$_{38}$) | 0.777             | 4.0                         | 254.5   | 1400   | -             | 11.43         |     |
| Se$_8$           | 4.30              | 631.7                       | 3.80    | 2060   | 1060          | -             |     |
| As$_2$S$_3$      | 3.20              | 246.05                      | 3.60−3.70 | 2650   | 1440          | -             |     |

The thermal equilibrium inside clusters is much faster than the thermal transport between neighbouring clusters. Such local order have been experimentally observed through radial distribution function (RDF) by X-ray diffraction. Staring from the fact that RDF shows clear peaks when the distance from a center atom is smaller than $2b$, we assume that average characteristic size of entity is approximately $4b$, where $b$ is the length of the covalent bond. This is consistent with the measured size of crystalline domain, for example, 7 Å for amorphous silica [23]. Alexander [25] has pointed out the existence of the negative internal stress regions whose correlation length is $3-10b$. The lattice dynamics of such materials is still unknown. We assume the amorphous solids are formed by random close packing of spherical clusters, whose volume is $V_c = \frac{4}{3} \pi (\frac{b}{2})^3$ where $\zeta$ is the diameter of cluster. According to the theory of random close packing, the average coordination number $Z = 6.91$ [18] and the filling factor $V_c \rho V = 0.637$ [13]. Therefore, the thermal conductivity can be evaluated by choosing $\zeta = 2$ and $\gamma = 1$

$$\kappa = \left( \frac{6.91 - 0.637}{6} \right)^{\frac{1}{2}} D_v k_B \bar{v}_s \frac{N_{cl}}{b},$$  \hspace{1cm} \text{for covalent solids.} \hspace{1cm} (9)

If we rewritten the mass density of solid as $\frac{N_{cl}}{V_c} = \rho$, where $N_{cl}$ is the number of atoms in each cluster. The numerical simulations showed that $N_{cl} = 14.2 + 1$ [20] which means 1 atom with 14.2 neighbourg atoms. One can easily reproduce the MTC model in Eq. (4) as $\kappa \approx 0.474 D_v k_B \bar{v}_s \frac{N_{cl}}{b}$ by choosing $D_v \approx 5/2$. We calculated the thermal conductivities of amorphous Si, Ge, CdGeAs$_2$, and SiO$_2$ with the parameters given in Table III. The calculated values are in good agreement with the measured ones as shown in Fig. 5 when $D_v$ is chosen to be 5/2.

B. Atomic clusters as entities: amorphous solids with bonded atoms

In amorphous solids such as Si, Ge, CdGeAs$_2$, and SiO$_2$ in which atoms are bonded, the selection of entities is not as apparent as the situations in Sections II.A. We point out that atomic clusters with local order should be chosen as entities.
C. Macromolecular chain segments as entities: polymer solids and polymer liquids

Polymers solids and polymer liquids consist of macromolecules with extremely long length, i.e., $L \gg a$. Therefore, it is not reasonable to consider an entire macromolecule as one entity. It has been pointed out that there are three processes when a heat current flow through polymers: inter-chain heat transfer and intra-chain heat transfer at contact points and thermal transport inside each segment between two adjacent contact points as shown in Fig. 1(d). It is obvious that thermal equilibrium of each entity is faster than inter-chain heat transfer because of the large intrinsic thermal conductivity of a single molecular chain. Therefore, $\tilde{n} = \frac{L}{v} n_{\text{mole}}$, $\Xi = 4$ and $Z = 6$ as shown in Fig. 1(d). Zhou et al. [16] have evaluated that $\xi = 4 \sqrt{\frac{m_{\text{unit}}}{l_{\text{unit}} \rho}}$ where $m_{\text{unit}}$ and $l_{\text{unit}}$ are the mass and length of repeating units, respectively. Moreover, in isotropic polymers, $\frac{1}{\kappa} = (1 - \gamma) R_{\text{intra}} + \gamma R_{\text{inter}} \approx \frac{R_{\text{per}}}{v}$ because $\gamma \approx (1 - \gamma) \approx 1/2$ where $R_{\text{intra}}$ is the intra-chain thermal resistance which is negligible compared to $R_{\text{inter}}$. Therefore, the average value of $h$ can be obtained as $2 \frac{C_{\text{per}} v_B}{s \bar{v}}$. Eq. (9) is then reduced to

$$\kappa = \left( \frac{l_{\text{unit}} \rho}{m_{\text{unit}}} \right)^{1/2} \frac{D_{\kappa} k_B \bar{v}_s}{\delta}, \text{ for polymers.}$$

It is easy to reproduce Eq. (5) by using $\frac{m_{\text{unit}} \rho}{l_{\text{unit}}^{\gamma D_{\kappa}}} = L_{\text{fl}}} \rho_{\text{mole}}$. The value of $\delta$ is determined by the size of functional groups, noted as $a'$, such as -CH$_3$, -F, -OH, =CO etc. Figure 6 shows the calculated thermal conductivity of several typical polymers in comparison with the experimentally measured data, where $D_{\kappa} = 2$ and other parameters are listed in Table. III.

D. Discussions

We summarize the selection of entities for different type of liquids and amorphous solids in Table. IV. The parameters $\Xi$, $\gamma$, $D_{\kappa}$, $\delta$ are also presented according to the results showed in above three subsections. We point out that the number density of entity is the key parameter in determining the thermal conductivity, as Eq. (6) indicated. When the entity is the entire small molecule, $\tilde{n}$ can be replace by $n_{\text{mole}}$. When the molecules are large in polymers, $\tilde{n}$ should be much larger than $n_{\text{mole}}$ by choosing chain segments as entities which contain tens of atoms. Similarly, $\tilde{n}$ should be the number density of atomic clusters which contains tens of atoms in covalent solids.

$C_{\text{per}}$ is the per particle heat capacity whose high temperature limit is $D_{\kappa} k_B$. Its value is related with the vibrational degree of freedom of atoms or functional groups. We find that our model is in excellent agreement with the experimental data when $2 \leq D_{\kappa} \leq 3$ for all substances. We further find that $D_{\kappa}$ is reduced to 2 when the shape of molecules is capsule-like or disk-like. This is probably due to the shape effect on the liquid relaxation process. In covalent solids, the
value of $D_v$ is found to be 5/2. We are not sure the origin of this value. Possible explanation is the strongly distorted atomic structure at the edge of entity where the internal stress shifts from negative value to positive one [25].

Another major difference of our model from Bridgman’s model and MTC model is the intermolecular/interatomic separation $\delta$. Bridgman’s model used $n^{-1/3}$ mole to be the intermolecular separation. This is true only for simple liquids with spherical-like molecules because $a \approx n^{-1/3}$. When the molecule is non-spherical, for example, Se$_8$ is disk-like and acetone is capsule-like, the intermolecular separation must not be the distance between the centers of adjacent molecules. The distance through which the energy transfers should be the separation between contact atoms or functional groups. Therefore, the value of $\delta$ is approximately a which is obviously smaller than $n^{-1/3}$ mole. It is much smaller than $n^{-1/3}$. In covalent solids, it is convenient to chose $\delta$ to be the bond length which is smaller than $n^{-1/3}$ atom. When the molecule is extremely long in polymer, $\delta$ is the average value of the size of atoms or functional groups which are attached to the backbone, $a'$.

### IV. CONCLUSIONS

We proposed a unified thermal conductivity model for liquids and amorphous solids, as they share the similarity of short range order structure. With properly defined entities, thermal conductivity is dominated by the thermal resistance between neighbouring entities as the thermal equilibrium is fast within the entity. The validity of our model has been proved by the good agreement with experiment measurements and the consistence with the existed well-accepted empirical/theoretical models. The chemical structure effect on thermal transport is taken into account in our model.

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### APPENDIX

In order to evaluate the coordination number of fluid molecules, the molecules are simplified into either spheres or cylinders with hemisphere at two ends, see Fig.2. The positions of fluid molecules are random, thus we adopted the Monte Carlo method to generate an equivalent fluid structure. We first evaluate the number $N_{MC}$ of particles to be generate in a given box, $N_{MC} = (L^3 \times \rho)/m_0$, where $\rho$ is the density of fluids, $m_0$ is the molecular weight of fluid particles, and $L$ is the size of the simulation box. In our simulation, $L = 1000 nm$. Then the position of particles is randomly generated and recorded. Once a new particle is generated, the distance between it and the previous generated particles in the box will be calculated. If the distance is smaller than the van der Waals diameter given in Table I, 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 $Z = 2 \times N_{contact}/N_{MC}$. 

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**TABLE V. Selections of entities and corresponding parameters for different type of materials.**

| Material type                      | Selection of entity | $\bar{n}$ | Typical size of entity | $\Xi$ | $\gamma$ | $D_v$ | $\delta$ |
|-----------------------------------|---------------------|-----------|------------------------|-------|---------|-------|---------|
| Molecular liquids and solids      | small nearly-spherical molecules | $= n_{mole}$ | $a \times a \times a$ | 2 | $\sim 3$ | $\approx a \approx n_{mole}^{-1/3}$ |
| Molecular liquids and solids      | small capsule-like molecules    | $= n_{mole}$ | $L \times a \times a$ | 2 | 1 | $\approx a \approx n_{mole}^{-1/3}$ |
| Molecular liquids and solids      | small disk-like molecules      | $= n_{mole}$ | $L \times L \times a$ | 2 | 1 | $\approx a \approx n_{mole}^{-1/3}$ |
| Covalent solids                   | atomic clusters          | $\ll n_{atom}$ | $\xi \times \xi \times \xi$ | 2 | 1 | $5/2 \approx b \approx n_{atom}^{-1/3}$ |
| Polymer liquids and solids        | chain segments          | $\gg n_{mole}$ | $\xi \times a \times a$ | 4 | 1/2 | $= a' \ll n_{mole}^{-1/3}$ |

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