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On the occurrence of size effects in the calculation of thermal conductivity by first-principles molecular dynamics: the case of glassy GeTe₄

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Abstract

The thermal conductivity of a glass can be obtained by first-principles molecular dynamics provided we exploit a methodology that has been termed the approach-to-equilibrium molecular dynamics (AEMD) [1] [2, Chap. 8]. In the present work, we investigate the occurrence of size effects by comparing the thermal conductivity of two g-GeTe₄ atomic models of different sizes. This issue is far from being trivial since, in principle, size effects are not expected to occur in disordered systems beyond a few interatomic distances. For this reason, it is important to search unambiguous pieces of evidence substantiating this point. The first system of length $L = 18 \text{ \AA}$ contains 185 atoms. By duplicating it along one direction we form the second system, that contains 370 atoms and features a double length $L = 36 \text{ \AA}$ and an identical cross section. The thermal conductivity increases by a factor 3 from $L = 18$ to 36 \AA , thereby approaching the experimental value. Our investigation exemplifies the crucial role of the system size to take full advantage of the AEMD methodology and bring the calculated values in better agreement with experiments.

Keywords: Thermal Conductivity, Glass, First-Principles Molecular Dynamics

1. Introduction

Molecular dynamics (MD) simulations are widely used to obtain the thermal conductivity of bulk systems, nanostructures and interfaces [3, 1, 4, 5, 6, 7]. In the literature, the forces between atoms are described by classical force fields with few exceptions. This is due to the need of extended MD trajectories to determine the thermal conductivity and obtain a fully converged auto-correlation function in the Green-Kubo approach [8], or to reach the steady state in the direct method [3]. However, it is highly desirable to go beyond the use of classical force fields, in particular in the case of glasses, since for disordered structures the use of quantitative models has found to be crucial [9, 10, 11]. This is specifically relevant for the class of chalcogenide glasses, for which empirical potentials often fail to quantitatively describe their structure and chemical interactions [12]. Recently [13], we have demonstrated that it is possible to determine the thermal conductivity of a glass, g-GeTe₄,

from a density functional (DFT) based first-principles MD (FPMD). The calculations have been performed by applying a methodology that we recently developed, the approach-to-equilibrium MD (AEMD) [1] [2, Chap. 8]. In this methodology, a transient regime is created and exploited to calculate the thermal conductivity in a way that proved to be faster and more effective than conventional approaches.

Past experience of application of the AEMD methodology provided evidence of the sensitivity to the system size of thermal conductivities obtained by AEMD. In particular, it has been shown that in crystalline Si (cSi), the thermal conductivity changes with the length of the system even up to $1.2 \mu\text{m}$. This length dependence is intimately related [14] to the existence of long phonon free paths in cSi (larger than $10 \mu\text{m}$) [15] [16]. In a disordered material like g-GeTe₄, the free paths of heat carriers are expected to be very short. At low temperature ($T \approx 130 \text{ K}$), a mean free path (MFP) of $4\text{-}5 \text{ \AA}$ has been measured by Zhang et al. [17]. However, it is known that the maximum heat carrier free paths can be considerably larger than the average value extracted from the thermal conductivity using the kinetic theory.

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43 It is therefore desirable to ascertain whether or not the
 44 thermal conductivity of g-GeTe₄ features a length de-
 45 pendence. This is exactly the objective of the present
 46 work. As a byproduct, one would like to understand
 47 whether the underestimate thermal conductivity found
 48 in [13] with a system of 185 atoms can be at least par-
 49 tially overcome by resorting to a longer system in the
 50 direction of the heat flux.

51 The article is organized as follows. In a first section,
 52 the two atomic models of g-GeTe₄ and the MD method-
 53 ology are presented. In a second section, the MD tra-
 54 jectories are analyzed, and the thermal conductivity of
 55 the two systems are extracted and discussed. Then, we
 56 critically analyze our results before drawing a final set
 57 of conclusions.

58 2. Method

59 The atomic model of g-GeTe₄ has been obtained by
 60 Car-Parrinello molecular dynamics (CPMD) [18] using
 61 the CPMD code ¹. This model yields structure factors
 62 and pair correlation functions in very good agreement
 63 with measurements [10]. In our first implementation of
 64 AEMD to the case of g-GeTe₄ [13] the cubic simulation
 65 box contained $N = 185$ atoms with a side $L = 18$ Å.
 66 Here the cubic box is doubled in the direction of thermal
 67 transfer to form a rectangular box containing $N = 370$
 68 atoms, with a length $L = 36$ Å and a cross section $S =$
 69 18×18 Å² (Fig. 1).

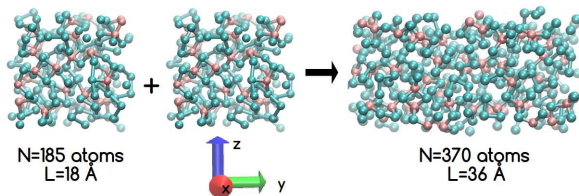


Figure 1: The atomic models containing respectively 185 and 370 atoms.

70 The atomic structure of the two systems is identical,
 71 as evidenced by the comparison of the total pair corre-
 72 lation functions $g(r)$ (Fig. 2).

73 The details of the CPMD calculations are as fol-
 74 lows. The Becke, Lee, Yang and Parr (BLYP) [19,
 75 20] exchange-correlation functional is used, with a
 76 norm-conserving pseudo-potentials [21] describing the
 77 valence-core interaction. Long-range dispersion forces

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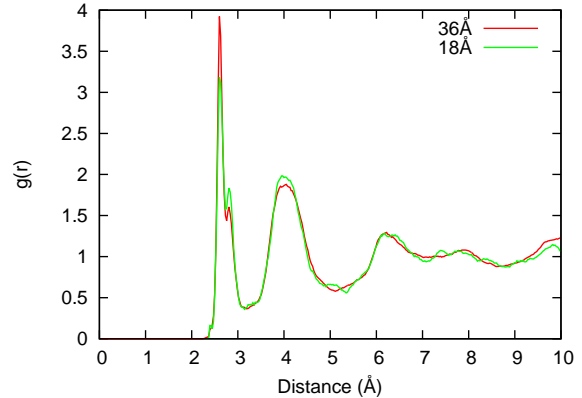


Figure 2: Pair correlation function $g(r)$ for the system of length $L = 18$ Å containing 185 atoms and the system of length $L = 36$ Å containing 370 atoms. The number of first neighbors as obtained from the integration of the first peak is equal to 3.8 in both cases.

78 are considered by following the formula by Grimme
 79 [22, 10]. Thermostats are applied to the fictitious elec-
 80 tronic degrees of freedom by following the Blöchl and
 81 Parrinello guidelines [23].

82 For each of the systems under study, the atomic struc-
 83 ture is equilibrated during 4 to 30 ps at the target tem-
 84 perature of $T_f = 130$ K since the MFPs are measured to
 85 be the lowest around this temperature [17]. The AEMD
 86 methodology is then applied to establish a thermal tran-
 87 sient. The simulation box is divided into two sub-parts
 88 along the y -direction, these bound to be the cold and hot
 89 parts. To this aim, two distinct Nosé-Hoover [24, 25]
 90 thermostats are applied to the blocks, with a tempera-
 91 ture difference ΔT_0 . Fig. 3 shows the time evolution
 92 of the temperature of the hot and the cold blocks in this
 93 phase 1 of AEMD for $\Delta T_0 = 200$ K. The temperature
 94 gap establishes in a few ps and it is stabilized by the
 95 application of the two thermostats along a time interval
 96 lasting 25 ps. Then, the thermostats are switched off
 97 to allow for the phase 2 of AEMD to begin. As a con-
 98 sequence, the temperature of the hot (cold) block de-
 99 creases (increases). The equilibrium temperature of 130
 100 K is reached faster for the smaller system (Fig. 3).

101 3. Results

102 The temperature difference during phase 2 of AEMD
 103 shown in Fig. 4 follows an exponential decay as ex-
 104 emplified by the linear variation on the semi-log graph.
 105 The decay time τ is extracted by a suitable fit.

106 We exploit the relationship between the decay time
 107 and thermal conductivity derived from the heat equation

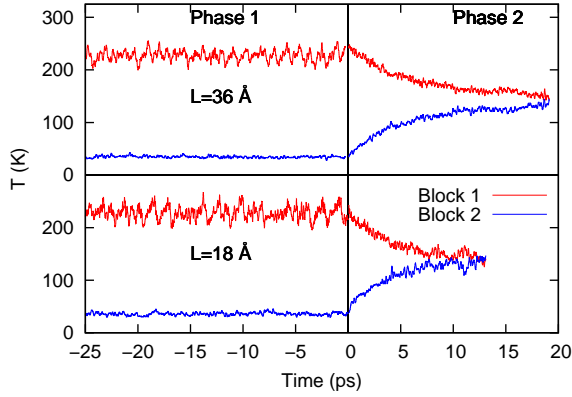


Figure 3: Time evolution of the hot block (red line) and cold block (blue line) during the two AEMD phases. Upper graph: $L = 36 \text{ \AA}$. Lower graph: $L = 18 \text{ \AA}$.

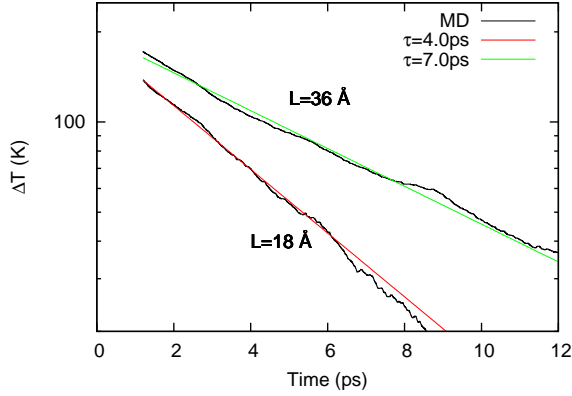


Figure 4: Time evolution of the temperature difference in phase 2 for the two systems and adjustment by a decaying exponential (the decay time is mentioned in label).

[1]:

$$\kappa = \frac{L^2}{4\pi^2} \frac{C_V \cdot \rho}{\tau} \quad (1)$$

where $\rho = N/L^3$ is the number density. The specific heat $C_V = 3k_B(0.78 \pm 0.02)$ is calculated from the energy fluctuations in a $\{NVT\}$ run at 130 K [26].

The thermal conductivity is plotted as a function of the system length in Fig. 5. For each size, the parameters of the simulation (like the initial temperature difference or the duration of phase 1) are varied in order to ascertain their impact on the thermal conductivity. The thermal conductivity varies without any clear cut dependence on the different parameters. The variations are taken as the statistical error on κ . The calculations result in averaged thermal conductivity equal to $0.013 \pm 0.003 \text{ W m}^{-1} \text{ K}^{-1}$ for $L = 18 \text{ \AA}$ and $0.044 \pm 0.001 \text{ W m}^{-1} \text{ K}^{-1}$

for $L = 36 \text{ \AA}$. Therefore, the thermal conductivity features a length dependence, and increases by a factor of 3 from $L = 18$ to 36 \AA . We recall that the experimental value obtained using a parallel temperature conductance technique is $0.14 \text{ W m}^{-1} \text{ K}^{-1}$ [17]. This technique is reportedly leading to an overestimate by 20-25 % of the thermal conductivity compared to a laser flash measurement [17]. This latest experimental framework is closer to our simulation methodology, and our experimental point of comparison is therefore a thermal conductivity of $\approx 0.1 \text{ W m}^{-1} \text{ K}^{-1}$.

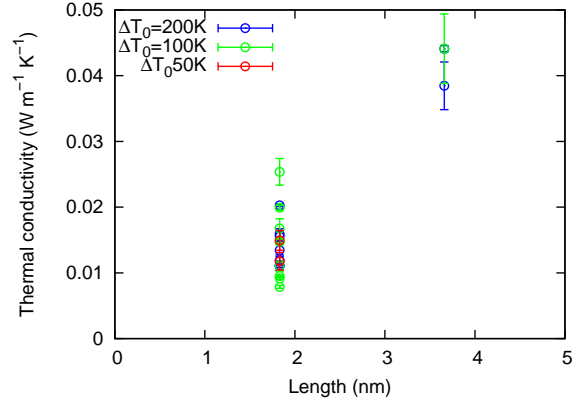


Figure 5: Thermal conductivity as a function of the length and for 3 values of the initial difference in temperature between hot and cold blocks ($\Delta T_0 = 200, 100$ or 50 K) for atomic models containing respectively 185 and 370 atoms.

4. Discussion

There are several examples of length dependence of the thermal conductivity obtained using the AEMD methodology. In bulk silicon and germanium [1] [14], the thermal conductivity changes on the entire range of lengths studied, from tens of nanometers up to $1.2 \mu\text{m}$. In α -quartz [14], the thermal conductivity varies up to $\approx 100 \text{ nm}$ before reaching a plateau. In silicon nanowires [5], the thermal conductivity always reaches a plateau only after a length that increases with the nanowire diameter. In silicon membranes [27], the same behavior is observed, with the plateau obtained at shorter length in presence of holes. All these cases were studied using classical force fields.

We have shown [14] that this behavior is due to the truncation at length L of the distribution of phonon mean free paths. In crystals, phonons encounter scattering events that make their lifetime finite, or the distance

they cover finite. The average mean free paths Λ_{ph} is estimated from the kinetic theory following:

$$\kappa = \frac{1}{3} C_V \nu \Lambda_{\text{ph}} \quad (2)$$

ν being the sound velocity. Nevertheless, phonon mean free paths can be distributed up to a maximum Λ_{max} considerably larger than Λ_{ph} . For example in silicon, $\Lambda_{\text{ph}} = 40$ nm and $\Lambda_{\text{max}} > 10 \mu\text{m}$.

In amorphous materials and glasses, heat carriers are not expected to cover long distances due to the disorder of the atomic structure that could be seen schematically as a distribution of defects beyond the first neighbor shell. Indeed, Zhang et al. [17] have estimated Λ_{ph} to 4-5 Å from their measurements of the thermal conductivity of g-GeTe₄. In amorphous silicon studied by classical force fields [14], the thermal conductivity does not exhibit any length dependence above 5 nm.

The variation of thermal conductivity obtained in the present work, ranging from $L = 18$ to 36 Å could be due to the fact that L is still smaller than the maximum phonon mean free path Λ_{max} . This conjecture can only be validated by looking for the saturation in the calculated values of the thermal conductivity. This requires the calculation of the thermal conductivity on a third, even more extended system. It remains true that the present calculations have the pleasing effect of approaching the AEMD value to the experimental counterpart. Also, it has to be observed that the size scaling of the CPMD method is prohibitive and by no means linear. For this reason, it might be of interest to resort to alternative schemes (as the so-called second generation CPMD [28]) in order to speed up the achievement of the planned calculation for a third, larger system size.

5. Conclusion

The thermal conductivity of a glass, g-GeTe₄ has been calculated from first-principles molecular dynamics. In particular, the dependence on the system length has been the focus of the work, since the AEMD methodology has shown such a dependence in many other materials. Although the disordered nature of g-GeTe₄ and an average phonon mean free paths measured to 4-5 Å in the literature were in favor of an absence of length dependence, we have obtained an increase by a factor 3 of the thermal conductivity when the cell length along the heat path changes from 18 to 36 Å. This amounts to a calculated value much closer to experimental data. Therefore, it appears that such a length dependence has some physical origins that can be traced back to the existence of maximum mean free

paths larger than the system size. Further investigations for even larger sizes will be instrumental to demonstrate that the combination of FPMD with the AEMD approach is able to provide fully size-converged, reliable values for the thermal conductivity, at least in the case of a prototypical disordered system.

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