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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 $GeTe_4$

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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-$GeTe_4$ 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 $L = 18$ Å contains 185 atoms. By duplicating it along one direction we form the second system, that contains 370 atoms and features a double length $L = 36$ Å and an identical cross section. The thermal conductivity increases by a factor 3 from $L = 18$ to 36 Å, 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.

1. Introduction

Molecular dynamics (MD) simulations are widely used to obtain the thermal conductivity of bulk systems, nanostructures and interfaces [1,3-7]. 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 [9-11]. 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-$GeTe_4$, 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 μm. This length dependence is intimately related [14] to the existence of long phonon free paths in cSi (larger than 10 μm) [15,16]. In a disordered material like g-$GeTe_4$, the free paths of heat carriers are expected to be very short. At low temperature ($T \approx 130$ K), a mean free path (MFP) of 4–5 Å 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. It is therefore desirable to ascertain whether or not the thermal conductivity of g-$GeTe_4$ features a length dependence. This is exactly the objective of the present work. As a byproduct, one would like to understand whether the underestimated thermal conductivity found in [13] with a system of 185 atoms can be at least partially overcome by resorting to a longer system in the direction of the heat flux.

The article is organized as follows. In a first section, the two atomic

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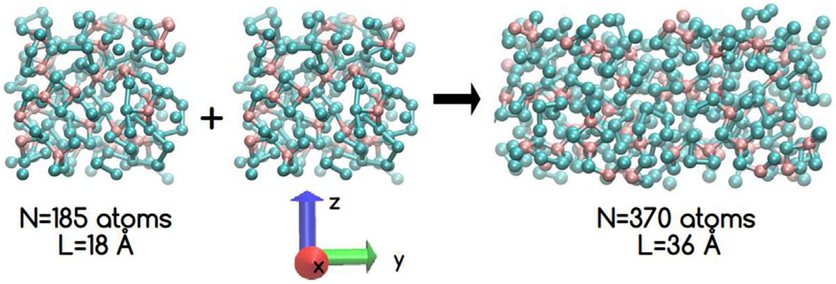

Fig. 1. The atomic models containing respectively 185 and 370 atoms.

models of g-GeTe$_4$ and the MD methodology are presented. In a second section, the MD trajectories are analyzed, and the thermal conductivity of the two systems is extracted and discussed. Then, we critically analyze our results before drawing a final set of conclusions.

2. Method

The atomic model of g-GeTe$_4$ has been obtained by Car-Parrinello molecular dynamics (CPMD) [18] using the CPMD code[1]. This model yields structure factors and pair correlation functions in very good agreement with measurements [10]. In our first implementation of AEMD to the case of g-GeTe$_4$ [13] the cubic simulation box contained $N = 185$ atoms with a side $L = 18$ Å. Here the cubic box is doubled in the direction of thermal transfer to form a rectangular box containing $N = 370$ atoms, with a length $L = 36$ Å and a cross section $S = 18 \times 18$ Å^2 (Fig. 1).

The atomic structure of the two systems is identical, as evidenced by the comparison of the total pair correlation functions $g(r)$ (Fig. 2).

The details of the CPMD calculations are as follows. The Becke, Lee, Yang and Parr (BLYP) [19,20] exchange-correlation functional is used, with a norm-conserving pseudo-potentials [21] describing the valence-core interaction. Long-range dispersion forces are considered by following the formula by Grimme [10,22]. Thermostats are applied to the fictitious electronic degrees of freedom by following the Blöchl and Parrinello guidelines [23].

For each of the systems under study, the atomic structure is equilibrated during 4 to 30 ps at the target temperature of $T_t = 130$ K since the MFPs are measured to be the lowest around this temperature [17]. The AEMD methodology is then applied to establish a thermal transient. The simulation box is divided into two sub-parts along the y-direction, these bound to be the cold and hot parts. To this aim, two distinct Nosé-Hoover [24,25] thermostats are applied to the blocks, with a temperature difference ΔT_0. Fig. 3 shows the time evolution of the temperature of the hot and the cold blocks in this phase 1 of AEMD for $\Delta T_0 = 200$ K. The temperature gap establishes in a few ps and it is stabilized by the application of the two thermostats along a time interval lasting 25 ps. Then, the thermostats are switched off to allow for the phase 2 of AEMD to begin. As a consequence, the temperature of the hot (cold) block decreases (increases). The equilibrium temperature of 130 K is reached faster for the smaller system (Fig. 3).

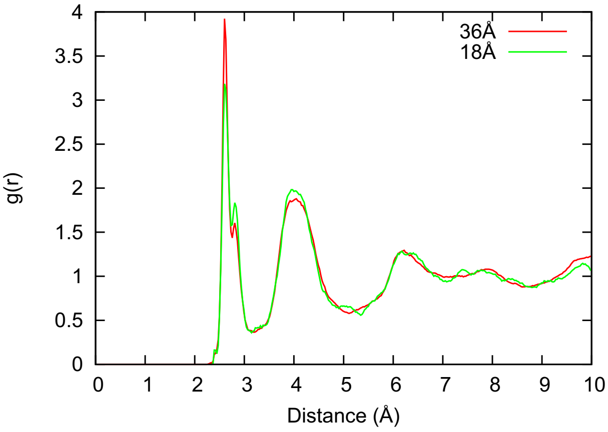

Fig. 2. Pair correlation function $g(r)$ for the system of length $L = 18$ containing 185 atoms and the system of length $L = 36$ containing 370 atoms. The number of first neighbors as obtained from the integration of the first peak is equal to 3.8 in both cases.

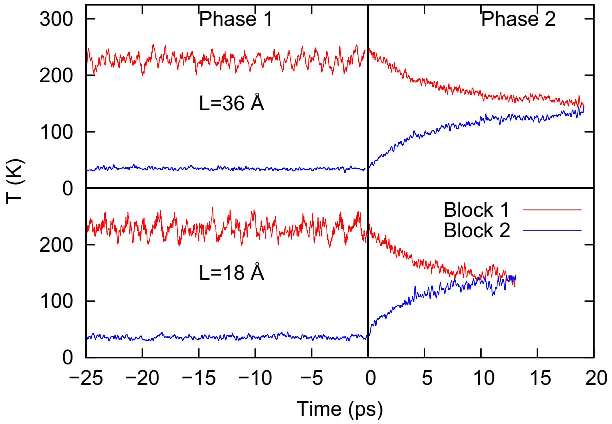

Fig. 3. Time evolution of the hot block (red line) and cold block (blue line) during the two AEMD phases. Upper graph: $L = 36$ Å. Lower graph: $L = 18$ Å.

3. Results

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

We exploit the relationship between the decay time and thermal conductivity derived from the heat equation [1]:

$$\kappa = \frac{L^2}{4\pi^2} \frac{C_V . \rho}{\tau} \tag{1}$$

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 $\{NV\,T\}$ 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

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[1] See http://www.cpmd.org, copyright 2000-2017 jointly by IBM Corporation and by Max Planck Institute, Stuttgart.