Estimating the thermal conductivity of the glassy phase-change memory material, Ge$_2$Sb$_2$Te$_5$, from non-equilibrium first-principles molecular-dynamics simulations

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An analysis of thermal transients from non-equilibrium ab initio molecular-dynamics simulations is used to calculate the thermal conductivity of materials with a short phonon mean-free path. We adapt the approach-to-equilibrium methodology to the three-dimensional case of a simulation that consists of a cubic core region at higher temperature approaching thermal equilibrium with a thermostatted boundary. This leads to estimates of the bulk thermal conductivity for the glassy state of the phase-change memory material, Ge$_2$Sb$_2$Te$_5$, which are close to previously reported experimental measurements. Self-atom irradiation of the material, modelled using thermal spikes and stochastic-boundary conditions, results in glassy models with a significant reduction of the thermal conductivity compared to the pristine glassy structure. This approach may prove to be useful in technological applications, e.g. for the suppression of thermal cross-talk in phase-change memory and data-storage devices.

The cost of computation is significantly impacted by the energy needed to keep key components cool, whether it is central processing units, accelerators, memory or data storage. Even when components are kept at reasonable temperatures during normal operation, there may still be thermal-throttling under peak-load which affects their performance and lifetime. Hence, the ability to predict the thermal properties of solids is critical for a comprehensive understanding of the thermal management of such devices and for the rational design of materials with targeted properties [1, 2].

Phase-change memory devices, which are widely believed to be a part of at least some commercial non-volatile solid-state drives, rely on the fast and reversible switching between a conductive crystalline phase (the “1” state of a bit), and a resistive glassy phase (the “0” state of a bit), of the same chalcogenide material, induced via Joule heating resulting from the application of appropriate voltage pulses [3]. Thermal conductivity is a key property for the device operation, since the phase changes of the material, corresponding to the memory writing/erasure processes, depend on heat dissipation and the thermal transport. Consequently, thermal cross-talk between adjacent memory cells can limit the size down-scaling in phase-change memory devices [4]. Therefore, an understanding of the thermal-transport properties of these materials at the atomic level is essential for their design and optimization [5].

The thermal conductivity of the phase-change memory material, GeTe, has been predicted successfully with quasi-static calculations [6], as well as with classical equilibrium [7] and non-equilibrium [7, 8] molecular-dynamics simulations by using a linear-scaling neural-network interatomic potential. First-principles calculations were also employed to estimate the thermal conductivity for the crystalline phases of different chalcogenide phase-change materials, including Ge$_2$Sb$_2$Te$_5$ [9], in good agreement with experimental observations. However, there are no previously reported modelling studies of the thermal conductivity for the glassy phase of Ge$_2$Sb$_2$Te$_5$, which is the prototypical material employed in phase-change random-access memory devices.

Methods for simulating thermal transport at the atomic level have seen a rapid evolution and are getting closer to quantitative agreement with experimental measurements [8, 10]. Ab initio methods, based on the Boltzmann transport equation [11, 12] and Green-Kubo dynamical formulations [13, 14] have been employed recently in the literature to provide a first-principles description of thermal transport, and they represent significant advances in the field. Nevertheless, these approaches are computationally very demanding within a density-functional-theory framework, while some of them are specifically designed for harmonic solids only at equilibrium.

Therefore, there is the necessity for an efficient and fully dynamical first-principles molecular-dynamics approach to model the thermal properties of glasses, which can be used for predictive calculations of the thermal conductivity of a material. A quantitative assessment of thermal-transport properties can be obtained from the approach-to-equilibrium molecular-dynamics (AEMD) method [15, 16], which has been deployed in ab initio (as well as with empirical force fields) molecular-dynamics simulations of several different materials [17]. The AEMD methodology can be applied in a straightforward manner to the calculation of the thermal conductivity using density-functional theory simulations, while the implementation of this approach requires only the calculation of molecular-dynamics trajectories and atomic forces, and hence it is computationally affordable.

In this Letter, the approach-to-equilibrium molecular-dynamics methodology has been adapted to the case of a cubic core region in contact with a thermostatted bound-
The Cartesian coordinates of atoms in the core region, assumed to be approximately homogeneous and isotropic. Based on our set-up, the simulation box is cubic and is also as-
duction is usually modelled by Fourier’s law \[16\]. Based on our previous work \[23, 24\]. and the molecular-dynamics simulations can be found in
the computational set-up, the radiation-damage cascades and the limitations of the approach.

The simulated system is a 315-atom melt-quenched model of glassy Ge$_2$Sb$_2$Te$_5$ \[18\]. The simulation box, which has a length of 21.65 Å, was divided into a core cubic region and an outer boundary shell of thickness 1 Å. This type of separation has been dubbed stochastic-boundary conditions, and it has a long history in the simulation of thermal transport at interfaces \[19\]. The core region samples a micro-canonical ensemble (NVE) while the boundary undergoes Langevin dynamics in the canonical ensemble (NVT) and dissipates the heat generated in the core region during an ionic cascade \[20\]. The thermostat parameters were chosen such that the thermostat damping time was 100 fs. \textit{Ab initio} molecular-dynamics simulations were carried out using the CP2K code \[21\], in which the stochastic-boundary-conditions approach is implemented, based on the Generalized Langevin Equation formulation \[22\]. We modelled radiation-induced non-equilibrium cascades by performing thermal-spike simulations with initial kinetic energies in the range of 15–200 eV. Further details related to the computational set-up, the radiation-damage cascades and the molecular-dynamics simulations can be found in our previous work \[23, 24\].

In the approach-to-equilibrium methodology, heat conduction is usually modelled by Fourier’s law \[16\]. Based on our set-up, the simulation box is cubic and is also assumed to be approximately homogeneous and isotropic. The Cartesian coordinates of atoms in the core region, \(x, y, z\), reside in the real interval \([0, L]\) where \(L = a - 2r\), \(a\) is the size of the periodic cubic simulation box and \(r\) is the thickness of the boundary region. In this case, the resulting heat equation can be written as:

\[
\frac{\partial T}{\partial t} = -\alpha \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \tag{1}
\]

where \(T\) is the temperature and \(t\) is the time. The thermal diffusivity \(\alpha\) is defined as:

\[
\alpha = \frac{\kappa}{C_v \rho} \tag{2}
\]

where \(\kappa\) is the thermal conductivity, \(C_v\) the constant-volume heat capacity and \(\rho\) the density of the system.

The general solution, assuming a separable form, is then given by:

\[
T(x, y, z, t) = T_0 + \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} a_{nml} e^{-\alpha l \lambda_{nl} t} \sin \left( \frac{n \pi x}{L} \right) \sin \left( \frac{n \pi y}{L} \right) \sin \left( \frac{n \pi z}{L} \right) \tag{3}
\]

The Fourier-series coefficients in the general solution, \(\lambda_{nml}\) and \(a_{nml}\), can be inferred from the boundary conditions and are given in the two equations below:

\[
\lambda_{nml} = \left( \frac{n \pi}{L} \right)^2 (n^2 + m^2 + l^2) \tag{4}
\]

\[
a_{nml} = -\Delta T_0 \left( \frac{2}{\pi} \right)^3 \frac{(1 - (-1)^n)(1 - (-1)^m)(1 - (-1)^l)}{nml} \tag{5}
\]

The temperature difference between the core region (undergoing NVE dynamics) and the boundary region (undergoing NVT dynamics) corresponds to: \(\Delta T = T(x, y, z, t) - T_0\). It has an initial value, \(\Delta T_0\), at the start of the thermal quench and it decays to zero during the quench. The exponential temporal decay of the temperature difference \(\Delta T\) between the core and the boundary, \(\Delta T \sim e^{-\frac{t}{\tau}}\), has a dominant contribution from the leading term \(a = m = l = 1\) of the Fourier series. Once the relaxation time \(\tau\) is obtained from simulations, it can be inserted into the time-dependent part of this dominant term. Hence, the thermal conductivity, \(\kappa\), can be calculated, based also on the equations 2 and 4, from the expression:

\[
\kappa = \frac{L^2 C_v \rho}{3\pi^2 \tau} \tag{6}
\]

It is noted that the above equation is related to the formula more commonly used in the quasi-1D setup for approach-to-equilibrium molecular-dynamics simulations \[25\]. In the standard AEMD approach, two thermal regions of the same size are initialized at different temperatures and are placed in contact along one Cartesian direction in a thin simulation box \[16\]. The expression for \(\kappa\) in equation 6 differs from the standard AEMD formula only by a geometric prefactor which is \(\frac{L^2}{3\pi^2}\) in the case of our adaptation, compared to \(\frac{L^2}{4\pi^2}\) in the standard approach. This reflects the different geometry of the 3D core/boundary setup.

The thermal transients of the non-equilibrium ion-irradiation simulations for glassy Ge$_2$Sb$_2$Te$_5$ can be directly fitted from the thermal quench of the core region as it reaches thermal equilibrium with the boundary layer. The trajectory of the radiation-induced cascade can be split into three intervals, based on the time evolution of the kinetic temperature, shown in figure 1 for
different initial thermal-spike kinetic energies: (a) The high-energy cascade generated by the thermal spike; (b) An approach-to-equilibrium transient that is reasonably well described by an exponential temporal decay of the temperature difference between the core and the boundary; and (c) An equilibrium region where the system as a whole fluctuates around the temperature of the thermostat. The computational procedure used in this case comprised the following steps: (1) Fix the atoms in the boundary region; (2) Initialize and equilibrate the velocities in the core region at a higher temperature; (3) Release the constraints on the boundary region; and (4) Release the thermostat from the core region. In this case, there is no radiation-induced cascade and the simulation consists simply of a thermal quench and equilibration with the boundary. The core-region initial maximum kinetic temperature was chosen to be 700 K in order to obtain a relatively long transient, without melting the structure.

After obtaining the transients for all the thermal-spike simulations, the approach-to-equilibrium methodology was applied to examine the pristine glassy Ge$_2$Sb$_2$Te$_5$ structure. The empirical criterion for this was to include as much of the transient as possible without exceeding an average kinetic temperature of 700 K in the core region. Examples of exponential fits to the approach-to-equilibrium region of the ion-irradiation simulations are shown in figure 2 for 50 eV, 100 eV and 200 eV initial thermal-spike energies.

FIG. 2. Log-linear plot of the temperature difference $\Delta T$ between the core region and the temperature of the boundary thermostat, viz. 300 K, as a function of time. Thermal transients in the approach-to-equilibrium are shown in different shades of red as a function of the energy of the thermal spike (darker is higher). The corresponding exponential fits are shown as black lines.
thermal spike. The temperature evolution is regularly analyzed after simulations of thermal spikes and a mechanical model predicts that the thermal relaxation time will scale as a power-law function of the thermal-spike energy, with an exponent around $\frac{2}{3}$ [26]. However, values for the power-law exponent below $\frac{2}{3}$ have been reported from computer simulations, suggesting that the exponent depends on the structure of the material [27]. From our simulations, an exponent of 0.43 was obtained for glassy Ge$_2$Sb$_2$Te$_5$, indicating a relatively subtle increase of the thermal relaxation time with the energy of the thermal spike.

An additional ingredient for the estimation of the thermal conductivity is the heat capacity of the material. In order to obtain the heat capacity, energy fluctuations, $\delta E = E - \langle E \rangle$, were sampled from equilibrium ab initio molecular-dynamics simulations. The starting point for each trajectory corresponds to the structural models at the end of each non-equilibrium thermal-spike simulation. In these subsequent molecular-dynamics runs, there is no longer a separation between core and boundary, and the entire system undergoes NVT dynamics with a single thermostat. A generalized Langevin equation (GLE), or colored-noise, thermostat [28, 29] was used for the sampling of the total-energy fluctuations. A molecular-dynamics trajectory of 10 ps was generated with a time-step of 1 fs for each glassy sample. The first 2 ps are discarded and the heat capacity is estimated, based on equation 3 in the Supplementary Information [30], from the remaining 8000 time steps.

The calculated heat capacity at 300 K for the pristine glassy phase of Ge$_2$Sb$_2$Te$_5$ was $181 \pm 14.4 \text{ Jkg}^{-1}\text{K}^{-1}$, which is quite close to the Dulong-Petit limit value of $219 \text{ Jkg}^{-1}\text{K}^{-1} (3Nk_B)$. This is in good agreement with experimental data from differential scanning calorimetry, viz. $220-230 \text{ Jkg}^{-1}\text{K}^{-1}$[31, 32], and with the fact that the Debye temperature of glassy (as-deposited) Ge$_2$Sb$_2$Te$_5$ was found to be below 111 K from inelastic neutron-scattering experiments [32]. In the Supplementary Information [30], details are provided for the calculation of the heat capacity in all the simulated systems.

The bulk thermal conductivity of glassy Ge$_2$Sb$_2$Te$_5$ was calculated from equation 6, following the approach described above, and was found to be $0.130\pm0.011 \text{ W K}^{-1} \text{ m}^{-1}$. This estimated value is in very good agreement with the lower limit of the experimentally reported values, which are in the range $0.19-0.3 \text{ W K}^{-1} \text{ m}^{-1}$ [33–35]. It should be noted that the effects of increased phonon-phonon scattering in a small simulation box can lead to an overestimation of the thermal conductivity, while the lack of longer wavelength phonons can be responsible for an underestimation of this quantity [36]. For this reason, the effect of the artificial Kapitza thermal resistance [37] at the core-boundary interface cannot be eliminated without accounting for finite-size effects [8, 17, 36]. Hence, the slight underestimation of the thermal conductivity of glassy Ge$_2$Sb$_2$Te$_5$ in this work suggests that the system size is still somewhat too small to fully account for the propagon contribution to the thermal conductivity [8, 38]. Moreover, the influence of the Langevin-thermostat damping time, applied in the boundary region, in the calculation of the thermal conductivity was explored and the results are shown in the Supplementary Information [30].

In a recent AEMD study for a related glassy chalcogenide material, namely GeTe$_4$, the authors reported a value of $0.013\pm0.003 \text{ W K}^{-1} \text{ m}^{-1}$ for the thermal conductivity [25], which is an order of magnitude lower than the experimental measurement for this material (0.1 W K$^{-1}$ m$^{-1}$) [39], as well as from our calculated value for glassy Ge$_2$Sb$_2$Te$_5$. This discrepancy is likely due to the small model system size (185 atoms), which illustrates the limitations of tractable ab initio molecular-dynamics simulations. The same authors, in a different study [40], doubled the simulated system size (up to 370 atoms) and obtained a value of $0.044\pm0.001 \text{ W K}^{-1} \text{ m}^{-1}$ for the thermal conductivity of glassy GeTe$_4$, closer to, but still smaller than, the experimental value, revealing the influence of size effects.

From figure 3, it can be seen that the irradiated glassy Ge$_2$Sb$_2$Te$_5$ models exhibit an increased thermal-relaxation time. The thermal conductivity of the irradiated glass systems was calculated for initial thermal-spike energies in the $15-200 \text{ eV}$ range, and it was found to be between $0.076$ and $0.106 \text{ W K}^{-1} \text{ m}^{-1}$. Hence, a reduction of the thermal conductivity of glassy Ge$_2$Sb$_2$Te$_5$, by up to $\approx 40\%$, can be achieved by ion irradiation of the pristine glassy phase. Reducing the thermal conductivity can help to increase the figure of merit, $ZT$, and therefore the performance of thermoelectric devices. It is noted that non-equilibrium doping has been used used success-
fully before to lower the thermal conductivity of ZnO nanowires [41], as well as, more recently, of Si nanowires [42].

In conclusion, an adaptation of the approach-to-equilibrium molecular-dynamics method is proposed for calculating the thermal conductivity of a cubic-core region in contact with a thermostatted-boundary layer. This approach has been applied to estimate the thermal conductivity of glassy Ge$_2$Sb$_2$Te$_5$ “on the fly” from non-equilibrium ab initio molecular-dynamics simulations using stochastic-boundary conditions. The thermal relaxation time is fitted using an appropriate time interval of the simulation, as the core approaches thermal equilibrium with the boundary. The good agreement between the calculated value for the thermal conductivity of pristine glassy Ge$_2$Sb$_2$Te$_5$ and the results of experimental measurements provides validation for this approach.

The thermal relaxation time increases as a power-law function of the thermal-spike energy, and it is the dominant effect, resulting in an overall decrease of the thermal conductivity compared to that of the pristine glassy structure. Our simulations suggest that radiation-induced cascades can reduce the thermal conductivity of glassy Ge$_2$Sb$_2$Te$_5$ by as much as 40%, and given the remarkable recovery of the electronic structure of the glass after irradiation, as already demonstrated for this material in our previous work [23], ion irradiation can therefore be a potential strategy for improving the thermoelectric figure of merit of this material. This might make glassy chalcogenide materials competitive with their crystalline counterparts in thermoelectric devices, and could also improve the performance of phase-change memory and data-storage devices by reducing thermal cross-talk between memory cells.

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See Supplemental Material at [URL will be inserted by publisher] for details about the calculation of the heat capacity in the simulated systems, the parametrization of the GLE thermostat used for the sampling of the total-energy fluctuations, and the effect of the Langevin-thermostat damping time during irradiation on the calculation of the thermal conductivity.

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