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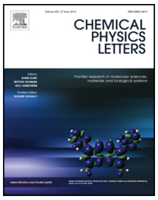

Understanding unusual thermal transport behavior in soft materials under mechanical strain – A molecular dynamics study

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ABSTRACT

Experiments have shown a dependence of the thermal conductivity of soft polymer materials on shear stress, which is common to several applications, such as film processing, fiber spinning, blow molding, and vacuum forming. Experiments reveal that the conductivity initially decreases with shear, but then increases as additional shear rate is applied. Based on molecular principles, we hypothesize that when molecules are initially placed under tension and extended, they disentangle, which reduces the number of points of interaction and diminishes the heat flux. Further molecular stretching increases this flux because the molecules are now better axially aligned. Molecular dynamics simulations confirm this competition and reproduce the inflection in the flux-strain relationship, which has not been previously explained.

Thermal transport in hard crystalline materials occurs through harmonic interactions between vibrating atoms. In contrast, soft materials that contain polymer chains experience both bonded interactions within a polymer molecule as well as anharmonic nonbonded interactions. The nonbonded interactions occur both between the constituents of a long molecule and among neighboring molecules [1]. Besides, polymer molecules can be entangled or disentangled, and unaligned or aligned with the direction of heat transfer. Thus, the dissimilar structures, and intra- and intermolecular interactions in soft [1–3] and hard [4–6] materials produce different thermal transport behaviors.

Experiments show that when polyethylene is sheared, its thermal conductivity k first decreases but then increases with higher shear [7]. This can be explained by examining the orientations of the polymer molecules. When they are unstretched, the molecules are entangled and have many points of interaction [8]. The initial imposition of stretch disentangles the molecules, removing the intermolecular intersections, which leads to weaker anisotropic molecular orientations. As the molecules disentangle and move apart, their nonbonded interactions decrease but there is little impact on their bonded interactions. This reduces the energy transport between the polymer chains, decreasing k, which is a behavior also exhibited by crystalline materials [5,6]. As the chains are stretched beyond a nominal value and further disentangled, they become more aligned with the direction of stretch as they lose their isotropic orientation. Orienting the direction of the applied stress, which aligns the chains, with the overall direction of heat transfer induces structural order within the bulk material, which decreases phonon scattering [2,3,9,10], and enhances k.

Consequently, we hypothesize that, while there is an initial decrease in the heat flux q when polymer molecules are placed in tension, it increases with further molecular stretching. This leads to an inflection in q with respect to molecular extension. Since the literature on the matter is sparse [2], we examine these interactions in an idealized system by either elongating or shortening each soft material chain directly in a homogeneous bulk material through molecular dynamics (MD) simulations.

The MD system consists of the hypercube shown in Figure 1 with dimensions of 10.6 nm in the x-direction, and 5.137 nm in the y- and z-directions. In the figure, z points into the plane of the paper. The x-direction traverses through two semipermeable fcc walls placed at $x^* = 2.65$ nm and 7.95 nm in y–z planes. The section between these walls is filled with the C_{32} linear alcohol shown in Figure 1(a). On the left and right sides of the walls are additional sections that contain CO. Periodic boundary conditions imply that the two end sections are connected as a contiguous CO compartment. Since the thermal conductivity of CO is well known, this allows us to obtain the system heat transfer rates even though k is not available for the C_{32}

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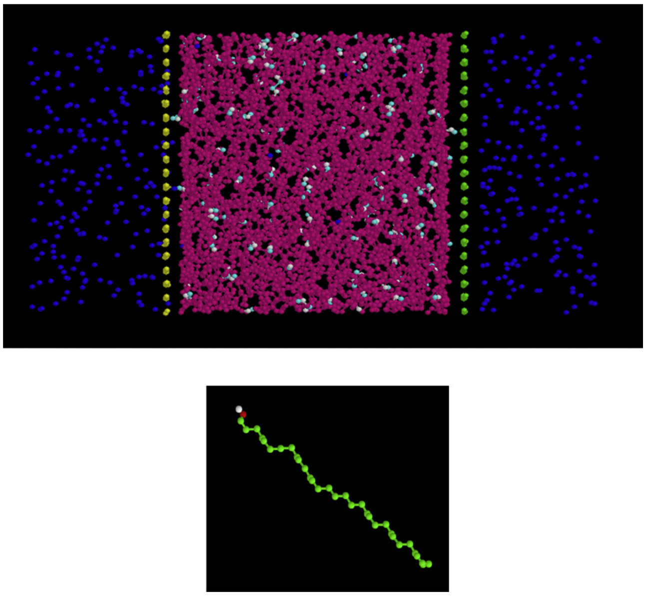

Figure 1. (a) The simulation system consists of a hypercube with dimensions 10.6 nm in the *x* direction, and 5.137 nm in the *y* and *z* directions (where *z* points into the plane of the paper). The *x* direction contains two semi-permeable fcc walls at 2.65 nm and 7.95 nm that contain the C_{32} linear alcohol between them. Due to periodic boundary conditions, additional sections on the left and right sides of the walls that are filled with CO form a single contiguous CO compartment. (b) Structure of the C_{32} linear alcohol, where the two end alkyl groups (two green sites at the extreme ends of the molecule) are tethered with a simple harmonic potential to produce either a tensile or compressive force in each alcohol molecule. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

alcohol under our conditions. The *x*-wise length of the system is divided into 53 rectangular slits of 0.2 nm width in which averaged slit temperatures and densities are sampled. The system is symmetric in the *y* and *z* directions so that no variations, other than thermal fluctuations, are expected.

We employ Lennard–Jones (LJ) potentials for the fcc walls, where,

$$u_{ij} = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right) + \frac{(q_i q_j)}{r_{ij}}, \qquad (1)$$

with $\varepsilon = 0.1591$ kcal/mol and $\sigma = 0.4$ nm. We have previously shown that if a hot wall is made more hydrophilic, the heat transfer rate through it to a soft material is enhanced [11]. Hence, the right wall of the system is made hydrophilic by increasing the energy parameter for its interactions with the C_{32} alcohol threefold. For the alcohol, we use united atom parameters [12], and for CO, we apply an LJ potential model with $\varepsilon = 0.3182$ kcal/mol and $\sigma = 0.376$ nm. The potential model used for alcohol includes bonded interactions (bonds, bond angles and dihederal angles that constrain two, three and four adjacent sites respectively) and non-bonded interactions which occur in our potential model between active sites that are separated by more than three bonds or between different molecules [12].

To accommodate mechanical straining, we add an additional stiff harmonic force to the system that either extends or shortens each alcohol molecule. This force is implemented by including a simple harmonic potential

$$\phi = K(\delta_{ij} - \delta_{eq})^2, \qquad (2)$$

where δ_{ij} denotes the scalar distance between the C_1 and C_{32} alkyl groups at the two ends of the alcohol molecules (thus avoiding any interference directly with the polar nature of the molecule), δ_{eq} is a simulation parameter that determines if a tensile or compressive force is being applied to the alcohol molecule in order to either extend or shorten it, and *K* is a fixed spring constant. The value of $K = 1$ kcal/(mol Å^2) is set deliberately small to ensure that the added tensile or compressive force is relatively weak. For the simulated system, the force due to *K* is almost three orders of magnitude smaller than the average covalent bond force. Simulations with no such force applied, or $\phi = 0$, are also conducted to examine the behavior of an unconstrained system in which the alcohol molecules are ‘unstretched’.

Our method differs from those used in previous studies that have included an externally imposed strain rate on the overall system

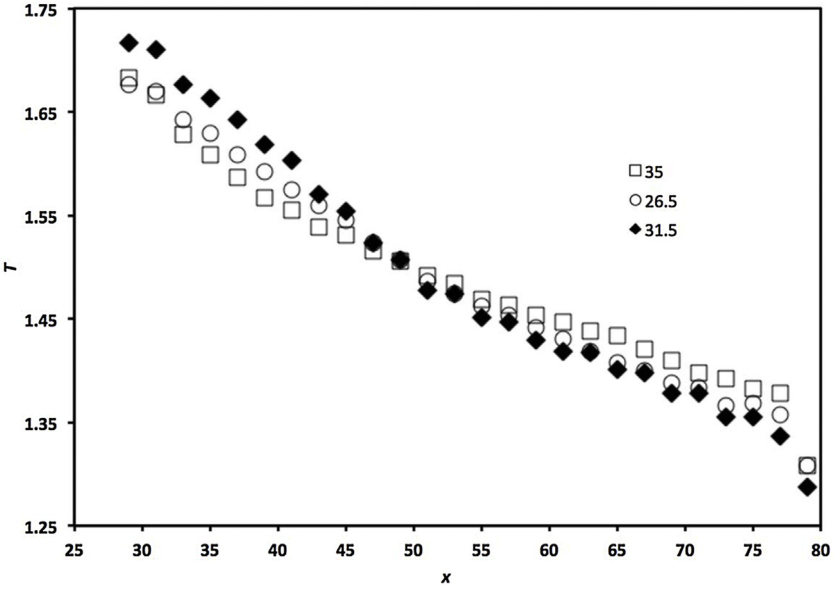

Figure 2. The temperature profiles for a bulk density $\rho = 1$, and mechanical stretch $r = 26.5$, 31.5 and 35. The hot and cold walls at $x = 79$ and 27 are maintained at dimensionless temperatures of 2.053 and 0.876, respectively. Results are presented for each position in dimensionless form where a length unit is equivalent to 0.1 nm and a temperature unit to 340 K. Moderate stretching of the molecules from $r = 26.5$ to 31.5 enhances the temperature gradient but higher molecular stretching decreases it.