Supporting Information: Energy Relaxation and Thermal Diffusion in IR Pump-Probe Spectroscopy of Hydrogen-Bonded Liquids

Riccardo Dettori,[†] Michele Ceriotti,[‡] Johannes Hunger,[¶] Luciano Colombo,[§] and Davide Donadio[*,†]

†*Department of Chemistry, University of California Davis, One Shields Avenue, Davis, California 95616, United States*

‡*Laboratory of Computational Science and Modeling, IMX, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*

¶*Max Planck Institute for Polymer research, Ackermannweg 10, 55128 Mainz, Germany*

§*Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, I-09042 Monserrato (Ca), Italy*

E-mail: ddonadio@ucdavis.edu

Thermal diffusivity calculations

Simulation cell set up

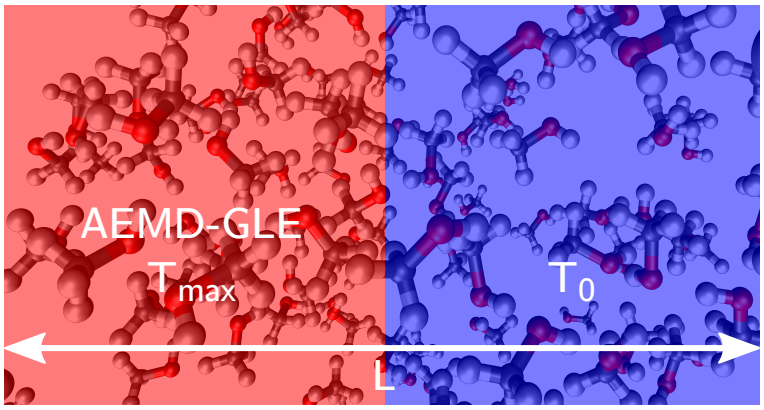

Figure 1: 1D set up of the simulation cell, where the GLE thermostat is adopted in the AEMD framework for a system with length L.

Results

Thermal diffusivity of deuterated methanol was computed at room temperature both by equilibrium MD and by AEMD. The results are reported in Fig. 2. Equilibrium MD simulations (blue triangles) were performed on cubic cells of increasing size, containing from 27 to 1000 molecules, equilibrated at 300 K and relaxed to the equilibrium density at 1 bar. The Green-Kubo relation allows us to compute the thermal conductivity (κ) from the time integral of the heat flux autocorrelation function. The diffusivity, $\bar{\kappa} = \kappa/\rho c_v = 10.1$ Å^2/ps with $c_v = 85.8$ J/mol K,[1] is size-independent and in excellent agreement with the experimental value of methanol $\bar{\kappa}^{exp.} = 10.1$ Å^2/ps.[2] This result validates the adopted force-field in comparatively small simulation cells, although it requires longer simulation times in order to converge the heat current autocorrelation function. However, the alternative strategy represented by AEMD allows one to investigate thermal transport in much larger systems within a considerably shorter time, which is more suitable for our purpose of non-equilibrium investigations. The AEMD simulation cell was prepared according to the geometry reported in Fig.1, but adopting a standard (white) Langevin thermostat. The initial temperature

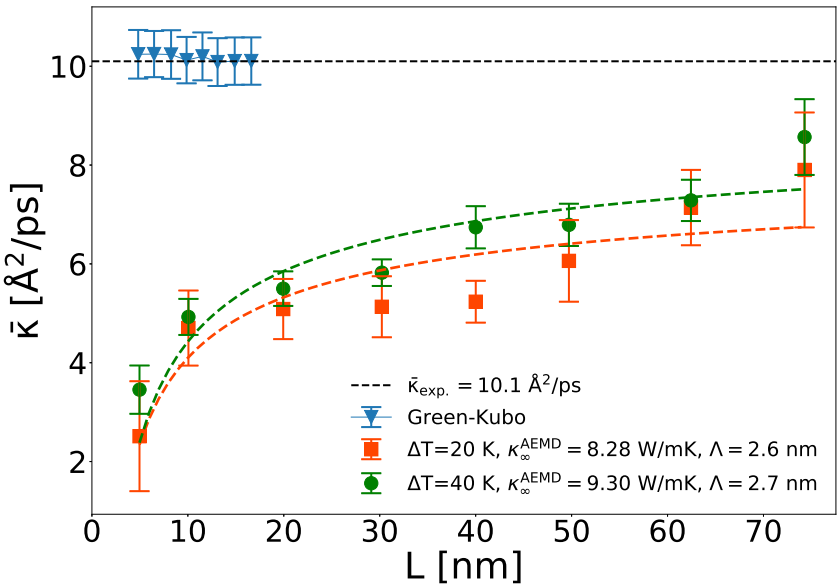

Figure 2: Thermal diffusivity calculated with Green-Kubo and with standard AEMD approach[3] for increasing system size, reported as a function of the simulation cell length (or the cell side in the case of the GK values). Dashed curves represent the fit performed with the model proposed in Ref.[4] and the bulk conductivity values are reported in the plot key.

profile is achieved by thermostatting the "hot" half of the simulation cell at $T_{\mathrm{H}} = 320$ and 340 K, while the "cold" half of the system is kept at $T_{\mathrm{C}} = 300$ K.

Similarly to what happens in other non-equilibrium methods, finite size effects are a common issue in the AEMD framework.[3] For this reason, we performed AEMD runs on simulation cells of increasing length L_z spanning the interval $4.0 \leq L_z \leq 74.3$ nm, with a fixed square cross section of 2.44×2.44 nm^2. The results display a remarkable size and temperature offset dependence as well. Fig. 2 shows that standard AEMD calculations do not converge for cell length up 80 nm. Usually, size-effect in AEMD are overcomed by considering the length dependence $\bar{\kappa} = \bar{\kappa}(L)$ (related to the mean free path -MFP- of phonons in the simulation cell) and by performing an extrapolation for $L \to \infty$. However, the investigated system is a molecular liquid and it is not possible to rely on the concept of MFP of vibrational modes. To our aim, we empirically adopted a $\bar{\kappa}(L) = \bar{\kappa}_{\infty}(1 - \sqrt{\Lambda/L})$ relation, where κ_{∞} is the bulk thermal conductivity. This relation is usually adopted for solid state systems,[4] with Λ being the MFP of the vibrational modes which contribute the most to heat transport. In our case, $\Lambda \sim 2.6$ nm: we argue that such length is the maximum

extension of intermolecular modes, which can contribute to thermal transport. This fitting relation would allow one to extrapolate the bulk value of $\bar{\kappa}$, yet with large uncertainties.

References

(1) Katayama, T. Heats of mixing, liquid heat capacities and enthalpy, concentration charts for methanol-water and isopropanol-water systems. *Kagaku Kogaku* **1962**, *26*, 361–372.

(2) Williams, M. L. CRC Handbook of Chemistry and Physics, 76th edition. *Occup. Environ. Med.* **1996**, *53*, 504–504.

(3) Melis, C.; Dettori, R.; Vandermeulen, S.; Colombo, L. Calculating thermal conductivity in a transient conduction regime: theory and implementation. *Eur. Phys. J. B* **2014**, *87*.

(4) Zaoui, H.; Palla, P. L.; Cleri, F.; Lampin, E. Length dependence of thermal conductivity by approach-to-equilibrium molecular dynamics. *Phys. Rev. B* **2016**, *94*, 054304.