Determination of thermal conductivity in liquids by the nonequilibrium MD simulations

Anže Hubman\textsuperscript{a,b} and Franci Merzel\textsuperscript{b}

\textsuperscript{a}Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia
\textsuperscript{b}Theory department, National Institute of Chemistry, Hajdrihova ulica 19, 1000 Ljubljana, Slovenia

Thermal conductivity is one of the fundamental material properties providing the rate at which thermal equilibrium is established. In recent years a substantial effort has been devoted to the development of atomistic computational methods which allow one to determine thermal conductivities in liquids by exploiting molecular dynamics (MD) simulations in its equilibrium and nonequilibrium flavors. Such \textit{in silico} approaches are especially important in cases where measurements of thermal conductivity become highly non-trivial as for example in ionic melts or liquids under extreme $pT$ conditions [1].

Equilibrium methods are rooted in the Green-Kubo (GK) theory of linear response [2,3] where the thermal conductivity is given as an integral of the heat flux autocorrelation function. Despite its apparent simplicity, the GK approach is troublesome due to poor convergence of the aforementioned integral. Alternatively, nonequilibrium methods [4] are generally based on either imposing thermal gradient or the heat flux along one direction of the simulation cell. Nonequilibrium methods converge faster but may have convection problems or significant finite size effects originating from periodic boundary conditions and continuum description of heat transfer.

We present a robust nonequilibrium MD method for efficient determination of thermal conductivity in liquids. Our approach exploits a transient regime where a system undergoes a relaxation towards thermal equilibrium after being subjected to a temperature perturbation. The method is simple to implement, converges rapidly with respect to system size and is compatible with periodic boundary conditions. We demonstrate performance of our approach on three carefully chosen systems: liquid argon and two water models (mW [5] and SPC/E [6]).

\textbf{Keywords}: thermal conductivity, molecular dynamics, atomistic simulations.

\textbf{References}


Corresponding author: Anže Hubman (anje.hubman@ki.si), Franci Merzel (franci.merzel@ki.si)