

Evaluating Thermal Conductivity in Molecular Simulation

David Keffer

Department of Materials Science & Engineering

University of Tennessee, Knoxville

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I. Purpose of Document

The purpose of this document is to provide a practical introduction to the evaluation of thermal conductivities in LAMMPS. The notes begin with some formal theory and conclude with practical implementation.

II. Macroscopic Description of Thermal Conductivity

Fourier (1768-1830) is responsible for an expression that is typically called “Fourier’s law of Heat Conduction”.

$$q_\alpha = -k_c \frac{\partial T}{\partial \alpha} \quad \text{for } \alpha = x, y, z \quad (1)$$

where T is temperature, α is a spatial dimension, q_α is a heat flux with units of energy per area per time, e.g. $J/s/m^2$, and k_c is the thermal conductivity, which possesses exactly those units required to convert a temperature gradient, e.g. K/m , to a heat flux, namely energy/temperature/time/length, e.g. $J/K/s/m$. For those familiar with heat transfer coefficients, the units of the thermal conductivity are not the same, since a heat transfer coefficient relates a heat flux to a temperature difference, units of K , rather than a temperature gradient, units of K/m .

Fourier’s law is an empirical relation that we can regard as a Taylor series expansion truncated at the linear term. It relates the heat flux to the temperature gradient. The presence of the negative sign in Fourier’s law and the corresponding requirement that the thermal conductivity is greater than zero dictates the common-sense observation that heat flows downhill.

As is the case with Fick’s law or Newton’s law of viscosity, Fourier’s law is intended to be inserted into a balance, in this case an energy balance, in order to describe the evolution of temperature in the system. When one derives the microscopic energy balance, one obtains

$$\frac{\partial \rho \left(\frac{1}{2} v^2 + \hat{U} + \hat{\Phi} \right)}{\partial t} = -\nabla \cdot \rho \left(\frac{1}{2} v^2 v + \hat{U} v + \hat{\Phi} v \right) - \nabla \cdot q - \nabla \cdot p v - \nabla \cdot (\tau \cdot v) , \quad (2)$$

where \hat{U} is the specific (per mass) internal energy, $\hat{\Phi}$ is the specific potential energy due to an external field, and q is the heat flux due to conduction, the vectorial form of Fourier’s heat flux in eqn (1). The term on the LHS is the accumulation term. The first term on the RHS is the convection term. The second term on the RHS is the conduction term. The third term on the RHS is the reversible rate of internal energy change per unit change in unit volume. Note that a compression will increase the internal energy. The last term on the RHS is the irreversible rate of internal energy increase per unit volume by viscous dissipation. This is equation (11.1-9) on page 336 of the second edition of Bird, Stewart and Lightfoot’s Transport Phenomena.[†]

We can add other terms to this energy balance to account for reactions and energy loss to the surroundings by other means.

The microscopic energy balance can also be written in terms of the enthalpy

$$\hat{H} = \hat{U} + p\hat{V} = \hat{U} + \frac{p}{\rho} . \quad (3)$$

Direct substitution and algebraic rearrangement yields

$$\frac{\partial \rho \left(\frac{1}{2} v^2 + \hat{H} + \hat{\Phi} \right)}{\partial t} - \frac{\partial p}{\partial t} = -\nabla \cdot \rho \left(\frac{1}{2} v^2 \cdot v + \hat{H}v + \hat{\Phi}v \right) - \nabla \cdot q - \nabla \cdot (\tau \cdot v) , \quad (4)$$

Let us consider a system, such as heat transfer in a solid, in which there is no flow, so all terms with a velocity can be deleted. Let us further consider an absence of gravitational potential energy. If we regard the solid as incompressible, then we can further ignore pressure changes, leaving

$$\frac{\partial \rho \hat{H}}{\partial t} = -\nabla \cdot q , \quad (5)$$

If we assume that the enthalpy is strictly a function of temperature, then we can write

$$\hat{H} = \int_{T_{ref}}^T \hat{C}_p(T') dT' \quad (6)$$

where \hat{C}_p is the specific (per mass) constant-pressure heat capacity and T_{ref} is a thermodynamic reference temperature. Using Leibniz's rule for differentiation under the integral sign we have

$$\frac{\partial \hat{H}}{\partial t} = \hat{C}_p(T) \frac{\partial T}{\partial t} - \hat{C}_p(T_{ref}) \frac{\partial T_{ref}}{\partial t} + \int_{T_{ref}}^T \frac{\partial \hat{C}_p(T')}{\partial t} dT' \quad (7)$$

If we further assume that the constant-pressure heat capacity is a constant, then we have

$$\frac{\partial \hat{H}}{\partial t} = \hat{C}_p \frac{\partial T}{\partial t} \quad (8)$$

Substituting equation (8) into the simplified energy balance of equation (5) yields

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = -\nabla \cdot q \quad (9)$$

If we limit ourselves to one-dimensional temperature gradients, e.g. in x , then we can substitute equation (1) into equation (9) to obtain

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = \frac{\partial T}{\partial x} \left(k_c \frac{\partial T}{\partial x} \right) \quad (10)$$

If we assume that the thermal conductivity is a constant, independent of temperature, then we can pull it out of the differential operator

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = k_c \frac{\partial^2 T}{\partial x^2} \quad (11)$$

Grouping the three constants into a single parameter yields

$$\frac{\partial T}{\partial t} = \frac{k_c}{\rho \hat{C}_p} \frac{\partial^2 T}{\partial x^2} = \alpha_T \frac{\partial^2 T}{\partial x^2} \quad (12)$$

where α_T is called the thermal diffusivity because it has units of diffusivity, e.g. length squared per time or m^2/s . Equation (12) is often called the heat equation. It is a partial differential equation that describes the evolution of a temperature profile. The unique solution to the heat equation depends upon the boundary conditions and the initial condition. Analytical solutions to the heat equation for a variety of conditions, geometries and additional generation terms are collected in Carslaw and Jaeger's Conduction of Heat in Solids, a seminal resource.[†]

As an example of a solution from Carslaw and Jaeger, consider the following one-dimensional problem of the infinite solid. Initially, a material is at temperature V from $-a < x < a$ and at temperature 0 for $x > a$. Then the solution to the heat equation (equation (12)) is given by

$$T(x, t) = \frac{1}{2} V \left[\operatorname{erf} \left(\frac{a-x}{\sqrt{t/\alpha_T}} \right) + \operatorname{erf} \left(\frac{a+x}{\sqrt{t/\alpha_T}} \right) \right] \quad (13)$$

where erf is the error function. This solution describes the conduction of heat from the hot central slab out into the object at any point in space or time. Many such solutions are provided in Carslaw and Jaeger for varying conditions and coordinate systems.

In this example, we have seen the number of approximations that were invoked to reach this solution in equation (13). Among these approximations was the assumption that the thermal conductivity was constant. This is in general not true. The thermal conductivity is generally a function of the thermodynamic state, with a practical consequence that it varies with temperature, density and composition.

[†]Bird, R.B., W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*. Second ed. 2002, New York: John Wiley & Sons, Inc.

^{††}Carslaw, H.S. and Jaeger, J.C., *Conduction of Heat in Solids*. Second ed. 1959, Oxford: Clarendon Press.

III. Mechanisms for Thermal Transport

At the macroscopic level, the mechanisms for thermal transport are categorized as convective (due to flow, e.g. center of mass motion in response to a pressure gradient), conductive (due to temperature gradient) and radiative. Heat transfer due to convection and conduction is caused by the movement of atoms. Radiative heat transfer, on the other hand, is carried by electromagnetic radiation.

Another way of looking at the same heat transfer phenomena is to think about the carriers of energy in the process. In general, energy can be transferred by four means

- photons (as is the case in radiative heat transfer),
- atoms (as is the case in convection and some conduction in fluids),
- phonons (as is the case in conduction in solids),
- electrons (as is the case in conduction in solids)

A good introduction to heat transfer via these four carriers is available at Wikipedia: https://en.wikipedia.org/wiki/Heat_transfer_physics.

Relevant to this course on classical molecular dynamics simulation, any phenomena which relies on photons or electrons is not captured in a typical MD simulation. (Exceptions exist; empirical reactive interaction potentials phenomenologically describe electron redistribution during chemical reaction.) However, for the purposes of heat transfer, MD simulations do not capture radiative heat transfer or heat transfer due to electrons.

MD simulations can describe heat transfer due to convection and conduction in fluids because the mechanisms for heat transfer are tied to motion of the nuclei. To the extent that a classical description suffices to describe the nuclei motion, MD simulations can describe the corresponding heat transfer.

A phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules usually in a solid. These lattice waves can be describe either classically or in quantum mechanics. Classical MD simulations can also be used to describe heat transfer in solids, because photons are perturbations of an equilibrium lattice and are constructed of groups of atoms. Again, to the extent that classical mechanics can describe motion of the nuclei, MD simulations can describe heat transfer via phonons.

As an aside, the heat capacity of electrons is small except at very high temperature when they are in thermal equilibrium with phonons. Electrons contribute to heat conduction (in addition to charge carrying) in solids, especially in metals. Thermal conductivity in a solid is the sum of electric and phonon thermal conductivities.

III. Thermal Conductivities from Equilibrium Simulation

The derivation for the expression of a viscosity comes from a Green-Kubo integral. See for example Chapters 7 and 8 (especially Table 8.1) of Hansen & McDonald.[†] The general Green-Kubo integral has the form

$$K_\alpha = \int_0^\infty d\tau \langle J_\alpha(t + \tau) J_\alpha(t) \rangle \quad (14)$$

where K is a transport property in direction α and J_α is a flux in the same direction.

For the case of the thermal conductivity, the argument of the Green-Kubo integral is the auto correlation function of the time derivative of the product of the position and the total (kinetic and potential) energy, where $K_\alpha = V k_B T^2 \lambda_\alpha$, λ_α is the thermal conductivity in dimension α and

$$J_\alpha(t) = \frac{d}{dt} \sum_{i=1}^N r_{i\alpha}(t) \left\{ \frac{1}{2} m_i \sum_{\beta=x}^z v_{i\beta}(t) v_{i\beta}(t) + \frac{1}{2} \sum_{j \neq i}^N U[r_{ij}(t)] \right\} \quad (15)$$

Using the product rule for differentiation, this expression can be rearranged as

$$J_\alpha(t) = \sum_{i=1}^N v_{i\alpha}(t) \left\{ \frac{1}{2} m_i \sum_{\beta=x}^z v_{i\beta}(t) v_{i\beta}(t) + \frac{1}{2} \sum_{j \neq i}^N U[r_{ij}(t)] \right\} + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \sum_{\beta=x}^z v_{i\beta}(t) r_{ij\beta}(t) f_{ij\alpha}(t) \quad (16)$$

$$V k_B T^2 \lambda_\alpha = \int_0^\infty d\tau \langle J_\alpha(t + \tau) J_\alpha(t) \rangle \quad (17)$$

In this expression, the angled brackets indicate an ensemble average, which is an average over all time origins, t . This latter fact means that every time step in the MD simulation can be used as a time origin in the calculation of the ACF.

[†]Hansen, J.-P. and McDonald, I.R., *Theory of Simple Liquids*. Second ed. 1986, San Diego: Academic Press.

A practical example of evaluating this integral can be found in the following reference.

Title: Molecular Dynamics Simulation of Polyethylene Terephthalate Oligomers

Authors: Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B.

Journal: *J. Phys. Chem. B* Vol. 114 Issue 2. pp. 786–795.

Published 2010

doi: <http://doi.org/10.1021/jp909762j>

From this paper (including citation numbers as specified in the reference), we quote, “The above atomic heat flux expression has been successfully applied to the systems governed by pair potentials as reported in many articles,^{41,46-48} in which the Green-Kubo integral is used to obtain thermal conductivity of small molecules (methane⁴⁷ and SiH₄⁴¹). These molecules can be treated as particles by ignoring the intramolecular bond stretching, bond bending, and bond torsion interactions so there will be only intermolecular Lennard-Jones interaction potential contributing to the heat flux. The simulation results based on this procedure are in good agreement with the experimental data. For larger molecules (butane,⁴⁹ alkanes⁵⁰), the heat flux expression is often taken as molecular based in order to calculate the molecular heat flux, a heat flux whose description is based on the view that the individual atomic contributions to the local energy density are localized at the molecular centers of mass.⁵¹ This expression applies well to polyatomic molecules with moderate chain length. When the chain length increases, this center of mass based heat flux will be problematic.⁵² If the chain is very long, the energy transport along each chain is not ignorable. Therefore, the atomic heat flux expression is needed for prediction of thermal conductivity of polymer chain molecules. Marechal and Ryckaert⁵³ derived the atomic heat flux expression for polyatomic molecules (n-butane), in which only bond torsion was included, but the thermal conductivity obtained is too large based on experimental comparison with alkanes. An alternative way for faithful prediction of thermal conductivity is to modify the force field or molecular dynamic model. Lussetti et al.⁵² transformed the molecule model for polyamide-6,6 by grouping some atoms in the chain together to have less quantum degree of freedoms in the system as they assume that the high value of thermal conductivity obtained from the MD simulation is due to the incorrect treatment of these fast quantum degrees of freedom in molecular dynamics. They compared the NEMD simulation results of thermal conductivity from different force fields and found that the united atom model with complete rigid bond generated the best result for comparison with the experimental data. Based on the collective conclusions of the work above, we only included nonbonded interactions in the heat flux of our PET oligomer molecules. These nonbonded interactions include both intramolecular and intermolecular Lennard-Jones and electrostatic interactions. Thus, we neglect stretching, bending, and torsion contributions.”

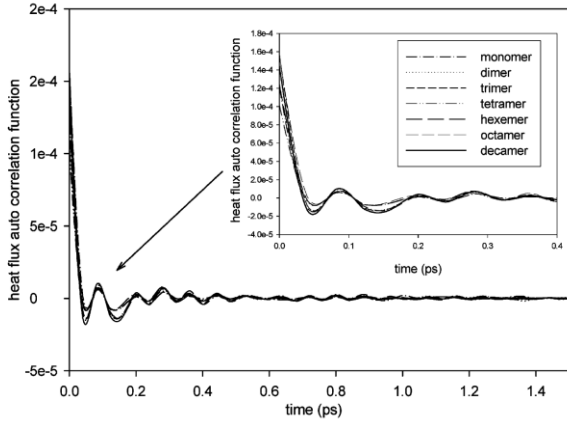


Figure 16. Heat flux autocorrelation functions as a function of observation time for all DP. The inset is a close-up of short-time behavior.

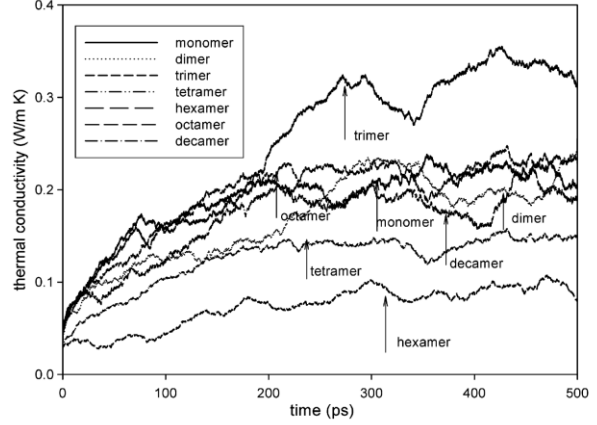


Figure 17. Thermal conductivity (λ) as a function of the upper limit of integration in eq 8. The arrows indicate the observation time at which a plateau begins.

Figure 1. Right: Energy flux autocorrelation functions as a function of observation time. Left: Thermal conductivity obtained from equation (16) as a function of the upper limit of integration.

One sees in Figure 1, that there is some uncertainty for practical system as to where the upper limit of integration should be fixed.

An alternative approach to obtaining the thermal conductivity is to use Bridgman's theory of energy transport in pure liquids.^{54,55}

$$\lambda = 3 \left(\frac{N}{V} \right)^{\frac{2}{3}} k_B v_s \quad (17)$$

where v_s is the speed of sound in the liquid, given by

$$v_s = \sqrt{\frac{C_p}{C_v} \left(\frac{\partial p}{\partial \rho} \right)_T} \quad (18)$$

where C_v is the constant volume heat capacity and ρ is the mass density. The partial derivative $\left(\frac{\partial p}{\partial \rho} \right)_T$ is contained within the isothermal compressibility, which we have already reported.

Typically, the ratio of constant-pressure and constant-volume heat capacities is close to unity for liquids. In order to test this assumption, we ran some additional MD simulations on the monomer at constant volume (NVT ensemble) to obtain C_v . We found the ratio to be 1.15, and this is what we used in eq 12 for all DP. The calculated data for velocity of sound is listed in Table 1. It is noted that empirically a coefficient of 2.8 gives a better fit to experimental data than 3 in eq 10,⁵⁴ so we used 2.8. The experiments of Bridgman were based on small molecules. Therefore, in eq 11, we used the number density not of chains but of repeat units, which taken independently constitute relatively small molecules. This prediction of the thermal conductivity is also shown in

Figure 18. On average the Bridgman thermal conductivity is 26% low. The Bridgman thermal conductivity shows almost a constant with DP (scaling exponent of -0.11), which is similar in the thermal conductivity obtained from the Green-Kubo integral.

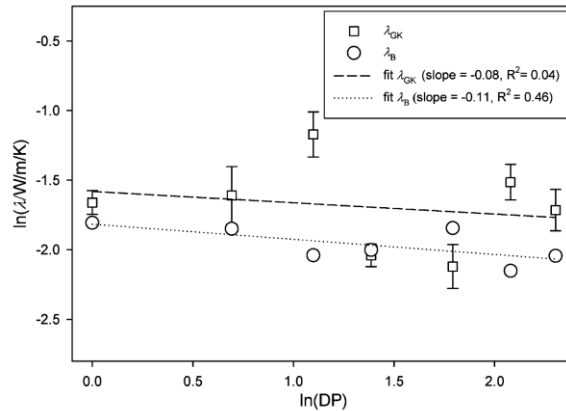


Figure 18. Thermal conductivity obtained from the Green-Kubo integral (λ_{GK}) and the Bridgman equation (λ_B) as a function of DP.

Here is another example of calculation of the thermal conductivity from the literature. [Patrick K. Schelling, Simon R. Phillpot, Pawel Keblinski, “Comparison of atomic-level simulation methods for computing thermal conductivity”, (2002) PHYSICAL REVIEW B, VOLUME 65, 144306.] In this paper, the Green-Kubo method is used to determine the thermal conductivity of solid Si.

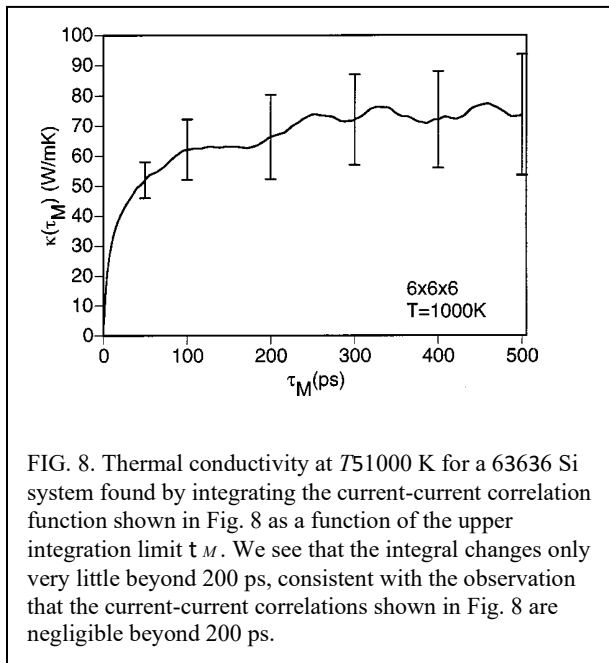


FIG. 8. Thermal conductivity at 751000 K for a 63636 Si system found by integrating the current-current correlation function shown in Fig. 8 as a function of the upper integration limit τ_M . We see that the integral changes only very little beyond 200 ps, consistent with the observation that the current-current correlations shown in Fig. 8 are negligible beyond 200 ps.

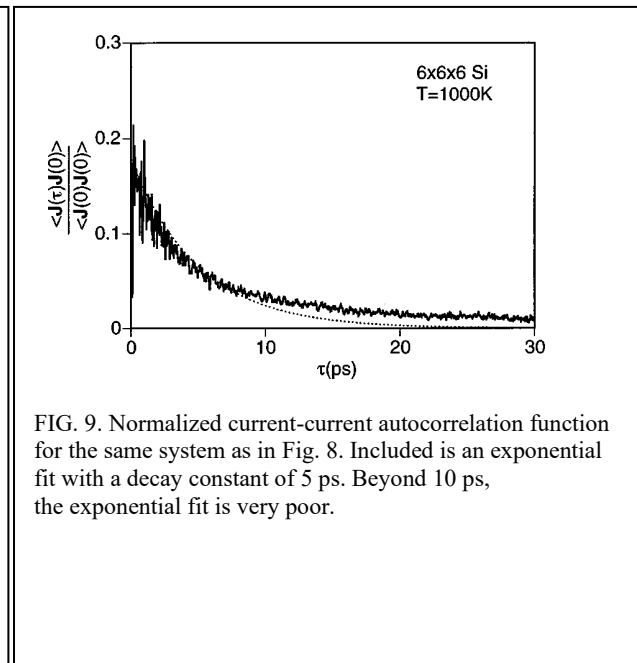


FIG. 9. Normalized current-current autocorrelation function for the same system as in Fig. 8. Included is an exponential fit with a decay constant of 5 ps. Beyond 10 ps, the exponential fit is very poor.

IV. Thermal Conductivity from Non-Equilibrium Simulation

Non-equilibrium molecular dynamics (NEMD) simulations can be performed to measure thermal conductivities. In these simulations, there is typically a hot region at T_{hot} and a cold region at T_{cold} , separated by an unthermostatted region in dimension α . of length l_α . One approach is to directly measure the energy flux, q_α , being transferred between hot and cold region. The temperature gradient can be approximated and substituted into Fourier's law

$$\frac{\partial T}{\partial \alpha} = \frac{T_{hot} - T_{cold}}{l_\alpha} \quad (19)$$

which can be solved for the thermal conductivity. The flux is measured at a plane in the midpoint of the system as the total kinetic and potential energy of all particles carried across the plane, E_{plane} , divided by the simulation duration, t_{sim} , and the cross-sectional area of the simulation, $A = l_\beta l_\gamma$, as

$$q_\alpha = \frac{E_{plane}}{t_{sim} l_\beta l_\gamma} \quad (20)$$

The temperature gradient and flux into Fourier's law

$$q_\alpha = -k_c \frac{\partial T}{\partial \alpha} \quad (21)$$

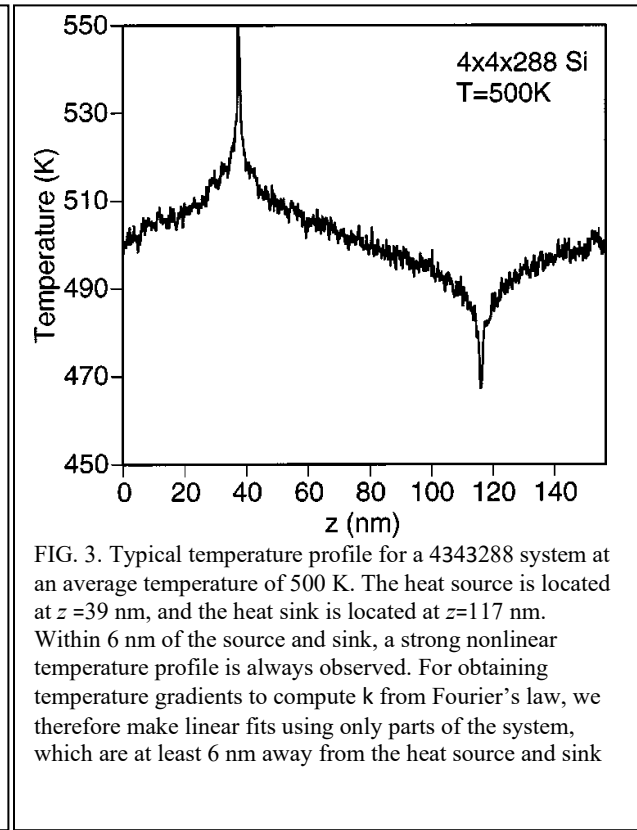
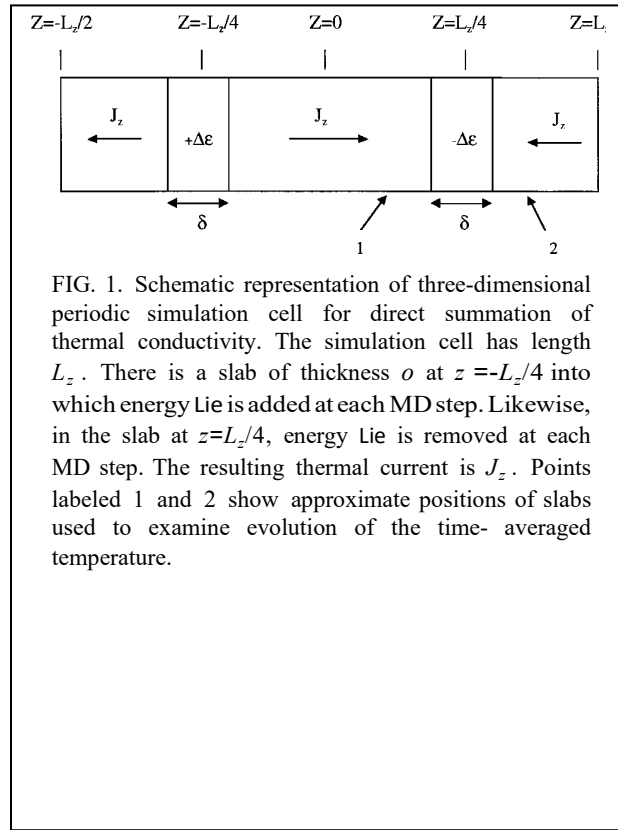
which can be solved for the thermal conductivity.

A second approach, which uses the same geometry, is to determine the flux not by direct measurement but by keeping track of the energy that the thermostat in the hot region pumps into the system, E_{hot} , and the energy that the thermostat in the cold region pumps out of the system, E_{cold} . These two quantities of energy should be the same and provide an equivalent way to determine E_{plane} as present in equation (20) as

$$E_{plane} = \frac{E_{hot}}{2} \approx \frac{E_{cold}}{2} \approx \frac{E_{hot} + E_{cold}}{4} \quad (22)$$

The factor of 2 is required because the system is periodic in all dimensions, including the α dimension in which the thermal gradient is present. As such heat can transfer along the positive α axis or the negative α axis from the hot reservoir to the cold. Thus the energy of the heat flux is half the energy removed or provided by the thermostats. Alternatively, we can think of this as a system with twice the cross-sectional area, which also halves the flux, per equation (20).

Below, we look at several examples from the literature. [Patrick K. Schelling, Simon R. Phillpot, Pawel Keblinski, “Comparison of atomic-level simulation methods for computing thermal conductivity”, (2002) PHYSICAL REVIEW B, VOLUME 65, 144306.]



In this paper, the authors note, “The direct method involves large ($>10^9$ K/m) temperature gradients. Because these temperature gradients are well outside of the experimental range, it is not clear *a priori* that results obtained using the direct method will be consistent with experiment. Specifically, very large temperature gradients may introduce significant nonlinear response effects such that Fourier’s law may not apply; therefore, it is important to test the effect of changing the magnitude of the thermal current on the resulting computed value of k . Below we shall establish that there exists a range of system dimensions where the degree of nonlinearity is acceptable.

This paper computed the thermal conductivity from both equilibrium MD and NEMD. A table of the comparisons is shown here. The agreement is pretty good. Clearly there is a system size effects. These simulations from 2002 are still pretty small and it is not clear that they have converged to a good value in terms of system size.

TABLE II. Dependence of κ on system size using the Green-Kubo method with definitions provided by Eqs. (17)–(19) and Eqs. (20)–(22). The system temperature was 1000 K. System length L was obtained using the lattice constant of 0.543 nm for Si.

Dimensions	L (nm)	Number of atoms	κ (W/mK) from Eqs. (17)–(19)	κ (W/mK) from Eqs. (20)–(22)
4×4×4	2.17	512	22	22
5×5×5	2.72	1000	82	90
6×6×6	3.26	1728	66	66
8×8×8	4.34	4096	62	61

There is another variety of NEMD simulation used for computing the thermal conductivity called transient NEMD.[R. J. Hulse, R. L. Rowley, W. V. Wilding, “Transient Nonequilibrium Molecular Dynamic Simulations of Thermal Conductivity: 1. Simple Fluids”, International Journal of Thermophysics, Vol. 26, No. 1, January 2005] In this case, a pulse of energy is input into a specified volume. The decay of that temperature profile is monitored as a function of time and is fit to the heat equation. In this case, they used spherical coordinates for which equation (11) becomes

$$\rho \hat{C}_v \frac{\partial T}{\partial t} = k_c \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \quad (23)$$

The least squares fit between the evolution of the temperature decay from simulation and the solution of the heat equation is optimized by varying the value of the thermal conductivity.

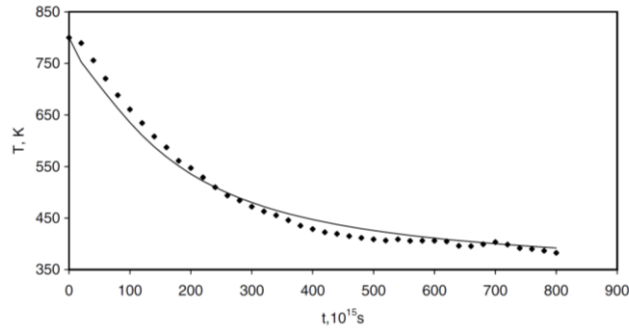


Fig. 1. Typical transient temperature trace for $T = 350$ K and $\rho = 25 \text{ kmol} \cdot \text{m}^{-3}$ with a ΔT of 450 K showing the averaged simulation temperature (points) and the solution to Eq. (7) with regressed λ (line).

A comparison of this method with NEMD and Green-Kubo methods is presented below.

Table V. Comparison of Proposed Method to Previous Methods

		$\lambda \text{ (mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\text{)}$						
$T \text{ (K)}$	$\rho \text{ (kmol} \cdot \text{m}^{-3}\text{)}$	Volegsang et al. [3] (EMD)	Paolini et al. [7] (NEMD)	Heyes [10] (NEMD)	Muller-Plathe [5] (NEMD)	Hoheisel [18] (EMD)	This Work	Correlation, Hanley et al. [15]
85.30	35.01	–	–	–	139.6–121.2	143.9	129.10	131.0
88.95	34.77	127.1	126.8	108.6	–	–	127.06	126.6
114.54	29.44	94.2	–	70.8	–	–	84.77	86.2
154.75	26.77	70	–	56.2	–	–	71.89	73.2

V. Built in LAMMPS Functionality

In the directory of LAMMPS examples, there is a directory called KAPPA. This contains five examples, each of which compute the thermal conductivity of a system. We discuss only three of the five examples.

V.A. Equilibrium Simulation

The input `in.heatflux` performs an equilibrium simulation from which a Green-Kubo integral is evaluated per equation (14). It is important to note that this implementation suffers

from the same egregious approach as does the evaluation of the autocorrelation functions used to calculate the diffusivity as implemented in LAMMPS. Namely, the angled brackets in equation 14, which indicate an ensemble average (an averaging over time origins in this case) is ignored. Only the starting point of the simulation is used as a time origin. Much better statistical reliability is obtained from post-processing based on saved values of the positions, velocities and stresses.

V.B. Non-Equilibrium Simulation

The input `in.langevin` performs a non-equilibrium simulation using the Langevin thermostats to keep one volume hot and one volume cold. The Langevin thermostat can keep track of how much heat is added or removed from the system, so the flux can be directly calculated.

The input `in.heat` performs a non-equilibrium simulation using the `fix heat` command to add or remove a fixed amount of energy per time for two volumes. The flux is again directly calculated.

The input `in.ehex` performs a non-equilibrium simulation using the `fix ehex` command to add or remove a fixed amount of energy per time for two volumes. The flux is again directly calculated. The method is described in Wirnsberger, Frenkel, and Dellago, *J Chem Phys*, 143, 124104 (2015).