Basics of thermal conductivity calculations

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1 Equilibrium Correlation

The basis of calculation of thermal conductivity and other transport coefficients using MD is linear response theory (Green 1954, Kubo 1957, Mori 1958, Kadanoff and Martin 1963). The thermal conductivity $\hat{\kappa}$ can be expressed in terms of equilibrium time autocorrelation function of the heat current $\mathbf{J}^q$:

$$\hat{\kappa} = \frac{1}{k_B T^2 \Omega} \int_0^\infty d\tau < \mathbf{J}^q(0)\mathbf{J}^q(\tau) >_0 \tag{1}$$

Here Ω is the total volume. The instantaneous heat current is given by

$$\mathbf{J}^q = \frac{d}{dt} \sum_i (E_i - h)\mathbf{r}_i \tag{2}$$

where E_i is the microscopic energy for each particle and h is the enthalpy per particle of the system. If the interaction is of pair potential type, then

$$E_i = \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{j \neq i} V(r_{ij}) \tag{3}$$

from which (2) can be written as

$$
\begin{aligned}
\mathbf{J}^q \quad &= \frac{d}{dt}\sum_i (E_i - h)\mathbf{r}_i \\
&= \sum_i \Big((E_i - h)\mathbf{v}_i + \mathbf{r}_i[\frac{\mathbf{p}_i}{m_i} \cdot \mathbf{F}_i + \frac{1}{2}\sum_{j\neq i}\frac{\partial V_{ij}}{\partial \mathbf{r}_i} \cdot (\mathbf{v}_i - \mathbf{v}_j)] \Big) \\
&= \sum_i [(E_i - h) - \frac{1}{2}\sum_{j\neq i}(\mathbf{r}_i - \mathbf{r}_j)\frac{\partial V_{ij}}{\partial \mathbf{r}_i}] \cdot \mathbf{v}_i \\
&= \sum_i (E_i - h)\mathbf{v}_i - \frac{1}{2}\sum_{pairs}(\mathbf{r}_i - \mathbf{r}_j)[\frac{\partial V_{ij}}{\partial \mathbf{r}_i} \cdot (\mathbf{v}_i + \mathbf{v}_j)] \qquad (4)
\end{aligned}
$$

On the other hand, when the interaction is of many-body nature, how to devide the potential energy among the interacting particles is not so obvious, and in fact can be quite arbitary. Yet when it's done $\mathbf{J}^q$ can be derived from the general formalism:

$$
\begin{aligned}
\mathbf{J}^q \quad &= \frac{d}{dt}\sum_i (E_i - h)\mathbf{r}_i \\
&= \sum_i \Big((E_i - h)\mathbf{v}_i + \mathbf{r}_i(\mathbf{v}_i \cdot \mathbf{F}_i + \sum_j \frac{\partial E_i}{\partial \mathbf{r}_j} \cdot \mathbf{v}_j) \Big) \\
&= \sum_i \Big((E_i - h)\mathbf{v}_i + \mathbf{r}_i \sum_j (-\mathbf{v}_i \cdot \frac{\partial E_j}{\partial \mathbf{r}_i}) + \mathbf{r}_i \sum_j \frac{\partial E_i}{\partial \mathbf{r}_j} \cdot \mathbf{v}_j \Big) \\
&= \sum_i \Big((E_i - h)\mathbf{v}_i + \sum_{j\neq i} \mathbf{r}_{ij}(\frac{\partial E_i}{\partial \mathbf{r}_j} \cdot \mathbf{v}_j) \Big) \qquad (5)
\end{aligned}
$$

(5) provides an obvious method to calculate the thermal conductivity in a model system, since all the dynamical variables in (5) are explicitly known in a molecular dynamics simulation. Although (1) was derived for a canonical ensemble, microcanonical ensemble is usually used in MD for it's much easier to implement, the difference is only trivial since the phase points generated in MD would be in the peak center of density distribution of the corresponding canonical ensemble. We will call this method **equilibrium correlation** method.

2 Nonequilibrium MD

Non-equilibrium molecular dynamics (NEMD) is a formalism which bypasses (1), and give the correct results. It is also based on the linear response theory, but with considerable originality and theoretical interest in itself, mainly, the concept of *equivalence* of equations of motions.

We know that when a physical system has Hamiltonian $\mathcal{H}(\mathbf{q}, \mathbf{p})$, the equation of motion can be readily written down:

$$\begin{cases} \dot{\mathbf{q}}_i = \partial\mathcal{H}/\partial\mathbf{p}_i \\ \\ \dot{\mathbf{p}}_i = -\partial\mathcal{H}/\partial\mathbf{q}_i \end{cases} \tag{6}$$

The Liouville operator is defined as

$$\begin{aligned} -i\mathcal{L}A(\mathbf{p}, \mathbf{q}) = & \quad \sum_i \left(\frac{\partial A}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{\partial A}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right) \\ = & \quad \sum_i \left(\frac{\partial A}{\partial \mathbf{q}_i} \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{q}_i} \right) \\ = & \quad \{A, \mathcal{H}\} \end{aligned} \tag{7}$$

so that from Liouville theorem

$$\begin{aligned} 0 \equiv & \quad -\mathrm{Tr}\left(\frac{\partial(\dot{\mathbf{p}}, \dot{\mathbf{q}})}{\partial(\mathbf{p}, \mathbf{q})}\right) \\ = & \quad \frac{Df}{Dt} \\ = & \quad \frac{\partial f}{\partial t} - i\mathcal{L}f \end{aligned} \tag{8}$$

there is $f(t) = \exp(it\mathcal{L})f(0)$, where $f(t)$ is the density distribution functional of phase points in Γ space. It can be shown that $\mathcal{L}$ is a Hermitian operator.

Because the measurement of $A(\mathbf{p}, \mathbf{q})$ is

$$\begin{aligned} \bar{A}(t) \quad & = \int_\Gamma d\Gamma f(t) A(\mathbf{p}, \mathbf{q}) \\ & = \int_\Gamma d\Gamma [\exp(it\mathcal{L}) f(0)] A(\mathbf{p}, \mathbf{q}) \end{aligned} \tag{9}$$

so

$$\begin{aligned}\frac{d\bar{A}(t)}{dt} &= \int_\Gamma d\Gamma[i\mathcal{L}\exp(it\mathcal{L})f(0)]A(\mathbf{p},\mathbf{q}) \\ &= \int_\Gamma d\Gamma\exp(it\mathcal{L})f(0)[-i\mathcal{L}A(\mathbf{p},\mathbf{q})] \\ &= \int_\Gamma d\Gamma[\exp(it\mathcal{L})f(0)]\dot{A}(\mathbf{p},\mathbf{q}) \qquad (10)\end{aligned}$$

where we have defined the time derivative of an arbitary dynamical variable to be

$$\begin{aligned}\dot{A}(\mathbf{p},\mathbf{q}) = &\quad -i\mathcal{L}A(\mathbf{p},\mathbf{q}) \\ = &\quad \sum_i\left(\frac{\partial A}{\partial \mathbf{q}_i}\cdot\dot{\mathbf{q}}_i + \frac{\partial A}{\partial \mathbf{p}_i}\cdot\dot{\mathbf{p}}_i\right) \qquad (11)\end{aligned}$$

where the second row conforms both to (7) and the physical interpretation of "time derivative".

From here we can derive the linear response formulae: suppose the system was originally governed by $\mathcal{H}_0$ and is already in thermal equilibrium:

$$\begin{cases} f_0 = \exp(-\beta\mathcal{H}_0) \\ \partial f_0/\partial t = -i\beta\exp(-\beta\mathcal{H}_0)(\mathcal{L}_0\mathcal{H}_0) \equiv 0 \end{cases} \qquad (12)$$

At $t = 0$ the perturbation $\mathcal{H}'$ was turned on, so

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \qquad (13)$$

and

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}',\ f(t) = f_0 + f'(t) \qquad (14)$$

The flow equation (8) remains valid as long as the system is described by a Hamiltonian,

$$\frac{\partial f}{\partial t} = i\mathcal{L}f$$

and to first order in perturbation strength it can be linearized,

$$\frac{\partial f'}{\partial t} = i\mathcal{L}_0 f' + i\mathcal{L}' f_0 \tag{15}$$

Multiplying both side by $\exp(-it\mathcal{L}_0)$, we have

$$\frac{\partial[\exp(-it\mathcal{L}_0)f']}{\partial t} = \exp(-it\mathcal{L}_0)i\mathcal{L}' f_0$$

which can be intergrated to give

$$\begin{aligned} f'(t) \quad &= \int_0^t d\tau \exp(i(t-\tau)\mathcal{L}_0)[i\mathcal{L}' f_0] \\ &= -\beta \int_0^t d\tau \exp(i(t-\tau)\mathcal{L}_0) f_0 [i\mathcal{L}'\mathcal{H}_0] \\ &= \beta \int_0^t d\tau \exp(i(t-\tau)\mathcal{L}_0) f_0 [i\mathcal{L}_0\mathcal{H}'] \\ &= -\beta \int_0^t d\tau \exp(i(t-\tau)\mathcal{L}_0) f_0 \dot{\mathcal{H}}'(\tau) \end{aligned} \tag{16}$$

For an arbitary dynamical variable A, the measurement of response to such perturbation at $t > 0$ is

$$\begin{aligned} \bar{\bar{A}}(t) - \bar{A} \quad &= \int_\Gamma d\Gamma f'(t) A(\mathbf{p},\mathbf{q}) \\ &= -\beta \int_0^t d\tau \int_\Gamma d\Gamma f_0 \dot{\mathcal{H}}'(\tau)[\exp(-i(t-\tau)\mathcal{L}_0)A(\mathbf{p},\mathbf{q})] \\ &= -\beta \int_0^t d\tau < A(t-\tau)\dot{\mathcal{H}}'(\tau) >_0 \end{aligned} \tag{17}$$

This is the central result of linear response theory.

3 NEMD scheme by Ciccotti *et al*

As to how (17) can be used to get $\hat{\kappa}$ without resorting to (1) explicitly, let's compare the two equations: suppose we let $A = \mathbf{J}_x^q(\mathbf{p},\mathbf{q})$ in (17), then the right hand side of (17) and (1) would look almost similiar, except that one has $\dot{\mathcal{H}}'(\tau)$, the other has $\mathbf{J}^q(\tau)$. However, we can *choose* a perturbation Hamiltonian to satisfy

$$\dot{\mathcal{H}}' = \lambda J_x^q \tag{18}$$

where λ is a very small constant, such that the RHS of (17) and (1) are identical except for a constant. Under such a perturbation, the thermal conductivity $\hat{\kappa}$ is simply

$$\hat{\kappa} = \lim_{t\to\infty}\lim_{\lambda\to 0}\left(\frac{-\tilde{J}_x^q(t)}{\lambda\Omega T}\right) \tag{19}$$

The above formulae assume $\hat{\kappa}$ to be an isotropic tensor, i.e., $\hat{\kappa} = \kappa\mathbf{I}$. When $\hat{\kappa}$ isn't isotropic, we can let

$$\dot{\mathcal{H}}' = \lambda J_i^q(t) \tag{20}$$

and

$$\kappa_{ij} = \lim_{t\to\infty}\lim_{\lambda\to 0}\left(\frac{-\tilde{J}_j^q(t)}{\lambda\Omega T}\right) \tag{21}$$

Whether $\hat{\kappa}$ is isotropic or not depend on the local symmetry of the crystal. When the local symmetry is cubic (solid argon) or tetrahedral (SiC), we can be sure that $\hat{\kappa}$ is isotropic from group theory.

The problem immediately follows that how can we choose a $\mathcal{H}'$ to satisfy (18). However, the answer is obvious once we note that $\mathbf{J}^q$ is defined by the equation

$$\mathbf{J}^q = \frac{d}{dt}\sum_i (E_i - h)\mathbf{r}_i$$

in (2), so that

$$\mathcal{H}' = \mathbf{b}\cdot\sum_i (E_i - h)\mathbf{r}_i \tag{22}$$

would satisfy (18) automatically, where $\mathbf{b}$ is a small constant. Up to now an ideal NEMD scheme had been completely set up. To implement it we need to put $\mathcal{H}'$ into the equation of motion:

$$\begin{aligned} \dot{\mathbf{r}}_i &= (\mathbf{p}_i/m_i)(1 + \mathbf{b}\cdot\mathbf{r}_i) \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i(1 + \mathbf{b}\cdot\mathbf{r}_i) - \left((E_i - h) - \frac{1}{2}\sum_{j\neq i}(\mathbf{r}_i - \mathbf{r}_j)\cdot\frac{\partial V_{ij}}{\partial \mathbf{r}_i}\right)\mathbf{b} \end{aligned} \tag{23}$$

For isotropic systems,

$$\kappa = \lim_{t\to\infty}\left(\frac{-\mathbf{b}\cdot\tilde{\mathbf{J}}^q(t)}{b^2\Omega T}\right) \tag{24}$$

This scheme, however, is only ideal and cannot be implemented on the computer because of the finite periodicity of the simulation cell. Imagine the situation described by (22) and (23): in order to generate a steady heat current in the system, a constant field had to be imposed on the *whole* space, i.e., the "potential" (22) describing this driving force should be a linear function of $\mathbf{r}_i$ (in strict mathematical sense), its value ranging from $-\infty$ to $+\infty$. The problem is that on a computer, instead of a straight line from $-\infty$ to $+\infty$, we can only generate potential functions of jigjaw shape, with periodicity of the simulation cell: discontinuity would happen on the boundary with finite jumps. In other word, there can be no absolute measures of $\mathbf{r}_i$'s that appear in (23). The measures in a peoriodic cell can only be of $\exp(i\mathbf{k}\cdot\mathbf{r}_i)$, with $\mathbf{k}$ commesurate to the cell, which means we can only have the finite $\mathbf{k}$ values of the thermal conductivity if we stick to the method.

Ciccotti *et al* (1978) show that we can study the finite $\mathbf{k}$ thermal conductivity of the system by taking

$$\mathcal{H}' = \lambda\sum_i (E_i - h)\phi_i, \quad \phi_i = \exp(i\mathbf{k}\cdot\mathbf{r}_i) \tag{25}$$

with the finite $\mathbf{k}$ heat flux defined by

$$\mathbf{J}^q_{\mathbf{k}} = \sum_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i)\left((E_i - h)\mathbf{I} - \frac{1}{2}\sum_{j\neq i}\mathbf{r}_{ij}\frac{\partial V_{ij}}{\partial \mathbf{r}_i}\right)\cdot\frac{\mathbf{p}_i}{m_i} \tag{26}$$

identify A in (17) by $\mathbf{J}^q_{-\mathbf{k}}\cdot\mathbf{k}$, we have

$$\tilde{\mathbf{J}}^q_{-\mathbf{k}}(t)\cdot\mathbf{k} = \frac{i\lambda\beta}{\Omega}\int_0^t d\tau\ \mathbf{k}\cdot < \mathbf{J}^q_{\mathbf{k}}(0)\mathbf{J}^q_{-\mathbf{k}}(\tau) > \cdot\mathbf{k} \tag{27}$$

from where we can get the finite $\mathbf{k}$ autocorrelation function of heat flux. And by extrapolating the finite $\mathbf{k}$ results onto $\mathbf{k} = 0$ we will arrive at what we want: the macroscopic thermal conductivity. The equation of motion described by (25) is

$$\dot{\mathbf{r}}_i \quad = (\mathbf{p}_i/m_i)(1 + \lambda\phi_i) \tag{28}$$

$$\dot{\mathbf{p}}_i \quad = \mathbf{F}_i(1 + \lambda\phi_i) - \lambda\left((E_i - h)\frac{\partial\phi_i}{\partial\mathbf{r}_i} - \frac{1}{2}\sum_{j\neq i}(\phi_i - \phi_j)\frac{\partial V_{ij}}{\partial\mathbf{r}_i}\right) \tag{29}$$

Ciccotti's scheme is a practical method to calculate $\mathbf{k}k$. The shortcoming lies in the non-trivial extrapolation procedure from finite $\mathbf{k}$ to $\mathbf{k} = 0$. Another strange feature about (28,29) is that the velocities $\dot{\mathbf{r}}_i$ are not simply given by the momenta $\mathbf{p}_i$ devided by mass.

4 Gillan and Dixon: Equivalence of Equation of Motions

Look at (27) and (28, 29), and let's think carefully of where the difficulty lies: obviously when we take the limit $\mathbf{k} \to 0$, there must be $\tilde{\mathbf{J}}^q_{-\mathbf{k}} \propto |\mathbf{k}|$ in order to satisfy (27). The second term on RHS of (29)

$$-\lambda\left((E_i - h)\frac{\partial \phi_i}{\partial \mathbf{r}_i} - \frac{1}{2}\sum_{j\neq i}(\phi_i - \phi_j)\frac{\partial V_{ij}}{\partial \mathbf{r}_i}\right)$$

satisfies this requirement explicitly, since $\partial\phi_i/\partial\mathbf{r}_i$, $(\phi_i - \phi_j) \propto |\mathbf{k}|$ in $\mathbf{k} \to 0$ limit: and we know that the response $\tilde{\mathbf{J}}^q_{-\mathbf{k}}$ is proportional to perturbation strength appearing in the equation of motion (in linear regime). The effect of other two terms, $\lambda\phi_i\mathbf{p}_i/m_i$ and $\lambda\phi_i\mathbf{F}_i$, on the other hand, are not so obvious, because there's no direct proportionality with $|\mathbf{k}|$ inside. To study them, let's seperate them out.

Consider the following equation of motion

$$\begin{aligned} \dot{\mathbf{r}}_i &= (\mathbf{p}_i/m_i)(1 + \lambda\phi_i) \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i(1 + \lambda\phi_i) \end{aligned} \tag{30}$$

The time evolution of an arbitary dynamical variable A under this equation of motion would be

$$\frac{DA}{Dt} = (\Lambda_0 + \lambda\Lambda_1)A \tag{31}$$

where the operators Λ_0 and Λ_1 are

$$\begin{aligned} \Lambda_0 &= \sum_i \left(\frac{\mathbf{p}_i}{m_i}\cdot\frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i\cdot\frac{\partial}{\partial \mathbf{p}_i}\right) \\ \Lambda_1 &= \sum_i \phi_i\left(\frac{\mathbf{p}_i}{m_i}\cdot\frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i\cdot\frac{\partial}{\partial \mathbf{p}_i}\right) \end{aligned} \tag{32}$$

Note that (30) is not being described by an Hamiltonian, thus although Λ_0 and Λ_1 looks similiar to the Liouville operator, they lack the Hermitian property of $\mathcal{L}$. Nevertheless, we can formulate a linear response theory like (17) because Hermicity is not required in the derivation. Since flow equation (8) is no longer valid here, we should use "Heisenberg" representation to do the ensemble average for the response to the perturbation.

Take $A(t) = A_0(t) + A'(t)$, where $A_0(t)$ satisfy $DA_0/Dt = \Lambda_0 A_0$, the time evolution of A in the corresponding unperturbed system. Linearize (31) into

$$\frac{DA'}{Dt} = \Lambda_0 A' + \lambda \Lambda_1 A_0(t) \tag{33}$$

multiply both side by $\exp(-t\Lambda_0)$, there is

$$\frac{D[\exp(-t\Lambda_0)A']}{Dt} = \exp(-t\Lambda_0)[\lambda\Lambda_1 A_0(t)]$$

which can be intergrated to give

$$\tilde{A}(t) - A_0(t) = \lambda \int_0^t d\tau \exp((t-\tau)\Lambda_0)[\Lambda_1 A_0(\tau)]$$

So, to linear order in λ, the measurement

$$\bar{\tilde{A}}(t) = \bar{A}_0(t) + \lambda \int_0^t d\tau \int_\Gamma d\Gamma f(0) \exp((t-\tau)\Lambda_0)[\Lambda_1 A_0(\tau)] \tag{34}$$

If at $t = 0$ the system is already in equilibrium, $\exp((t-\tau)\Lambda_0)$ can be replaced by unity, which reads

$$\begin{aligned} \bar{\tilde{A}}(t) \quad &= \bar{A}_0(t) + \lambda \int_0^t d\tau \int_\Gamma d\Gamma f_0 [\Lambda_1 A_0(\tau)] \\ &= \bar{A}_0(t) + \lambda \int_0^t d\tau < \Lambda_1 A_0(\tau) >_0 \end{aligned} \tag{35}$$

Plug in the expression for Λ_1

$$\begin{aligned} \bar{\tilde{A}}(t) \quad &= \bar{A}_0(t) + \lambda \int_0^t d\tau \int_\Gamma d\Gamma f_0 [\sum_i \phi_i \left(\frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) A_0(\tau)] \\ &= \bar{A}_0(t) - \lambda \int_0^t d\tau \int_\Gamma d\Gamma f_0 \left(\sum_i \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial \phi_i}{\partial \mathbf{r}_i} \right) A_0(\tau) \end{aligned} \tag{36}$$

since if ϕ_i is a constant we should get zero by turning around both $\partial/\partial\mathbf{r}_i$ and $\partial/\partial\mathbf{p}_i$, and ϕ_i is only a function of $\mathbf{r}_i$. Because

$$f_0\frac{\mathbf{p}_i}{m_i} = -k_BT\frac{\partial f_0}{\partial\mathbf{p}_i}$$

(36) can be rewritten as

$$\begin{aligned}
\bar{\bar{A}}(t) \quad &= \bar{A}_0(t) + \lambda k_BT\int_0^t d\tau\int_\Gamma d\Gamma\sum_i\frac{\partial f_0}{\partial\mathbf{p}_i}\cdot\frac{\partial\phi_i}{\partial\mathbf{r}_i}A_0(\tau) \\
&= \bar{A}_0(t) - \lambda k_BT\int_0^t d\tau\int_\Gamma d\Gamma f_0\sum_i\frac{\partial\phi_i}{\partial\mathbf{r}_i}\cdot\frac{\partial A_0(\tau)}{\partial\mathbf{p}_i} \\
&= \bar{A}_0(t) + \lambda\int_0^t d\tau < \Lambda_2A_0(\tau) >_0 \qquad (37)
\end{aligned}$$

with

$$\Lambda_2 = -k_BT\sum_i\frac{\partial\phi_i}{\partial\mathbf{r}_i}\cdot\frac{\partial}{\partial\mathbf{p}_i} \qquad (38)$$

Compare (37) with (35), we see that although perturbation operators Λ_1 and Λ_2 are algebriacally different, the responses they would induce for an arbitary dynamical variable are totally identical after ensemble averaging. This is a truly amazing conclusion, since it proves the existence of a family of dynamical systems with different equation of motions, but with the *same* macroscopic properties (in linear regime). For instance, Λ_2 can be generated by the following equation of motion

$$\begin{aligned}
\dot{\mathbf{r}}_i \quad &= \mathbf{p}_i/m_i \\
\dot{\mathbf{p}}_i \quad &= \mathbf{F}_i - \lambda k_BT\frac{\partial\phi_i}{\partial\mathbf{r}_i} \qquad (39)
\end{aligned}$$

Although (30) and (39) are different equation of motions, they are actually equivalent.

Now let's go back to thermal conductivity and see how old problems can easily be solved by transferring the equation of motion. Since perturbations are additive in linear regime, (28, 29) are equivalent to

$$\begin{aligned}
\dot{\mathbf{r}}_i \quad &= \mathbf{p}_i/m_i \\
\dot{\mathbf{p}}_i \quad &= \mathbf{F}_i - \lambda\left((E_i + k_BT - h)\frac{\partial\phi_i}{\partial\mathbf{r}_i} - \frac{1}{2}\sum_{j\neq i}(\phi_i - \phi_j)\frac{\partial V_{ij}}{\partial\mathbf{r}_i}\right) \qquad (40)
\end{aligned}$$

As perturbations terms are all explicitly proportional to $|\mathbf{k}|$ now, we can take the $\mathbf{k} \to 0$ limit directly, and get

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{p}_i/m_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{b} \cdot \left((E_i + k_B T - h)\mathbf{I} - \frac{1}{2} \sum_{j \neq i} \mathbf{r}_{ij} \frac{\partial V_{ij}}{\partial \mathbf{r}_i} \right) \end{aligned} \tag{41}$$

with the $\mathbf{k} = 0$ heat current $\tilde{\mathbf{J}}^q(t)$ given by (4), and

$$\kappa = \lim_{t \to \infty} \left(\frac{\mathbf{b} \cdot < \tilde{\mathbf{J}}^q(t) >}{b^2 \Omega T} \right) \tag{42}$$

Another way to look at it is to take $\phi_i = \mathbf{b} \cdot \mathbf{r}_i$ and do equivalence transformation for (23). All the formalisms above were first given by Gillan and Dixon (1983).

We know that $< \mathbf{J}^q >_0 = 0$ for an equilibrated system. However, $\tilde{\mathbf{J}}^q(\tau)$ and $\mathbf{J}^q(\tau)$ are highly correlated random variables, so instead of calculating $< \tilde{\mathbf{J}}^q(t) >$ directly, we calculate the ensemble average of their difference $< \tilde{\mathbf{J}}^q(t) - \mathbf{J}^q >$, which must possess much higher statistical accuracy as ensemble fluctuations largely cancel each other.

5 Implementation on Argon

As a model system for the calculation of thermal conductivity, we choose LJ6-12 argon. There are several purposes in doing this:

- To verify the NEMD algorithm theoretically derived by Gillan and Dixon.
- To compare the accuracy between equilibrium correlation method and NEMD.
- To see the difference between liquid state and solid state calculations.
- To check the sensitivity of results with respect to cell size, i.e., how many $\mathbf{k}$ points are enough.
- In the possible future, put defects into the system and get empirical functional dependence between defect concentration and thermal conductivity.

Following the work by Gillan and Dixon (1983), we implemented both the equilibrium correlation and NEMD algorithms on LJ6-12 argon systems. In order to get reasonable results, we must ensure the phase trajectories we generated by MD are highly smooth, so that the differnce between the perturbed trajectory and the unperturbed trajectory, which is very small, won't be inundated by numerical noise. This requires us to use a smooth truncated LJ6-12 potential, as any discontinuity in the potential function would cause "jumps" in the phase trajectory:

$$V(r) = \begin{cases} 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] & r < r_0 \\ \\ -\gamma(r_1 - r)^2 & r_0 < r < r_1 \\ \\ 0 & r_1 < r \end{cases} \tag{43}$$

where, for a given r_1, the constants r_0 and γ are chosen to ensure the continuity of V and its first derivative at $r = r_0$. We introduced the cutoff at $r_1 = 2\sigma$, same as Gillan and Dixon (1983), and get

$$r_0 = 1.20129951\sigma, \quad \gamma = 1.39214916\frac{\epsilon}{\sigma^2} \tag{44}$$

All variables are of double precision in the program to ensure numerical accuracy.

Fig.(1) shows a run at $TR = 0.69, DR = 0.84, NP = 256$. The thermal conductivity is in reduced unit, the X axis showing the time steps, with one step $\Delta t = 10ps$. A total number of 2745 NEMD runs had been taken within the range of 340000 running steps. For the equilibrium correlation method, 329380 different origins had been taken (each running step after equilibration as a new origin), with correlation length = 120 steps: the number of effective origins is much smaller than the number of 329380 as these origins are highly correlated, but since it's a long run we are quite sure that the phase space was fully sampled. The calculated κ for liquid argon at this condition is 0.99 ± 0.03, close to the publishd results by Gillan and Dixon.

As we can see from Fig.(1), the comparison between equilibrium correlation method and the NEMD method by Gillan and Dixon should be considered as quite satisfactory: not only are the asymptotic value for thermal conductivity close, but also for the whole time range of the autocorrelation integral. This directly proved the theory developed in previous sections of the "equivalence transformation" of dynamical systems, based on which this NEMD algorithm was put forward.

Fig.(2) shows one run at $TR = 0.2983, DR = 0.90, NP = 256$ for solid argon. A total number of 1887 NEMD runs had been taken within the range of one million steps, the correlation length being 450, which is almost 4 times the length needed for the liquid to converge.

Since thermal conductivity in a crystal mainly results from the aharmonicity of the lattice, i.e., inelastic phonon-phonon collisions, the size of the simulation cell is an important issue here, as it directly controls how many $\mathbf{k}$ points we have. A run had been taken with exactly the same condition as Fig.(2), except that $NP = 108$. The result is shown in Fig.(3): We can see that the equilibrium correlation curve changed very little, but the NEMD curve became shaky after about 150 steps. For overall considerations we decided that it does not make much difference between 108 and 256 particles if we use equilibrium correlation method.

There are several subtle points concerning the accuracy of the NEMD method:

1. We must ensure that at $t = 0$ the perturbation force be instantaneously added onto the copy of the original system, not a step later or something (for implementation in a 5th order Gear method see *ball.f*).

2. As numerical error (in the finite-step intergration process) will set in for both the perturbed and unperturbed systems, their trajectories would eventually drift away what they should be. This makes the delicate business of taking the differences between two trajectories more and more precarious as time goes on. We therefore do not recommend NEMD for a very long correlation run if numerical accuracy can not be guaranteed. The best way to see this is to test the reversibility of the system after a certain time, by checking how much the heat current has changed and compare to the difference in heat current generated by the perturbation $\mathbf{b}$.

3. To reduce the error discussed above, we can either shorten the intergration step, which is costly, or to increase perturbation strength $\mathbf{b}$ to suppress the noise (however, this will undermine the validity of the entire algorithm since it only works in linear regime). There would be an optimum value depending on how many NEMD runs one is going to take (the more you're going to take, the smaller the optimum $\mathbf{b}$ should be). Usually $\mathbf{b}$ is around $1 \times 10^{-8}/\sigma$ for argon systems.

A The Argon Code: ball.f

ball.f (650 lines) is a simple molecular dynamics code for LJ6-12 system with interaction potential of Eq.(43) type, able to perform both equilibrium correlation method and NEMD to get the thermal conductivity of the model system. It uses the temperature coupling method proposed by Berendsen *et al* (1984), with coupling time constant of about 300 ps. Be aware of the fact that temperature coupling must be stopped before NEMD starts, so that the smoothness of the phase trajectory could be guaranteed. *ball.f* usually generates 5 output files:

- *temp.out*: This is the overall record of instantaneous thermodynamical variables during the run, such as the potential energy, pressure and MSD.
- *gr.out*: Radial distribution function. Sometimes you'll find 'B' in the file which means paragraph breaking, after which the counter is reset and $G(r)$ is re-measured for a new period of time.
- *config*: Configuration file which saves the positions and velocities of particles, so that later programs can continue from previous runs.
- *corr.out*: Autocorrelation function of heat current in the system, starting from the second row: first column is the steps, second column is the $< \mathbf{J}^q(0) \cdot \mathbf{J}^q(t) >$ functional, third column is the time integral of it. The first row is the system parameters: temperature, density and Δt.
- *nemd.out*: Heat current of the perturbed system, starting from the third row: $(\tilde{J}^q_x,\tilde{J}^q_y,\tilde{J}^q_z)$. The first row is system parameters: temperature, density and Δt, the second row is perturbation strength $\mathbf{b} : (b_x, b_y, b_z)$.

The input parameters are put in a file (suppose called *con*), which usually looks like this:

```
256       0.2983   0.90  0
1000000   150000   500   300.
1         1        450
2.E-8     0.       0.
```

The first row means 256 particles with $TR = 0.2983, DR = 0.90$, the 0 means *not* reading from the config files (if it's 1, then the *config* file of previous run should be appended behind

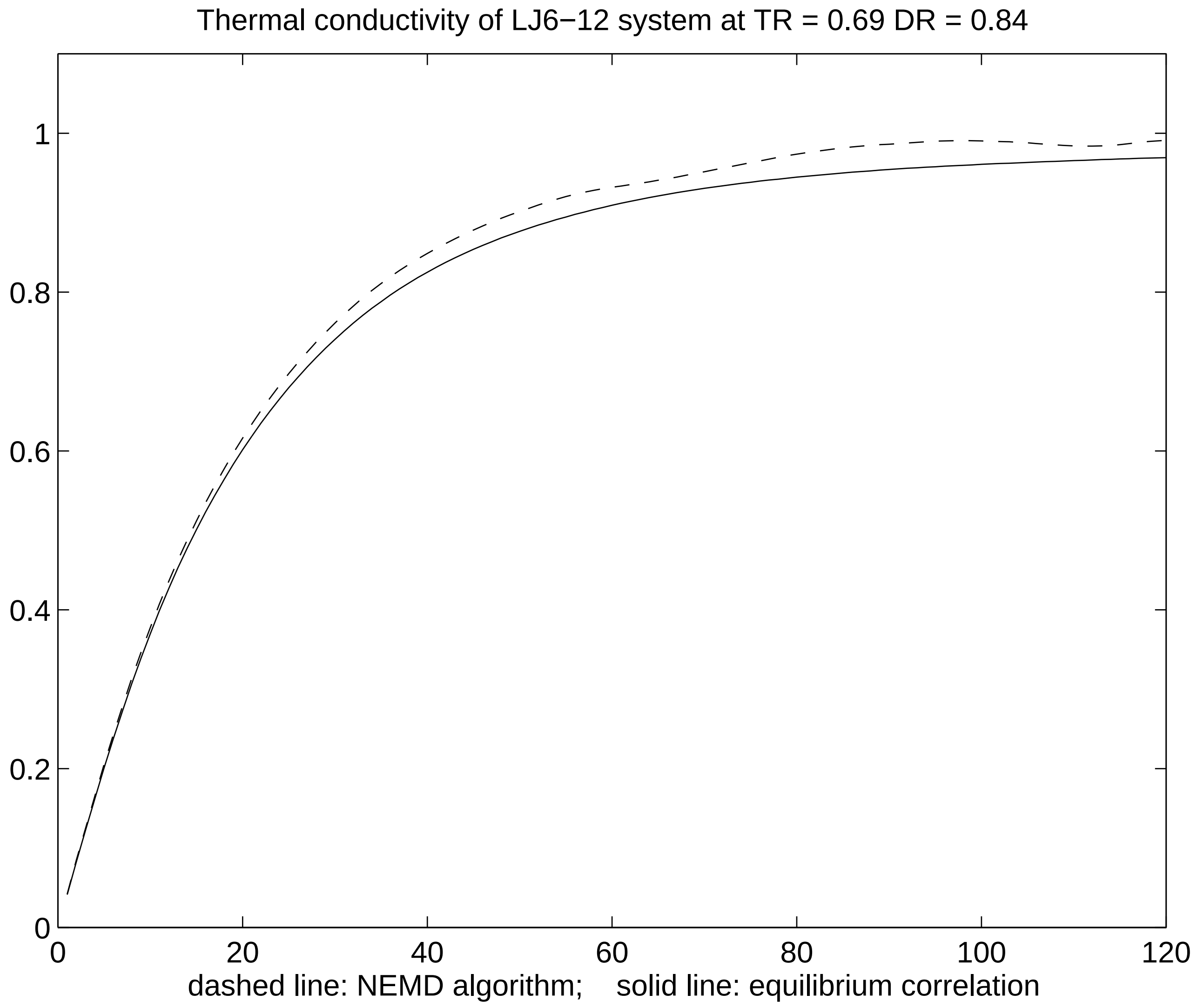

Figure 1: Fluid near triple point, NP = 256

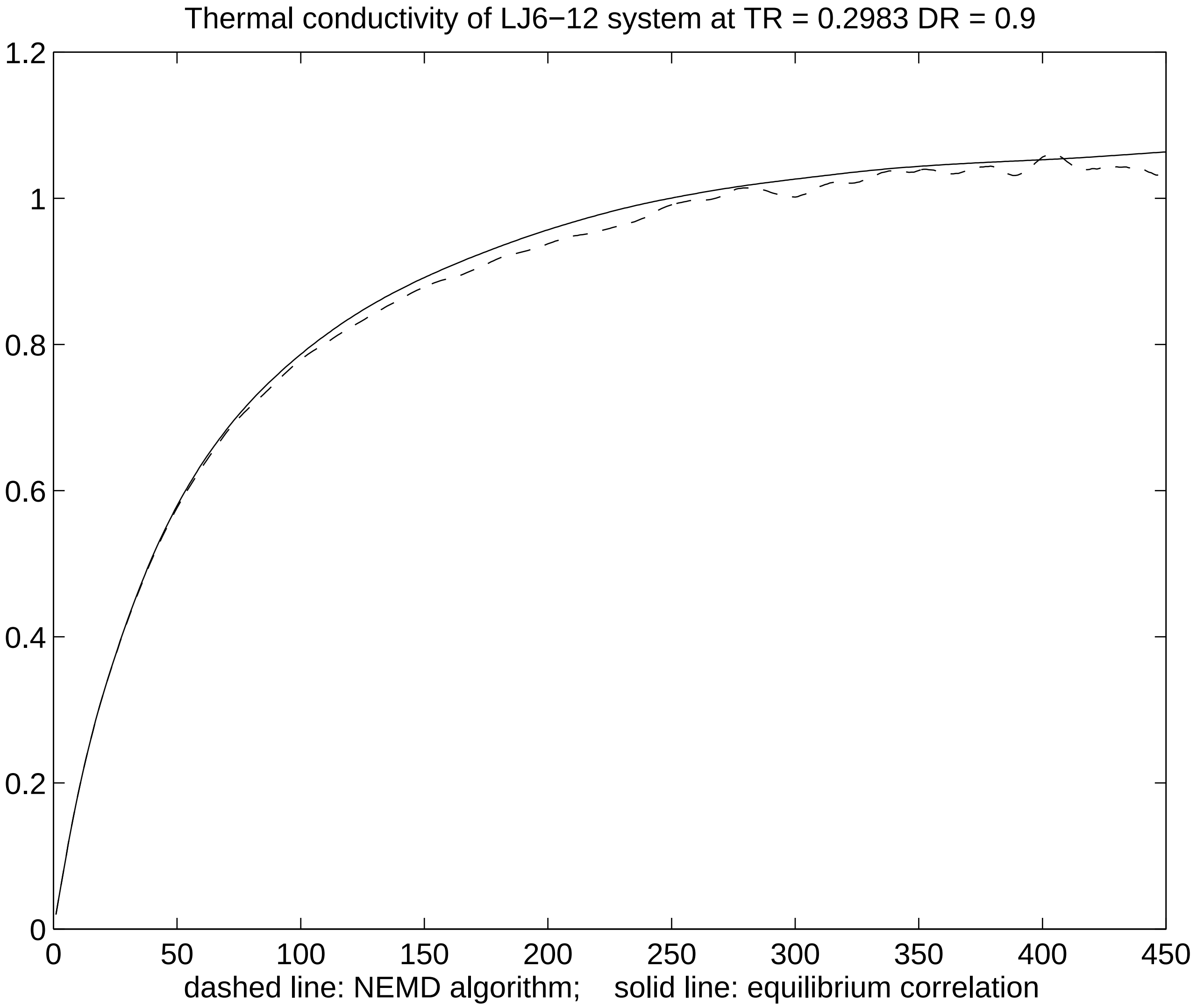

Figure 2: Solid argon, NP = 256

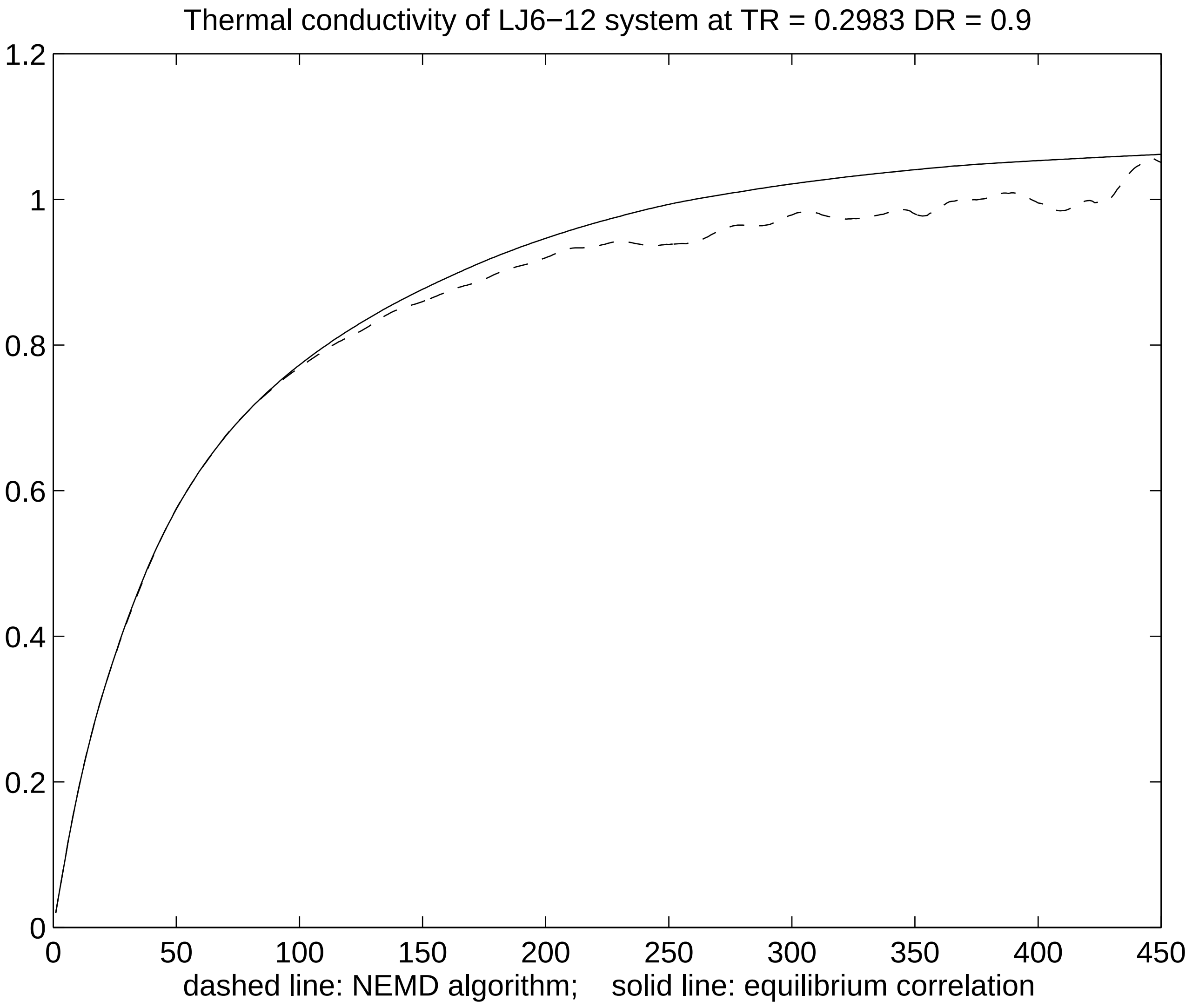

Figure 3: Solid argon, NP = 108

the *4th* row). The second row means the total run is 1000000 steps with the first 150000 steps as temperature coupling (the coupling constant is 300. ps), and writing on *temp.out* thermodynamical variables every 500 steps. The third row: the first 1 means equilibrium correlation turned on, second 1 means NEMD turned on, 450 is correlation length of both methods (they are the same). The fourth row is perturbation strength $\mathbf{b} : (b_x, b_y, b_z)$. To run, just type:

```
% ball < con &
```

where *con* is the above condition file.

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