Low-temperature Crystalline Lattice Thermal Conductivity from Molecular Dynamics Simulation's View

Ju Li

Department of Nuclear Engineering

Massachusetts Institute of Technology, Cambridge, MA 02139

1 Past Problems

In the past years, we numerically calculate the lattice thermal conductivity of dielectric solids using the Green-Kubo fluctuation-dissipation formula and molecular dynamics simulation based on classical Newtonian dynamics using well-tested interatomic potential [1], with a crude temperature rescaling scheme due to Lee *et al* [2] to account for the quantum-mechanical heat capacities at low temperature. It is found that in the high temperature region ($T > T_D/2$) and for perfect crystal (Ar, Si and SiC), where κ follows $T^{-\alpha}$ behavior ($\alpha \sim 1$), the calculations yield reliable results as compared with experiments. It also provides a qualitatively correct picture of the drastic defect-induced reduction of thermal conductivity at high defect concentration. On the other hand, the simulation fails to produce the low-temperature thermal conductivity of these crystals, where κ has the form of $e^{\theta/T}$, while our model continues to give $T^{-\alpha}$ behavior and becomes much lower in absolute magnitude in comparison with the experiments. In view that the Debye temperature for Si is 550K and

[1] J. Li, L. J. Porter, S. Yip, *Journal of Nuclear Materials*, vol 255, pp. 139 (1998).
[2] Y. H. Lee, R. Biswas, C. M. Soukoulis, C. Z. Wang, C. T. Chan, K. M. Ho, Phys. Rev. B 43 (1991) 6573.

SiC > 1000K, this includes room temperature and is a severe drawback to the usefulness of our simulation.

At extremely low temperatures ($T < T_D/20 - T_D/10$), the experimental κ heads for a drastic decrease ($\kappa \propto T^3$) as the phonon mean free path becomes limited by the macroscopic sample size. Our model produce qualitatively the same result by coincidence.

2 The Reason

To see why the simulation fails at low temperatures, we must concede that the conventional classical MD simulation describes a fictitious world where classical mechanics and statistical mechanics always hold true at any given temperature. Consider a spring with Hamiltonian,

$$\mathcal{H}(p, q) = \frac{p^2}{2} + \frac{1}{2}\omega^2 q^2, \tag{1}$$

whose trajectories on pq-plane are closed ellipses with size dependent on its total energy E, and encloses area $A = 2\pi E/\omega$. In classical mechanics, all E's are allowable, and so all ellipses could exist, which fills up the phase plane as a continuum. The density of states on the pq-plane is the continuous integral $\int dpdq$, and the partition function is

$$Z_{\text{classical}} = \int dpdq e^{-\mathcal{H}/k_B T}. \tag{2}$$

In this world, the property averages are just Gaussian integrals and one can easily show that

$$\langle E \rangle = k_B T, \tag{3}$$

independent of ω, which is the famous equi-partition theorem, provided that the classical Newtonian mechanics are followed.

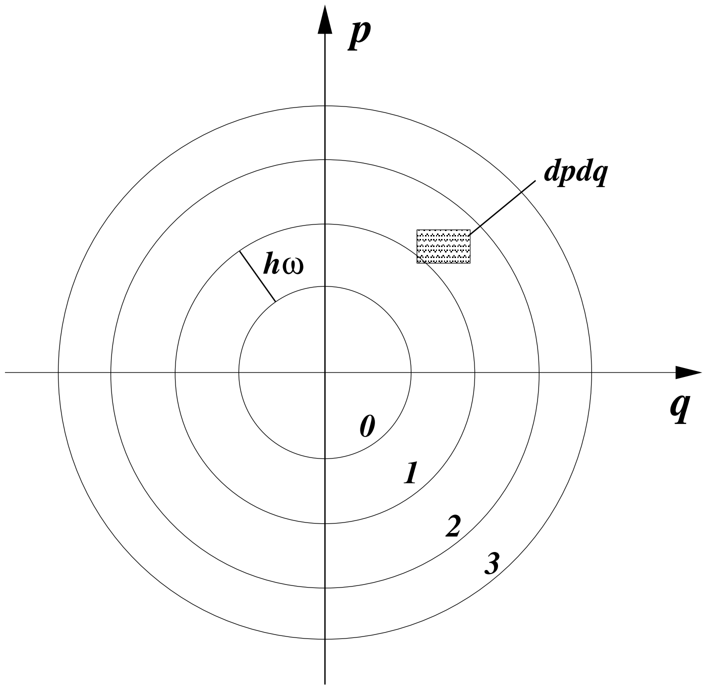

Fig. 1. Phase space trajectories of an harmonic oscillator and its quantization

But, in our real world, a quantum world, the energy is quantized instead of continuous. The only allowable E's are

$$E_N = (N + 1/2)\hbar\omega. \tag{4}$$

It is still helpful to consider the pq-plane, for a so-called semi-classical picture which is the same as the classical one except only a countable number of ellipses *can* exist, satisfying the Bohr-Sommerfeld quantization condition [3]

$$\oint pdq = 2\pi(N + 1/2)\hbar, \tag{5}$$

which is seen to be equivalent to (4). So, in the quantum world, the density of states is a discrete sum $\sum_N$ instead of continuous integral $\int dpdq$,

$$Z_{\mathrm{QM}} = \sum_N e^{-\mathcal{H}/k_B T}. \tag{6}$$

[3] The original formulation for Hydrogen electron is without the $\frac{1}{2}$ factor.

(6) and (2) would not differ by much if the scale of available energy, $k_B T$, is much greater than the energy separation between two nearest ellipses, $\hbar\omega$; just like a man standing far away cannot distinguish the subtleties of a painting – which is the "approach to continuum" or "correspondence principle" between quantum and classical physics. But if the available energy is comparable to $\hbar\omega$, then the system can *distinguish* the discrete ellipses, which then could modify its behavior profoundly.

The most illustrious example worked out by Einstein is that of the "anomalous" heat capacity of solids at low temperature. From (6),

$$Z = e^{-\hbar\omega/2k_B T} + e^{-3\hbar\omega/2k_B T} + e^{-5\hbar\omega/2k_B T} + ... = \frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}}, \tag{7}$$

and thus

$$\langle E \rangle = (\langle N \rangle + 1/2)\,\hbar\omega = -\frac{\partial \log Z}{\partial(1/k_B T)} = \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} + 1/2\right)\hbar\omega. \tag{8}$$

Here

$$\langle N \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}, \tag{9}$$

is the Bose-Einstein distribution for bosons. (8) can be shown to approach (3) asymptotically as $\mathcal{O}(1/T)$ when $T \to \infty$.

One can see that the heat capacity of a quantum oscillator (slope of Fig. 2) – the derivative of average internal energy with respect to T, only approaches the constant k_B value predicted by the equi-partition theorem (3) at high enough temperatures. When $k_B T/\hbar\omega$ is on the order of unity, there is a severe discrepancy between the quantum and classical results. Same thing would happen for the thermal conductivity κ.

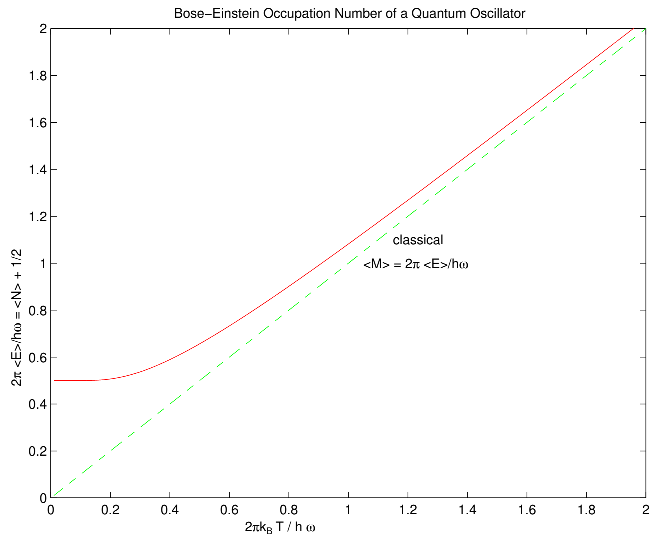

Fig. 2. Occupation number of a quantum oscillator as compared to a classical one (dash line).

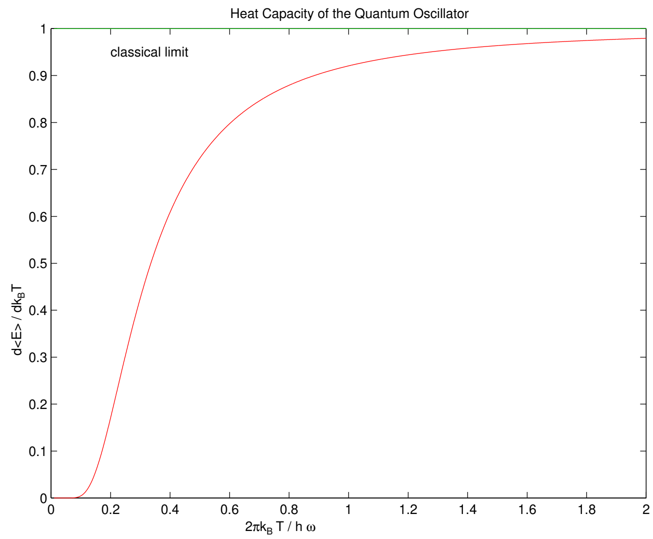

Fig. 3. Comparison of heat capacity between a quantum oscillator and a classical one (dash line).

In a solid, there exist not just a single oscillator but a whole bunch (in fact, $3N$) of them, each with different ω's. Labelling them can be difficult; but for a perfect crystal with translational symmetry, a great simplification happens (Bloch theorem) where one can label them by $\mathbf{k}$ and branch number j's. These vibrations with space-time periodicity $e^{i\mathbf{k}\cdot\mathbf{R}_n - i\omega_j(\mathbf{k})t}$ are called phonons; and $\omega_j(\mathbf{k})$ is called the phonon dispersion relation. When $\mathbf{k}$ is small (long waves), there exist three j-branches that have almost linear dispersion: $\omega_j(\mathbf{k}) \simeq c_j|\mathbf{k}|$; they are nothing other than the sound and shear waves in a solid corresponding to macroscopic elastic deformations. They are special because only at small $|\mathbf{k}|$ do $\omega_j(\mathbf{k})$'s approach 0.

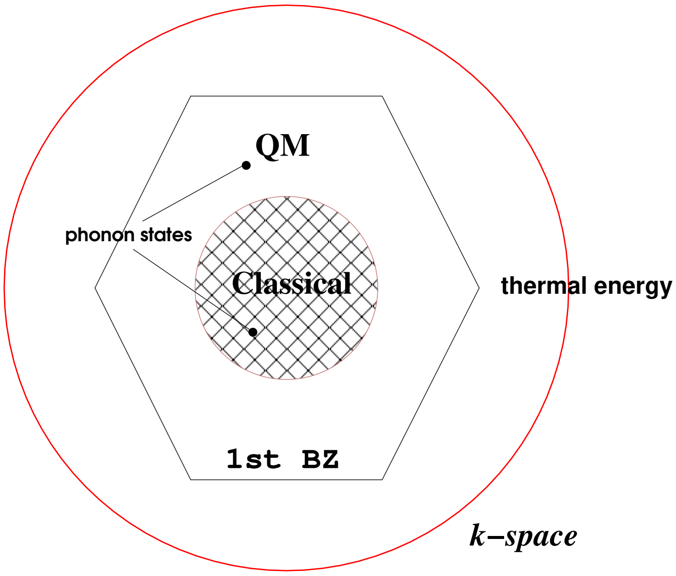

Fig. 4. Two scenarios in the activation of phonons. When $k_B T \gg \hbar\omega_D$, the thermal energy (large) circle encloses the entire BZ; so the classical equi-partition theorem is good for all phonons and thermal (representative) phonons are those on the BZ boundary. On the other hand, when $k_B T < \hbar\omega_D$, the activation circle is in BZ: inside the occupation is still classical, but outside the Bose-Einstein distribution must be used, which is exponetially small. The thermal phonons are those on the circle.

A continuum can support arbitrarily large $\mathbf{k}$; but a discrete lattice can only support up to $2\pi/a$ where a is the lattice spacing of a pedagogical 1D lattice. It can be easily seen that $k + 2\pi/a$ and k represent the *same* wave on this lattice, which is called *aliasing*. Thus, $k + 2\pi/a$ and k are exactly the same label for vibrational eigenstates and so, we only need to label the eigenstates by $k \in (-\pi/a, \pi/a)$, which is called the first Brillouin Zone. If one traces the lowest ω of a given $\mathbf{k}$, it usually achieves maxima on $\pm\pi/a$, the BZ boundary; with maximum on the order of the so-called Debye frequency ω_D.

Depending on temperature, some phonons (grouped according to frequency) are more populous than others; the most populous is called *thermal phonon* frequency ω_T, which dominates the thermodynamics of the system. ω_T exists because there are more phonon states at large k ($\propto 4\pi k^2 dk$), but larger k also means larger ω which means smaller $\langle N \rangle$ in (9). The situation is thus divided into two scenarios: If $k_B T \gg \hbar\omega_D$, i.e., if the available thermal energy (signified by the big circle) is enough to excite even the highest available frequency, ω_D, at the

BZ boundary, then $\omega_T = \omega_D$. In this case all phonon excitations can be well-approximated by the classical "effective" occupation number

$$M_{\mathbf{k}j} = k_B T / \hbar\omega_{\mathbf{k}j} \tag{10}$$

and it is valid to study the entire system using classical mechanics. On the other hand, if the thermal energy is smaller than $\hbar\omega_D$ (small circle in BZ), then $\omega_T = k_B T/\hbar$; modes inside the circle are still excited according to classical equi-partition theorem, but those outside the circle ($\omega > \omega_T$) are not and (9) is essential. So it is inappropriate to describe such a system using classical mechanics without modification.

In the above we regard the phonon modes as perfect normal modes of the system, where the occupation number $N_{\mathbf{k}j}$, once assigned, has no reason to change. This is not so once nonlinearities exists in the interaction potential[4], the leading order of which are the cubic terms, that can annihilate a phonon $\mathbf{k}_1$ and create two ($\mathbf{k}_2$, $\mathbf{k}_3$), and vice versa, which makes the BZ look rather like a boiling pot of water. But, not any triplets of $\mathbf{k}$ can scatter; energy must be conserved:

$$\omega_1 = \omega_2 + \omega_3, \tag{11}$$

and so is the quasi-momentum

$$\mathbf{k}_1 = \mathbf{k}_2 + \mathbf{k}_3 (+\mathbf{G}), \tag{12}$$

because, as we said, a discrete lattice can not support real momentum, so there is only a conservation law for the *quasi*-momentum. If the reciprocal vector $\mathbf{G}$ in the bracket ($2\pi/a$ for the 1D lattice) is not involved, it is called a Normal or N-process; otherwise it is called

[4] see *Phonon interactions and thermal conductivity* at http://mmm.mit.edu/~liju99/phonon.ps.

Umklapp or U-process, which in German means "flip over" [5]. One can see that in order to "flip over", at least two of the three $|\mathbf{k}|$'s must be greater than $|\mathbf{G}|/2$, so at least two ω's involved are quite large. This means that the rate of Umklapp process will drop drastically in scenario II, because quite generally, it can be shown that the *rate* of a three-phonon process is proportional to

$$[N_1(+1)] \times [N_2(+1)] \times [N_3(+1)], \tag{13}$$

where N_1, N_2, N_3 are the current occupation numbers of the phonons involved; since N is exponentially small if it lies outside the activation circle, one can see that the rate of Umklapp process becomes exponentially small ($\propto e^{-\theta/T}$) in the low temperature regime of $\omega_T \ll \omega_D$, when the rate of Normal process only decreases as algebraic powers of T. This is going to have important consequences on the crystal's thermal conductivity.

Why do we have to distinguish between N- and U-processes? The reason lies in the form of the phonon transport equation (for details see the last reference),

$$\frac{\partial N_{\mathbf{k}j}}{\partial t} + \nabla \cdot (N_{\mathbf{k}j}\mathbf{v}_G) = \left.\frac{\partial N_{\mathbf{k}j}}{\partial t}\right|_{collision} = I_N[N] + I_U[N]. \tag{14}$$

RHS of (14) describes the local phonon collisional processes that we mentioned above; it can be further categorized as N- and U- collision rate functionals $I_N[N]$ and $I_U[N]$. Note that their contributions to the rate of change in $N_{\mathbf{k}j}$ does not only depend on $N_{\mathbf{k}j}$ itself, but also on other phonon occupation numbers [6]. $I_N[N]$ and $I_U[N]$ can further be shown to have the

[5] That is like playing some sort of Black Jack! Suppose one wins \$11, but he is greedy and wins another \$13. Oops, that is larger than \$21, and he owns \$2!

[6] An effort to ignore that is the *relaxation time* approximation, which only makes sense in scenario I where $\tau_U \sim \tau_N$ and there is no clear distinction between mechanisms.

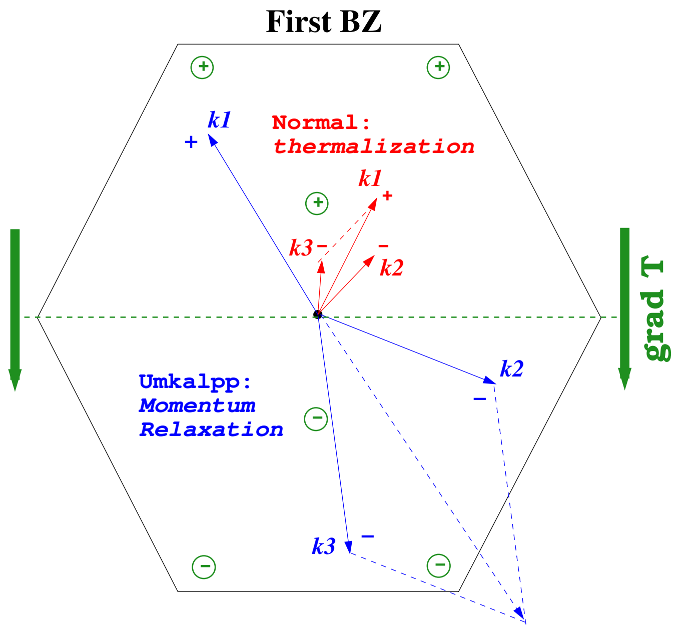

Fig. 5. Character of the streaming, Normal and Umklapp-collisional terms.

Bose-Einstein distribution $N_{BE}(\mathbf{k}j)$ as zero-modes, which means

$$I_N[N_{BE}] = I_U[N_{BE}] = 0; \quad N_{BE}(\mathbf{k}j) = \frac{1}{e^{h\omega_{\mathbf{k}j}/k_BT} - 1}, \tag{15}$$

so complete equilibrium is only achievable when T is constant everywhere.

The second term on LHS is the so-called *streaming* term, which for steady state ($\frac{\partial N_{\mathbf{k}j}}{\partial t} = 0$) heat flow, is the only input or inhomogeneous term of this integro-differential equation. It has the important feature that it carries net quasi-momentum [7] with it,

$$\sum_j \int \frac{d\mathbf{k}}{8\pi^3} \mathbf{k} \nabla \cdot (N_{\mathbf{k}j} \mathbf{v}_G) = S \nabla T \neq 0, \tag{16}$$

where S is the entropy per volume of the crystal. By analogy, one can think of a 2D BZ phonon distribution as a pile of sand, whose height is the highest at zone center and lowest on zone boundaries. The streaming term is to such effect that the amount of sand is increased on one side ($\mathbf{k}$'s along the temperature gradient $-\nabla T$) and decreased on the opposite side. The overall result is that the center of mass of this sand dune is shifted toward $-\nabla T$.

[7] V. L. Gurevich, *Transport in Phonon Systems*, Elsevier Science Publishers (1986).

Without counteractive processes, this shifting of center of mass will simply continue. Because each phonon mode carries certain amount of energy and propagates it by group velocity $\mathbf{v}_G = d\omega/d\mathbf{k}$ which is often along the $\mathbf{k}$-direction, the net effect is to induce a *macroscopic* heat current $\mathbf{J}^q$ in the $-\nabla T$ direction; and in fact $\mathbf{J}^q$ will just increase without bound. So without counteractive or scattering processes, the thermal conductivity will just be infinite.

Both Normal and Umklapp process are counteractive processes which tries to revoke whatever changes the streaming term causes to the phonon distribution. They cannot fully win, but they do strike a balance with it; so in the end the center of mass *is* displaced but is not growing, and a finite instead of infinite $\mathbf{J}^q$ will be established.

We must distinguish between Normal and Umklapp processes because they play different roles in this struggle against the streaming term. To see this, we must understand that the Normal process cannot change the total quasi-momentum of the system, since by definition $\mathbf{k}_1 = \mathbf{k}_2 + \mathbf{k}_3$. So whatever the center of mass displacement the system currently has, Normal process cannot recover. The job, called *momentum relaxation*, has to be done by the Umklapp process, which catches anything that spills over the BZ and put it on the other side, in effect reducing the center of mass displacement of the system.

Then, what is the role of Normal process? Normal process induces *thermalization*, or approach to *local* equilibrium. This comes from the observation that not only $N_{BE}(\omega)$, but also $N'_{BE}(\omega) = N_{BE}(\omega - \mathbf{k}\cdot\mathbf{V})$ for arbitrary $\mathbf{V}$ having the dimensionality of velocity, are zero-modes of $I_N[N]$. $N'_{BE}(\omega)$ can be thought of as nothing other than a Bose-Einstein distribution with a displaced center of mass $\mathbf{V}$. Thus the Normal process is a mason with a good eye for details but cannot correct for the systematic deviation of the sand pile. It measures the average "center of mass" of the BZ at a given $\mathbf{x}$ and then tries to re-shape the pile according to $N'_{BE}(\omega)$. If somewhere there is a notch (some $\mathbf{k}$-modes are under-excited), it can propagate the energy from surplus regions to this deficient region by many small Normal collisions. And, as we said, when $\omega_T \ll \omega_D$, such thermalization has a much shorter time scale (τ_N) than the momentum relaxation time scale (τ_U), since the rate of Umklapp process decreases exponentially with T while that of the Normal process only decreases algebraicly. Thus the low-temperature crystalline thermal conductivity is controlled by Umklapp process rather than the Normal process, which is the *weaker* of the two in fighting against the streaming term. And at any given moment, the leading-order phonon distribution should have the form $N'_{BE}(\omega)$, as if relaxed instantaneously by I_N.

In exact analogy, a box of gas can only be at global equilibrium as $e^{-m|\mathbf{v}|^2/2k_BT}$, but a local equilibrium distribution $e^{-m|\mathbf{v}-\bar{\mathbf{v}}(\mathbf{r})|^2/2k_BT}$, which is also a zero mode of the gas collisional operator, can exist and persist for quite a while. Suppose one gives the gas an initial random distribution at $t = 0$, under suitable conditions (dense gas, namely) we will find that within a very short time τ_L, the system approaches local equilibrium; beyond τ_L, the macroscopic variable $\mathbf{v}(\mathbf{r})$ evolves with timescale τ_H with the leading order particle distribution $e^{-m|\mathbf{v}-\bar{\mathbf{v}}(\mathbf{r})|^2/2k_BT}$ co-moving[8]. The reduced equations (as a function of $\mathbf{r}$ only) are called *hydrodynamics* equations, or fluid mechanics equations. The transition from kinetic to hydrodynamics theory relies critically on this separation of timescales and the assumption of leading-order local equilibrium. By the same token, when $\omega_T \ll \omega_D$ and $\tau_N \ll \tau_U$, we can concentrate how $\mathbf{V}(\mathbf{r})$ evolves with time rather than the full $N_{\mathbf{k}j}$ description, which is appropriately named *phonon hydrodynamics*.

It should be quite clear now why classical MD cannot be used to study the low-temperature thermal conductivity without modification, since in that fictitious world the equi-parition theorem ordains that there should always be significant excitations for **all** phonon modes (think of $\hbar \to 0$ and the activation circle goes to infinity). So τ_U is always as big as as τ_N,

[8] There are, of course, next-order terms, without which there can be no shear stress or heat current; their relations to $\mathbf{v}(\mathbf{r})$ and its spatial gradients can be systematically calculated by the Chapman-Enskog expansion of the Boltzmann equation, which is essentially a τ_L/τ_H expansion.

and there is no separation of timescales, no phonon hydrodynamics, and no $e^{\theta/T}$ like thermal conductivity rise.

3 Remedies

3.1 Wigner-Kirkwood $\hbar$-Expansion

It can be shown that any two-point correlation function of the quantum world can be expanded in a power series of $\hbar$, the coefficients of which are classical n-point correlation functions. Besides being quite complicated analytically and numerically, I also doubt that a power series expansion can be useful in the deep quantum domain, as all previous applications were for liquids, where the quantum effect is indeed a small correction. Nevertheless, it is a trodden path and when we have nowhere to turn, we may try this.

3.2 Path-Integral MD

PIMD seems to be something new that just appear recently in the simulation study of water[9]. The path integral MC is a rigorous way to sample quantum mechanical partition function, by linking many identical systems in a closed loop with springs $\propto \hbar/T$, and then do plain classical MC sampling. I am not sure that the extension of MC to MD yields the correct dynamics, although the quantum partition function *is* exactly reproduced.

This method looks hopeful because it has a clear picture and is not hard to implement.

[9] There is a close analogy between a flexible water model and a quantum solid, and we have unfortunately met both.

Furthermore, I think the Wigner-Kirkwood expansion can be derived as a result of this approach.

3.3 Quasi-Momentum Relaxation Method?

One may think of our low-temperature trouble as a terrible complication; but the establishment of phonon hydrodynamics may also be a great simplification as in the theory of fluids, once we have means to deal with them in a fundamental way. For example, the following hydrodynamics equation [10],

$$\frac{d\mathbf{P}}{dt} + \frac{TS^2}{\kappa p}\mathbf{P} = 0, \quad \mathbf{P} = p\mathbf{V}, \tag{17}$$

for a spatially homogeneous system may be used to calculate κ directly, where S and p are the entropy and "mass density" of the phonon system, both of which have explicit expressions. What we need is a numerical "lab" in which $\mathbf{V}(0)$ can be assigned and $d\mathbf{V}/dt$ measured, and this lab must be quantum mechanical (at least for a short while), by which we mean the correct quantum mechanical evolution of $\mathbf{V}$ must be reproduced. This is achievable by a simple equivalence rule and a specially conditioned *classical* MD system.

4 Quantum to classical bridge through the phonon Boltzmann equation

In above I described the critical differences between classical and quantized phonon *excitation amplitudes* at low temperatures, and why that leads to exponentially rare occurrence of the

[10] Gurevich, pp. 137.

Umklapp processes and the establishment of local "drifted equilibrium"

$$N_{\mathbf{k}j} \approx N_{BE}(\omega - \mathbf{k} \cdot \mathbf{V}) \;\; (+\Delta_2 N, \; ...), \tag{18}$$

by the more frequent Normal processes. One can derive, by τ_N/τ_U expansion, homologous to the Chapman-Enskog development, a set of phonon hydrodynamics equations (Gurevich, pp. 138) which looks much simpler than the Boltzmann equation but are exact [11] . A simplified version is (17) (Gurevich, pp.137), which describes the temporal relaxation of the total quasi-momentum, or "center of mass" of a spatially homogeneous phonon distribution, to zero due to U-processes. Its relaxation time τ_κ ($\sim \tau_U$) is thus directly related to the thermal conductivity by

$$\kappa = \frac{TS^2}{p}\tau_\kappa, \tag{19}$$

where

$$S = \frac{k_B}{\Omega}\sum_{\mathbf{k}j}(N_{\mathbf{k}j}+1)\log(N_{\mathbf{k}j}+1) - N_{\mathbf{k}j}\log(N_{\mathbf{k}j}) \tag{20}$$

is the entropy density, and

$$p = \frac{\hbar^2}{3\Omega k_B T}\sum_{\mathbf{k}j}|\mathbf{k}|^2 N_{\mathbf{k}j}(1+N_{\mathbf{k}j}) \tag{21}$$

is the "mass density" of the phonon system, relating $\mathbf{V}$ to the total quasi-momentum density

$$\mathbf{P} = \sum_{\mathbf{k}j}\hbar\mathbf{k}N_{\mathbf{k}j} \tag{22}$$

[11] They are on the same footing as the Navier-Stokes equations, so as "exact" as the Navier-Stokes equations are "exact".

as

$$\mathbf{P} = p\mathbf{V} + \mathcal{O}(\mathbf{V}^2). \tag{23}$$

Please note that this relation is exact as long as phonon hydrodynamics holds, unlike the well-used expression

$$\kappa = \sum_{\mathbf{k}j} C_V(\mathbf{k}j)|\mathbf{v}_G(\mathbf{k}j)|^2 \tau_{\mathbf{k}j}/3, \tag{24}$$

that comes by the single-relaxation time approximation, which represents a physical picture of "broken rank" of the phonon system which is only valid at high temperatures. However, there is a close symmetry between the exact (19) and the empirical (24) which we shall heavily exploit later on.

The big surprise is that the crux of the matter: the relaxation of the total quasi-momentum by (17), whose origin is purely quantum physics, can be faithfully investigated by classical molecular dynamics.

The bridge is phonon Boltzmann equation, quantum and classical. It is my feeling that the full quantum *dynamics*, as described by the Schroedinger equation, cannot be simulated in a fool-proof manner as the classical world by MD, where if one needs something and computer is available, he can just blindly go through the procedure and get whatever he needs [12]. In this case, we have to learn about the specific problem, whose main theoretical tool is the quantum phonon Boltzmann equation, based on three-phonon scattering [13]. It is the unique symmetry of the phonon Boltzmann equation that leads to a simplified, "semi-classical"

[12] That is not true if complexity of the real problem is involved, but let me just naively call that a "computer time" problem.

[13] The validity of this kinetic description has been verified in M. Omini and A. Sparavigna, Phys. Rev. B 53 (1996) 9064, and hopefully this work.

approach.

We are going to study the relaxation of $\mathbf{V}$ in $N_{BE}(\omega - \mathbf{k}\cdot\mathbf{V})$ at low T due to phonon collisions, in the absence of spatial gradients such as ∇T, so there is no streaming term and the full equation reads

$$
\begin{aligned}
&\frac{\partial\langle N_{\mathbf{k}j}\rangle}{\partial t} = \left.\frac{\partial\langle N_{\mathbf{k}j}\rangle}{\partial t}\right|_{collision} = I_N[N] + I_U[N] = \\
&\sum_{j'}\int\frac{d\mathbf{k}'}{8\pi^3}\left[\sum_{j''}\beta_{jj'j''}(\mathbf{k},\mathbf{k}',-\mathbf{k}'')\langle N''(N'+1)(N+1) - (N''+1)N'N\rangle\delta(\omega''-\omega-\omega')\right. \\
&\left.+\frac{1}{2}\sum_{j'''}\beta_{j'j'''j}(\mathbf{k}',\mathbf{k}''',-\mathbf{k})\langle(N+1)N'N''' - N(N'+1)(N'''+1)\rangle\delta(\omega-\omega'-\omega''')\right].
\end{aligned}
\tag{25}
$$

following Gurevich pp. 55, (6.15), where

$$
\begin{aligned}
&\beta_{j_1j_2j_3}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = \frac{\pi\hbar}{4\rho\omega_1\omega_2\omega_3(\rho\Omega)^2}\times \\
&\left|\sum_{\mathbf{n}_1\mathbf{n}_2\mathbf{n}_3}\sum_{\gamma_1\gamma_2\gamma_3}B^{\mathbf{n}_1\mathbf{n}_2\mathbf{n}_3}_{\gamma_1\gamma_2\gamma_3}e^{\mathbf{k}_1j_1}_{\gamma_1}e^{\mathbf{k}_2j_2}_{\gamma_2}e^{\mathbf{k}_3j_3}_{\gamma_3}\exp\left[i(\mathbf{k}_1\cdot\mathbf{a}_{\mathbf{n}_1}+\mathbf{k}_2\cdot\mathbf{a}_{\mathbf{n}_2}+\mathbf{k}_3\cdot\mathbf{a}_{\mathbf{n}_3})\right]\right|^2,
\end{aligned}
\tag{26}
$$

and $B^{\mathbf{n}_1\mathbf{n}_2\mathbf{n}_3}_{\gamma_1\gamma_2\gamma_3}$ are the cubic nonlinear coefficients of the potential,

$$
\mathcal{U}_3 = \frac{1}{6}\sum_{\mathbf{n}_1\mathbf{n}_2\mathbf{n}_3}\sum_{\gamma_1\gamma_2\gamma_3}B^{\mathbf{n}_1\mathbf{n}_2\mathbf{n}_3}_{\gamma_1\gamma_2\gamma_3}u_{\mathbf{n}_1\gamma_1}u_{\mathbf{n}_2\gamma_2}u_{\mathbf{n}_3\gamma_3},
\tag{27}
$$

as defined in Gurevich, (6.3), (6.5) and (6.10).

The idea is that although we use (25) theoretically, practically we do not want to deal with $\beta_{jj'j''}(\mathbf{k},\mathbf{k}',\mathbf{k}'')$'s, which are hard to calculate, hard to store, and RHS integral of (25) with δ-functions are hard to evaluate. The next order, quatic terms will be even more complicated. We want to realize (25) by doing a real MD simulation using the full interatomic potential, from which the $\beta_{jj'j''}(\mathbf{k},\mathbf{k}',\mathbf{k}'')$'s are derived.

However, although the $\beta_{jj'j''}(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ coefficients in (25) are inherited exactly in a classical MD simulation, (25) itself, which is derived from Fermi's Golden Rule in quantum perturbation theory, does not. In fact the $+1$ factors after N', N, etc. are the unique property of boson operators. How can that be inherited by a classical simulation?

To show the symmetry of (25), let me concentrate on the first term (second term follows identically) of the collisional integral and omit all inconsequential symbols, and write it as

$$\begin{aligned}\frac{\partial\langle N\rangle}{\partial t} &= \hbar\,\langle N''(N'+1)(N+1)-(N''+1)N'N\rangle\,\delta(\omega''-\omega-\omega')+...\\ &= \hbar\,\langle N''N'+N''N+N''-N'N\rangle\,\delta(\omega''-\omega-\omega')+...\end{aligned} \tag{28}$$

One can readily check that if

$$1+N^{-1}=\exp(\mathrm{const}\cdot\omega)\equiv\exp(\frac{\omega}{k_BT}) \tag{29}$$

then RHS of (28) vanishes identically. So (29) is in fact the necessary and sufficient condition for the establishment of equilibrium Bose-Einstien distribution [14].

The corresponding Boltzmann equation in a fictitious, classical lattice vibrational system can be derived purely based on classical mechanics. However a much simpler way is to let $\hbar\to 0$ in (25) while one keeps the energy E fixed,

$$\hbar\to 0,\ \ N\to\infty,\ \ N\hbar\to M\equiv\frac{E}{\omega}=(N+\frac{1}{2})\hbar\ \text{ fixed.} \tag{30}$$

[14] For the same reason, if only N-process is present, local equilibrium $N_{BE}(\omega-\mathbf{k}\cdot\mathbf{V})$ can be established because we have an additional conserved quantity $\mathbf{k}$ for *every* Normal collision. This development is entirely analogous to the gas Boltzmann equation and $e^{-m|\mathbf{v}-\bar{\mathbf{v}}(\mathbf{r})|^2/2k_BT}$. In a sense, the U-process is the only thing new, as a crystal is discrete while space-time is continuous.

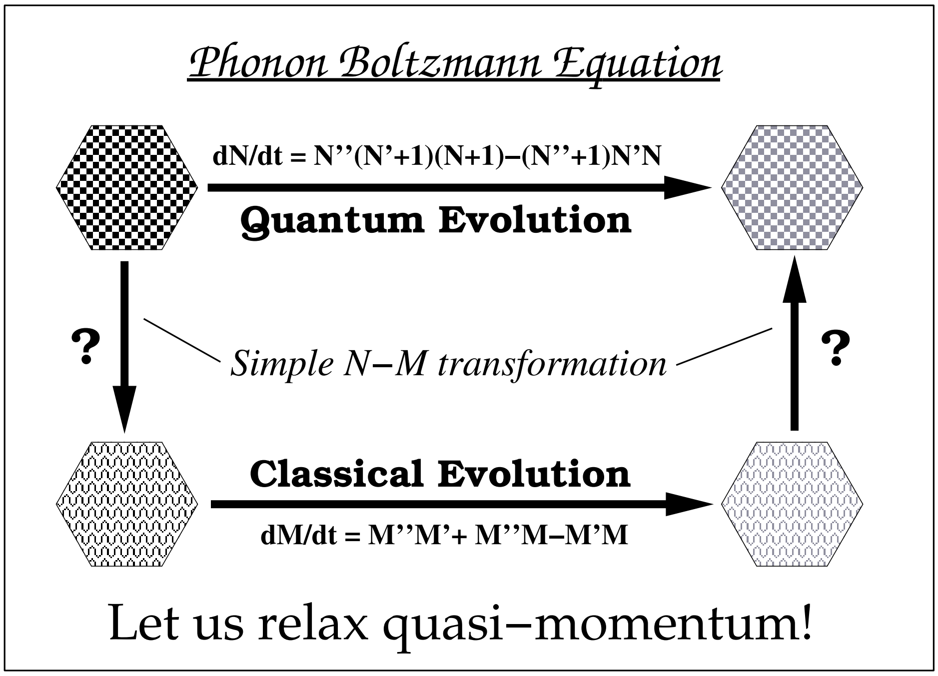

Fig. 6. Schematics of quantum↔classical partial equivalence transformation.

Then (28) becomes, after multiplying both sides by $\hbar$,

$$\frac{\partial\langle\hbar N\rangle}{\partial t} = \Big\langle(\hbar N'')(\hbar N') + (\hbar N'')(\hbar N) + \hbar^2 N'' - (\hbar N')(\hbar N)\Big\rangle\,\delta(\omega'' - \omega - \omega') + ... \tag{31}$$

Thus in the classical limit the third term $\hbar^2 N''$ vanishes and one obtains

$$\frac{\partial\langle M\rangle}{\partial t} = \langle M''M' + M''M - M'M\rangle\,\delta(\omega'' - \omega - \omega') + ..., \tag{32}$$

where $M \equiv E/\omega$ can be related to the classical vibrational amplitude. Eqn (32) is then the Boltzmann equation of a fictitious classical vibrational system, which MD simulation realizes in full. One can easily check that the necessary and sufficient condition for RHS of (32) to vanish is

$$E = \text{const} \equiv k_B T, \quad M = \frac{k_B T}{\omega}, \tag{33}$$

re-confirming the classical equi-partition theorem.

Since we have (32) at our **full** disposal (through MD), can we learn something about the **real** equation (25) by studying a fictitious classical MD system? More specifically, we need an equivalence transformation between N and M that guarantees the evolution of certain properties, in this case $\mathbf{V}$, is exactly reproduced by a classical simulation, at least *for a short while*. The idea is sketched in Fig. 6.

Despite their seemingly small differences, (28) and (32) are in fact quite different, because N at low temperatures is exponentially *small*. As a consequence of keeping the third term N'', the quantum (28) has

$$N_{\mathbf{k}j} = \frac{1}{e^{\hbar\omega_{\mathbf{k}j}/k_BT} - 1} \tag{34}$$

as its zero-mode, while the classical (32) has

$$M_{\mathbf{k}j} = \frac{k_BT}{\omega} \tag{35}$$

as its zero-mode (see Fig. 2). A complete one-to-one mapping between (28) evolution and (32) evolution seems impossible.

However, let us just think about what it would take to get there anyway, keeping in mind the physical picture of phonon scattering. Phonons scatter because of potential nonlinearities. How much potential nonlinearity an atom sees clearly depend on how far it leaves its origin, or $\langle \Delta x^2 \rangle$, which both *classically* and *quantum mechanically* can be shown to be related to the total vibrational energy as

$$\langle \Delta x^2 \rangle = \frac{E}{m\omega^2}. \tag{36}$$

The harmonic approximation would be very good if $\langle \Delta x^2 \rangle$ is very small, hence phonons collide less frequently and the thermal conductivity is high, or vice versa. That is why $T \downarrow$, $\kappa \uparrow$. However, there is a clear distinction between quantum phonon total energy and classical phonon total energy at a given T, as shown in Fig. 2. The most extreme case is $T = 0$K: a classical vibrational system would just sit at the potential well bottom, and any infinitesimal excitation leads to purely harmonic oscillations; but a quantum phonon at $T = 0$K still has $k_B T/2$ total energy, *still* has a non-negligible $\langle \Delta x^2 \rangle$, and so is *still* sampling potential nonlinearities. Thus we see that the only chance we have to mimic the quantum behavior is to let the classical phonons having the same total energy as its corresponding quantum phonon; otherwise a quantum phonon will be sampling parts of the interatomic potential where the classical phonon does not have enough energy to access; and then how could it reproduce the thermal conductivity correctly!

This is not a brand-new idea. Lee *et al*'s temperature re-scaling scheme is an attempt to treat the above problem. However, they equate the total energy of a phonon *system* instead of individual phonons, with the equi-partition theorem still holding internally in the MD simulation. One can understand that this definitely will lead to wrong thermal conductivity at low T, as indeed we discovered. The entire fact about the role of U-process and the existence of phonon hydrodynamics depends on the highly unequal distribution of "wealth" in the BZ "population", not the "total wealth".

But, we just showed that the zero-mode of (32) can only be $E = k_B T$, so one cannot have $(N_{BE}(\omega) + 1/2)\hbar\omega$ as the *equilibrium* energy distribution in *any* classical simulation. Does it mean that we have met the dead-end?

The answer is no: it is OK to use a non-equilibrium distribution as the *initial condition* of a classical MD simulation as long as one is concerned with the correct properties, and only for a short time. Fortunately I can prove that for $\mathbf{V}$ using (28) and (32).

Let the NM partial-equivalence transformation be

$$M = \alpha(\tilde{N} + \frac{1}{2})\hbar, \tag{37}$$

where $\hbar$ is the Planck constant of our quantum world and α is a constant. Plug this into (32), we get, after dividing both sides by $\alpha^2\hbar$,

$$
\begin{aligned}
&\frac{\partial\langle\tilde{N}\rangle}{\partial(\alpha t)} \\
&= \hbar\left\langle(\tilde{N}''+\frac{1}{2})(\tilde{N}'+\frac{1}{2})+(\tilde{N}''+\frac{1}{2})(\tilde{N}+\frac{1}{2})-(\tilde{N}'+\frac{1}{2})(\tilde{N}+\frac{1}{2})\right\rangle\delta(\omega''-\omega-\omega')+\ldots \\
&= \hbar\left\langle\tilde{N}''\tilde{N}'+\frac{\tilde{N}''}{2}+\frac{\tilde{N}'}{2}+\frac{1}{4}+\tilde{N}''\tilde{N}+\frac{\tilde{N}''}{2}+\frac{\tilde{N}}{2}+\frac{1}{4}-\tilde{N}'\tilde{N}-\frac{\tilde{N}'}{2}-\frac{\tilde{N}}{2}-\frac{1}{4}\right\rangle+\ldots \\
&= \hbar\left\langle\tilde{N}''\tilde{N}'+\tilde{N}''\tilde{N}+\tilde{N}''-\tilde{N}'\tilde{N}+\frac{1}{4}\right\rangle\delta(\omega''-\omega-\omega')+\ldots \qquad (38)
\end{aligned}
$$

For the moment let $\alpha = 1$. Comparing (38) with (28), we see that we recover back the lost N'' term, which is the critical difference between the classical (32) and quantum (28), and N is much greater than the N^2 terms at low temperatures! But we also get an additional $1/4$ factor; so we cannot achieve complete victory in this mapping, since $\tilde{N}$ still have a different time-evolution than N in (32).

However since it is a constant, the $1/4$ term does not contribute to the evolution of $\mathbf{V}$ in the short time-window when $\tilde{N} \approx N$, because $\mathbf{V}$ is an odd moment of the occupation distribution. The way to see it is to imagine $\tilde{N} = 0$ for all $\mathbf{k}$'s in (38), meaning initially in a classical simulation we only give each vibrational mode its zero-point energy $\hbar\omega/2$. Then only the $1/4$ term operates in (38); but clearly the "center of mass" of the distribution will not change with time but stays at $\mathbf{V} = 0$![15] What does happen due to the $1/4$ term is that the quantum zero-point energy distribution $E_{\mathbf{k}j} = \hbar\omega_{\mathbf{k}j}/2$ will be transformed into a classical profile $E_{\mathbf{k}j} = k_B T'$ as the simulation is carried out for a long enough time, i.e., the shape of E will change from a bowl to a flat surface, but the "center of mass" will not change because of it. What does relax the "center of mass" is the Umklapp part of the

[15] This can be shown rigorously using the time-reversal symmetry of $\beta_{jj'j''}(\mathbf{k},\mathbf{k}',\mathbf{k}'')$, but it suffices here to just see the picture.

$\tilde{N}''\tilde{N}' + \tilde{N}''\tilde{N} + \tilde{N}'' - \tilde{N}'\tilde{N}$ terms in (38), whose rate the classical simulation reproduces exactly, as long as $\tilde{N}$ stays close to N; in this case N is of the known form $N_{BE}(\omega - \mathbf{k}\cdot\mathbf{V})$, due to the *simplifications* of phonon hydrodynamics.

Thus, eqns. (17), (20), (21), (22) and

$$E_{\mathbf{k}j}(0) = \Big(N_{BE}(\omega_{\mathbf{k}j} - \mathbf{k}\cdot\mathbf{V}) + 1/2\Big)\,\hbar\omega_{\mathbf{k}j} \tag{39}$$

specifies an MD scheme to calculate the low-temperature lattice thermal conductivity. Detailed prescriptions are,

(i) Evaluate the force constants numerically or analytically at the equilibrium volume of the crystal structure at a given temperature.

(ii) Choose an MD simulation box with PBC and find out the $\mathbf{k}$-points of the unit cell that are compatible with the supercell PBC. Identify those on the BZ boundary which needs special treatment.

(iii) Assemble the dynamical matrix $\mathbf{D}(\mathbf{k})$ for all $\mathbf{k}$'s and diagonalize them. Save $\omega_{\mathbf{k}j}$ and eigenvectors $\mathbf{e}_{\mathbf{k}j}$. Calculate the group velocities $\mathbf{v}_G$ using Hellman-Feymann theorem.

(iv) Calculate S and p using (20) and (21). Also, calculate the total zero-point energy, Debye-Waller factor $\langle \Delta x^2\rangle$, C_V. Estimate the sound speeds; infer the Debye temperature and shear/bulk moduli.

(v) Choose an initial $\mathbf{V}(0)$, usually a small percentage of the sound speed. Its direction can be random if κ is isotropic.

(vi) Assign particle $\{\mathbf{x}_i,\ \mathbf{p}_i\}$ in the supercell all vibrational modes with energy (39) and random phases. BZ boundary $\mathbf{k}$-points are treated as $1/2\ \mathbf{k}$ and $1/2\ -\mathbf{k}$.

(vii) Do NEV MD simulation on the particle system, in essence letting the phonons collide according to (38), and $\mathbf{V}$ is relaxed by the U-processes among them.

(viii) At intervals, do normal mode analysis on $\{\mathbf{x}_i,\ \mathbf{p}_i\}$ to get $N_{\mathbf{k}j}(t)$. Calculate $\mathbf{P}(t)$ using (22).

(ix) Monitor $\langle N_{\mathbf{k}j}(t)\rangle$. When they change *significantly* from the assigned distribution, stop the MD simulation. Choose a new $\mathbf{V}(0)$ and repeat the experiment. The lower T is, the shorter time-window one has, and the more experiments one needs to do in order to get rid of the fluctuations [16].

(x) Least-square fit $\langle \mathbf{P}(t)\rangle$ to determine the quasi-momentum relaxation time constant τ_κ and its statistical error. Use hydrodynamic formula (19) to evaluate κ.

Now, let us consider $\alpha \neq 1$ in (37), which seems devoid of any "physical" meaning. But the algebra carries through and one can easily show that, instead of (17),

$$\frac{d\mathbf{P}}{d(\alpha t)} + \frac{TS^2}{\kappa p}\mathbf{P} = 0, \tag{40}$$

i.e., the relaxation of $\mathbf{P}$ in the classical system is *accelerated* by a factor of α in comparison with the quantum system, since we pump more energy into it. α can be thought of as the scaling factor between "quantum time" and "classical time", which exploits the x^3 scaling of the leading cubic nonlinearity. This reminds us the fictitious nature of our MD "lab", whose only connection with the quantum reality at low T is through the phonon Boltzmann equation. The partial-equivalence transformation (37), $\alpha = 1$ or not, is only a physically inspired **algebraic** transformation, which should not be attached too much meaning or to be used to predict other properties.

Depending on whether there is "too little" or "too much" nonlinearity in the system at a given temperature, $\alpha > 1$ or $\alpha < 1$ can be used to enhance the computational efficiency, leveraging between quantum real time and classical simulation time.

[16] After all, the Boltzmann equation is a coarse-grained description, and is for $\langle N_{\mathbf{k}j}(t)\rangle$ instead of $N_{\mathbf{k}j}(t)$.

As one can see, the scheme is already of considerable complexity; yet compared with explicitly tabulating $\beta_{jj'j''}(\mathbf{k}, \mathbf{k}', \mathbf{k}'')$'s and solving the integral equation (25), it is still much simpler, both conceptually and computationally. As long as it can yield satisfactory results with the same order of computational cost as a) the explicit Boltzmann equation solver, b) the Green-Kubo method, this technique could prove superior since it can be fully automated. The current program only requires the user to provide interatomic force routine.

5 Successful Extension to High Temperature

At high temperature, the N-process no longer dominates over the U-process, and one can not expect the steady-state phonon distribution to be in drifted equilibrium form, (18). The phonons behave more "individualisticly", each is scattered more "independently" or "stochastically" rather than as a collective whole specified by a single parameter $\mathbf{V}$. This is the basis of the relaxation time approximation

$$\left.\frac{\partial\langle N_{\mathbf{k}j}\rangle}{\partial t}\right|_{collision} = I_N[N] + I_U[N] \approx -\frac{\Delta N_{\mathbf{k}j}}{\tau_{\mathbf{k}j}}, \tag{41}$$

from which the well-known formula

$$\kappa = \sum_{\mathbf{k}j} C_V(\mathbf{k}j)|\mathbf{v}_G(\mathbf{k}j)|^2\tau_{\mathbf{k}j}/3 \tag{42}$$

is derived.

Let me rewrite (42) as

$$\kappa = W\bar{\tau}, \tag{43}$$

where

$$W \equiv \sum_{\mathbf{k}j} C_V(\mathbf{k}j)|\mathbf{v}_G(\mathbf{k}j)|^2/3, \tag{44}$$

and

$$\bar{\tau} \equiv \left(\sum_{\mathbf{k}j} C_V(\mathbf{k}j)|\mathbf{v}_G(\mathbf{k}j)|^2\tau_{\mathbf{k}j}\right) \Big/ \left(\sum_{\mathbf{k}j} C_V(\mathbf{k}j)|\mathbf{v}_G(\mathbf{k}j)|^2\right) \tag{45}$$

is a "properly averaged" relaxation time. Although (43) is essentially a high temperature formula, it is nevertheless interesting to compare with (19), since they are quite alike in that both are some prefactor multiplied by a relaxation time. As TS^2/p must have the same dimension as W, how do they compare with each other in magnitude at high and low T?

Consider the entropy density S first. Since

$$C_V \equiv T\frac{\partial S}{\partial T}, \tag{46}$$

and it is well-known that

$$C_V \propto T^3 \ \text{ as } \ T \to 0, \tag{47}$$

there must be

$$S \to \frac{C_V}{3} \ \text{ at } \ T \to 0. \tag{48}$$

Also, since C_V approaches a constant at high T, there is

$$S \sim \log T \ \text{ at } \ T \to \infty. \tag{49}$$

How about the phonon "mass density" p? For systems with isotropic κ,

$$p \equiv \frac{\hbar^2}{3\Omega k_B T}\sum_{\mathbf{k}j} |\mathbf{k}|^2 N_{\mathbf{k}j}(1+N_{\mathbf{k}j}).$$

At low enough T, $N_{\mathbf{k}j}$ for finite $|\mathbf{k}|$ is exponentially small, as illustrated in Fig. 4, and only those modes within the "thermal activation circle" are excited. They are long-wave acoustic phonons in the limit, which then have approximately linear dispersion with $\mathbf{k}$ [17],

$$\omega_{\mathbf{k}j} \simeq c|\mathbf{k}|, \quad |\mathbf{v}_G| \equiv \left|\frac{d\omega_{\mathbf{k}j}}{d\mathbf{k}}\right| \simeq c, \tag{50}$$

and they are the main contributors to p. Thus

$$p \simeq \frac{\hbar^2}{3\Omega k_B T c^2} \sum_{\mathbf{k}j} \omega_{\mathbf{k}j}^2 N_{\mathbf{k}j}(1+N_{\mathbf{k}j}). \tag{51}$$

But RHS of (51) is proportional to C_V! In fact,

$$C_V \equiv \frac{1}{\Omega} \sum_{\mathbf{k}j} \frac{\exp(\frac{\hbar\omega_{\mathbf{k}j}}{k_B T})\frac{\hbar^2\omega_{\mathbf{k}j}^2}{k_B T^2}}{\left(\exp(\frac{\hbar\omega_{\mathbf{k}j}}{k_B T})-1\right)^2} = \frac{\hbar^2}{\Omega k_B T^2} \sum_{\mathbf{k}j} \omega_{\mathbf{k}j}^2 N_{\mathbf{k}j}(1+N_{\mathbf{k}j}). \tag{52}$$

So,

$$p \simeq \frac{TC_V}{3c^2} \tag{53}$$

in the low temperature limit, which, combined with (48), gives

$$\frac{TS^2}{p} \to \frac{T(C_V/3)^2}{(TC_V/3c^2)} = \frac{C_V c^2}{3} \simeq W, \quad \text{as } T \to 0, \tag{54}$$

without missing a single coefficient!

So there is a remarkable symmetry between (19) and (43) in that the prefactors before the relaxation time, TS^2/p and W, approach each other asymptotically at low T. This prediction had been explicitly verified using the definitions of TS^2/p and W, and the numerically calculated $\omega_{\mathbf{k}j}$ and $\mathbf{v}_G(\mathbf{k}j)$'s of Si perfect crystal with $11\times 11\times 11$ $\mathbf{k}$-sampling (2662 atom MD supercell), and the agreement is within 10% below 70K.

[17] Actually c should be a matrix, with $\det|\omega^2\mathbf{I} - \mathbf{k}\underline{\underline{c}}^2\mathbf{k}| = 0$, but that subtlety has a negligible effect.

Now let us think about why and how we should extend the previous methodology to high temperature. It comes rather as a necessity than as an additional improvement, since TS^2/p rises too quickly even at a moderate T. As I found out, the ideal phonon hydrodynamics regime is possibly below 100K for Si, which is too narrow for our method to be practically useful. The vast intermediate region between 100 and 400K are of mixed character, neither purely low T (hydrodynamics) or high T (classical) behavior. There, the prefactor TS^2/p is already too large for (19) to be correct, and even the temperature dependence becomes wrong. One can show that TS^2/p blows up as $(\log T)^2$ while W approaches a constant at $T \to \infty$, though they agree with each other asymptotically at low T, as T^3. This information, combined with the fact that (43) is a high temperature formula, suggest that we use a modified formula

$$\kappa = W\tau_\kappa, \tag{55}$$

that is of considerable validity in both low and high temperature regime and smoothly link the two behaviors. Here τ_κ is the quasi-momentum relaxation time constant defined by (17) in an MD relaxation experiment, except now we *also* do it at high temperature. (55) is equivalent to (19) at low T since W agrees with TS^2/p then, but it also makes sense at high T because

$$\tau_\kappa \sim \tau_U \simeq \tau_N \simeq \bar{\tau} \ \text{ at high } \ T, \tag{56}$$

where $\bar{\tau}$ is the "properly averaged" phonon relaxation time in (45). The rationale at high temperature is that since individual phonon relaxation times $\tau_{\mathbf{k}j}$ are probably too many to be calculable, and we only need a "proper average" of them anyway, why don't we just pick a collective mode whose relaxation rate at high T reflects the average rate of phonon relaxations? And what collective mode is simpler than a displaced center of mass? That is, we acknowledge the $\mathbf{V}(t)$ relaxation suffers a mechanism change from low T to high T, where at

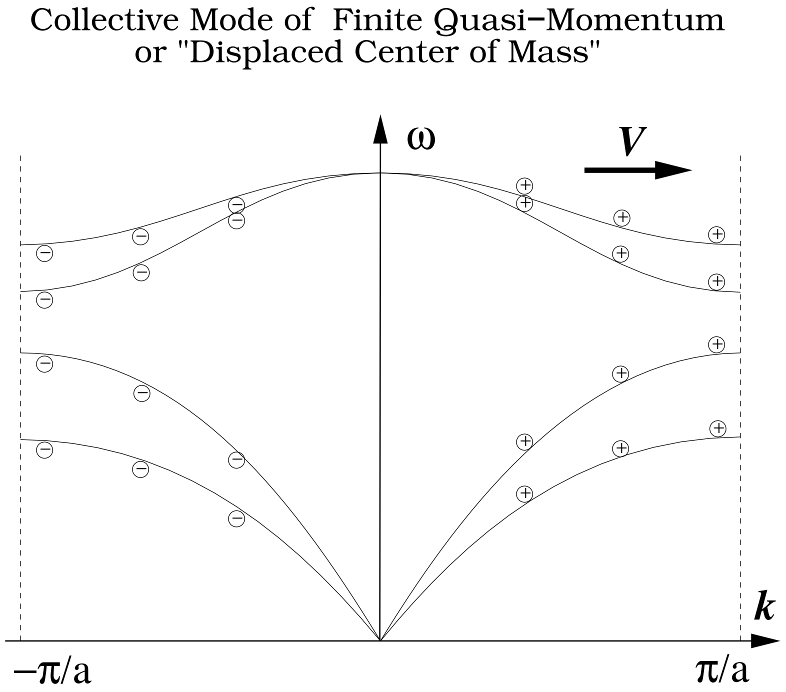

Fig. 7. Schematics of a collective deformation mode (18) in phonon occupation. $\pm$ means increase or decrease from its global equilibrium distribution.

low T $N_{\mathbf{k}j}$ stays close to drifted-equilibrium form (18) and $\mathbf{V}(t)$ relaxation is a real physical process described by phonon hydrodynamics; but at high T everything is chaotic and $\mathbf{V}(t)$ relaxation does not even describe a real process because the steady-state $N_{\mathbf{k}j}$ distribution is no longer (18), we nevertheless pick a deformation mode of the equilibrium distribution which is the most straightforward and do a fictitious relaxation of it in an MD simulation. It is like in order to determine the "average" crawl speed of ants, we put $10,000$ of them in a bucket, left side slightly more than the right, and measure how the surface levels off. Because (42) is itself only an approximation, and $\tau_N \sim \tau_U$, (55) does not do gross injustice to (42), and we expect it to provide a good estimate at high T. In fact it works perfectly for Si perfect crystal up to 1200K, using the Tersoff potential.

Once we have both limits right, the intermediate temperature region should be satisfactory because (55) is smooth.