On-line Supplemental Material for Phonon thermal conductivity by non-local non-equilibrium molecular dynamics

Philip B. Allen*
Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794-3800, USA

Yerong Li†
Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794-3800, USA and
Department of Intensive Instruction, Nanjing University, Nanjing 210093, China

(Dated: November 30, 2016)

This supplement contains details of the FAT algorithm used to find the best value of $\pm\Delta\vec{v}$ to use in the heating algorithm. It also contains details of the analytic integrations shown in Appendix A.

I. HEAT EXCHANGE ALGORITHM

The Müller-Plathe recipe is: find the hottest atom in the cold ($\ell = N_S/2$) slab, and the coldest atom in the hot ($\ell = 0$) slab. Interchange their velocities. Energy and momentum are both conserved, and the system is driven from equilibrium in a way that must be monitored. Cao and Li[1] among others, have suggested modified algorithms of this type. Furtado, Abreu, and Tavares[2] (FAT) devised a gentler and more versatile method. An earlier version of the present paper, which was was posted on the arXiv[3], derived the same procedure. We call it the FAT algorithm, because Furtado *et al.* discovered it simultaneously and published it first.

In our computation, driving is done by spatially periodic injection ($\dot{e}(\ell) \propto \cos(2\pi\ell/N_s)$) and simultaneous removal of heat. Examine a slab ℓ (with $0 \le \ell < N_S/4$), and its conjugate slab $N_S/2 - \ell$. The former is "hotter" than the latter because $\dot{e}(\ell) > 0 > \dot{e}(N_S/2 - \ell) = -\dot{e}(\ell)$. Find the coldest atom (meaning least kinetic energy) of all atoms of mass m_i in the hotter slab, denoting its velocity as $\vec{v}_C$. Find the hottest atom of the same mass in the colder slab, denoting its velocity $\vec{v}_H$. Given the large fluctuations of the Maxwell-Boltzmann ensemble, it is certain that $v_H^2 > v_C^2$. Choose an appropriate velocity $\vec{w}$ and add it to the velocity $\vec{v}_C$ and subtract it from $\vec{v}_H$:

$$\begin{aligned} \vec{v}_H &\to \vec{v}_H - \vec{w} \\ \vec{v}_C &\to \vec{v}_C + \vec{w} \end{aligned} \tag{1}$$

The same operation should be done for the pair of slabs $-\ell$ and $\ell - N_S/2$. All slabs can be done simultaneously, or different random times can be used for different slabs.

There are three criteria for an appropriate $\vec{w}$, which uniquely fix the desired choice. (i) The cold atom's kinetic energy should increase by Δ, an energy that can be specified in advance as $(\dot{e}\Omega_S\tau)\cos(2\pi\ell/N_S)$, where τ is the average time interval between random interventions, and Ω_S is the volume of a slab. (ii) The hot atom's kinetic energy should decrease by Δ. Then both momentum and energy are conserved. Heating has the desired sinusoidal form, with $\dot{e}$ chosen not too different from $k_BT/\Omega_S\tau$. Trial calculations should test for the best choices of $\dot{e}$ and τ. (iii) There is still a one-dimensional family of vectors $\vec{w}$; from these, choose the smallest $|\vec{w}|$, which gives the least impulse to the affected atoms. Except for the sinusoidal spatial variation of Δ, these are exactly the criteria chosen by Furtado *et al.*. Their implementation of these criteria is also exactly like ours. We present our derivation here for the convenience of the reader.

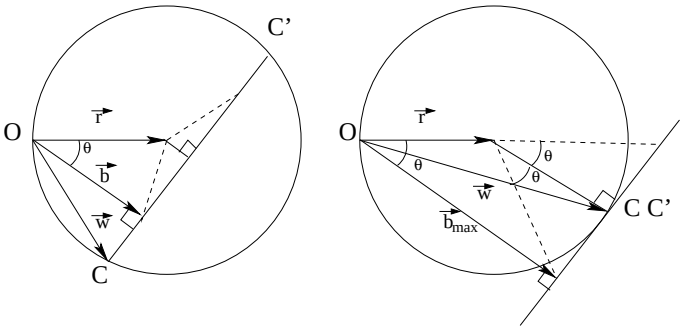

FIG. 1. Geometric construction for finding the smoothest velocity change $\vec{w}$ of the coldest atoms (with velocity $\vec{v}_C$ in the hotter region and the hottest atoms (with velocity $\vec{v}_H$ in the colder region. Both figures represent a sphere of radius $\vec{r} = (\vec{v}_C - \vec{v}_H)/2$. The plane perpendicular to $\vec{b}$, intersects the sphere in a circle, which is the locus of solutions $\vec{w}$ obeying energy and momentum conservation rules. The points C and C' (in the $\vec{r}$–$\vec{b}$ plane) give the solutions with least and greatest impulse. The right-hand version shows the largest vector $\vec{b}$ which allows solutions for $\vec{w}$. The minimum and maximum impulse solutions have merged to a point.

The energy shift criteria (i) and (ii) give equations $-2\vec{v}_H \cdot \vec{w} + w^2 = -2\Delta/m \equiv -\delta$, and $2\vec{v}_C \cdot \vec{w} + w^2 = +\delta$. Adding and subtracting these equations give

$$\begin{aligned} \delta &= (\vec{v}_H + \vec{v}_C) \cdot \vec{w} \\ w^2 &= (\vec{v}_H - \vec{v}_C) \cdot \vec{w}, \end{aligned} \tag{2}$$

a linear and a quadratic equation for $\vec{w}$. These have a simple geometric interpretation shown in Fig. 1. The first equation restricts the projection of $\vec{w}$ along the vector $\vec{v}_H + \vec{v}_C$. Geometrically, this means that $\vec{w}$ lies on the plane (shown by C, C' in Fig. 1) perpendicular to the vector $\vec{b} \equiv \delta(\vec{v}_C + \vec{v}_H)/|\vec{v}_C + \vec{v}_H|^2$, where the origin of $\vec{w}$ coincides with the origin of $\vec{b}$. The second equation re-

stricts $\vec{w}$ to the surface of a sphere of radius $|\vec{v}_H - \vec{v}_C|/2$, centered at the end of the vector $\vec{r} \equiv (\vec{v}_H - \vec{v}_C)/2$, whose origin also coincides with the origin of $\vec{w}$. The sphere and the plane intersect on a circle, indicated by C, C' in Fig. 1. This circle is the one-dimensional family of solutions $\vec{w}$ satisfying Eqs.(2). It is also clear from the geometry that the shortest vector $\vec{w}$ (the one that satisfies criterion (iii)) is the one shown, from O to C. This lies in the same plane as the two known vectors $\vec{r}$ and $\vec{b}$ (also the same plane as $\vec{v}_H$ and $\vec{v}_C$). Therefore

$$\begin{aligned} \vec{w} &= \alpha\vec{r} + \beta\vec{b} \\ \vec{r} &= (\vec{v}_H - \vec{v}_C)/2 \\ \vec{b} &= \frac{\delta(\vec{v}_H + \vec{v}_C)}{|\vec{v}_H + \vec{v}_C|^2}. \end{aligned} \tag{3}$$

These definitions allow Eqs.(2) to be written as

$$\begin{aligned} b^2 &= \vec{w}\cdot\vec{b} \\ w^2 &= 2\vec{r}\cdot\vec{w}. \end{aligned} \tag{4}$$

The solution for $\vec{w}$ is

$$\begin{aligned} \beta &= 1 - \alpha\frac{\vec{r}\cdot\vec{b}}{b^2} \\ \alpha &= 1 - \sqrt{1-X} \\ X &= \frac{(b^2 - 2\vec{b}\cdot\vec{r})b^2}{b^2r^2 - (\vec{b}\cdot\vec{r})^2} \end{aligned} \tag{5}$$

To derive this, substitute Eq.(3) for $\vec{w}$ in terms of the unknown coefficients α and β into the Eqs.(2). The linear equation is used to find β in terms of α. Eliminating β in favor of α in the quadratic equation gives a quadratic equation for α. The appropriate solution is displayed in Eq.(5). An alternate version directly in terms of the velocities $\vec{v}_H$ and $\vec{v}_C$ is

$$X = (2\Delta/m)\frac{(2\Delta/m) - (v_H^2 - v_C^2)}{v_H^2 v_C^2 - (\vec{v}_H\cdot\vec{v}_C)^2} \tag{6}$$

$$\vec{w} = \frac{\alpha}{2}(\vec{v}_H - \vec{v}_C) + \left[\frac{2\Delta}{m} - \frac{\alpha}{2}(v_H^2 - v_C^2)\right]\frac{\vec{v}_H + \vec{v}_C}{|\vec{v}_H + \vec{v}_C|^2} \tag{7}$$

Notice that X in Eq.(6) has a non-negative denominator that becomes zero in an accidental event where $\vec{v}_H$ and $\vec{v}_C$ are parallel; X is then ill-defined, because no solution exists. An alternate pair of C and H atoms must be chosen. In the simulations reported in subsequent sections, we find that Δ should be chosen small, making the numerator of X in Eq.(6) negative. Thus both X and α are negative, contrary to the version shown in Fig. 1. This does not adversely affect anything.

There is a second solution, $\alpha = 1 + \sqrt{1-X}$, corresponding to the maximum $|\vec{w}|$, designated as C' in Fig. 1. For $|\vec{b}| > b_{\max}$, there are no real solutions. This corresponds to $X > 1$. The condition for the two solutions to coincide is $X = 1$, which agrees with $b_{\max} = r(1 + \cos\theta)$, where θ is the angle between $\vec{b}$ and $\vec{r}$. This can be understood from the right hand part of Fig. 1, illustrating the case where the circle collapses to a point. For reasonable choices of the parameter $m\delta/2 = \Delta$, meaning values smaller than or similar to k_BT/N_S, solutions should always exist.

II. DEBYE-RTA MODEL, ESPECIALLY p=2

Appendix A gives formulas in the Debye-RTA model. Here are details. Equation 13 of ref. 4 is

$$\kappa_{\rm RTA}(q) = \frac{k_B}{\Omega}\sum_Q \frac{v_{Qx}^2}{1/\tau_Q + iqv_{Qx}}. \tag{8}$$

This is the classical limit of the solution of the Boltzmann equation in the relaxation time approximation (RTA). Now make a Debye model, and model the scattering rate as $1/\tau_Q = (1/\tau_D)(Q/Q_D)^p$. Multiplying numerator and denominator by τ_D, and using $x = Q/Q_D$, $\mu = v_x/v = \cos\theta$, and $\lambda = qv$, this generates Eq.(A1),

$$\tilde{\kappa}_p(q) = \frac{9}{2}\kappa_0\int_0^1 dx x^2\int_{-1}^1 d\mu\frac{\mu^2}{x^p + i\lambda\mu}, \tag{9}$$

where $\kappa_0 = Nk_Bv^2\tau/\Omega$. One way to perform the integrations is to do the μ-integral first.

$$\frac{\tilde{\kappa}_p(q)}{\kappa_0} = \frac{9}{\lambda}\int_0^1 dx x^2\left[\frac{x^p}{\lambda} - \left(\frac{x^p}{\lambda}\right)^2\tan^{-1}\left(\frac{\lambda}{x^p}\right)\right]. \tag{10}$$

The most important case is $p = 2$, and also the trickiest to integrate further. Using $u = x^2$, this can be written as

$$\frac{\tilde{\kappa}_2(q)}{\kappa_0} = \frac{9}{2\lambda^2}\int_0^1 du u^{3/2}\left[1 - \frac{u}{\lambda}\cot^{-1}\frac{u}{\lambda}\right]. \tag{11}$$

This uses $\tan^{-1}(1/x) = \cot^{-1}x$. The answer can be written as

$$\frac{\tilde{\kappa}_p(q)}{\kappa_0} = \frac{9}{7\lambda^2}[h(1) - h(0)] \tag{12}$$

where $h(u)$ is

$$\begin{aligned} h(u) &= \frac{7}{2}\int du\left[u^{3/2} - \frac{u^{5/2}}{\lambda}\cot^{-1}\frac{u}{\lambda}\right] \\ &= u^{5/2} + 2\lambda^2u^{1/2} - \frac{u^{7/2}}{\lambda}\cot^{-1}\frac{u}{\lambda} \\ &- \frac{\lambda^{5/2}}{\sqrt{2}}\left[\frac{1}{2}\log\left(\frac{u + \sqrt{2u\lambda} + \lambda}{u - \sqrt{2u\lambda} + \lambda}\right)\right. \\ &\left. + \tan^{-1}\left(\sqrt{2u/\lambda} + 1\right) + \tan^{-1}\left(\sqrt{2u/\lambda} - 1\right)\right] \end{aligned} \tag{13}$$

This gives the result of Eq.(A4).

Going back to Eq.(9), an alternate route that is often simpler is to do the radial (x) integral before the angular (μ) integral. In the tricky $p = 2$ case, this gives

$$\frac{\tilde{\kappa}_2(q)}{\kappa_0} = 9\int_0^1 d\mu\mu^2\left[1 - \frac{\pi}{2}\sqrt{\frac{\lambda\mu}{2}} + \mathcal{R}\mathrm{e}\frac{r}{2}\log\left(\frac{1-r}{1+r}\right)\right], \tag{14}$$

where $r = \sqrt{\lambda\mu}\exp(-i\pi/4)$. By numerical integrations, we have convinced ourselves that both integrals (Eq.(10) and Eq.(14)) give the same result as the fully integrated formula in Eq.(A4). These results are used in Appendix D to confirm the conjecture of Refs. 4 and 5 that MD results, which are likely to conform to the $p = 2$ case, should be extrapolated by plotting $\kappa_{\mathrm{eff}}(L)$ *versus* $\sqrt{(1/L)}$.

* philip.allen@stonybrook.edu
† yerong.li@outlook.com

[1] B.-Y. Cao and Y.-W. Li, The Journal of Chemical Physics **133**, 024106 (2010), URL http://scitation.aip.org/content/aip/journal/jcp/133/2/10.1063/1.3463699.
[2] F. A. Furtado, C. R. A. Abreu, and F. W. Tavares, AIChE Journal **61**, 2881 (2015), ISSN 1547-5905, URL http://dx.doi.org/10.1002/aic.14803.
[3] Y. Li and P. B. Allen, arXiv:1412.3099v1 (2014).
[4] P. B. Allen, Phys. Rev. B **90**, 054301 (2014), URL http://link.aps.org/doi/10.1103/PhysRevB.90.054301.
[5] D. P. Sellan, E. S. Landry, J. E. Turney, A. J. H. McGaughey, and C. H. Amon, Phys. Rev. B **81**, 214305 (2010), URL http://link.aps.org/doi/10.1103/PhysRevB.81.214305.