Calculating the lifetimes of the vibrational normal modes in solids using Jazz

Jazz: a new Python wrapper for LAMMPS

Hengjia Wang
Advisor: *Dr. Murray S. Daw*
Department of Physics and Astro.
Clemson University, SC

Collaborators:
Dr. Yang Gao
Dr. Ted Dickel

Thank DOE grant Award ER 46871

why studying lifetime?

lifetime of a vibrational mode is the entire duration for this mode to diminish.

it describes the thermal and transport properties of materials, such as thermal conductivity.

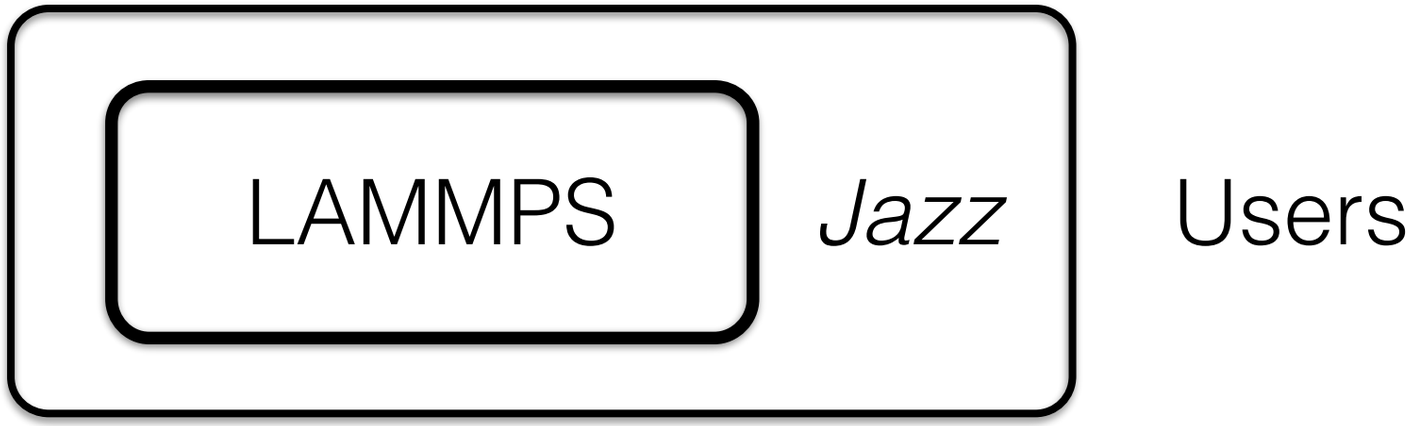
many ways to obtain lifetimes

Experimental: raman spectra, neutron scattering, pump-probe and etc.

Theoretical: boltzmann transport equation + first-principle, lattice dynamics + auto-correlation, etc.

What is *Jazz*?

Jazz is a new python wrapper for LAMMPS to calculate the lifetimes of vibrational normal modes



*Thanks to Dr. Steven Plimpton's Python Interface for LAMMPS

Theory Background (1)

Amplitude $A_k(t)$ of normal mode k

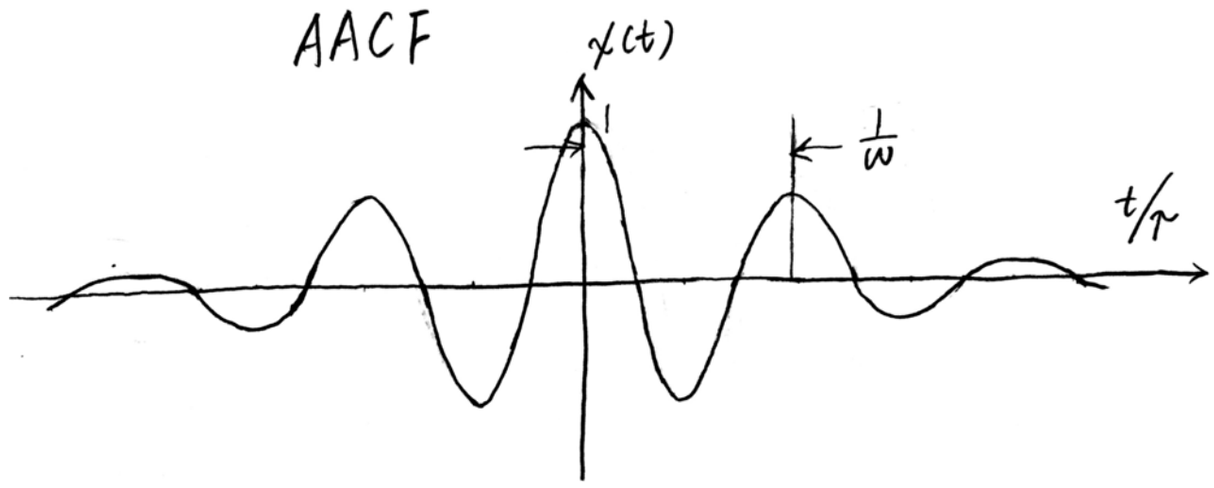
Auto-correlation between values of A at different times

Auto-correlation Function:

$$\chi(t) = \frac{< A(0)A(t) >}{< A^2 >}$$

<—Ensemble Average

* A is the amplitude of a normal mode

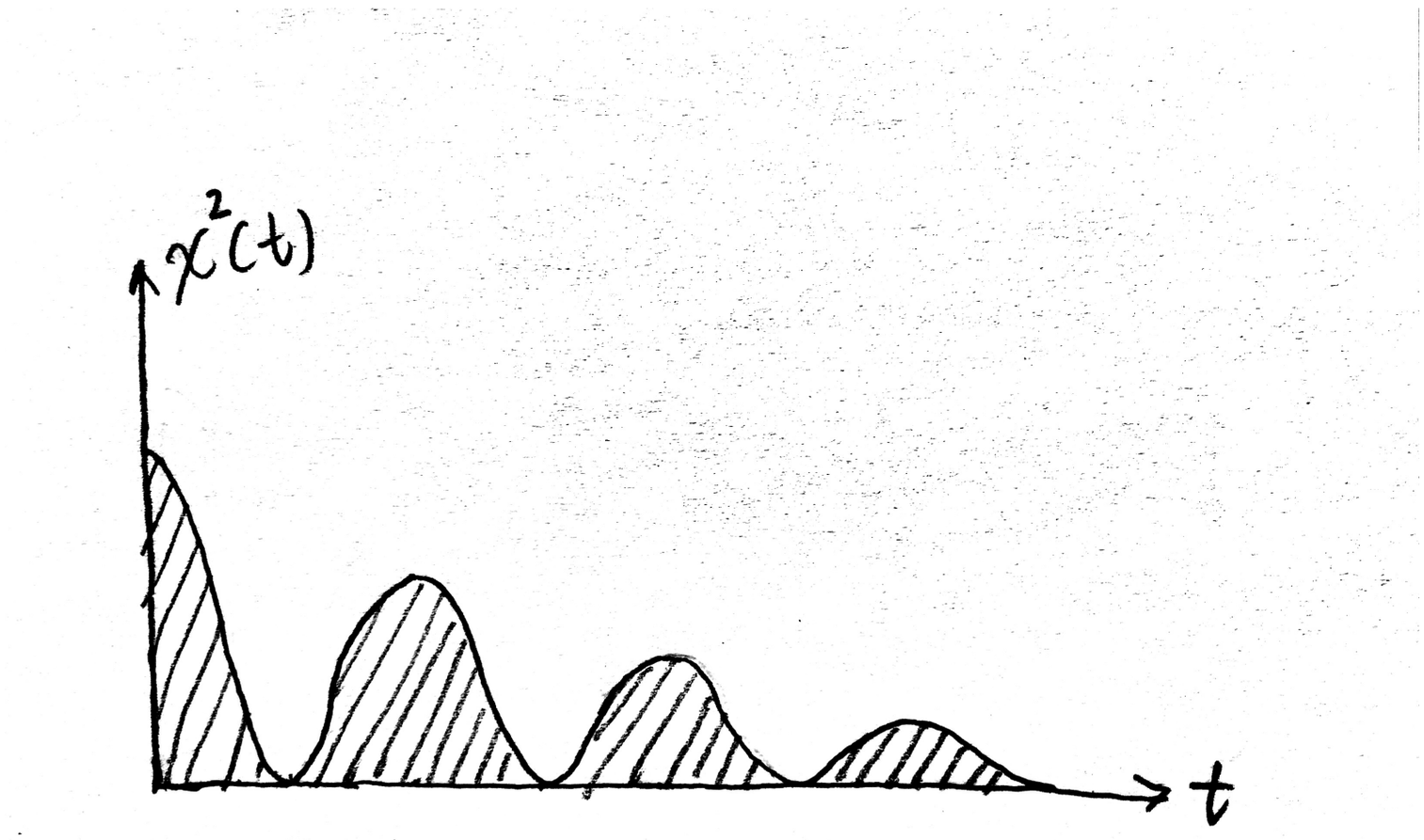


Theory Background (2)

what is *lifetime*?

Gao & Daw proposed to use the area under the square of the auto-correlation function as a measurement of *lifetime*.

$$\tau = \int_{-\infty}^{+\infty} dt\, \chi^2(t)$$



Theory Background (3)

the Liouvillian helps to explain *Jazz*

$$\frac{\partial f}{\partial t} = -i\hat{L}f$$

the Liouvillian operator:

$$\hat{L} = i\{H,\} = i\sum_l \left(\frac{\partial H}{\partial x_l}\frac{\partial}{\partial P_l} - \frac{\partial H}{\partial P_l}\frac{\partial}{\partial x_l}\right)$$

$$A(t) = e^{-it\hat{L}}A(0) \quad \rightarrow \quad \chi(t) = \frac{< Ae^{-it\hat{L}}A >}{< A^2 >}$$

Expressing the moments

Taylor series: $$\chi(t) = 1 - \mu_2 \frac{t^2}{2!} + \mu_4 \frac{t^4}{4!} - \mu_6 \frac{t^6}{6!} + \ldots$$

coefficient: $$\mu_n = \frac{< A \hat{L}^n A >}{< A^2 >}$$

2nd moment:

$$\mu_2 = \frac{< \dot{A}^2 >}{< A^2 >} = \frac{- < \ddot{A} A >}{< A^2 >}$$

4th moment:

$$\mu_4 = \frac{< \ddot{A}^2 >}{< A^2 >}$$

lifetime τ can be expressed as a function of the moments

$$\tau = F(\mu_2, \mu_4, \mu_6, \ldots)$$

Dimensional analysis

$$[\tau] = T$$

$$[\mu_n] = T^{-n}$$

$$[G] = 1$$

$$\tau \cdot \sqrt{\mu_2} = G(\gamma_4, \gamma_6, \ldots)$$

in which $\gamma_n = \dfrac{\mu_n}{(\mu_2)^{n/2}}$ <——Dimensionless

$$\tau \cdot \sqrt{\mu_2} = G(\gamma_4)$$

Gao & Daw ran Molecular Dynamics to determine the G function.(2013)

Jazz doesn't do MD.

Finally,

$$\tau_\kappa = \frac{1.41}{\sqrt{\mu_{2,\kappa}}(\gamma_{4,\kappa} - 1)}$$

$$\tau_{\kappa} = \frac{1.41}{\sqrt{\mu_{2,\kappa}(\gamma_{4,\kappa} - 1)}}$$

Jazz does MC averages for amplitudes and forces for all the modes given the cell and potential. From that Jazz gives frequency and lifetime mode-by-mode.

Moments calculation involving only Monte Carlo is many orders of magnitude faster than MD calculation.

Three primary python modules in Jazz

1. genvecs0: determines normal modes from dynamic matrix;

Dynamic Matrix $\longrightarrow$ $$D_{i\alpha,j\beta} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial u_{i\alpha}\, \partial u_{j\beta}}\Big|_0$$

$$\omega_\kappa^2 \eta_{i\alpha}^{(\kappa)} = \sum_{j\beta} D_{i\alpha,j\beta} \eta_{j\beta}^{(\kappa)}$$

$$Y_{i\alpha,\kappa} = \frac{1}{\sqrt{m_i}} \eta_{i\alpha}^{(\kappa)}$$

$$\underline{u} = \underline{\underline{Y}} \cdot \underline{A} \qquad \Longrightarrow \qquad \underline{F} = \underline{\underline{Y}} \cdot \underline{\ddot{A}}$$

How it's done in *Jazz*

Metropolis MC

$$A_k \rightarrow A_k + \Delta A_k$$

What *LAMMPS* does

u

E F

Y^{-1}

$\ddot{A}_k$

used to make MC decision

2. calcavgs: does the MC averaging, produces the averages;

$$S_{1,k} = \left\langle A_k{}^2 \right\rangle \qquad S_{2,k} = \left\langle A_k \ddot{A}_k \right\rangle \qquad S_{3,k} = \left\langle \ddot{A}_k{}^2 \right\rangle$$

3. calcmoments: combines the averages to calculate moments and lifetime.

$$\mu_{2,k} = \frac{S_{2,k}}{S_{1,k}} \qquad \mu_{4,k} = \frac{S_{3,k}}{S_{1,k}} \qquad \gamma_{4,k} = \frac{S_{3,k} S_{1,k}}{(S_{2,k})^2}$$

A detail that might be interesting

Jazz sets positions in the **numpy array**.

but “extract” command lets LAMMPS return positions/forces in form of **a double ** pointer**.

The copying is slow.

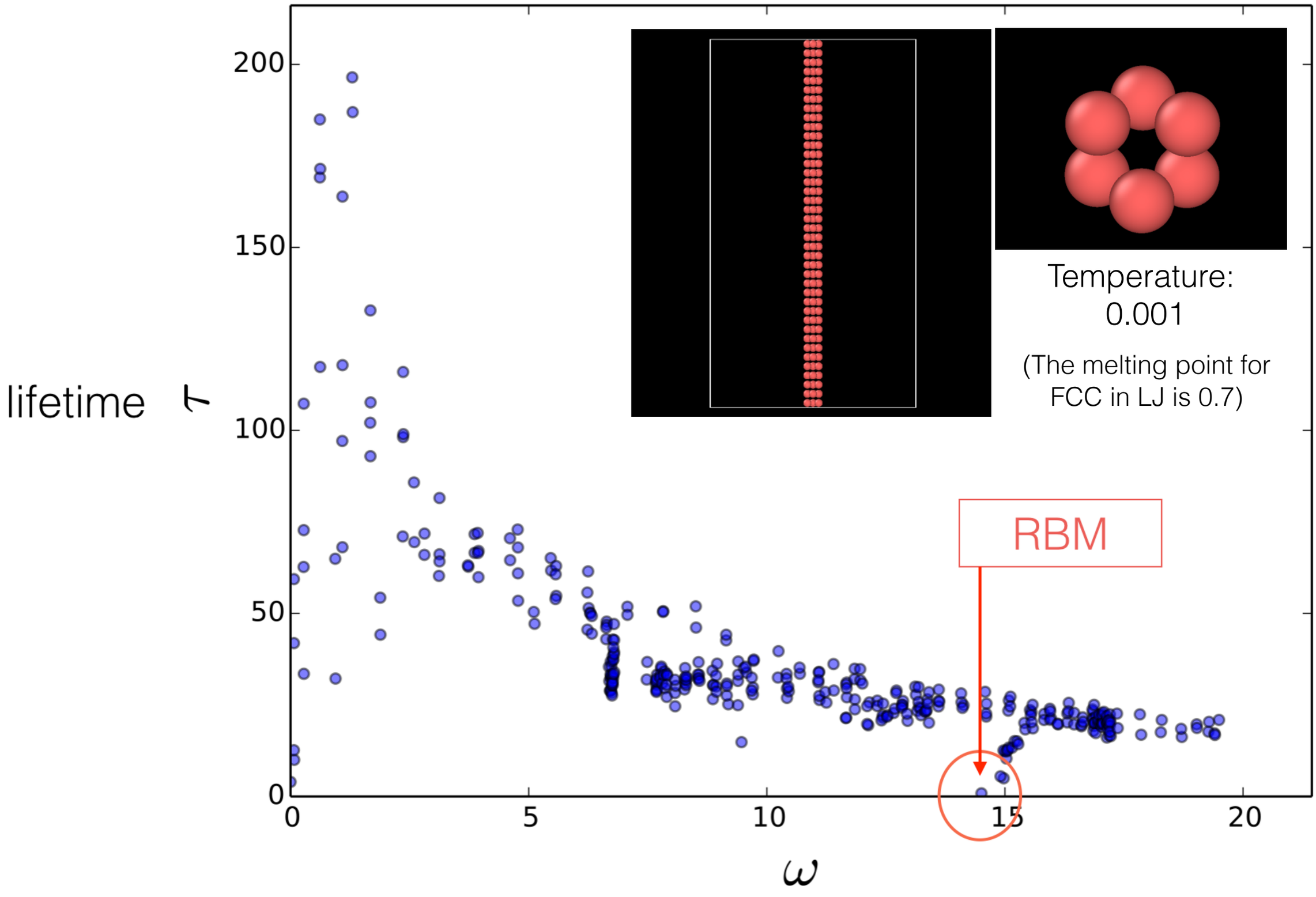
To speed it up, we modified src/atom.cpp extract() by adding two lines to extract “xp”/ “fp” as &x[0][0] / &f[0][0] instead of “x”/“f” as double **.

```
if (strcmp(name,"xp") == 0) return (void *) &x[0][0] ;   /* added by m. s. daw on 29 may 2015 */
if (strcmp(name,"fp") == 0) return (void *) &f[0][0] ;   /* added by m. s. daw on 29 may 2015 */
```

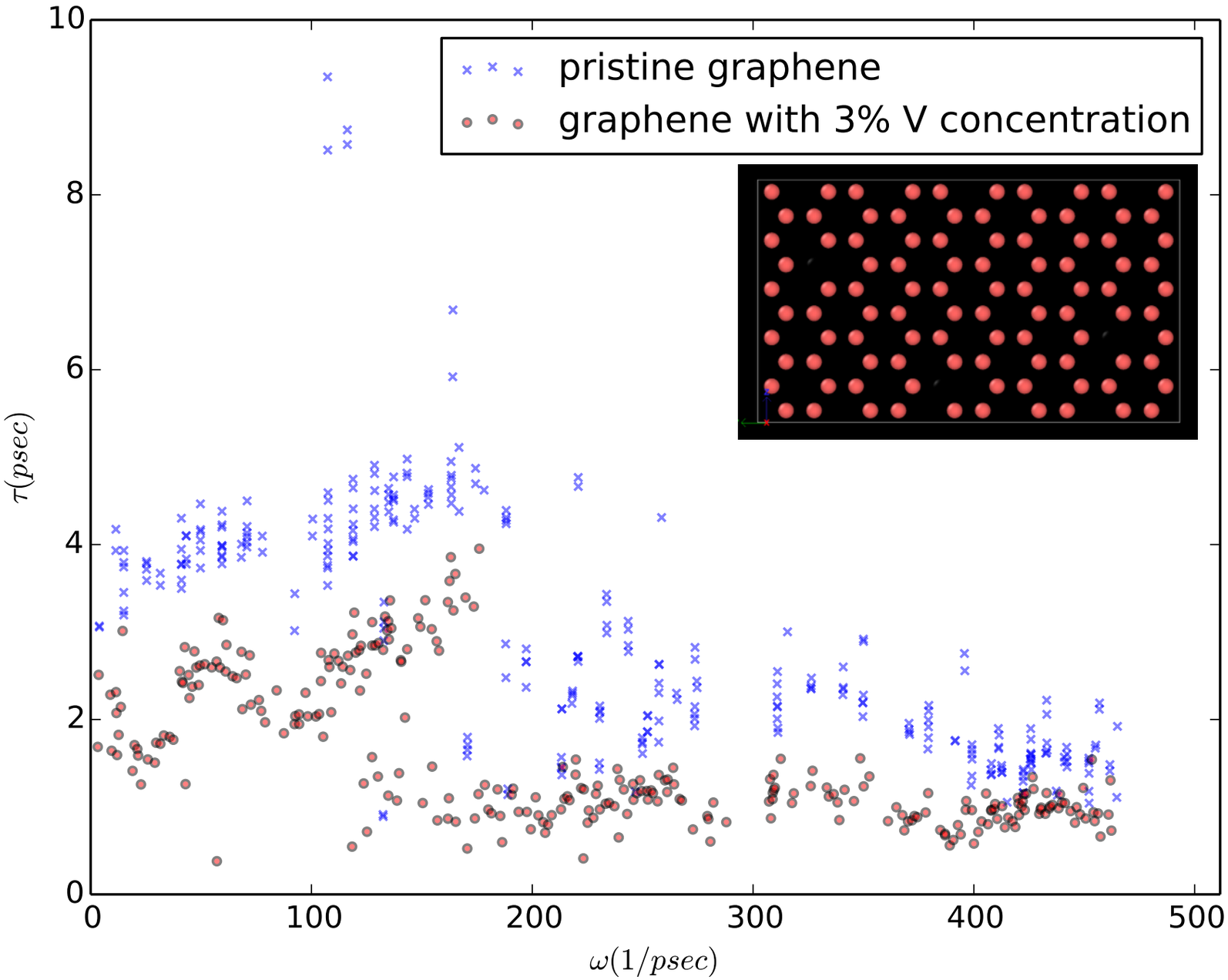
It makes the calculation ~3 times faster!

For more information, see ctypeslib in numpy

Example1: Radial Breathing Mode of simple nanowire with LJ



Example2: comparison of modes of pristine and defected graphene



# of atoms in the cell: 100

Temp : 0.002

NMCsteps: 10^7

The calculations cost ~65 minutes on a laptop

We are working on making connection to experimental Raman graphene results.

Future Work

- Parallelization of Jazz
- First Principles (“Socorro”?)

Jazz (public version) is available at

http://sourceforge.net/projects/jazzforlammps/

manual and examples included

Thank you!

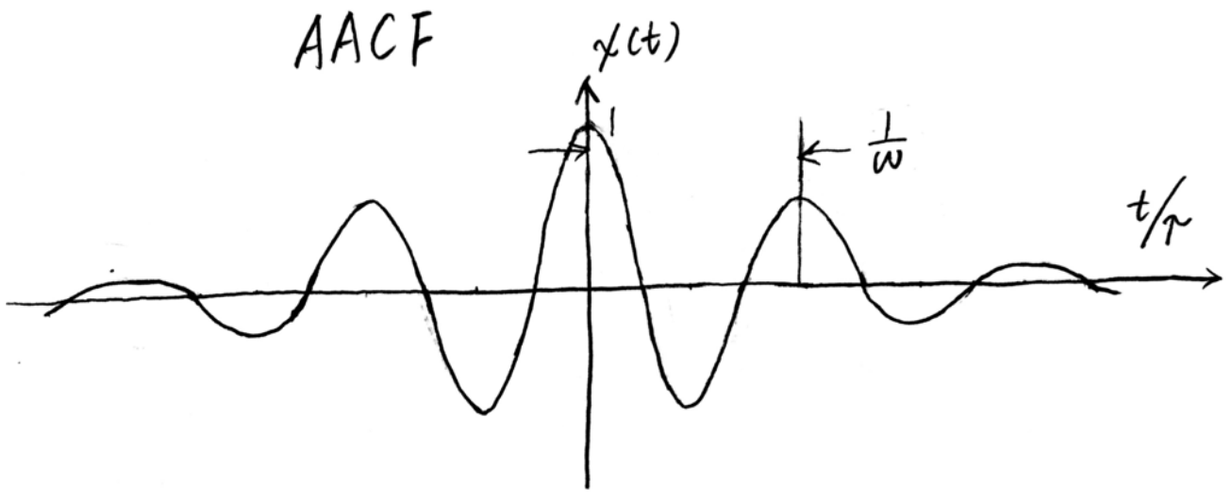
Questions:

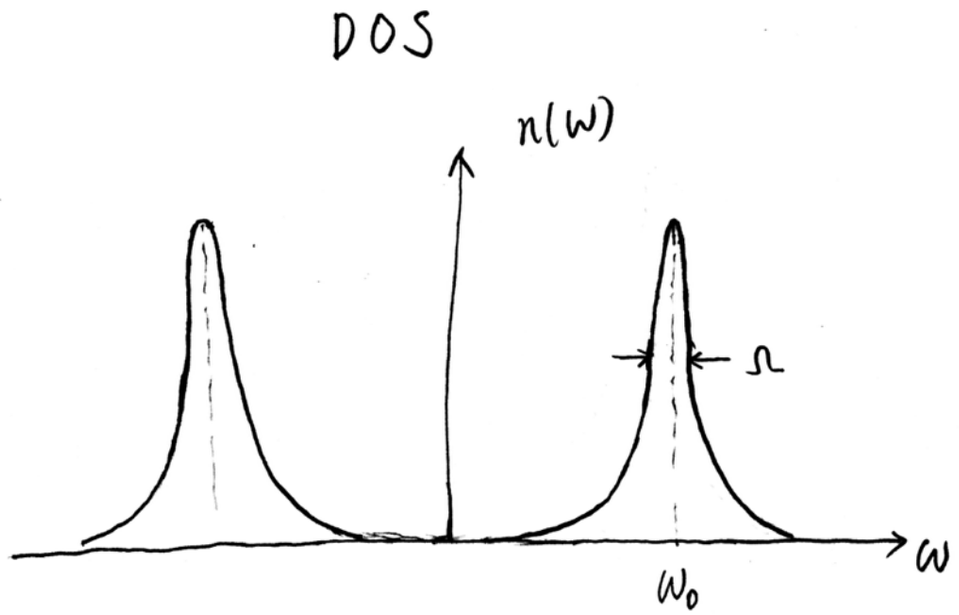
1. Why can we use two moments(2nd and 4th) to express lifetime?

2. What are the physical meanings of μ_2, μ_4, γ_4 ?

The moments of the Liouvillian are also the moments of the density of states derived from $\chi(t)$

Fourier transform: $$n(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \chi(t) e^{-i\omega t} dt$$





Parseval's Theorem: $$\tau = \int_{-\infty}^{+\infty} dt\, \chi^2(t) = \int_{-\infty}^{+\infty} d\omega n^2(\omega)$$

harmonic system: $F \propto -A$

Quasi-harmonic system: define an effective force constant K

construct a function:

$$\alpha = \frac{\left\langle (F + KA)^2 \right\rangle}{\left\langle F^2 \right\rangle}$$

compare with:

$$\omega \sim \sqrt{\frac{k}{m}}$$

$$\alpha' = \frac{\left\langle 2AF + 2KA^2 \right\rangle}{\left\langle F^2 \right\rangle} = 0 \quad \Rightarrow \quad K_{eff} = \frac{-\left\langle AF \right\rangle}{\left\langle A^2 \right\rangle} = \mu_2 m$$

$$\alpha_{\min} = 1 - \frac{\left\langle A\ddot{A} \right\rangle^2}{\left\langle A^2 \right\rangle \left\langle \ddot{A}^2 \right\rangle} = 1 - \gamma_4^{-1}$$

The meanings of the two moments

$$K_{eff} = \frac{-\langle AF \rangle}{\langle A^2 \rangle} = \mu_2 m$$

μ_2 : quasi-harmonic frequency(squared)

$$\alpha_{\min} = 1 - \gamma_4^{-1}$$

γ_4 : a measurement of the degree of anharmonicity of the mode beyond the quasiharmonic