SAND2013-10042C

Lecture 9: Macroscale Property Estimation with Molecular Dynamics

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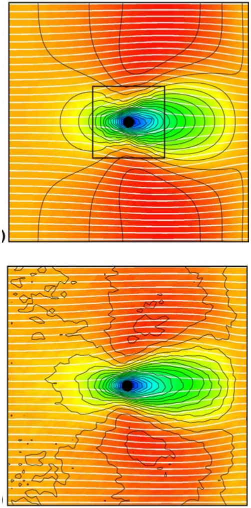
add I&K/Hardy

please ask questions as we go



flow around a CNT
top: continuum, bottom: MD

[Werder et al *JCompPhys* 2005]

History

- [Clausius *PhilMag* 1870] [Maxwell *TransRoySocEdin* 1870] "virial" expression for stress
- [Onsager *PhysRev* 1931] discovery that decay from perturbation is same as that from equilibrium fluctutaion
- [Born *ProcCamPhilSoc* 1940] Cauchy-Born model of molecular response
- [Irving&Kirkwood *JChemPhys* 1950] correspondence between molecular dynamics and continuum mechanics
- [Metropolis *JChemPhys* 1953] generated ensemble response with Monte-Carlo method
- [Green *JChemPhys* 1954] [Kubo *JPhysSocJap* 1957] calculated transport properties from decay of fluctuations

Macroscale properties

Material properties can be calculated from (empirical) potentials (and structure):

Non-transport

- Surface/defect energies
- Energy of formation
- Mass density
- Heat capacity

Transport

- Elastic constants (solid): bulk,shear, & Young's modulus
- Viscosity (fluid)
- Thermal conductivity

Since there are no explicitly-represented electrons, no electronic properties can be computed directly (see DFT and other *ab initio* methods) but ion conductivity is possible.

Mass density

The mass density of a system with volume V is simply

$$\rho = \frac{1}{V} \sum_{\alpha} m_{\alpha}$$

where the mass of atom α is m_{α}.

- For a NVT system $\rho \equiv \frac{N}{V} m_{\alpha}$.
- For a NPT system $\rho = \rho(P, T)$ is non-trivial since $V = V(P, T)$.

A brief aside: correlation

Temporal correlation of a vector $\mathbf{v}(t)$ is simply the product $\mathbf{v}(0)\mathbf{v}(t)$ averaged over the ensemble.

To make this computable in MD, first use the ergodic hypothesis to convert the ensemble to a time average

$$\langle \mathbf{v}(0) \otimes \mathbf{v}(t) \rangle \quad = \quad \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \mathbf{v}(s) \otimes \mathbf{v}(s+t)\, ds$$

and use time invariance of the product i.e. steady state statistics.

Next translate to discrete time

$$\langle \mathbf{v}(0) \otimes \mathbf{v}(i\,\Delta t) \rangle \quad \approx \quad \frac{1}{N_t} \sum_{j=1}^{N_t} \mathbf{v}_j \otimes \mathbf{v}_{i+j}$$

Spatial correlations are similar.

Heat capacity

Recall that the Dulong-Petit law implies that the heat capacity (per unit volume) for classical dynamics is $c_v = 3k_B\frac{N}{V}$.

The heat capacity can also be calculated from the variance of fluctuations in the internal energy U (potential + thermal energy)

$$c_v = \left.\frac{\partial U}{\partial T}\right|_V = \frac{\langle U^2\rangle - \langle U\rangle^2}{k_B T^2}$$

using a derivation based on the partition function (see my last lecture).

The idea of material properties being related to fluctuations will come up again in the discussion of Green-Kubo methods.

Heat capacity

To take account of significant quantum effects at low temperatures, the internal energy of the phonons (lattice vibrations) can be modeled as a collection of harmonic oscillators

$$\begin{aligned} U &= \sum_{\mathbf{k},p} \frac{\hbar\omega_{\mathbf{k},p}}{\exp\left(\hbar\omega_{\mathbf{k},p}/k_B T\right) - 1} \\ &\approx \sum_{p} \int k_B T \epsilon(\omega)\, \varphi(\omega)\, D_p(\omega)\, d\omega \end{aligned}$$

where the first sum is over wave-vectors **k** & polarizations p.

The (reduced) energy of oscillator is $\epsilon(\omega) = \frac{\hbar\omega}{k_B T}$, the distribution is $\varphi(\epsilon) = \left(\exp\left(\epsilon\right) - 1\right)^{-1}$, and $\varphi d\epsilon \sim \varphi\, D\, d\omega$.

$D(\omega)$ is the density of states (DOS) and can be computed by MD.

Heat capacity

Density of states (DOS) is the Fourier transform of the velocity auto-correlation $\mathcal{A}_{\mathbf{v}}(t) = \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$

$$D(\omega) = \int_0^\infty \mathcal{A}_{\mathbf{v}}(t) \cos(\omega t)\, dt$$

where

$$\mathcal{A}_{\mathbf{v}}(i\,\Delta t) \equiv \langle \mathbf{v}(0) \cdot \mathbf{v}(i\,\Delta t) \rangle = \frac{1}{N_\alpha N_t} \sum_\alpha \sum_j \mathbf{v}_{\alpha,i} \cdot \mathbf{v}_{\alpha,i+j}$$

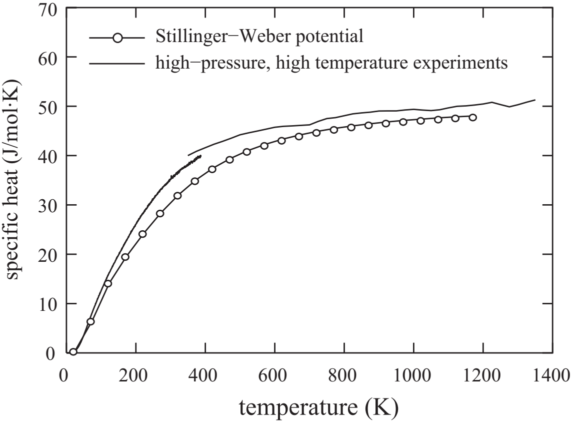
and is typically normalized by $\langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle$ so that $\mathcal{A}_{\mathbf{v}}(0) = 1$.

Notice this is essentially the Wiener-Kinchine theorem relating spectral density to the auto-correlation.

Heat capacity

Finally, using the chain rule $\frac{d}{dT} = \frac{dT}{d\epsilon}\frac{d}{d\epsilon}$

$$c_v = \frac{\partial U}{\partial T} = k_B \sum_p \int \frac{\epsilon^2(\omega)\exp\left(\epsilon(\omega)\right)}{\left(\exp\left(\epsilon(\omega)\right) - 1\right)^2} D_p(\omega)\, d\omega$$



Equilibrium vs. Non-equilbrium

Equilibrium is defined by the average macro-scale fluxes zero and the relevant statistics are steady. Transport involves non-equilibrium but potentially steady processes.

So what is a flux? It is conjugate to a force, e.g.

$$\dot{\Psi} = \frac{\partial \Psi}{\partial \mathbf{F}} \dot{\mathbf{F}} = \mathbf{P} \dot{\mathbf{F}}$$

the stress–rate-of-deformation pair, and

$$\dot{S} = \frac{\partial S}{\partial \mathbf{X}} \dot{\mathbf{X}} = \boldsymbol{\nabla} \left(\frac{1}{T} \right) \ \mathbf{q}$$

where the energy current density/heat flux **q** is a dissipative flux i.e. one that directly contributes to entropy S production.

Linear response means that the flux J is linearly related to the (external) force F_e

$$\mathrm{J} = L(\mathrm{F}_e = 0)\mathrm{F}_e$$

Macroscale transport

Fick's law: the flux in concentration flows its gradient

$$\mathbf{j} = -D\boldsymbol{\nabla} c$$

plus conservation of species

$$\frac{\partial}{\partial t} c + \boldsymbol{\nabla}\mathbf{j} = 0$$

together give a diffusion equation

$$\frac{\partial}{\partial t} c = D\boldsymbol{\nabla}^2 c$$

The question is can we determine the diffusion coefficient D from MD?

Macro-micro connection

Apparently, macroscale laws do apply in aggreate at atomic scale but there can be strong size effects.

One of the foundations of this observation is the Onsager regression hypothesis (1931) which states:

> The equilibrium fluctuations in a phase variable are governed by the same transport coefficients as is the relaxation of that same phase variable to equilibrium

In other words, the decay of an equilibrium fluctuation is indistinguishable from that of a (small) external perturbation.

We will see that Green-Kubo theory makes this discovery computable.

Microscopic fluxes

Irving & Kirkwood, 1950 made a correspondence between Newton's law for the ion cores to the Euler balances of mass, momentum & energy for a continuum.

Stress (this is essentially the virial)

$$\boldsymbol{\sigma} = \frac{1}{V} \sum_{\alpha} \left(m_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha + \frac{1}{2} \sum_{\beta} \mathbf{f}_{\alpha\beta} \otimes \mathbf{x}_{\alpha\beta} \right)$$

and heat flux

$$\mathbf{q} = \frac{1}{V} \sum_{\alpha} \left(\phi_\alpha \mathbf{I} + \boldsymbol{\sigma}_\alpha^T \right) \mathbf{v}_\alpha$$

note the PE $\phi_\alpha = \frac{1}{N_\beta} \sum_\beta \phi(r_{\alpha\beta})$ is per atom not per bond.

Recall $\mathbf{x}_\alpha$ are the positions, $\mathbf{v}_\alpha$ the velocities, & $\mathbf{f}_\alpha$ the forces.

Methods

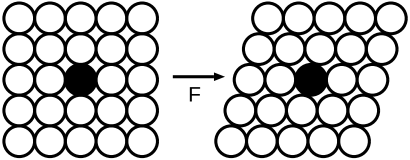
There are three main methods with variants:

- Analytical : usually involve derivatives of potential & simplified structure. These methods can be complex/tedious and have limited applicability due to strong assumptions.
- Direct : based on a macroscale analogue. They usually involve non-equilibrium with unphysically large gradients and large systems (variants include Müller-Plathe for conductivity)
- Green-Kubo : use equilibrium fluctuations and small systems (non-equilibrium variants: Evans, SLLOD). The noise/errors in the estimates must be handled correctly.

Analytical: Cauchy-Born rule

Potential energy is function of positions $\Phi = \Phi(\{\mathbf{x}_\alpha\})$

Cauchy-Born rule assume a homogeneous (local) deformation from a perfect lattice reference $\mathbf{x}_\alpha = \mathbf{F}\mathbf{X}_\alpha$



Stress, which identical in form to the virial

$$\boldsymbol{\sigma} \approx \mathbf{P} = \partial_{\mathbf{F}}\Phi = \frac{1}{V}\sum \frac{\phi'}{r_{\alpha\beta}}\mathbf{x}_{\alpha\beta} \otimes \mathbf{x}_{\alpha\beta} = \frac{1}{V}\sum \mathbf{f}_{\alpha\beta} \otimes \mathbf{X}_{\alpha\beta}$$

The elastic constants

$$\begin{aligned} \mathbb{C} \approx \mathbb{B} &= \partial^2_{\mathbf{F}}\Phi = \partial^2_{\mathbf{u}}\Phi\partial_{\mathbf{F}}\mathbf{u}\,\partial_{\mathbf{F}}\mathbf{u} = \mathbb{D}\partial_{\mathbf{F}}\mathbf{u}\,\partial_{\mathbf{F}}\mathbf{u} \\ &= \frac{1}{2V}\sum_\alpha \left(\phi'' - \frac{\phi'}{r_\alpha}\right) r_\alpha^2 \frac{\mathbf{x}_\alpha}{r_\alpha} \otimes \frac{\mathbf{X}_\alpha}{r_\alpha} \otimes \frac{\mathbf{x}_\alpha}{r_\alpha} \otimes \frac{\mathbf{X}_\alpha}{r_\alpha} \\ &\quad + \frac{1}{r_\alpha}\phi'\delta_{ij}\,\mathbf{e}_i \otimes \frac{\mathbf{X}_\alpha}{r_\alpha} \otimes \mathbf{e}_j \otimes \frac{\mathbf{X}_\alpha}{r_\alpha} \end{aligned}$$

Analytical: Finite temperature Cauchy-Born

The zero temperature C-B rule can be extended to finite temperatures using the same harmonic oscillator model seen earlier.

The Helmholtz free energy is $\Psi = \Phi - TS$. The necessary entropy S can be constructed via dynamical matrix

$$\mathbb{D}_\alpha = \frac{1}{m} \frac{\partial^2 \Phi}{\partial \mathbf{x}_0 \partial \mathbf{x}_\alpha}$$

which is essentially a stiffness matrix, so that

$$\Psi = \Phi + \frac{k_B T}{V_\alpha} \log \left(\left(\frac{\hbar}{k_B T} \right)^3 \sqrt{\det \mathbb{D}} \right) .$$

where $\det \mathbb{D} = \prod_i \omega_i$.

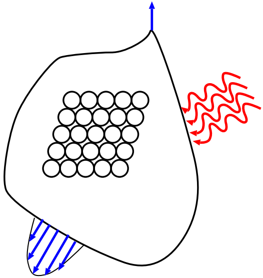
Then the stress and elastic constants can be derived via the first and second derivatives of Ψ with respect to $\mathbf{F}$ at constant T.

Direct methods

The methods are typically based on making an analogue with continuum test, e.g. a tensile test.

Like the continuum experiments these computer “experiments” are usually quasi-one dimensional.

The basic issue is how to set up & support a gradient via boundary conditions which mimic the external environment.

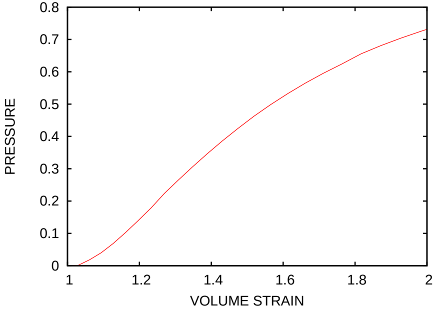


a material subject to external mechanical loads and heat flux

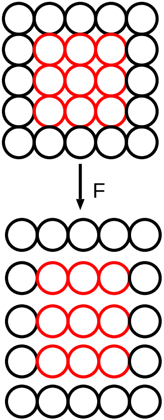
Control regions, ghost/periodic image atoms can be employed.

Direct determination of elastic constants

The bulk modulus K is the constant of proportionality between the pressure $p = \frac{1}{3}\,\mathrm{tr}\,\boldsymbol{\sigma}$ and the dilational strain $p = K\,\mathrm{tr}\,\boldsymbol{\epsilon} \approx K\frac{\Delta V}{V}$

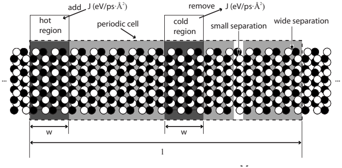


To obtain this elastic constant we simply stretch the periodic box & take derivative of curve at any particular volume strain.



tension via box stretch

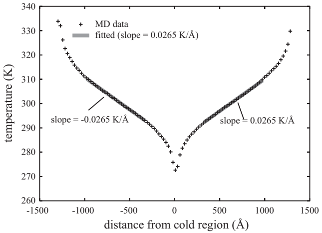
Direct determination of thermal conductivity



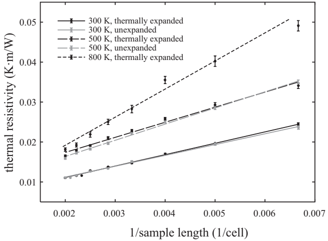
A steady-state temperature gradient is supported by injected energy in the “hot” region and extracting the same amount from the “cold” region via

- rescaling velocities
- a thermostat
- swapping hot atoms for cold ones (Müeller-Plathe)

[Schelling *PRB* 2002]
[Zhou *PRB* 2009,2010]



temperature profile



size effects & extrapolation to bulk

Einstein relation

Generally, correlations $\mathcal{A}_c$ satisfy same PDE as phase variable c

$$\frac{\partial}{\partial t}\mathcal{A}_c = D\boldsymbol{\nabla}^2\mathcal{A}_c$$

Similarly $\langle r^2\rangle \equiv \langle r(0)r(0)\rangle$ where $r^2 = \mathbf{x}\cdot\mathbf{x}$ & $c = c(r,t)$

$$\frac{\partial}{\partial t}\langle r^2\rangle \;\;=\;\; D\int r^2\boldsymbol{\nabla} c\,dV = 2D\int \boldsymbol{\nabla}\cdot\mathbf{x}\,c\,dr = 6D$$

via integration by parts and a normalized $\int c\,dV = 1$.

This is called an Einstein (1905) relation.

Green-Kubo

Using the Einstein relation & $\mathbf{x} = \int_0^t \mathbf{v}\, dt$, D can be connected to a correlation:

$$\begin{aligned} 6D &= \lim_{t\to\infty} \frac{\partial}{\partial t}\langle r^2\rangle \\ &= \lim_{t\to\infty} \frac{\partial}{\partial t}\int_0^t \int_0^t \mathbf{v}(t_1)\cdot\mathbf{v}(t_2)\, dt_1\, dt_2 = \lim_{t\to\infty}\int_0^t \mathbf{v}(0)\cdot\mathbf{v}(s)\, ds \end{aligned}$$

using the symmetry and time invariance of the correlation $\mathbf{v}(t_1)\cdot\mathbf{v}(t_2)$. The limit is necessary to eliminate a $1-\frac{t_1}{t}$ factor that is significant at short times.

Evans derives the general Green-Kubo relation

$$L(F_e = 0) = \frac{V}{k_B T}\int_0^\infty \langle J(0) J(s)\rangle_{F_e=0}\, ds$$

using the fluctuation and central limit theorems

Self-diffusion

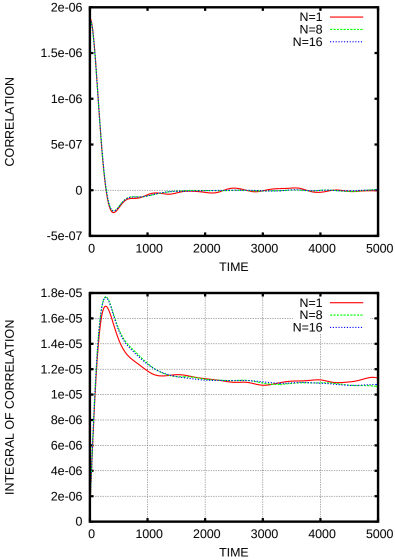
So the self diffusion constant for a material can be calculated

$$D = \frac{1}{3}\int_0^{\infty} \langle \mathbf{v}_\alpha(0) \otimes \mathbf{v}_\alpha(t) \rangle \; dt$$

for a set of α to get ensemble.

Notice the correlation must decay & in a reasonable amount of time to get an answer.

Also, the Fast Fourier transform is sometimes used instead of simple sums to get fast correlations.



correlation & integral for 1, 8, 16 atoms

Green-Kubo

Specific formulas exist:

- for elastic constants,

$$\left(\mathbb{C}\,\mathbf{k}\otimes\mathbf{k}\right)^{-1}=\frac{V}{k_B T}\left\langle\tilde{\mathbf{u}}(\mathbf{k})\otimes\tilde{\mathbf{u}}(\mathbf{k})\right\rangle$$

$\tilde{\mathbf{u}}$ Fourier transform of displacements & $\mathbf{k}$ is the wave vector.

- for viscosity,

$$\boldsymbol{\nu}=\frac{V}{k_B T}\int_0^\infty\left\langle\boldsymbol{\varsigma}(0)\otimes\boldsymbol{\varsigma}(t)\right\rangle\,dt$$

$\boldsymbol{\varsigma}$ is a vector of off-diagonal components of stress

- for thermal conductivity

$$\boldsymbol{\kappa}=\frac{V}{k_B T^2}\int_0^\infty\left\langle\mathbf{q}(0)\otimes\mathbf{q}(t)\right\rangle\,dt\ .$$

$\mathbf{q}$ is the heat flux (whose “affinity” is $\frac{1}{T}$ thus the extra T)

Homework: set-up

Use LAMMPS and the Green-Kubo method to calculate the viscosity of liquid Argon

```
# parameters
variable  T equal 86.4956
variable  dt equal 4.0 # time-step
variable  s equal 4     #  sample interval in steps
variable  p equal 2000  # correlation length in units of $s steps
variable  d equal $p*$s # output interval
# convert from LAMMPS real units to SI
variable kB     equal 1.3806504e-23 # [J/K] Boltzmann
variable kCal2J equal 4186.0/6.02214e23
variable atm2Pa equal 101325.
variable A2m    equal 1.e-10
variable fs2s   equal 1.e-15
variable convert equal ${atm2Pa}*${atm2Pa}*${fs2s}*${A2m}*${A2m}*${A2m}
```

Homework: create system

```
units     real
dimension 3
boundary  p p p
pair_style    lj/cut 13.0
lattice   fcc  5.719025032 # sets density of system
region    box block 0 4 0 4 0 4
create_box    1 box
create_atoms  1 box
mass    1 39.948
pair_coeff    1 1 0.2381 3.405
velocity all create $T 31456 mom yes rot yes dist gaussian
variable V equal vol
variable scale equal ${convert}/(${kB}*$T)*$V*$s*${dt}
```

Homework: your turn

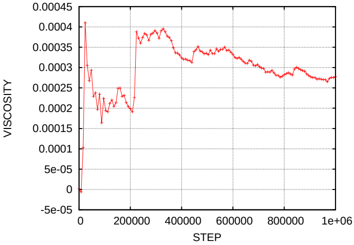
```
timestep  ${dt}
thermo    $d
variable pxy equal pxy  # off-diagonal stress
fix NVT all nvt temp $T $T 10 drag 0.2
run 32000 # transient
reset_timestep  0
# hint use ave/correlate to calculate J(0).J(t)
# hint use trap to integrate the correaltion
# hint run for a long time
run 1000000
```

Homework: solution for Ar viscosity

Solution

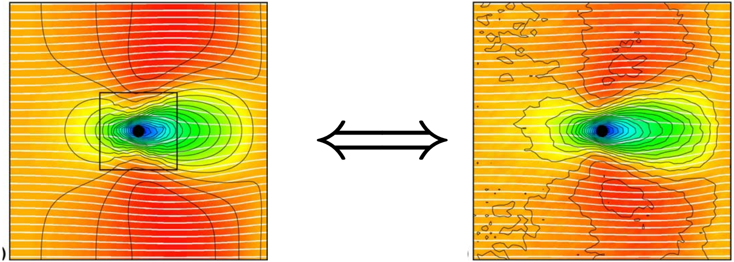
```
...
fix SS all ave/correlate $s $p $d v_pxy type auto ave running
variable v11 equal trap(f_SS[3])*${scale}
thermo_style  custom step temp press v_v11
run 1000000
```

- experimental value is approximately 0.0003 Pa-s
- what could make the estimate better? think size of the ensemble
- extra credit : calculate the thermal conductivity (see http://lammps.sandia.gov/doc/compute_heat_flux.html)



Conclusion

With a well-verified potential and appropriate atomic structure, we can use molecular dynamics to predict a variety of material properties.



Further reading

- Allen & Tildesley,*Computer Simulation of Liquids*, 1987
- Evans & Morriss, *Statistical Mechanics of Non-equilibrium Liquids*, 1990
- Haile, *Molecular Dynamics Simulation: Elementary Methods*, 1992
- Leach, *Molecular Modelling - Principles and Applications*, 2001
- Schlick, *Molecular Modeling and Simulation: An Interdisciplinary Guide*, 2002
- Frenkel & Smit, *Understanding Molecular Simulation*, 2002
- Rappaport, *The Art of Molecular Dynamics Simulation*, 2004
- http://lammps.sandia.gov