3.320: Lecture 15 (Mar 31 2005)

First-Principles Molecular Dynamics

…and let us, as nature directs,
begin first with first principles.
Aristotle (Poetics, I)

Simulated Annealing

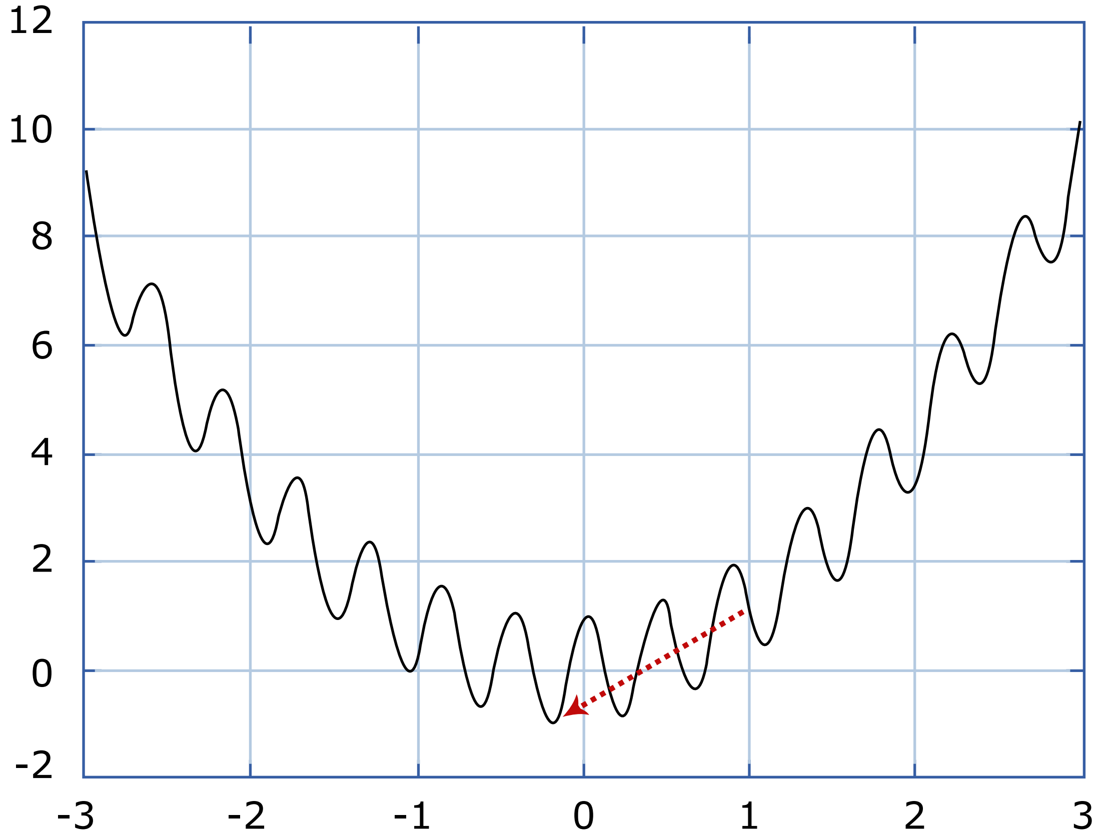


Figure by MIT OCW.

Micro- to macro- : diffusion coefficient

- From Fick to Einstein:

$$\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t)$$

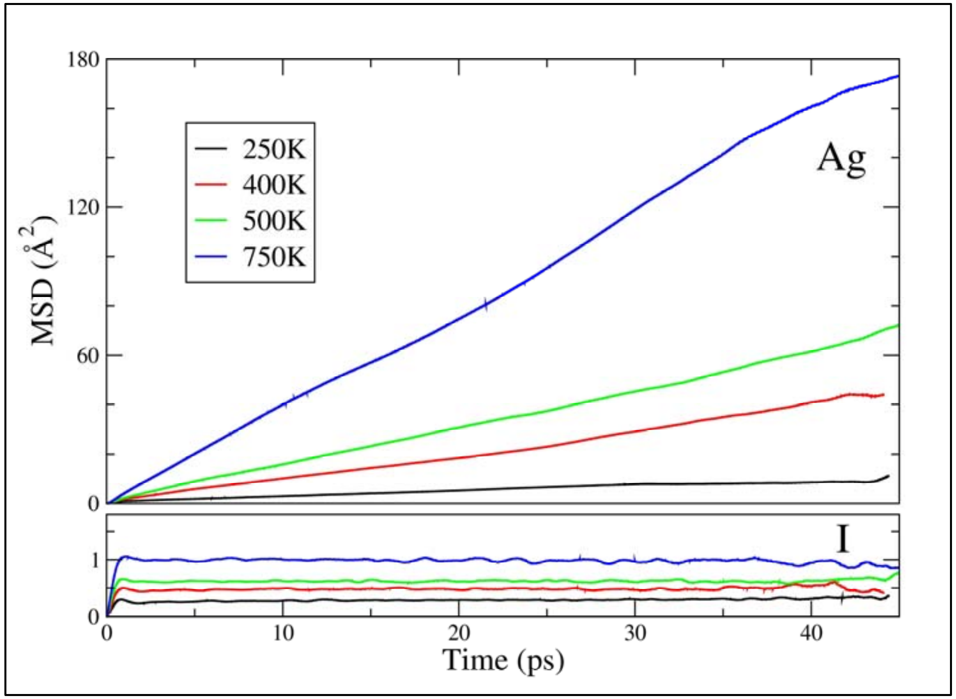
$$\frac{\partial}{\partial t}\int d\vec{r}\, r^2 c(r,t) = D\int d\vec{r}\, r^2 \nabla^2 c(r,t)$$

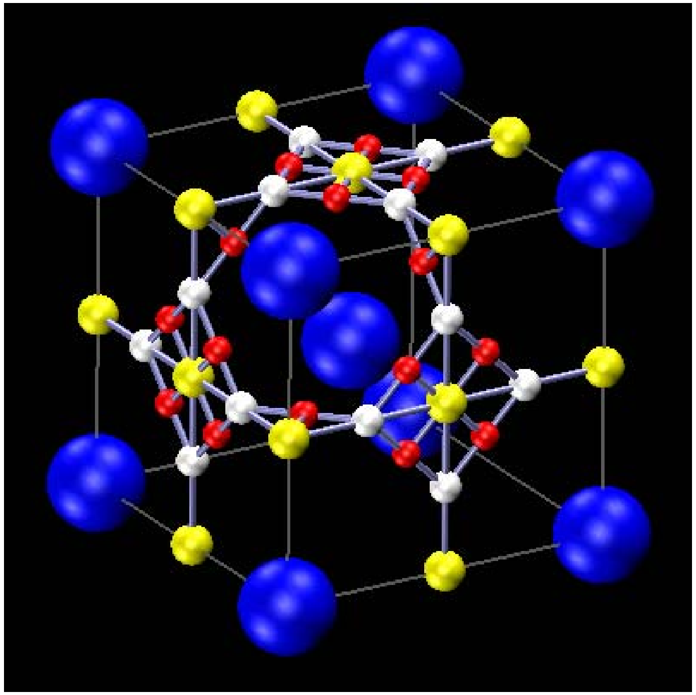
$$\frac{\partial}{\partial t}\left\langle r^2(t)\right\rangle = 2dD$$

Mean Square Displacements

$$\left\langle \Delta r(t)^2 \right\rangle = \frac{1}{N}\sum_{i=1}^{N} \Delta r_i(t)^2$$

Mean Square Displacements





Velocity Autocorrelation Function

$$\left\langle \Delta x(t)^2 \right\rangle = \frac{1}{N}\sum_{i=1}^{N} \Delta x_i(t)^2 \qquad \Delta x(t) = \int_0^t dt'\, v_x(t')$$

$$\left\langle \Delta x(t)^2 \right\rangle = \left\langle \left(\int_0^t dt' v_x(t') \right)^2 \right\rangle = \int_0^t dt' \int_0^t dt'' \left\langle v_x(t') v_x(t'') \right\rangle$$

$$= 2 \int_0^t dt' \int_0^{t'} dt'' \left\langle v_x(t') v_x(t'') \right\rangle$$

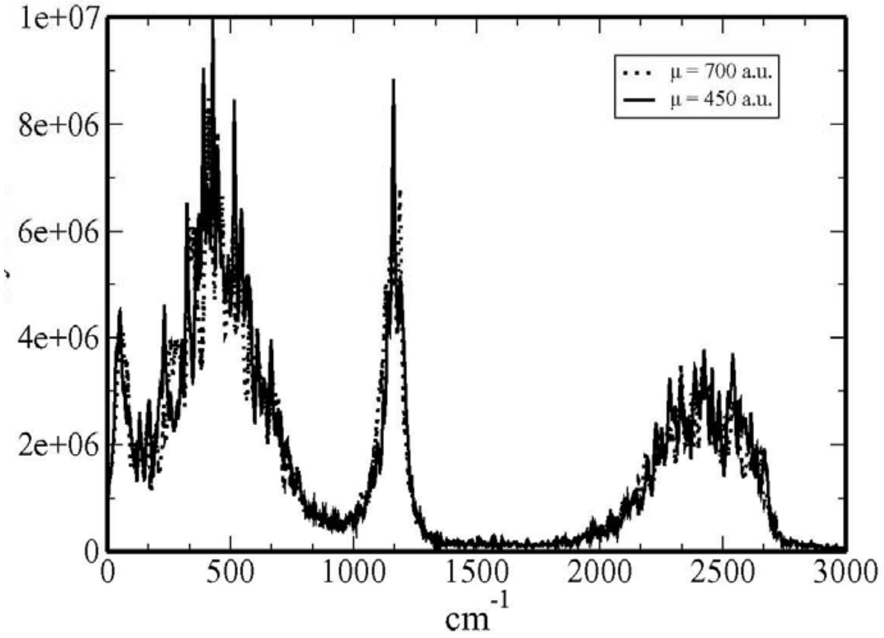
Green-Kubo relations

$$2D = \lim_{t\to\infty} \frac{\partial\left\langle x^2(t)\right\rangle}{\partial t} = \lim_{t'\to\infty} 2\int_0^{t'} dt'' \left\langle v_x(t')v_x(t'')\right\rangle$$

$$\left\langle v_x(t')v_x(t'')\right\rangle = \left\langle v_x(t'-t'')v_x(0)\right\rangle$$

$$D = \lim_{t'\to\infty} \int_0^{t'} dt'' \left\langle v_x(t'-t'')v_x(0)\right\rangle = \int_0^{\infty} d\tau \left\langle v_x(\tau)v_x(0)\right\rangle$$

Velocity Autocorrelation Function



More Green-Kubo

- Other transport coefficients:
  - Shear viscosity, from the stress
  - Electrical conductivity, from the charge current
  - IR adsorption, from the polarization

Dynamics, Lagrangian style

- First construct L=T-V
- Then, the equations of motion are given by

$$\boxed{\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right)-\frac{\partial L}{\partial q_j}=0}$$

(the dot is a time derivative)

- Why ? We can use generalized coordinates. Also, we only need to think at the two scalar functions T and V

Newton's second law, too

- 1-d, 1 particle: $T=1/2\ mv^2$, $V=V(x)$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right)-\frac{\partial L}{\partial q_j}=0$$

$$\frac{d}{dt}\left(\frac{\partial\left(\frac{1}{2}m\dot{x}^2\right)}{\partial \dot{x}}\right)+\frac{\partial V}{\partial x}=0 \quad \Rightarrow \quad \frac{d}{dt}\left(m\dot{x}\right)=-\frac{\partial V}{\partial x}$$

Hamiltonian

- We could use it to derive Hamiltonian dynamics (twice the number of differential equations, but all first order). We introduce a Legendre transformation

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \qquad\qquad H(q,p,t) = \sum_i \dot{q}_i p_i - L(q,\dot{q},t)$$

$$\boxed{\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad\qquad -\dot{p}_i = \frac{\partial H}{\partial q_i}}$$

Thermostats, barostats…

- We might want to sample a constant-temperature ensemble, or constants pressure
  - Stochastic approach
  - Extended system
  - Constraint method

Nose' extended Lagrangian

$$L_{NOSE} = \sum_i \frac{1}{2} m_i s^2 \dot{r}_i^2 - V + \frac{1}{2} Q \dot{s}^2 - \frac{(3N+1)}{\beta} \ln s$$

Ergodicity issues

Very harmonic solids (e.g. 1 harmonic oscillator !)

Classical MD Bibliography

- Allen and Tildesley, *Computer Simulations of Liquids* (Oxford)
- Frenkel and Smit, *Understanding Molecular Simulations* (Academic)
- Ercolessi, *A Molecular Dynamics Primer* (http://www.fisica.uniud.it/~ercolessi/md)

First-principles molecular dynamics

Graph removed for copyright reasons.
Shows dramatic increase in number of citations per year of "CP PRL 1985" and "AIMD" beginning around 1990.

Plane waves basis set

$$\vec{G}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$$

It's really kinetic + potential

$$\hat{H} = -\frac{1}{2}\nabla^2 + V(\vec{r})$$

$$\psi_n(\vec{r}) = \sum_{\vec{G}} c_{\vec{G}}^n \exp(i\vec{G}\cdot\vec{r})$$

$$E = \sum_n \varepsilon_n = \sum_n \left\langle \psi_n \middle| \hat{H} \middle| \psi_n \right\rangle$$

Kinetic energy

$$E_{kin} = \sum_n \left\langle \psi_n \right| -\frac{1}{2}\nabla^2 \left| \psi_n \right\rangle \qquad \psi_n(\vec{r}) = \sum_{\vec{G}} c_{\vec{G}}^n \exp(i\vec{G}\cdot\vec{r})$$

$$\left\langle G \left| -\frac{1}{2}\nabla^2 \right| G' \right\rangle = \int dr \exp(-iGr)\left[-\frac{1}{2}\nabla^2\right]\exp(iG'r) = \frac{1}{2}G^2\delta_{G,G'}$$

$$E_{kin} = \sum_n \frac{1}{2}\sum_{\vec{G}} \left\| c_{\vec{G}}^n \right\|^2 G^2$$

Total energy (non-SCF)

$$E_{pot} = \sum_n \left\langle \psi_n \middle| V\left(\vec{r}\right) \middle| \psi_n \right\rangle \qquad \psi_n(\vec{r}) = \sum_{\vec{G}} c_{\vec{G}}^n \exp(i\vec{G}\cdot\vec{r})$$

$$\left\langle G \middle| V(r) \middle| G' \right\rangle = \int dr \exp(-iGr) V(r) \exp(iG'r) = V(G-G')$$

$$E_{tot} = \sum_n \left(\frac{1}{2} \sum_{\vec{G}} \left\| c_{\vec{G}}^n \right\|^2 G^2 + \sum_{\vec{G},\vec{G}'} c_{\vec{G}}^{n\,*} c_{\vec{G}'}^n V(\vec{G}-\vec{G}') \right)$$

Dynamical evolution of c's

$$E_{tot} = \sum_n \left(\frac{1}{2} \sum_{\vec{G}} \left\| c_{\vec{G}}^n \right\|^2 G^2 + \sum_{\vec{G},\vec{G}'} c_{\vec{G}}^{n\,*} c_{\vec{G}'}^n V(\vec{G} - \vec{G}') \right)$$

We need the force

$$E = E[\{\psi_i\}] \Longrightarrow F_i = -\frac{\delta E[\{\psi_i\}]}{\delta \psi_i}$$

$$= -\hat{H}\psi_i$$

Skiing down a valley

$$\mu \ddot{\psi}_i = -H\psi_i$$

$$\dot{\psi}_i = -H\psi_i$$

Conjugate-gradients minimization

Hellmann-Feynman theorem

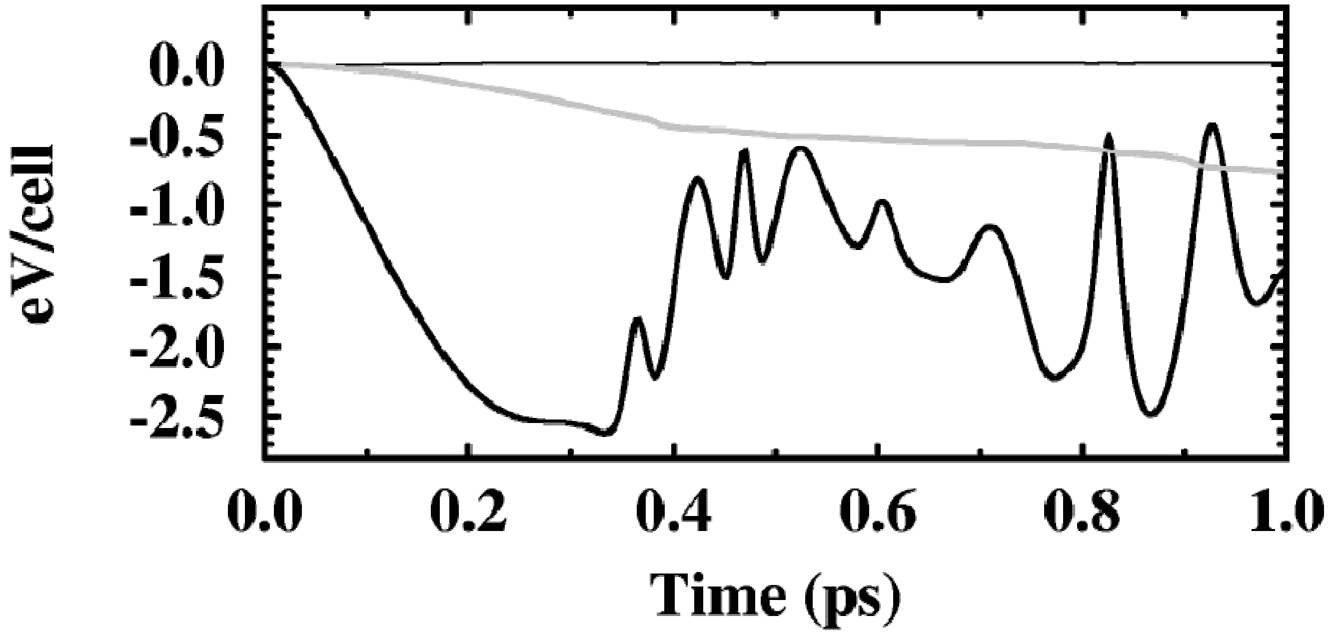
$$\vec{F}_i = -\frac{dE}{d\vec{R}_i} = -\frac{d\left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle}{d\vec{R}_i} =$$

$$= \left\langle \Psi \middle| -\frac{d\hat{H}}{d\vec{R}_i} \middle| \Psi \right\rangle = \left\langle \Psi \middle| -\frac{d\hat{V}}{d\vec{R}_i} \middle| \Psi \right\rangle$$

Proof of Hellmann-Feynman

Born-Oppenheimer Molecular Dynamics

$$m_i \ddot{\vec{R}}_i = \vec{F}_i = \left\langle \Psi \left| -\frac{d\hat{V}}{d\vec{R}_i} \right| \Psi \right\rangle$$



The extended Car-Parrinello Lagrangian

$$\mathcal{L}_{\mathrm{CP}} = \underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2} \mu_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle}_{\text{kinetic energy}} - \underbrace{\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle}_{\text{potential energy}} + \underbrace{\mathit{constraints}}_{\text{orthonormality}}$$

Equations of motion

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle$$

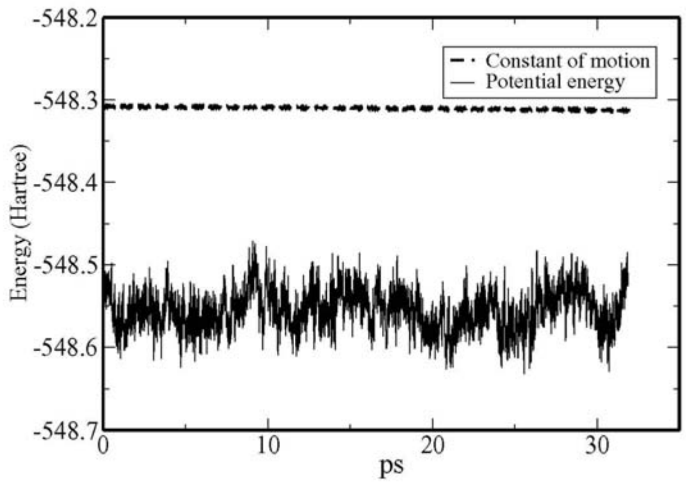
$$\mu_i \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^\star} \langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle + \frac{\delta}{\delta \psi_i^\star} \{constraints\}$$

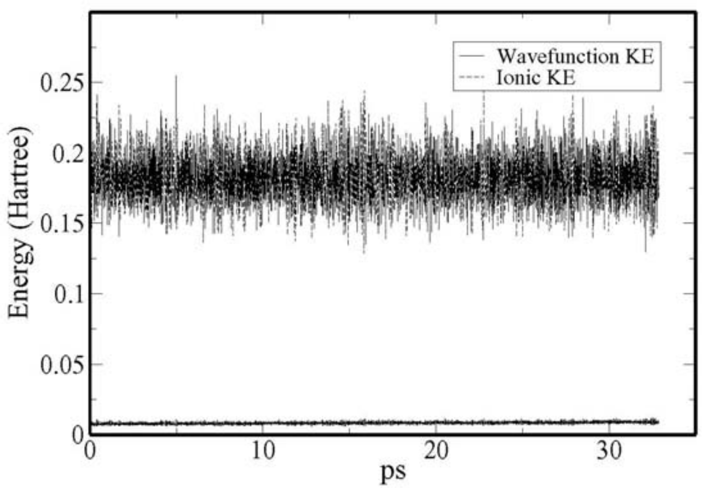
$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I}$$

$$\frac{d}{dt} \frac{\delta \mathcal{L}}{\delta \dot{\psi}_i^\star} = \frac{\delta \mathcal{L}}{\delta \psi_i^\star}$$

Constant of Motion

$$\underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle}_{\text{kinetic energy}} + \underbrace{\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle}_{\text{potential energy}}$$





Born-Oppenheimer vs Car-Parrinello

BO vs CP forces

Kolmogorov-Arnold-Moser invariant tori

Quantum MD Bibliography

- Payne, Teter, Allan, Arias, Joannopoulos, *Rev Mod Physics* 64, 1045 (1992).
- Marx, Hutter, "Ab Initio Molecular Dynamics: Theory and Implementation", in "Modern Methods and Algorithms of Quantum Chemistry" (p. 301-449), Editor: J. Grotendorst, (NIC, FZ Jülich 2000)
- http://www.theochem.ruhr-uni-bochum.de/research/marx/cprev.en.html