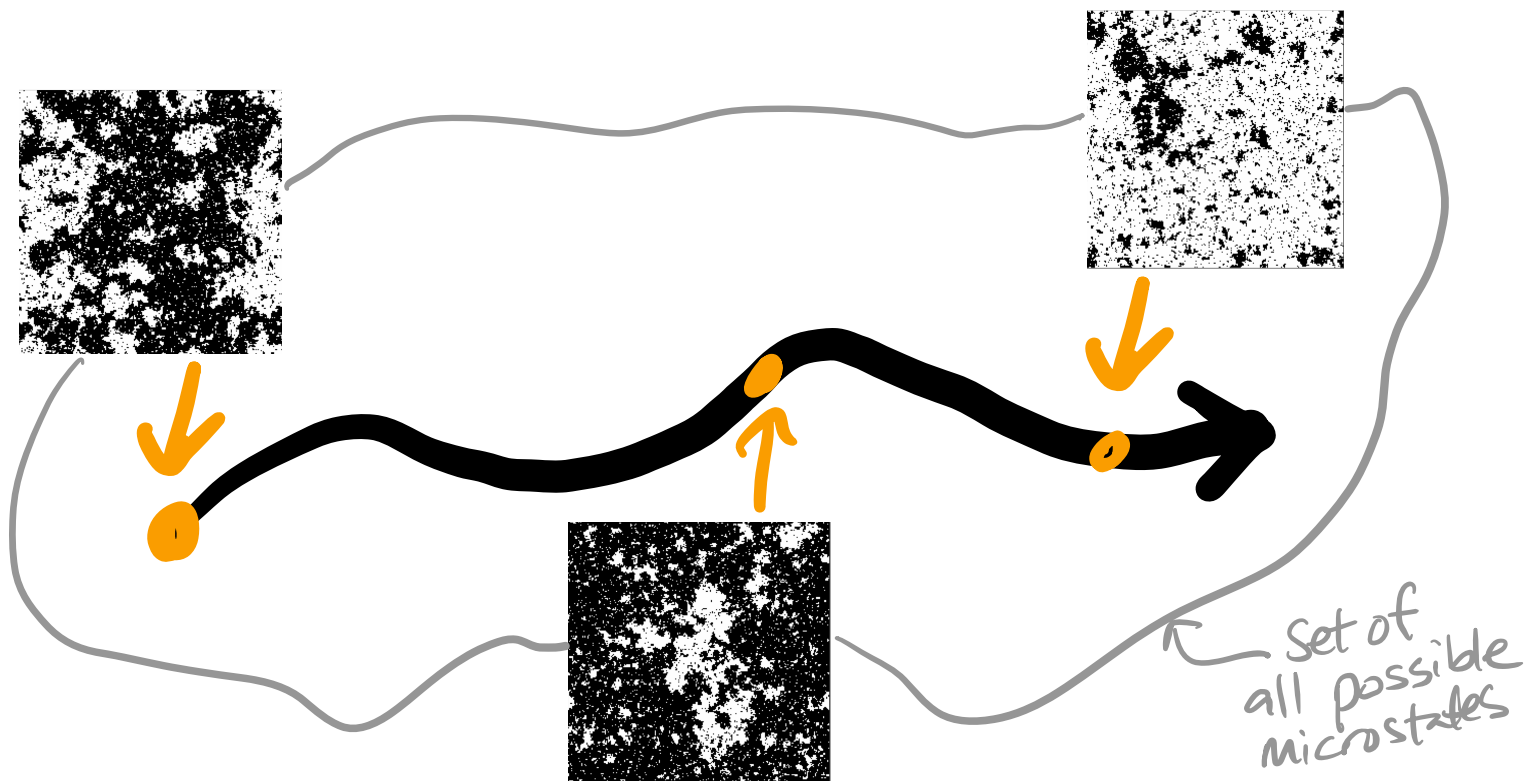


Lecture 18

Recall from last lecture...

How should we sample spin configurations from the canonical ensemble?

Use Dynamics!



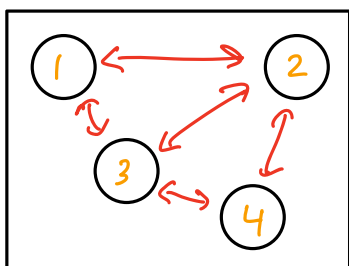
A "made up" Monte Carlo dynamics.

Is this really how spins evolve in time...? Discuss.

If not, what good is such a make believe dynamics?

From make believe spin dynamics to "real" molecular dynamics

Newton says classical particles feel forces, which cause them to move:



$$\vec{F}_i = m \vec{a}_i = m \ddot{\vec{r}}_i$$

i : Particle #

\rightarrow : vector (1d, 2d, 3d...)

$\ddot{\cdot}$: two time derivatives

This is a function of positions $\{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\} \equiv \{\vec{r}_i\}$

(shorthand)

$$\left\{ \begin{array}{l} \vec{F}_1(\{\vec{r}_i\}) = m \ddot{\vec{r}}_1 \\ \vec{F}_2(\{\vec{r}_i\}) = m \ddot{\vec{r}}_2 \\ \vdots \\ \vec{F}_N(\{\vec{r}_i\}) = m \ddot{\vec{r}}_N \end{array} \right.$$

Look, it is a system of second order differential equations!

(Eqn. relating two derivatives of \vec{r} to a fn. of \vec{r})

This requires two initial conditions to solve.

$\{\vec{r}_i(0)\}$ and $\{\vec{r}_i(t)\}$: Initial and final positions
Lagrangian Mechanics

OR

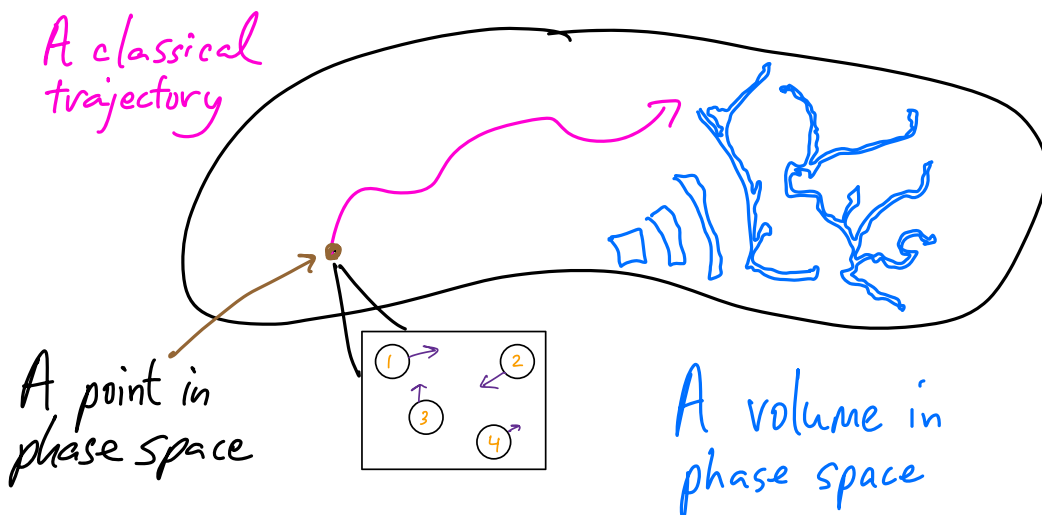
$\{\vec{r}_i(0)\}$ and $\{\dot{\vec{r}}_i(0)\}$: Initial positions
Initial velocities

Hamiltonian Mechanics

In the Hamiltonian picture, we define $\dot{\vec{r}}_i(t) = \vec{v}_i(t)$, the velocity at time t , and we recognize that the entire trajectory is specified by the initial values

$$(\vec{r}(t), \vec{v}(t))$$

The combined position-velocity space is called "phase space"



$$\begin{array}{ccc}
 \vec{F}_i = m_i \ddot{\vec{r}}_i & \Leftrightarrow & \left\{ \begin{array}{l} \dot{\vec{r}}_i = \vec{v}_i \\ \dot{\vec{v}}_i = \vec{F}_i / m_i \end{array} \right. & \Leftrightarrow & \left\{ \begin{array}{l} \dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} = \frac{\partial H}{\partial \vec{p}_i} \\ \dot{\vec{p}}_i = -\frac{\partial U}{\partial \vec{r}_i} = \frac{\partial H}{\partial \vec{r}_i} \end{array} \right. \\
 \text{Newton} & & & & \text{Hamilton}
 \end{array}$$

$$(H = K + U = \frac{p^2}{2m} + U(r))$$

Isn't the world quantum?

Indeed, classical models would struggle with very light particles (electrons, protons, etc.) with energy scales of order \hbar , but classical models can be very useful for thinking about many phenomena, especially when the effects of light degrees of freedom (e^- 's) are baked into a classical model for the energy of the heavier degrees of freedom, e.g.

$$U(\{r_i\})$$

↑ positions of atomic nuclei, not e^- 's.

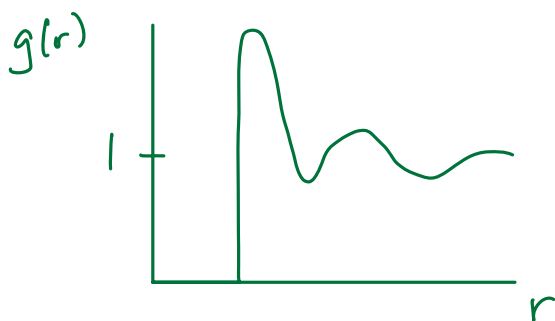
- Aha! So I can:
- Freeze all the nuclei
 - Use QM to solve for the energy of those nuclear positions
 - Use $\frac{\partial U}{\partial \vec{r}}$ to get forces
 - Move the nuclei
 - Repeat

Good thinking! You can do that (Car-Parinello molecular dynamics), but the QM part of that is very expensive and it may well be overkill.

There are actually lots of different ways to smear out the difference between quantum and classical dynamics. These things are called "semiclassical methods". They help us understand conditions under which classical + quantum models might be expected to agree or disagree.

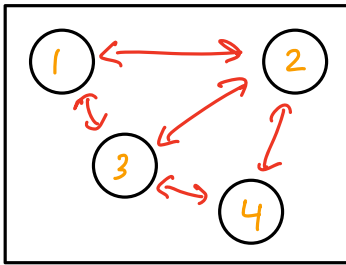
Keywords if you are interested: "Old quantum theory", WKB, Bohr-Sommerfeld, Wigner functions, Bill Miller, Ring Polymer Molecular Dynamics.

If you're interested in many chemistry problems (H_2O , protein dynamics, lipid membranes, nanoparticle assembly, etc.), it is often more useful to work with classical models. For example, x-ray scattering expts. can give correlations between where particles are in space:

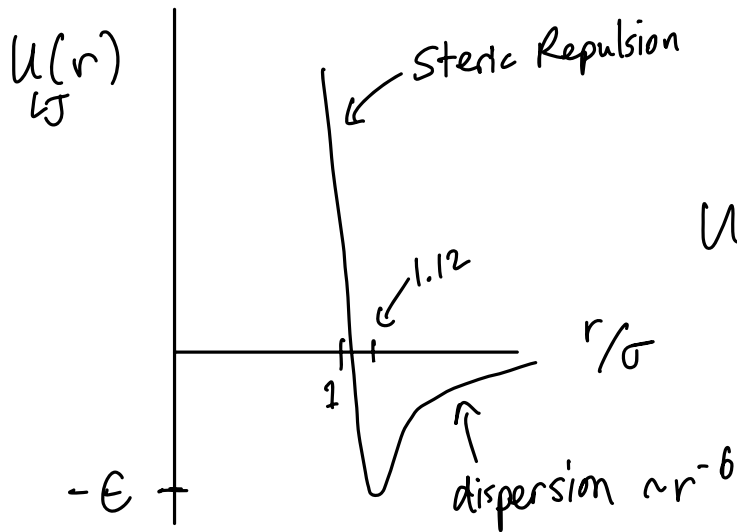


Do I really need QM to explain how charge/solvation effects change the way atoms organize?

What should a classical model for liquids look like?



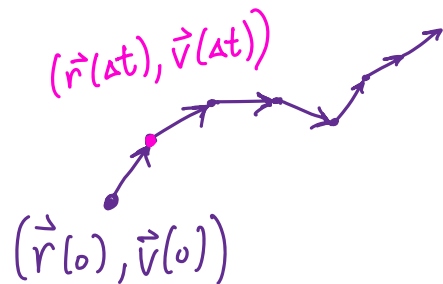
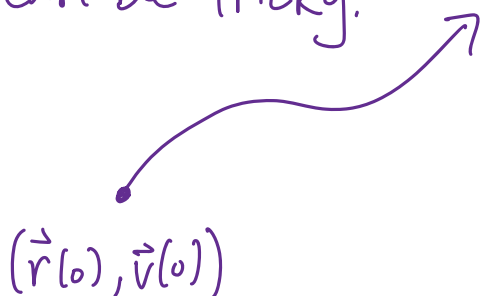
Assume energetics is pairwise decomposable
 [Why is this an assumption. Aren't all fundamental forces pairwise?]



$$U_{LJ}(r) = 4E \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Now, can we just run Newton's laws on this model to make predictions for $g(r)$?

Well, kind of. But we must discretize time, and even that can be tricky.



Real classical dynamics
 (smooth)

Discretized classical dynamics
 Compute forces at $(\vec{r}(t), \vec{v}(t))$ and assume Δt is so small that the force is constant for all time $t \rightarrow t + \Delta t$

For a very small time interval Δt ,

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \underbrace{\Delta t \dot{\vec{r}}(t)}_{\vec{v}(t)} + \frac{1}{2} \Delta t^2 \underbrace{\ddot{\vec{r}}(t)}_{\vec{F}(t)/m} + \mathcal{O}(\Delta t^3)$$

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \Delta t \dot{\vec{v}}(t) + \frac{1}{2} \Delta t^2 \underbrace{\ddot{\vec{v}}(t)}_{?} + \mathcal{O}(\Delta t^3)$$

To clarify ?, let's differentiate LHS and RHS wrt time...

$$\dot{\vec{v}}(t + \Delta t) = \dot{\vec{v}}(t) + \Delta t \ddot{\vec{v}}(t) + \mathcal{O}(\Delta t^2)$$

$$\Rightarrow \ddot{\vec{v}}(t) = \frac{\dot{\vec{v}}(t + \Delta t) - \dot{\vec{v}}(t)}{\Delta t} + \mathcal{O}(\Delta t)$$

Hence

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \Delta t \dot{\vec{v}}(t) + \frac{1}{2} \Delta t^2 \left[\frac{\dot{\vec{v}}(t + \Delta t) - \dot{\vec{v}}(t)}{\Delta t} \right] + \mathcal{O}(\Delta t^3)$$

$$= \vec{v}(t) + \frac{1}{2} \Delta t [\dot{\vec{v}}(t) + \dot{\vec{v}}(t + \Delta t)] + \mathcal{O}(\Delta t^3)$$

$$= \vec{v}(t) + \frac{1}{2} \frac{\Delta t}{m} [\vec{F}(t) + \vec{F}(t + \Delta t)] + \mathcal{O}(\Delta t^3)$$

Dropping terms of order Δt^3 or higher...

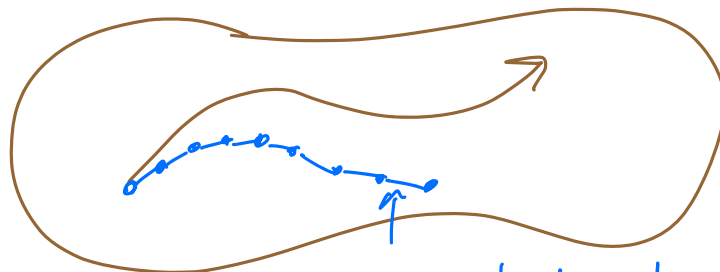
$$\vec{r}(t+\Delta t) = \vec{r}(t) + \Delta t \vec{v}(t) + \frac{\Delta t^2}{2m} \vec{F}(t)$$

$$\vec{v}(t+\Delta t) = \vec{v}(t) + \frac{\Delta t}{2} [\vec{F}(t) + \vec{F}(t+\Delta t)]$$

Verlet Algorithm [Accurate to $\mathcal{O}(\Delta t^3)$]

What goes wrong by dropping these terms of $\mathcal{O}(\Delta t^3)$?
Will all our trajectories be wrong?

Well, we already should have expected them to be "wrong". We are not talking about plotting the motion of planets here (massive, few bodies), we must expect strong chaos. Nevertheless, the statistics of which states are visited could be very accurate, even if trajectories can stray.



Discrete trajectory strays from the continuous solution.

We accept that dynamics will drift, but maybe that's not the end of the world so long as conservation laws are conserved!

Does Verlet conserve energy? Not exactly.

Verlet generates the trajectory

$$\vec{r}(t) = \vec{r}^*(t) + \Delta \vec{r}(t)$$

↑ "exact" soln ↖ error: $\mathcal{O}(\Delta t^3)$

$$E(\vec{r}(t)) = E(\vec{r}^*(t) + \Delta \vec{r}(t)) = E(\vec{r}^*(t)) + \underline{\underline{\mathcal{O}(\Delta t^3)}}$$

More naive discretization schemes would have bigger errors in energy here: $\mathcal{O}(\Delta t^2)$

Does Verlet conserve momentum $\vec{p}(t) = \sum_i m_i \vec{v}_i(t)$?

Yes! (If $U(\vec{r})$ is translationally symmetric, e.g.)
($U(r_1 + \Delta r, r_2 + \Delta r, \dots) = U(r_1, r_2, \dots)$)

Does Verlet conserve angular momentum?

$$\vec{L} = \sum_j \vec{r}_j \times \vec{p}_j$$

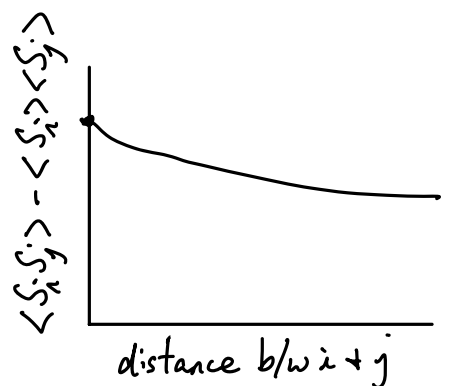
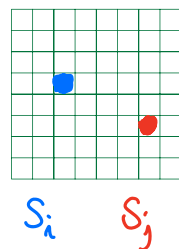
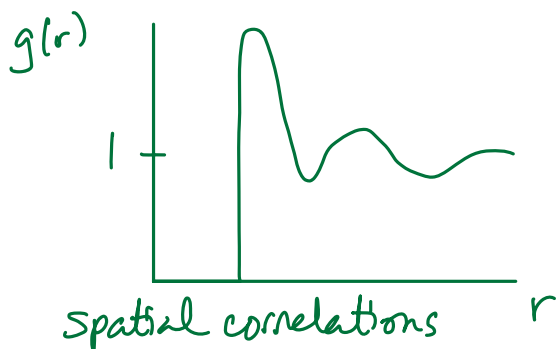
Yes! (If $U(\vec{r})$ is rotationally symmetric
(Note: Periodic boundary conditions break that symmetry.)

Does Verlet conserve the volume of phase space?

Not exactly, but up to $\mathcal{O}(\Delta t^2)$. This conservation is again an order better than a naive algorithm, and it is related to the time-reversibility of this "symplectic" integrator. See Frenkel + Smit.

Congratulations! You just simulated a movie.
Now what do you actually do with it?

BIG IDEA: Many things you measure in physical chemistry experiments can be expressed as correlation functions.

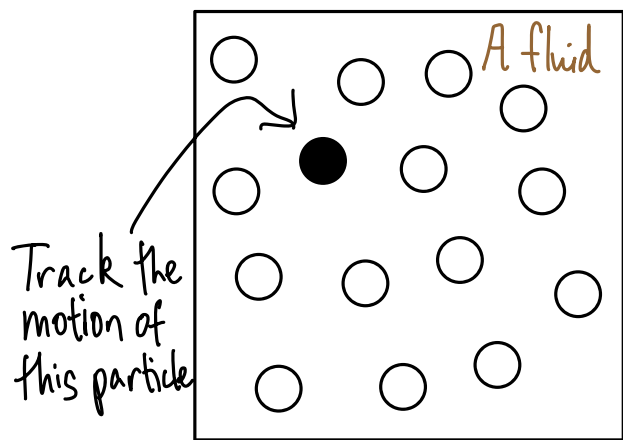


These correlation functions do not depend on time!
 They can be computed by MC (Problem Set 8), but MD both samples the distribution and gives a physical dynamical model. That means MD can also be used for time-correlation functions! Things like

$$\langle \vec{v}(0) \cdot \vec{v}(t) \rangle \text{ or } \langle \delta \vec{v}(0) \cdot \delta \vec{v}(t) \rangle$$

(How similar is the velocity to the velocity a time t later?)

Let's close out the class by seeing how that time-correlation function is related to diffusion.

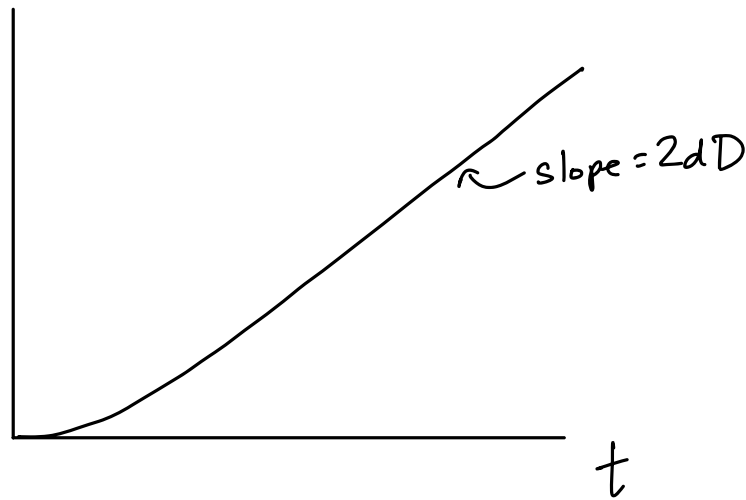


$$\langle |\Delta \vec{r}(t)|^2 \rangle = 2dDt \text{ at long times.}$$

Over short times, $\vec{r}(t) = \vec{r}(0) + \vec{v}(0)t$

$$\Rightarrow \langle |\Delta \vec{r}(t)|^2 \rangle = \langle \vec{v}^2 \rangle t^2$$

$$\langle |\Delta \vec{r}(t)|^2 \rangle$$



How would you compute D from an MD simulation?

1. As the slope of this mean squared displacement curve.

2. Using a velocity autocorrelation function:

$$\vec{r}(t) = \vec{r}(0) + \int_0^t dt' \vec{v}(t')$$

$$\Rightarrow \langle |\Delta \vec{r}(t)|^2 \rangle = \langle \left(\int_0^t dt' \vec{v}(t') \right)^2 \rangle$$

By differentiating each side, we get

$$\frac{d \langle (\Delta r(t))^2 \rangle}{dt} = \left\langle 2 \left(\int_0^t dt_i \vec{v}(t_i) \right) \cdot \frac{d}{dt} \left(\int_0^t dt_i \vec{v}(t_i) \right) \right\rangle$$

Fundamental
Theorem of
Calculus.

$$= 2 \int_0^t dt_i \langle \vec{v}(t_i) \cdot \vec{v}(t) \rangle$$

How does $\langle \vec{v}(0) \cdot \vec{v}(t) \rangle$ differ from $\langle \vec{v}(t_1) \cdot \vec{v}(t+t_1) \rangle$?

I've shifted the origin of time, but if we've already equilibrated, that can't affect the average

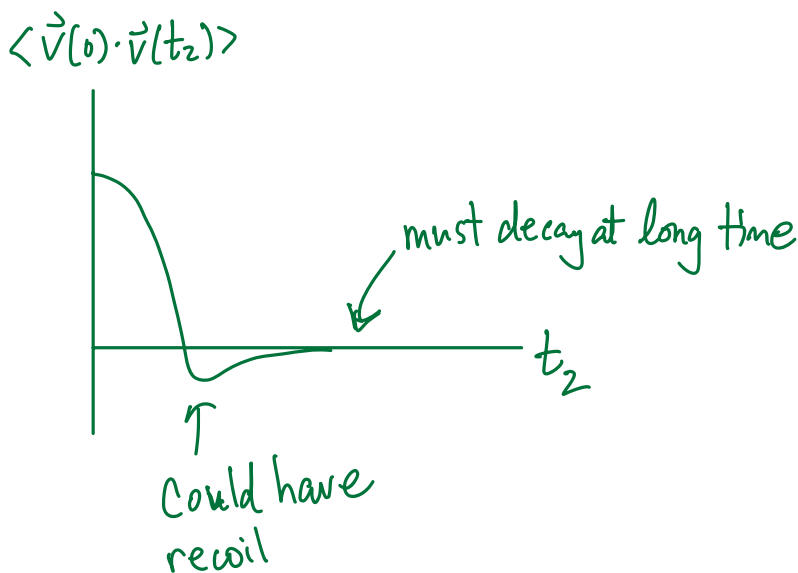
$\Rightarrow \langle \vec{v}(0) \cdot \vec{v}(t) \rangle$ really only depends on the difference b/w times

So...

$$\frac{d \langle (\Delta \vec{r}(t))^2 \rangle}{dt} = 2 \int_0^t dt_1 \langle \vec{v}(0) \cdot \vec{v}(t-t_1) \rangle$$

$$= -2 \int_t^0 dt_2 \langle \vec{v}(0) \cdot \vec{v}(t_2) \rangle \text{ using } t_2 \equiv t-t_1$$

$$= 2 \int_0^t dt_2 \langle \vec{v}(0) \cdot \vec{v}(t_2) \rangle$$



At long times, the RHS limits to

$$2 \int_0^{\infty} dt_2 \langle \vec{v}(0) \cdot \vec{v}(t_2) \rangle$$

But we know from earlier that

$$\langle (\vec{v}(t))^2 \rangle \sim 2Dt \Rightarrow \lim_{t \rightarrow \infty} \left(\frac{d \langle (\vec{v}(t))^2 \rangle}{dt} \right) = 2Dd$$

Hence

$$D = \frac{1}{d} \int_0^{\infty} d\tau \underbrace{\langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle}_{\text{Spontaneous fluctuations}}$$

Transport coefficient

A Green-Kubo Relation

A lot like our relation b/w C_V and $\langle \delta E^2 \rangle$.
Another fluctuation-dissipation result.

Bitti