Dynamics in Classical Fluids

The potential, $U(r^N) = \sum_{i>j=1}^{N} u_{ij}(r_{ij})$

$$u_{ij}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$\sigma \rightarrow$ defines a length scale
$\epsilon \rightarrow$ defines an energy scale
$m \rightarrow$ defines mass (also time!)

To do dynamics, we'll just use $F = ma$:

$$m_i \ddot{\vec{r}}_i = \vec{F}_i = \text{force acting on particle } i$$

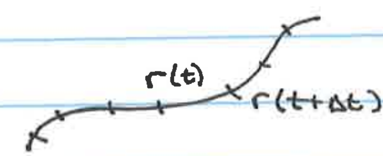
$$= \frac{-\partial}{\partial \vec{r}_i} U(r^N) = -\sum_{j \neq i} \left(\frac{\vec{r}_{ij}}{|\vec{r}_{ij}|}\right) \frac{d u_{ij}(r_{ij})}{\partial r_{ij}}$$

where:

$$\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$$

This equation is a second-order coupled differential equation for $3N$ variables $x_1(t), \dots z_N(t)$

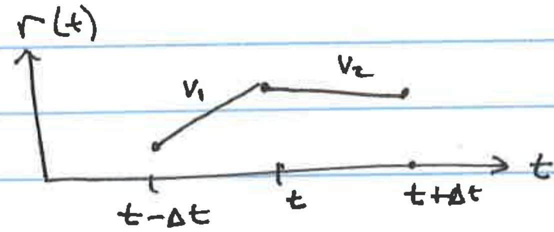
To integrate this, we imagine a path that is locally parabolic in time:



$$r(t+\Delta t) = r(t) + \Delta t\, v(t) + \frac{1}{2}(\Delta t)^2 \frac{F[r(t)]}{m} + \dots$$

Where $v(t) = \dot{r}(t)$ is the velocity

We can approximate $v(t)$



Slope of 1st segment $v_1 = \dfrac{r(t) - r(t-\Delta t)}{\Delta t}$

Slope of 2nd segment $v_2 = \dfrac{r(t+\Delta t) - r(t)}{\Delta t}$

Average slope $v(t) \simeq \dfrac{v_1 + v_2}{2} = \dfrac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$

$\therefore$

$$r(t+\Delta t) = r(t) + \Delta t \,\frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + \frac{1}{2}(\Delta t)^2 \frac{F[r(t)]}{m}$$

$$\boxed{r(t+\Delta t) = 2r(t) - r(t-\Delta t) + (\Delta t)^2 \frac{F[r(t)]}{m}}$$

Verlet's leap frog algorithm. Given r at 2 different times and the forces at time t we can predict the future positions at time $t+\Delta t$

For a Lennard-Jones fluid: $\vec{r}_i^{\,*} = \dfrac{\vec{r}_i}{\sigma}$

$$\vec{r}_i^{\,*}(t+\Delta t) = 2\vec{r}_i^{\,*}(t) - \vec{r}_i^{\,*}(t-\Delta t) - (\Delta t)^2 \left(\frac{48\epsilon}{m\sigma^2}\right) \sum_{j\neq i} \frac{\vec{r}_{ij}^{\,*}}{|\vec{r}_{ij}^{\,*}|} \left[\left(\frac{1}{r_{ij}^*}\right)^{13} - \frac{1}{2}\left(\frac{1}{r_{ij}^*}\right)^{7}\right]$$

The natural (reduced) unit of time is therefore:

$$\tau = \left(\frac{m\sigma^2}{48\epsilon}\right)^{1/2}$$

For Argon, $\frac{\epsilon}{k_B} = 119.8\ K$

$$\sigma = 3.405\ \text{Å}$$

$$\tau \simeq 10^{-13}\ \text{sec} \approx 0.1\ \text{psec}$$

The errors in verlet are higher order than $(\Delta t)^2$ and can be made small by setting Δt small

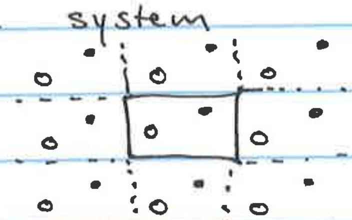
For LJ fluids

$$\Delta t^* \simeq 0.03\tau \qquad (\text{i.e. } 3\ \text{fs})$$

is good for Argon.

Boundary Conditions

We usually imagine a bulk fluid by simulating a small portion of an infinitely replicated system



This is a fairly good model for bulk systems. We can't observe any fluctuations larger than the box length.

Equipartion can help set Initial Conditions

$$K = \sum_{i=1}^{N} \frac{1}{2} m_i \vec{v}_i^{\,2} = \sum_{i=1}^{N} \frac{1}{2} m_i \left({v_i^x}^2 + {v_i^y}^2 + {v_i^z}^2 \right)$$

↳ 3N "squared" terms

$$\langle K \rangle = \frac{3}{2} N k_B T$$

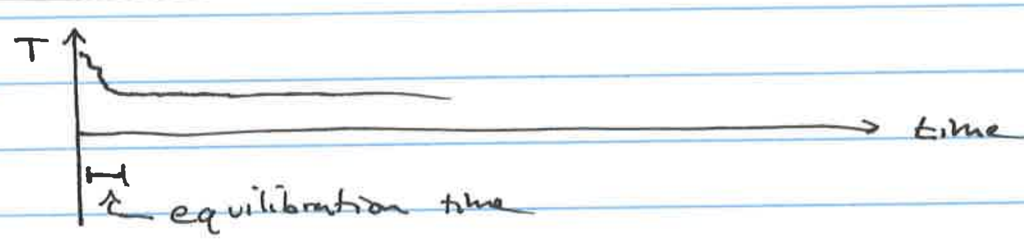
If all the velocities are uniformly distributed,

$$3N \left\langle \tfrac{1}{2} m (v_x^i)^2 \right\rangle = \frac{3N}{2} k_B T$$

$$\left\langle (v_x^i)^2 \right\rangle = \frac{k_B T}{m_i}$$

We can distribute velocities based on some average temperature we want to simulate.

If we start the atoms in a regular lattice, and pick some velocities, do you expect T to go <u>up</u> or <u>down</u> in time? Why?



Dynamics after equilibration

By the ergodic hypothesis:

$$\langle G \rangle = \frac{1}{\tau} \int_0^{\tau} dt\, G\left[r^N(t), v^N(t) \right]$$

initial lattice

If you focus your attention on a single tagged particle over time:  the path is highly irregular:

To quantify what we see in a liquid we use correlation functions:

$$\rho(\vec{r},t) = \sum_{i=1}^{N} \delta[\vec{r}-\vec{r}_i(t)]$$

equilibrium average is time independent

$$\langle \rho(\vec{r}) \rangle = \left\langle \left(\sum_{i=1}^{N} \delta[\vec{r}-\vec{r}_i] \right) \right\rangle$$

particles are identical

$$= \langle N\, \delta(\vec{r}-\vec{r}_1) \rangle$$

in isotropic systems, the average is also independent of $\vec{r}$:

$$\langle \rho \rangle = \frac{N}{V}$$

Generalities about fluctuating quantities:

For any fluctuating quantity $\hat{x}$,

$$P(x) = \langle \delta(x-\hat{x}) \rangle_{\hat{x}}$$ = probability of finding fluctuating quantity $\hat{x}$ with value x.

How we know: consider $f(\hat{x})$ = arbitrary function

$$\langle f \rangle = \int dx\, P(x) f(x)$$

Also:

$$\langle f \rangle = \left\langle \int dx\, \delta(x-\hat{x}) f(x) \right\rangle_{\hat{x}}$$

$$= \int dx\, \langle \delta(x-\hat{x}) \rangle_{\hat{x}} f(x)$$

$\therefore$

$$P(x) = \langle \delta(x-\hat{x}) \rangle_{\hat{x}}$$

Why this matters:

$$\left\langle \sum_{i\neq j=1}^{N} \delta(\vec{r}-\vec{r}_i)\delta(\vec{r}\,'-\vec{r}_j) \right\rangle = \langle N(N-1)\delta(\vec{r}-\vec{r}_1)\delta(\vec{r}\,'-\vec{r}_2) \rangle$$

That is,

the average probability of any particle being found at $\vec{r}$ and another being found at $\vec{r}\,'$

$$= \langle N^2 \delta(\vec{r}-\vec{r}_1)\delta(\vec{r}\,'-\vec{r}_2)\rangle - \langle N \delta(\vec{r}-\vec{r}_1)\delta(\vec{r}\,'-\vec{r}_2)\rangle$$

$$= \langle \rho(\vec{r})\rho(\vec{r}\,')\rangle - \delta(\vec{r}-\vec{r}\,')\langle\rho(\vec{r})\rangle$$

$$= \langle\rho(\vec{r})\rangle\langle\rho(\vec{r}\,')\rangle\, g(\vec{r},\vec{r}\,')$$

$g(\vec{r},\vec{r}\,') =$ probability that a particle will be found at $\vec{r}\,'$, when on is at $\vec{r}$.

This is closely related to the density-density fluctuations at 2 points in space:

$$\chi(\vec{r},\vec{r}\,') = \langle [\rho(\vec{r}) - \langle\rho(\vec{r})\rangle]\cdot[\rho(\vec{r}\,') - \langle\rho(\vec{r}\,')\rangle]\rangle$$

$$= \langle\rho(\vec{r})\rho(\vec{r}\,')\rangle - \langle\rho(\vec{r})\rangle\langle\rho(\vec{r}\,')\rangle$$

$$= \underbrace{\langle\rho(\vec{r})\rangle\delta(\vec{r}-\vec{r}\,')}_{\text{self correlations}} + \underbrace{\langle\rho(\vec{r})\rangle\langle\rho(\vec{r}\,')\rangle[g(\vec{r},\vec{r}\,')-1]}_{\text{interparticle correlations}}$$

For an ideal gas, or a collection of uncorrelated particles, $g(r) = 1$. In that case, only self correlations contribute to $\chi(\vec{r},\vec{r}\,')$

Dynamics

Single particle:

$$F_s(\vec{r}-\vec{r}_1', t-t') = \langle \delta(\vec{r}-\vec{r}' - \vec{r}_1(t) + \vec{r}_1(t')) \rangle$$

average probability that particle 1 was at $\vec{r}$ at t and at $\vec{r}_1$ at t'

$$= \frac{1}{N} \left\langle \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}' - \vec{r}_i(t) + \vec{r}_i(t')) \right\rangle$$

If the system is uniform:

$$= \frac{V}{N} \left\langle \sum_{i=1}^{N} \delta[\vec{r}-\vec{r}_i(t)]\, \delta[\vec{r}' - \vec{r}_i(t')] \right\rangle$$

Therefore

$F_s(\vec{r}, t)$ = probability density that a particle is at position $\vec{r}$ at time t given it was at the origin at time 0

The <u>second moment</u> of $F_s(\vec{r}, t)$ is the mean squared distance travelled by a particle in the interval $t - t'$:

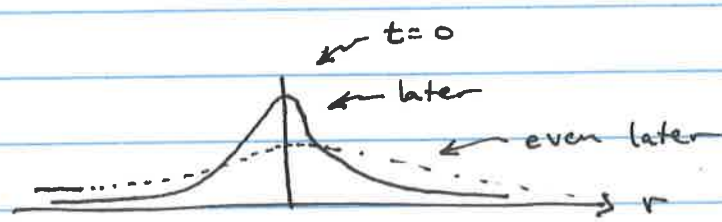
$$\int d\vec{r}\; r^2 F_s(\vec{r}, t-t') = \langle |\vec{r}_1(t) - \vec{r}_1(t')|^2 \rangle$$

$$= R^2(t-t')$$

In random walks, $F_s(\vec{r}, t)$ is a gaussian

$$F_s(r,t) = \underbrace{c(t)}_{\text{normalization}}\, e^{-3r^2/2R^2(t)}$$

That is:



$R^2(t)$ is one example of a __time__ __correlation function__

In general:

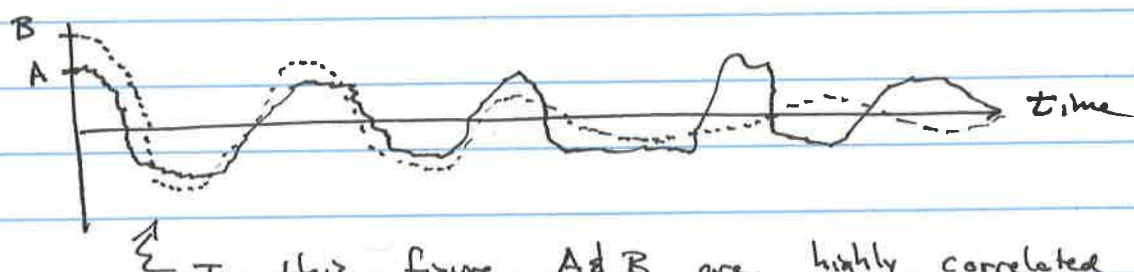
$$\langle A(0)B(t)\rangle = \frac{1}{\tau}\int_0^{\tau} dt'\, A(t')\, B(t'+t)$$

$A(t)$ & $B(t)$ are two (possibly different) variables

$$A(t) = A\left[r^N(t),\ p^N(t)\right]$$

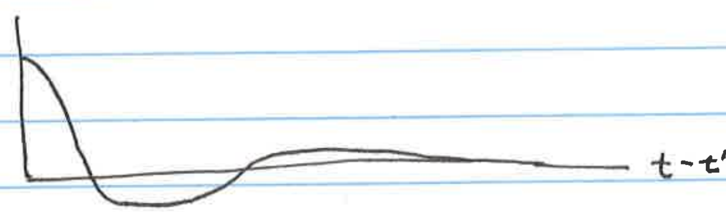
these evolve in time

this property evolves in time



In this figure A & B are highly correlated at short times and anti correlated later

$\langle A(t)\,B(t')\rangle$



At equilibrium:

$$\langle A(0)\,B(t)\rangle = \langle A(t_1)\,B(t_2)\rangle \quad \text{where } t_2 - t_1 = t$$

$\uparrow$ time origin doesn't matter

and

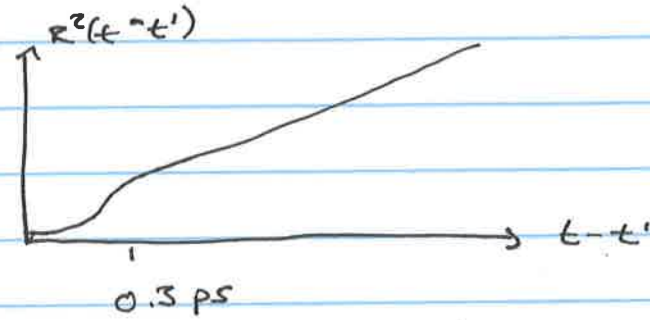
$$\langle A(0)\,B(t)\rangle = \langle A\rangle\langle B\rangle \quad \text{when } t\to\infty$$

That is, loss of correlation & relaxation are identical concepts.

Back to $R^2(t)$:

$$R^2(t) = \langle|\vec{r}_1(t)-\vec{r}_1(t')|^2\rangle = \langle|\vec{r}_1(t)-\vec{r}_1(0)|^2\rangle$$
$$= \langle(\vec{r}_1(t)-\vec{r}_1(0))\cdot(\vec{r}_1(t)-\vec{r}_1(0))\rangle$$
$$= \langle\vec{r}_1^{\,2}(t)\rangle - 2\langle\vec{r}_1(t)\cdot\vec{r}_1(0)\rangle + \langle\vec{r}_1^{\,2}(0)\rangle$$

What it looks like:



After a short transient, $R^2(t-t')$ becomes linear as a function of $t-t'$

Slope = $6D$ where D is the self-diffusion constant:

$$D = \lim_{t\to\infty}\frac{1}{6t}\langle|\vec{r}(t)-\vec{r}(0)|^2\rangle$$

For LJ argon, $D \approx 10^{-5}\ \mathrm{cm^2/s}$

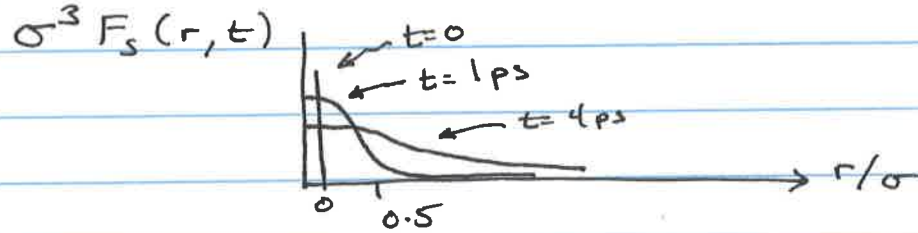
How long will it take an argon atom ($\sigma = 3.4\,\text{Å}$) to move a distance σ in a liquid?

$$D = \frac{\sigma^2}{6t}$$

← what's that?

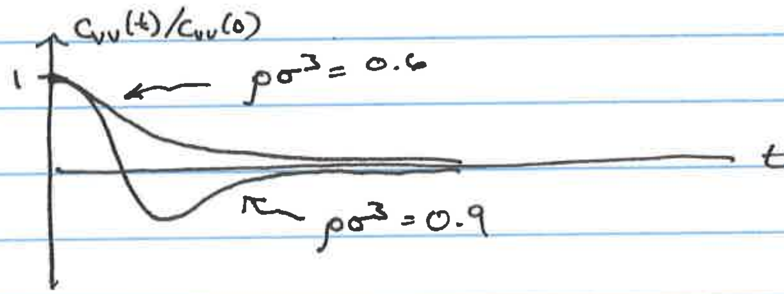
$$t = \frac{\sigma^2}{6D} = \frac{(3.4\times10^{-8}\,\text{cm})^2\ \text{sec}}{6\quad 10^{-5}\ \text{cm}^2} \approx 10\ \text{ps}$$

So:

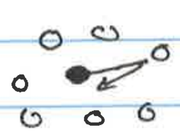


Consider this correlation function

$$C_{vv}(t) = \langle \vec{v}_1(0)\cdot\vec{v}_1(t)\rangle = 3\langle v_{1z}(0)\, v_{1z}(t)\rangle$$



This indicates back-scattering at high densities



← initial velocity is nearly reversed after 1 collision and is pointing in the opposite direction!

We can connect $R^2(t)$ and $C_{vv}(t)$

$$\vec{r}_1(t) = \vec{r}_1(0) + \int_0^t dt' \, \vec{v}_1(t')$$

$$\vec{r}_1(t) - \vec{r}_1(0) = \int_0^t dt' \, \vec{v}_1(t')$$

$$|\vec{r}_1(t) - \vec{r}_1(0)|^2 = \left(\int_0^t dt' \, \vec{v}_1(t')\right)\left(\int_0^t dt'' \, \vec{v}_1(t'')\right)$$

$$= \int_0^t dt' \int_0^t dt'' \, \vec{v}_1(t') \cdot \vec{v}_1(t'')$$

$$\langle |\vec{r}_1(t) - \vec{r}_1(0)|^2 \rangle = \int_0^t dt' \int_0^t dt'' \langle \vec{v}_1(t') \cdot \vec{v}_1(t'') \rangle$$

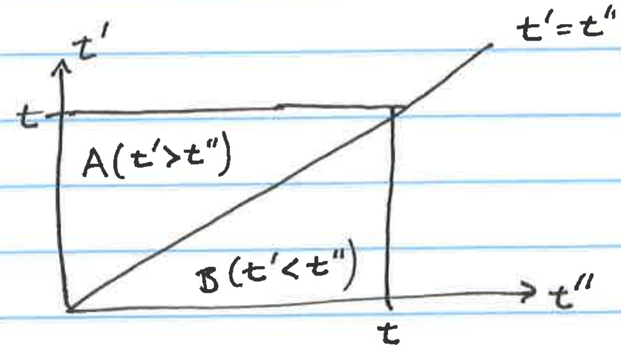
We need to make some assumptions:

1) $\vec{v}$ is a stationary random process, so $\langle \vec{v}(t_1) \vec{v}(t_2) \rangle$ is independent of the origin of time: $\langle \vec{v}(t_1) \cdot \vec{v}(t_2) \rangle = \langle \vec{v}(0) \cdot \vec{v}(t_2 - t_1) \rangle$

2) Eventually velocities will decorrelate:
$\langle \vec{v}(0) \cdot \vec{v}(t) \rangle = 0$ as $t \to \infty$

3) $\langle \vec{v}(0) \cdot \vec{v}(t) \rangle$ is an <u>even</u> function of time
$\langle \vec{v}(0) \cdot \vec{v}(-t) \rangle = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle$

<u>Integration Method</u>:



Integral above is actually 2* Integral over region B

$$R^2(t) = 2\int_0^t dt'' \int_0^{t''} dt' \langle v(0) \cdot v(t'' - t') \rangle$$

Assumption 2

Now we can introduce a new set of variables:

$y = t'' - t'$ ← replaces t' with limits $(t'', 0)$

$x = t''$

$$R^2(t) = 2\int_0^t dx \int_0^x dy \, \langle \vec{v}(0)\cdot\vec{v}(y)\rangle$$

Integration by Parts: $\int u\,dv = uv - \int v\,du$

$$R^2(t) = 2\int_0^t \underbrace{\int_0^x dy \, \langle \vec{v}(0)\cdot\vec{v}(y)\rangle}_{u} \; \underbrace{dx}_{dv} .$$

$du = \langle \vec{v}(0)\cdot\vec{v}(x)\rangle$ $\qquad v = x$

$$R^2(t) = 2\left[x\int_0^x \langle \vec{v}(0)\cdot\vec{v}(y)\rangle dy \Big|_0^t - \int_0^t x\,\langle \vec{v}(0)\cdot\vec{v}(x)\rangle dx\right]$$

$$= 2\left[t\int_0^t \langle \vec{v}(0)\cdot\vec{v}(y)\rangle dy - \int_0^t x\,\langle \vec{v}(0)\cdot\vec{v}(x)\rangle dx\right]$$

$$R^2(t) = 2\int_0^t (t-x)\langle \vec{v}(0)\cdot\vec{v}(x)\rangle dx$$

Since $\displaystyle D = \lim_{t\to\infty} \frac{1}{6t} R^2(t) = \lim_{t\to\infty} \frac{1}{3t}\int_0^t (t-x)\,\langle \vec{v}(0)\cdot\vec{v}(x)\rangle dx$

As $t\to\infty$, $(t-x) \sim t$, so

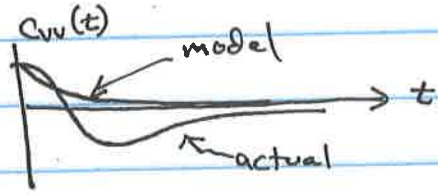
$$\boxed{D = \frac{1}{3}\int_0^\infty dx \,\langle \vec{v}(0)\cdot\vec{v}(x)\rangle}$$

← Green-Kubo relation

Models for $C_{vv}(t)$

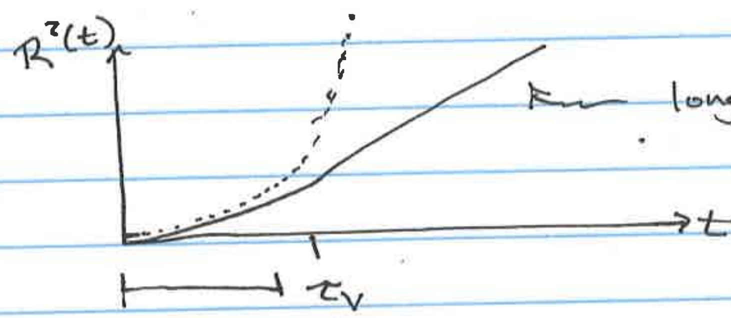
$$C_{vv}(t) \approx \langle v^2 \rangle e^{-t/\tau_v}$$ ← Exponential relaxation model

(Models random walks with τ_v^{-1} = collision frequency)



In this model, $R^2(t) = \langle v^2 \rangle 2 \int_0^t dx\, (t-x)\, e^{-x/\tau_v}$

$$R^2(t) = 2\langle v^2 \rangle \left[t\tau_v - \tau_v^2 \left(1 - e^{-t/\tau_v}\right) \right]$$



long time slope: $= 2\langle v^2 \rangle \tau_v = \frac{6 k_B T}{m} \tau_v$

At short times this model predicts: $\langle v^2 \rangle t^2$

This simple model predicts diffusion!

$$D = \frac{k_B T \tau_v}{m}$$ i.e. rate of momentum relaxation ↑ → Diffusion ↓

or frequent collisions slow down diffusion

or a collision that occurs before a particle can move will slow down transport.

Independent of this relaxation model for $C_{vv}(t)$ we can define:

$$\tau_v = \int_0^\infty dt \, \frac{\langle \vec{v}(t) \cdot \vec{v}(0) \rangle}{\langle v^2 \rangle}$$

And therefore

$$\frac{mD}{k_B T} \equiv \tau_v \quad \text{is an } \underline{\text{identity}}$$

At short times,

$$\vec{r}_i(t) = \vec{r}_i(0) + t\vec{v}_i(0) + \underbrace{O(t^2)}_{\text{All interparticle forces}}$$

The definition of the self-correlation function:

$$F_s(\vec{r}, t) = \langle \delta[\vec{r}_1(t) - \vec{r}_1(0) - \vec{r}] \rangle$$

$$\approx \langle \delta[t\vec{v}_1 - \vec{r}] \rangle$$

$$= \int d\vec{v}_1 \, \phi_{MB}(\vec{v}_1) \, \delta(\vec{v}_1 t - \vec{r})$$

where

$$\phi_{MB}(\vec{v}) = e^{-m\vec{v}^2/2k_B T}$$ is the Maxwell-Boltzmann distribution

$$\delta(\vec{v}_1 t - \vec{r}) \Rightarrow \vec{v}_1 = \frac{\vec{r}}{t}$$

$$\therefore \quad F_s(\vec{r}, t) = c \, e^{-r^2/(2t^2 \beta m)}$$

$\therefore$

$F_s(r,t)$ is Gaussian & $R^2(t)$ is <u>quadratic</u> at small times

$F_s(r,t)$ is Gaussian & $R^2(t)$ is <u>linear</u> at long times