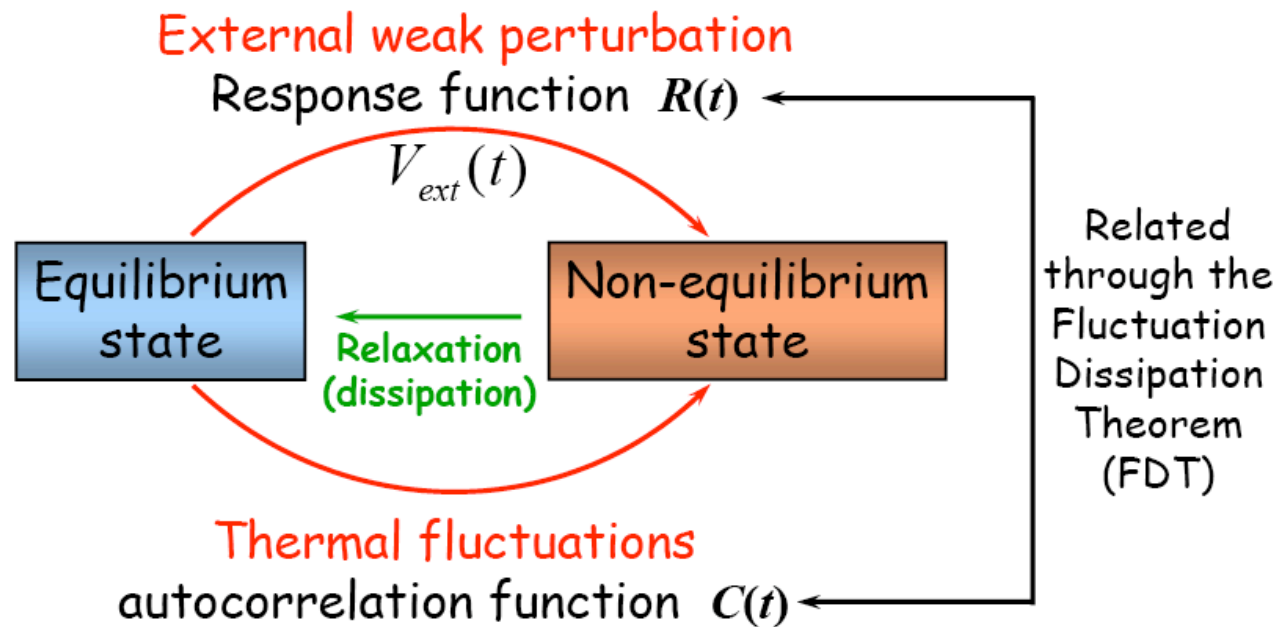


Linear Response Theory



$$\frac{V_{ext}}{kT} \langle \delta A(t) \delta A(0) \rangle = \bar{A}(t) - \langle A \rangle$$

$$V_{ext}(t) = -Af(t)$$

$$\langle A(t) \rangle = \int_0^{\infty} dt' R(t') f(t-t')$$

$$R(t) = -\frac{1}{kT} \frac{d}{dt} \langle \delta A(0) \delta A(t) \rangle$$

The Experiment: Molecular Dynamics Simulations

Goal:

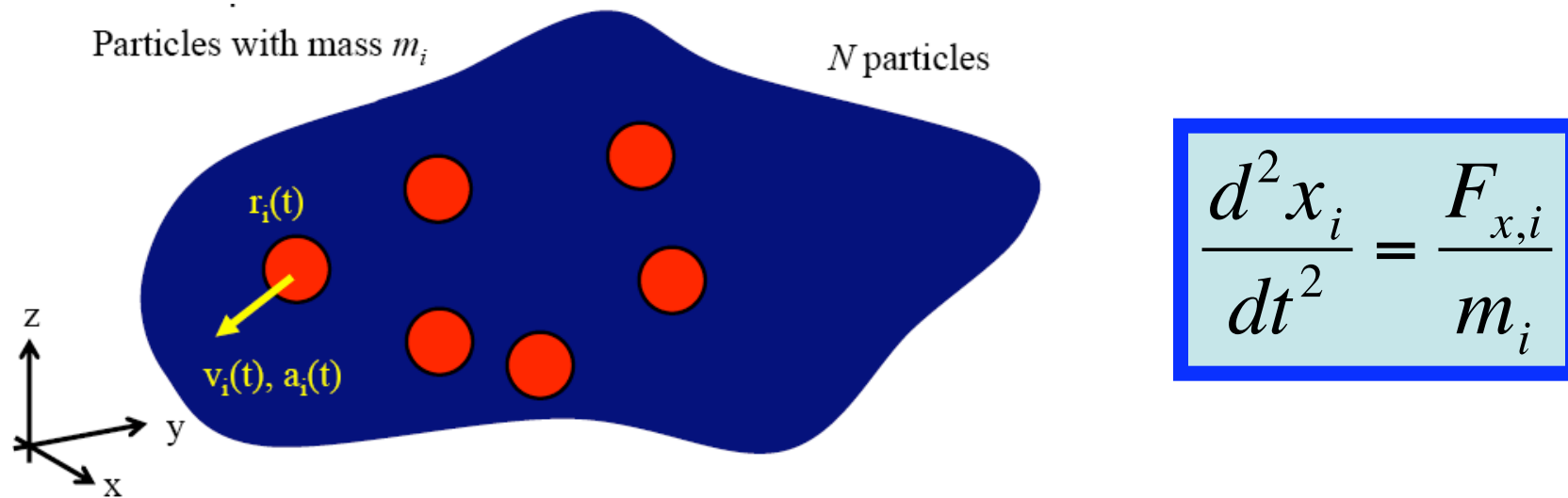
extract dynamical information (?) from a system

Two ways:

- equilibrium simulations
- non equilibrium simulations

Core of any Molecular Dynamics program:

MD generates the **dynamical trajectories** of a system of **N particles** by **integrating Newton's equations of motion**.



dynamical trajectories:

time evolution of the system in phase space
(positions(t) and velocities(t) for all the N particles)

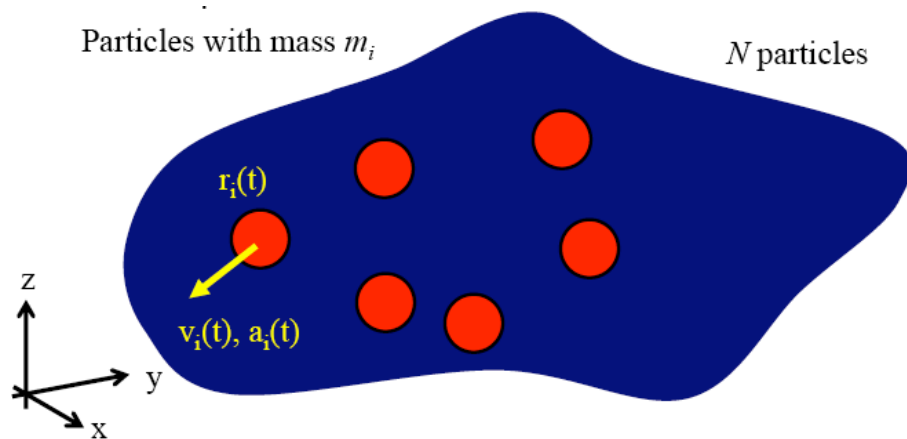
MD generates the **dynamical trajectories** of a system of **N particles** by **integrating** Newton's equations of motion.

$$\frac{d^2 r_i}{dt^2} = \frac{F_i(r_1, \dots, r_N)}{m_i} = -\nabla_{r_i} U(r_1, \dots, r_N)$$

Intermolecular potential U :
simple, analytical function of
all atomic positions.

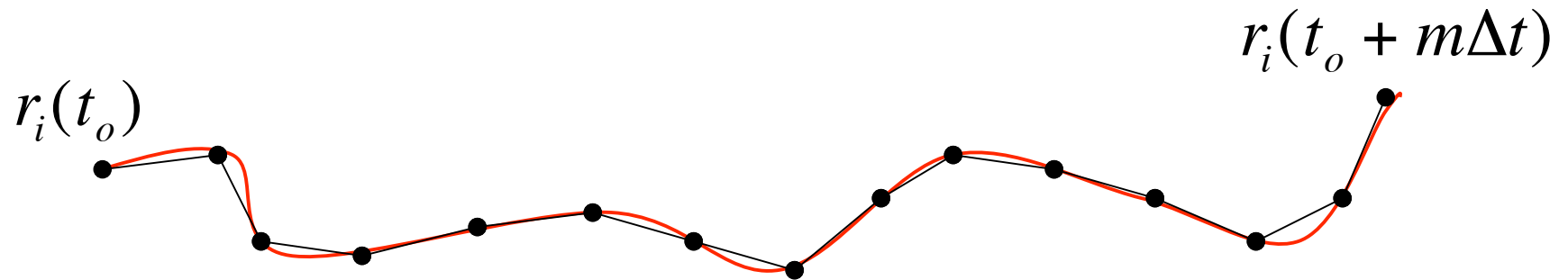
N coupled non-linear
differential equations

N-body problem cannot
be solved exactly for $N > 2$!



**solved by discretizing the time
and evolving the system in
finite time steps**
(atoms already discretize space)

To evolve the particles' positions we discretize the time evolution:



m steps of time step Δt

$$r_i(t_0) \rightarrow r_i(t_0 + \Delta t) \rightarrow r_i(t_0 + 2\Delta t) \rightarrow \dots \rightarrow r_i(t_0 + m\Delta t)$$

Approximation made to advance a time step: Taylor series expansion of positions, velocities, accelerations.

Taylor expansion of positions, velocities and accelerations

$$r_i(t + \Delta t) = r_i(t) + v_i(t)\Delta t + \frac{1}{2}a_i(t)\Delta t^2 + \frac{1}{6}b_i(t)\Delta t^3 + \dots$$

$$v_i(t + \Delta t) = v_i(t) + a_i(t)\Delta t + \frac{1}{2}b_i(t)\Delta t^2 + \dots$$

$$v_i = \frac{dr_i}{dt}$$

$$a_i(t + \Delta t) = a_i(t) + b_i(t)\Delta t + \dots$$

$$a_i = \frac{d^2r_i}{dt^2}$$

How do we implement this to integrate newton's?

We use finite difference methods such as the Verlet algorithm

Compute forces, advance one step:

algorithm based on the current time position $r(t)$ and acceleration $a(t)$,
and the positions at the previous step $r(t-\Delta t)$

$$r_i(t + \Delta t) = r_i(t) + v(t)\Delta t + \frac{1}{2}a_i(t)\Delta t^2 + \dots$$

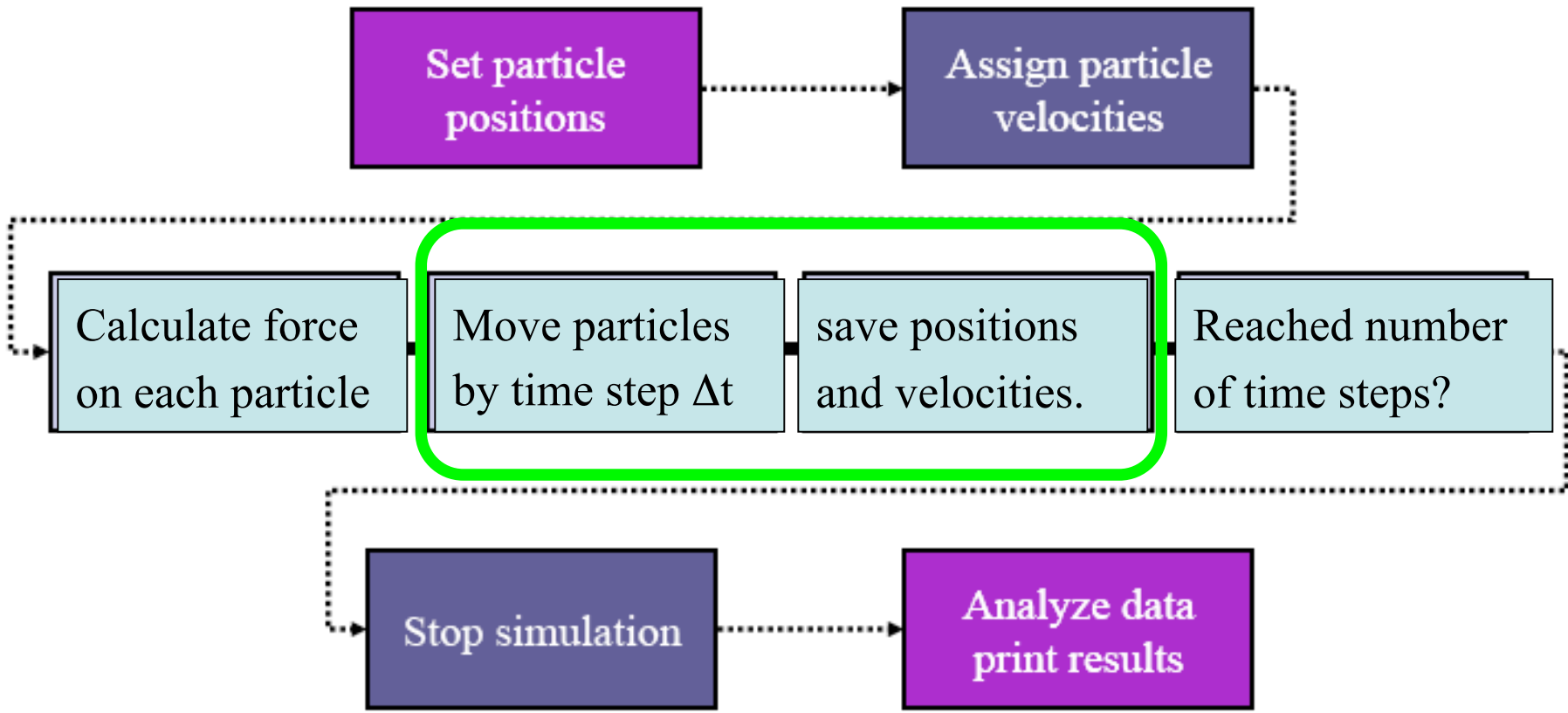
$$r_i(t - \Delta t) = r_i(t) - v(t)\Delta t + \frac{1}{2}a_i(t)\Delta t^2 + \dots$$

Adding the two equations we get rid of $v(t)$:

$$r_i(t + \Delta t) = 2r_i(t) - r_i(t - \Delta t) + a_i(t)\Delta t^2$$

$f_i(t) = ma_i(t)$

future position current position past position current acceleration need to compute Current forces



What thermodynamic ensemble is produced by evolving the dynamics with Verlet's algorithm?

no external forces acting on the system
nor particles entering or leaving, the algorithm :

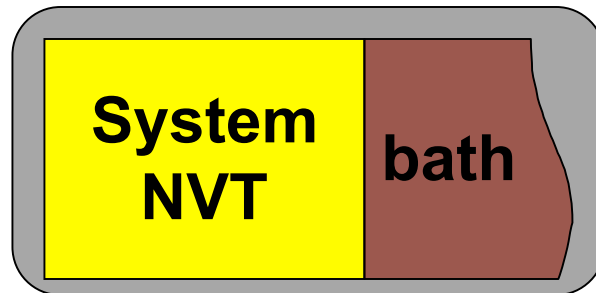
- 1) Conserves the energy E
- 2) Conserves the number of particles N
- 3) Conserves the volume V

The integration of Verlet's equations yields the microcanonical ensemble (NVE).

Other ensembles (NVT, NPT, NPH, etc) can be realized by modifying the equations of motions.

Fluctuations depend on the thermodynamic ensemble!

Equilibrium simulations in the canonical ensemble: Nose-Hoover thermostat coupled to the system



(System + Bath)
together is NVE

Purely **deterministic** canonical MD.
(**no stochastic forces or randomizations**)

The thermostat has its own degree of freedom **s** with
corresponding momentum **p_s**. (**imagine a piston!**)

Energy flows between thermostat and system's degrees of freedom.
Coupling time.

stages of a MD experiment

INITIALIZATION

prepare initial conditions of model system.



EQUILIBRATION

Evolve this system in time by solving newton's equations of motion until the properties do not change with time.



COLLECT EQUILIBRIUM DATA

Evolve this system in time by solving newton's equations of motion for the system in equilibrium. Collect data vs time.



ANALYSIS

Compute observables from the data collected



From the eq-MD we have the time evolution of:

Atomic positions
Atomic velocities
Atomic forces
Atomic masses
Potential energy
Volume

↓ structure

Radial distribution functions
Structure factors
Conformations ...

thermodynamics →

We may **want to** compute:

Total energy
Kinetic energy
Temperature
Pressure
Volume
Potential energy
Heat capacity

dynamics →

Entropy
Gibbs free energy
Helmholtz free energy
Chemical potential

Diffusivity
Viscosity
Responses ...

In italics are properties that cannot be computed for an individual time of the trajectory

Some thermodynamic properties are computed as time averages over the equilibrium run.

$$\langle E \rangle_t = \lim_{t \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} E(p^N(t), r^N(t)) dt \quad \text{If time were continuous...}$$

Potential Energy

$$E_p = \langle U(t) \rangle_t = \frac{1}{M} \sum_{k=1}^M U(t_k)$$

$$U(t_k) = U(r_1(t_k), \dots, r_N(t_k))$$

The potential energy is a known function of the coordinates for each configuration.

Time in MD is not continuous but a succession of steps. Average is over discrete number of steps.

To compute an average, we should discard the equilibration (non-stationary) part of the trajectory.

Kinetic Energy & Temperature

$$K(t_j) = \sum_{i=1}^N \frac{v_i^2(t_j)}{2m_i}$$

$$K = \langle K(t) \rangle_t = \frac{1}{M} \sum_{j=1}^M K(t_j)$$

$$K = \frac{k_b T}{2} (3N - n_c)$$

$$T = \frac{2K}{2k_b (3N - n_c)}$$

Instantaneous kinetic energy is the sum of the instantaneous atomic k.e. (computed from particles velocities and masses)

The **thermodynamic kinetic energy** is a time average of the instantaneous values of K on an equilibrium trajectory.

The temperature is obtained from K through the equipartition theorem (valid because these are classical trajectories)

If center of mass of the system is fixed $n_c=3$

Instantaneous and thermodynamic temperatures are defined as for K.

Pressure

$$\langle W \rangle = \frac{1}{3} \sum_{i=1}^N \vec{r}_i \cdot \vec{f}_i$$

Instantaneous pressure is obtained from the virial theorem.

$$P = \rho k_b T + \langle W \rangle / V$$

The calculation of the pressure requires knowledge of forces, positions and temperature (i.e. velocities)

$$P = P^{ideal} + P^{excess}$$

↗ ↖

kinetic interactions

Heat Capacity

$$C_v = \left(\frac{dE}{dT} \right)_V$$

from simulations at different energy
(temperature)

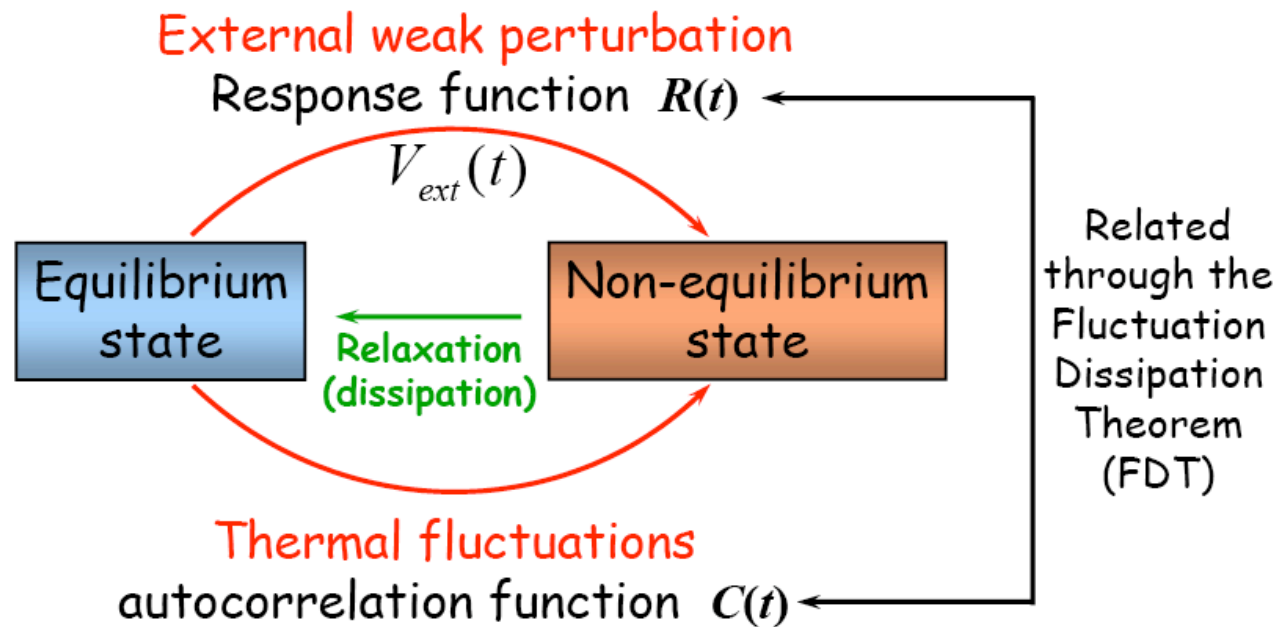
We cannot define an instantaneous value of C_v nor for any other response function (note difference with V , E , K , T)

In canonical (NVT) simulations, the heat capacity can be computed from the fluctuations of total energy over an equilibrium trajectory.

$$C_v = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_b T^2}$$

And in NVE ensemble?

Linear Response Theory



$$\frac{V_{ext}}{kT} \langle \delta A(t) \delta A(0) \rangle = \bar{A}(t) - \langle A \rangle$$

$$V_{ext}(t) = -A f(t)$$

$$\langle A(t) \rangle = \int_0^{\infty} dt' R(t') f(t-t')$$

$$R(t) = -\frac{1}{kT} \frac{d}{dt} \langle \delta A(0) \delta A(t) \rangle$$

Diffusion

$$D = \frac{1}{3} \int_0^{\infty} dt \langle v_i(t) v_i(0) \rangle$$
$$2tD = \frac{1}{3} \langle |r_i(t) - r_i(0)|^2 \rangle$$

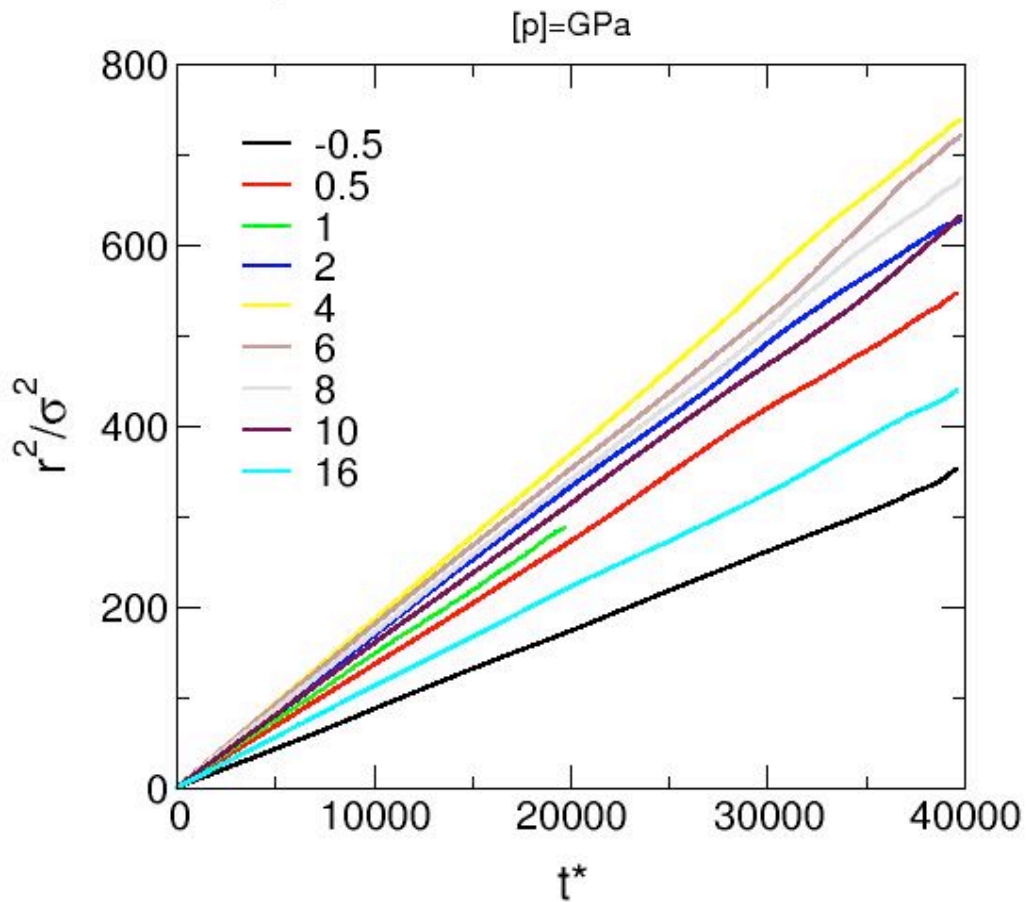
We compute the average over all the particles at each time t .

For an equilibrium simulation, all times are equivalent, so we also average over all possible initial times.

Short t , long t

Mean square displacement (diffusion)

MSD vs pressure for SW Silicon at T=1150K



Is this equation valid for all times and circumstances?

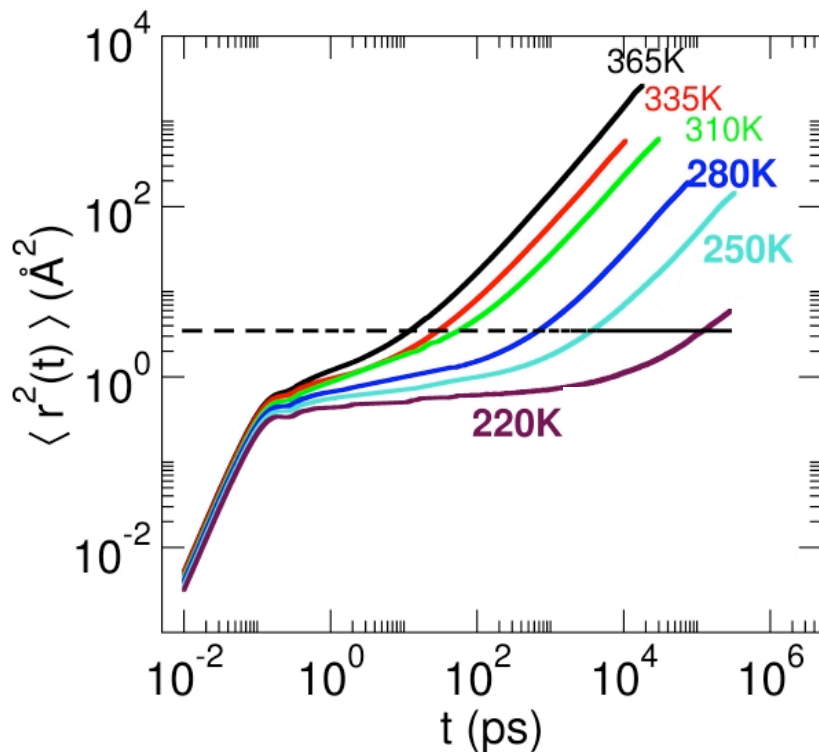
$$\langle \Delta r(t)^2 \rangle = 6Dt$$

Mean square displacement (diffusion)

Is this equation valid for all times and circumstances?

$$\langle r^2(t) \rangle = 6D t$$

THE ANSWER IS NO.



- 1) at short times (< 1 ps) the motion is not diffusive but ballistic.
- 2) Diffusion in viscous liquids may show a plateau due to caging of the neighbors.
- 3) But at long times (long compared with the time for individual displacements) it approaches Einstein's

Dipole/Rotational correlations

$$C_1(t) = \frac{\langle \mu_\alpha(0) \mu_\alpha(t) \rangle}{\langle \mu_\alpha(0) \mu_\alpha(0) \rangle}$$

Single molecule dipole autocorrelation
(**first rank**; average over all $\alpha = 1, \dots, N$ molecules)

Difficult to measure in experiments

$$M(t) = \left\langle \left(\sum_{\alpha=1}^N \mu_\alpha(0) \right) \left(\sum_{\beta=1}^N \mu_\beta(t) \right) \right\rangle$$

Total dipole autocorrelation (**first rank**)

dielectric spectroscopy measures its Laplace transform. (cross $\alpha\beta$ terms make it different from the single molecule above)

$$C_2(t) = \frac{3\langle \mu_\alpha(0) \mu_\alpha(t) \rangle - 1}{3\langle \mu_\alpha(0) \mu_\alpha(0) \rangle - 1}$$

Single molecule dipole autocorrelation
(**second rank**; average over all $\alpha = 1, \dots, N$ molecules)

Can be measured by Spin Echo NMR

Pressure correlations

$$\eta = \frac{V}{9kT} \int_0^{\infty} \langle \delta P(0) \delta P(t) \rangle dt$$

Bulk viscosity

Autocorrelation of the diagonal elements of the pressure (stress) tensor P_{xx} , P_{yy} , P_{zz}

$$\eta = \frac{V}{kT} \int_0^{\infty} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \rangle dt$$

Shear viscosity

Autocorrelation of the off-diagonal elements of the pressure (stress) tensor P_{xy} , P_{xz} , P_{yz}

$$P_{\alpha\beta} = \frac{1}{V} \left(\sum_{i=1}^N \frac{p_{i\alpha} p_{i\beta}}{m_i} + \sum_{i=1}^N \frac{r_{i\alpha} f_{i\beta}}{m_i} \right)$$

kinetic

virial

Energy fluctuations

$$C_v(\omega) = \frac{\langle \delta E^2 \rangle}{k_b T^2} - \frac{i\omega}{k_b T^2} \int_0^{\infty} \langle \delta E(0) \delta E(t) \rangle e^{-i\omega t} dt$$

(Nielsen & Dyre, 1996)

Frequency dependent Heat Capacity

Note that the heat capacity is NOT the response to a field perturbing the system!

We will compute:

-static c_v

-autocorrelation of E

-difficult to converge...