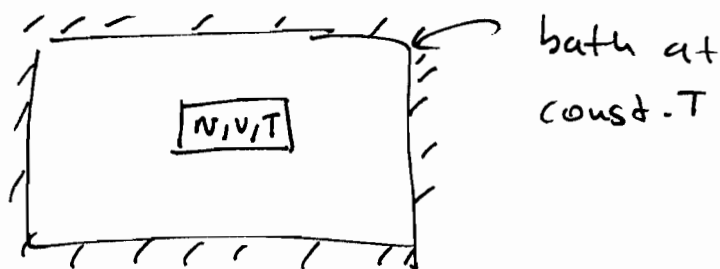
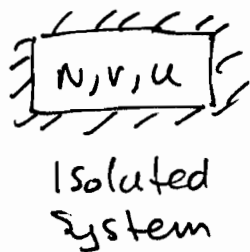


Constant-T Molecular Dynamics



Newton's equations of motion naturally sample N, v, u ensemble. How can we measure the instantaneous (fluctuating) temperature of such a system?

$$\text{Average kinetic energy} = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

(For any system - in monoatomic ideal gases this) gives $C_v = \frac{3}{2} R$

$$\text{Apparent "kinetic" temperature: } T_k = \frac{m}{3k_B} \frac{\sum_{i=1}^N v_i^2}{N}$$

The apparent kinetic temperature fluctuates even for a system under NVT conditions.

From Maxwell-Boltzmann distribution, $P(v) = \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\frac{\beta v^2}{2}}$

$$\text{can be shown that } \frac{\langle T_k^2 \rangle - \langle T_k \rangle^2}{\langle T_k \rangle^2} = \frac{\langle v^4 \rangle - \langle v^2 \rangle^2}{\langle v^2 \rangle^2} =$$

$$= \frac{2}{3N} \quad (\sim 1\% \text{ for } N=100)$$

This means that we cannot simply rescale the velocities every now and then to keep T constant.

Berendsen Thermostat / Barostat

(used in Hyperchem - approximate, does not follow proper NVT ensemble) - see J. Chem. Phys. 81:3684 (1984)

Coupling to a "heat bath" with coupling constant τ

$$\frac{dT_k}{dt} = \frac{(T_0 - T_k)}{\tau}$$

\uparrow target value of T \nwarrow instantaneous kinetic T

$\left\{ \begin{array}{l} \tau \text{ must} \\ \text{be } > \Delta t \\ \text{of simulation} \end{array} \right.$

$$\Rightarrow \text{Scale velocities by factor } \lambda = \left[1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{T_k} - 1 \right) \right]^{1/2}$$

If τ is short ($\ll 0.1$ ps) one gets essentially no fluctuations in T_k , but deviations from correct NVT behavior are greatest.

A similar approach can be used to control pressure for constant-pressure simulations

$$\frac{dP}{dt} = (P_0 - P) / \tau_p$$

Scale volume at each step by factor

$$\lambda = 1 - \frac{B_T \Delta t}{\tau_p} (P_0 - P)$$

\nwarrow isothermal compressibility of system

Andersen Thermostat

Stochastic collisions with phantom particles

J. Chem. Phys. 72:2384 (1980)

- ① Start with initial positions + velocities, integrate
- ② for every time step, check for probability of collision $p\Delta t$; if there is a collision, new velocity for a randomly selected particle is drawn from Maxwell-Boltzmann distribution

→ Dynamics are influenced, since randomization of velocities leads to rapid loss of correlations

Nose-Hoover Thermostat

JCP 81:511 (1984)

Deterministic MD with an extended Lagrangian (additional degree of freedom, s)

Time step scales with s (fluctuates)

→ Dynamics only mildly perturbed

→ m_s (thermal mass associated w/ s) influences how quickly system responds to perturbations

→ extended Lagrangian approach can be extended to pressure, polarizability etc

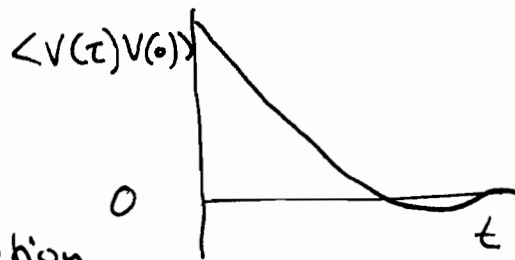
For all NVT cases, energy $U_{\text{tot}} = U_{\text{kin}} + U_{\text{pot}}$

is no longer constant

Measuring Transport Coefficients

Obtaining transport properties from equilibrium MD simulations involves "Green-Kubo" relationships. The simplest of these is for the self-diffusion coefficient D :

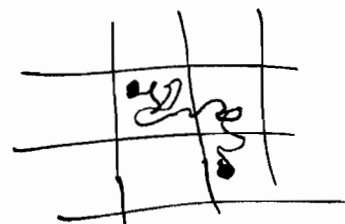
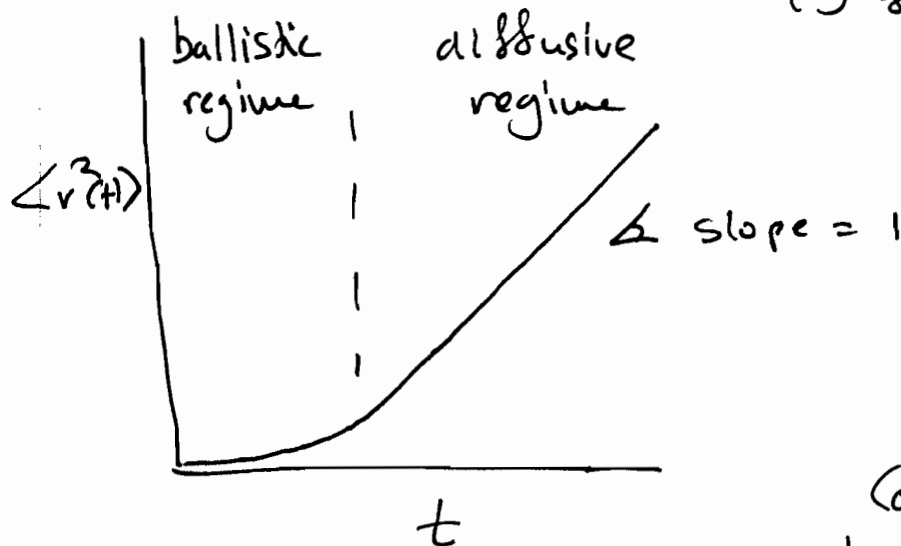
$$D = \int_0^{\infty} d\tau \underbrace{\langle V(\tau)V(0) \rangle}_{\text{velocity autocorrelation function}}$$



An alternative approach for D is provided by the Einstein relationship for a particle that starts at position $r(0) = 0$

$$\lim_{t \rightarrow \infty} \frac{\partial \langle r^2(t) \rangle}{\partial t} = 2dD$$

↓
dimensionality of space
(3 for normal systems)



Care needs to be taken to correct for periodic boundary conditions

Other Green-Kubo relationships:

Viscosity $\eta = \frac{1}{Vk_B T} \int_0^\infty dt \langle \sigma^{xy}(0) \sigma^{xy}(t) \rangle$

(off-diagonal components of pressure tensor)

Thermal Conductivity $\lambda = \frac{1}{Vk_B T} \int_0^\infty dt \langle j_z(0) j_z(t) \rangle$

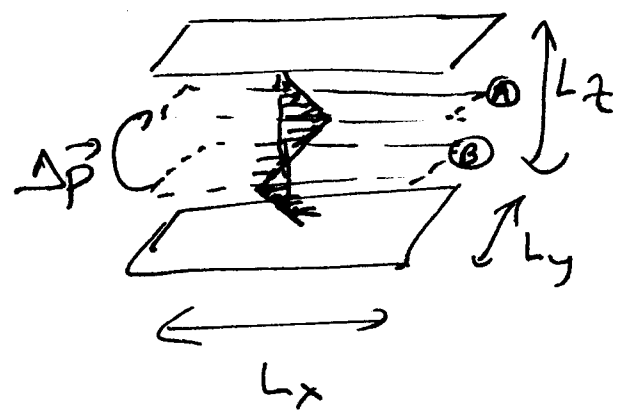
energy fluxes

Transport coefficients can also be measured by non-equilibrium molecular dynamics simulations in which an explicit gradient (e.g. of concentration for D , or velocity for η) is set up and the response measured (e.g. flux for D , stress for η).

- very large gradients relative to experiments to obtain statistically meaningful results (small box dimensions)
- need for temperature control (shearing a system heats it up)
- extrapolations to low gradients needed

Reverse Non-Equilibrium Simulation

Florian Müller-Plathe, J. Chem. Phys. 106:6082 (1997)



Periodically exchange momentum by selecting particles in slabs A and B } most negative p_x^- (A) } most positive p_x^+ (B)

Swap p_x^- with p_x^+

Shear Stress

$$\tau_{xx} = \frac{\langle \Delta P_x \rangle}{2L_x L_y \Delta t} \leftarrow \begin{matrix} \text{momentum transfer} \\ \text{time} \end{matrix}$$

Linear flow field in $v_x(z)$

$$\text{viscosity } \eta = \frac{\tau_{xx}}{\langle \partial v_x / \partial z \rangle}$$

A good idea, but see movie for issues...