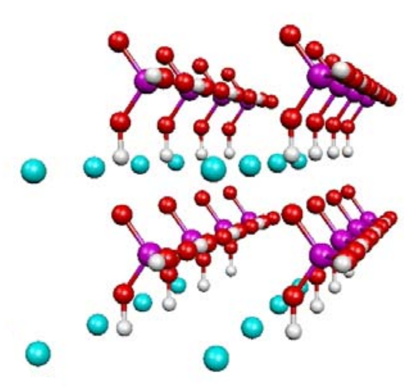
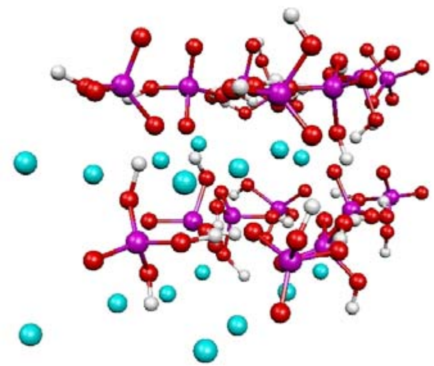
Statistical Mechanics and Molecular Dynamics

IMA Workshop on
Classical and Quantum Approaches in Molecular Modeling





Mark Tuckerman

Dept. of Chemistry

and Courant Institute of Mathematical Science

100 Washington Square East

New York University, New York, NY 10003

Lecture Outline

- **Hamiltonian systems and Liouville's theorem**
- **The Liouville equation and equilibrium solutions**
- **The microcanonical ensemble**
- **The canonical ensemble**
- **Linear response theory and transport properties**

Molecular Dynamics

- A physical system described at an atomistic level consists of N atoms

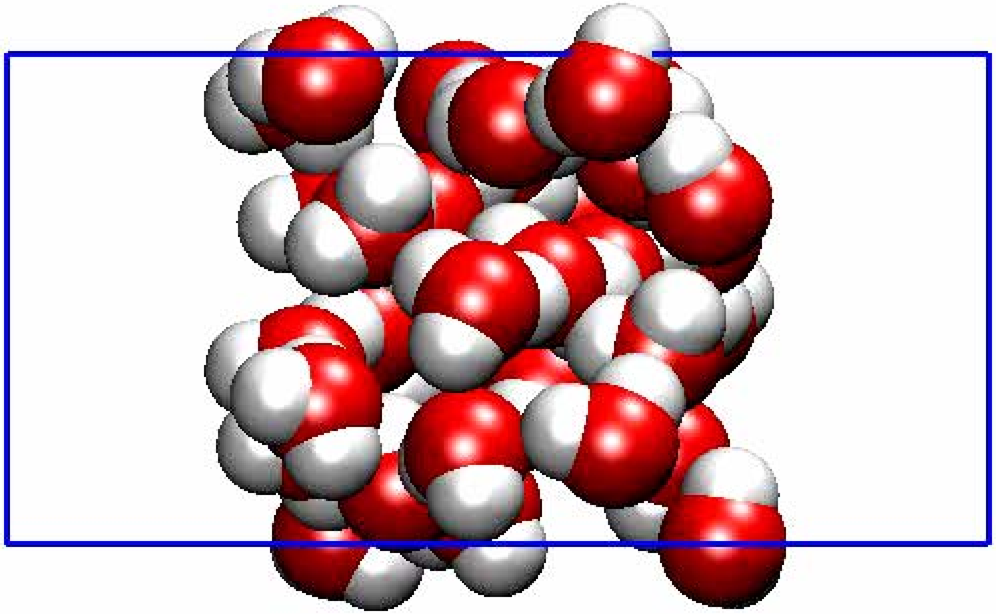
- The dynamics of the system can be described using the laws of classical mechanics

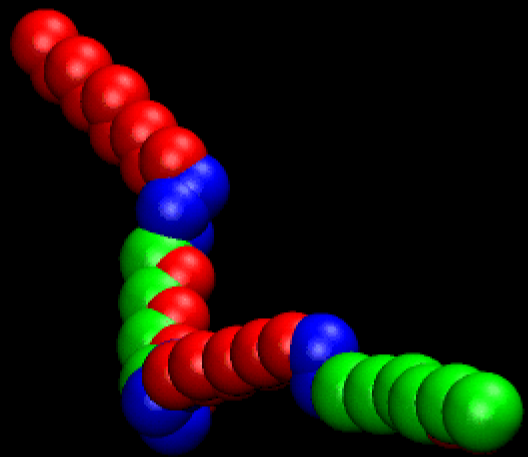
- Each atom experience a force due to all the other atoms in the system and any other external influences. Hence, at any instant in time, there will be N forces $\mathbf{F}_1,\ldots,\mathbf{F}_N$.

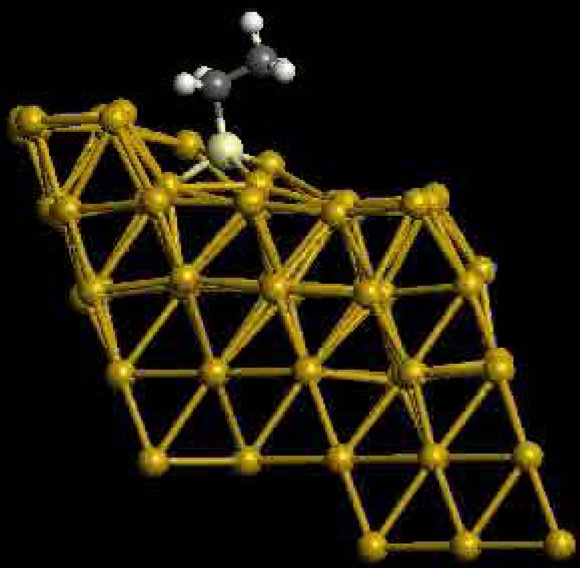
- The forces give rise to accelerations $\mathbf{a}_1,\ldots,\mathbf{a}_N$ according to Newton's second law of motion:

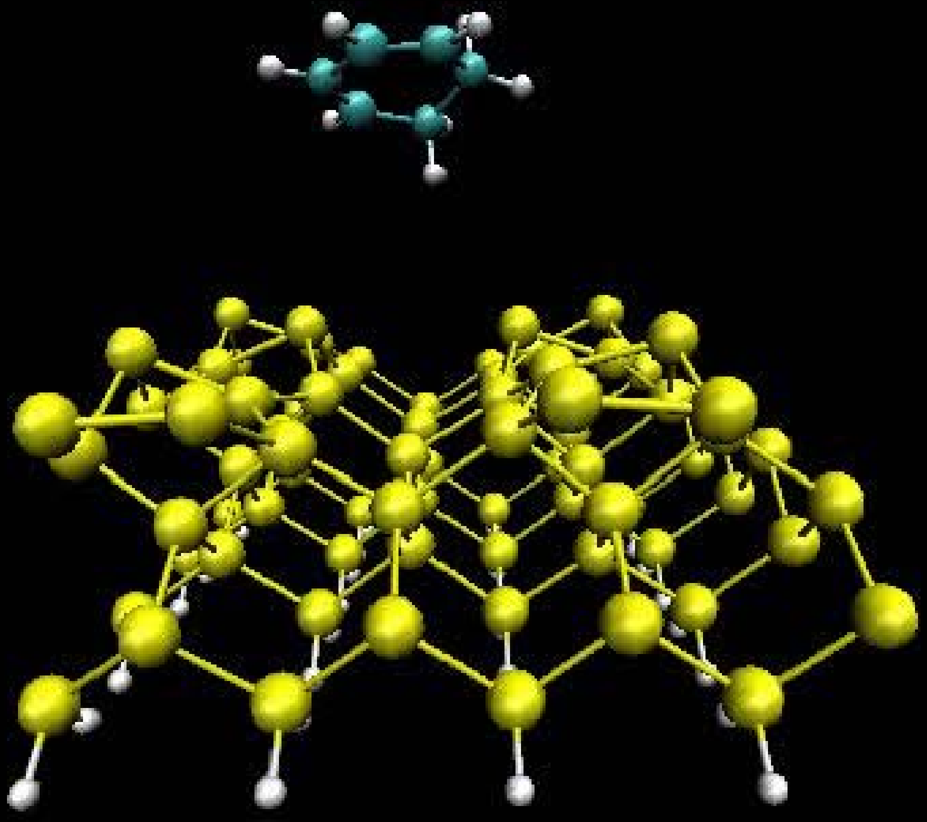
$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2} \qquad i = 1,\ldots,N$$

- From these equations, we seek to determine the positions $\mathbf{r}_1(t),\ldots,\mathbf{r}_N(t)$ and velocities $\mathbf{v}_1(t),\ldots,\mathbf{v}_N(t)$ of all atoms in the system as functions of time.









Hamiltonian Mechanics

Hamiltonian:

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

Equations of motion:

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= -\frac{\partial H}{\partial \mathbf{r}_i} = -\frac{\partial U}{\partial \mathbf{r}_i} = \mathbf{F}_i(\mathbf{r}_1, ..., \mathbf{r}_N) \\ &= m_i \ddot{\mathbf{r}}_i \end{aligned}$$

Initial conditions: $\{\mathbf{p}_1(0), ..., \mathbf{p}_N(0), \mathbf{r}_1(0), ..., \mathbf{r}_N(0)\}$

Energy conservation:

$$\begin{aligned} \frac{dH}{dt} &= \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i}{m_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial U}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i \right] \\ &= \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i}{m_i} \cdot \mathbf{F}_i - \mathbf{F}_i \cdot \frac{\mathbf{p}_i}{m_i} \right] \\ &= 0 \end{aligned}$$

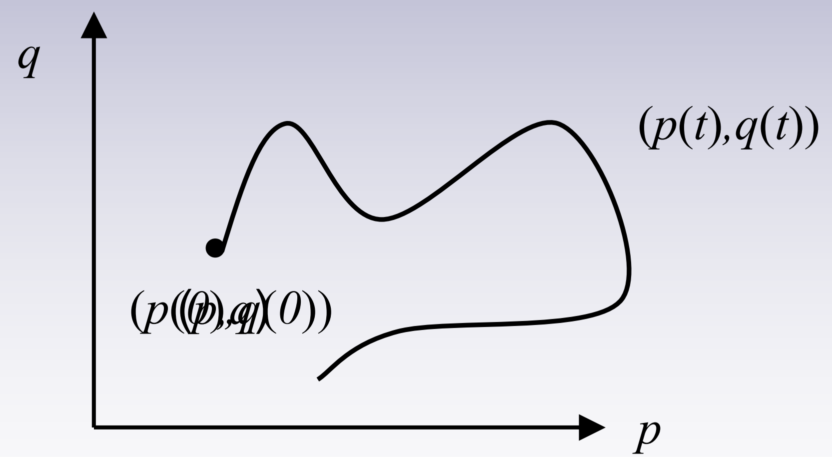
Phase Space

Collect all momenta and coordinates into a Cartesian vector:

$$\mathrm{x} = (\mathbf{p}_1, ..., \mathbf{p}_N, \mathbf{r}_1, ..., \mathbf{r}_N)$$

that lives in a $6N$-dimensional space called *phase space.*

For a one-dimensional system with coordinate q and momentum p phase space can be visualized:

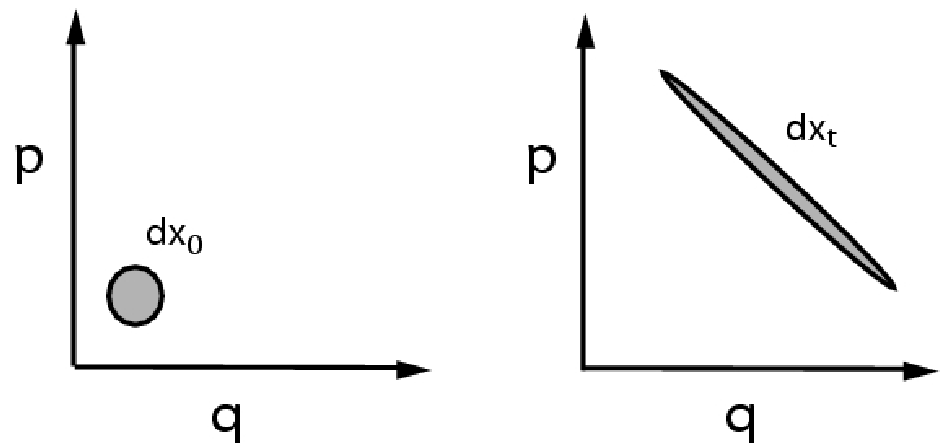


Solution of Hamilton's equations yields $\mathrm{x}(t)$ given initial conditions $\mathrm{x}(0)$

Phase space volume evolution

Generic recasting of Hamilton's equations:

$$\dot{x} = \eta(x)$$



Time evolution as a coordinate transformation (one-parameter diffeomorphism):

$$x_t = \phi_t(x_0)$$

Phase-space volume evolution depends on Jacobian:

$$dx_t = J(x_t; x_0)dx_0$$

Phase-space volume evolution

Jacobian of the transformation $\mathrm{x}_0 \to \mathrm{x}_t$

$$J(\mathrm{x}_t, \mathrm{x}_0) = \left| \frac{\partial \mathrm{x}_t}{\partial \mathrm{x}_0} \right| = \det(\mathrm{M}) = e^{\mathrm{Tr}(\ln \mathrm{M})}$$

$$M^i_{\ j} = \frac{\partial \mathrm{x}^i_t}{\partial \mathrm{x}^j_0} \qquad \left(M^{-1}\right)^i_{\ j} = \frac{\partial \mathrm{x}^i_0}{\partial \mathrm{x}^j_t} \qquad \frac{dM^i_{\ j}}{dt} = \frac{\partial \dot{\mathrm{x}}^i_t}{\partial \mathrm{x}^j_0}$$

Take the time derivative of both sides:

$$\frac{d}{dt} J(\mathrm{x}_t, \mathrm{x}_0) = J(\mathrm{x}_t, \mathrm{x}_0) \mathrm{Tr}\left(\frac{d\mathrm{M}}{dt} \mathrm{M}^{-1} \right)$$

$$\mathrm{Tr}\left(\frac{d\mathrm{M}}{dt} \mathrm{M}^{-1} \right) = \sum_{i,j} \frac{\partial \dot{\mathrm{x}}^j_t}{\partial \mathrm{x}^i_0} \frac{\partial \mathrm{x}^i_0}{\partial \mathrm{x}^j_t} = \sum_j \frac{\partial \dot{\mathrm{x}}^j_t}{\partial \mathrm{x}^j_t} = \nabla \bullet \dot{\mathrm{x}}_t = \nabla \bullet \eta(\mathrm{x}_t) = \kappa(\mathrm{x}_t)$$

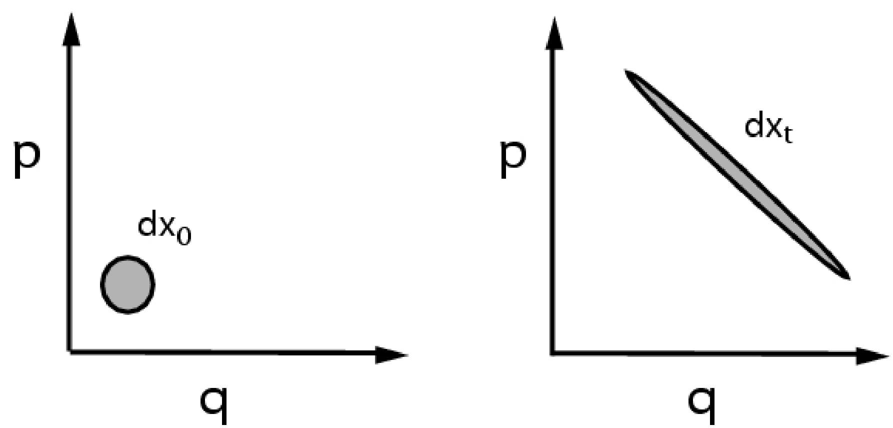
Phase-space volume evolution

Equation of motion for Jacobian:

$$\frac{d}{dt} J(\mathrm{x}_t, \mathrm{x}_0) = \kappa(\mathrm{x}_t) J(\mathrm{x}_t, \mathrm{x}_0) \qquad\qquad J(\mathrm{x}_0, \mathrm{x}_0) = 1$$

Hamiltonian systems incompressible:

$$\kappa(\mathrm{x}_t) = \sum_{i=1}^{N} \left[\nabla_{\mathbf{p}_i} \bullet \dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i} \bullet \dot{\mathbf{r}}_i \right] = \sum_{i=1}^{N} \left[-\nabla_{\mathbf{p}_i} \bullet \nabla_{\mathbf{r}_i} H + \nabla_{\mathbf{r}_i} \bullet \nabla_{\mathbf{p}_i} H \right] = 0$$



Phase-space volume conserved (Liouvlle's Theorem):

$$d\mathrm{x}_t = d\mathrm{x}_0$$

The ensemble concept

- Each phase-space point $x = (\mathbf{p}_1, ..., \mathbf{p}_N, \mathbf{r}_1, ..., \mathbf{r}_N)$ is a complete specification of a system and is, therefore, called a *microstate*.

- Macroscopic matter consists of 10^{23} particles.

- Macroscopic observables should not depend sensitively on the specific details of each particle's motion.

- Many microstates give rise to the same macroscopic observables, e.g. temperature:

$$T \Leftrightarrow \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}$$

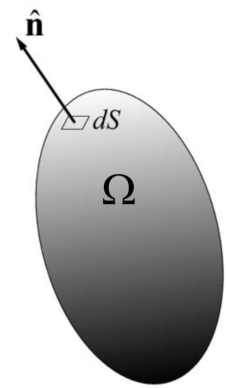
- Ensemble concept: Imagine a collection of systems governed by the same Hamiltonian H, all sharing common macroscopic properties (e.g. same total energy, volume, numer of particles,…). Each system evolves according to the microscopic laws of motion from a different initial condition so that at each instant in time, each system in the ensemble is in a unique microstate. ***Macroscopic observables are expressible as averages over the systems in a given ensemble.***

Ensembles and the Liouville equation

Fraction of ensemble members in a phase space volume $d\mathrm{x}$ at time t:

$$f(\mathrm{x},t)d\mathrm{x}$$

$$f(x,t) \geq 0 \qquad\qquad \int d\mathrm{x}\, f(\mathrm{x},t) = 1$$



$$\text{Fraction of ensemble members in } \Omega = \int_\Omega d\mathrm{x}_t f(\mathrm{x}_t,t)$$

Rate of decrease of ensemble members in Ω

$$-\frac{d}{dt}\int_\Omega d\mathrm{x}_t f(\mathrm{x}_t,t) = -\int_\Omega d\mathrm{x}_t \frac{\partial}{\partial t} f(\mathrm{x}_t,t)$$

Flux out of the surface

$$\int_S dS\; \dot{\mathrm{x}}_t \cdot \hat{\mathbf{n}} f(\mathrm{x}_t,t) = \int_\Omega d\mathrm{x}_t \nabla \bullet \left[\dot{\mathrm{x}}_t\, f(\mathrm{x}_t,t)\right]$$

Ensembles and the Liouville equation

$f(x,t)$ has a constant normalization:

$$\int_\Omega d\mathrm{x}_t \nabla \bullet \left[\dot{\mathrm{x}}_t \, f(\mathrm{x}_t,t) \right] = -\int_\Omega d\mathrm{x}_t \frac{\partial}{\partial t} f(\mathrm{x}_t,t)$$

$$\int_\Omega dx_t \left[\frac{\partial}{\partial t} f(\mathrm{x}_t,t) + \nabla \bullet \left(\dot{\mathrm{x}}_t \, f(\mathrm{x}_t,t) \right) \right] = 0$$

Since $\nabla \cdot \dot{\mathrm{x}}_t = \kappa(\mathrm{x}_t) = 0$ and choice of Ω is arbitrary, obtain Liouville equation:

$$\boxed{\frac{\partial}{\partial t} f(\mathrm{x}_t,t) + \dot{\mathrm{x}}_t \cdot \nabla f(\mathrm{x}_t,t) = 0}$$

Liouville equation implies $f(x,t)$ conserved along a trajectory $df/dt=0$

“Passive” form of Liouville equation:

$$\boxed{\frac{\partial}{\partial t} f(\mathrm{x},t) + \eta(\mathrm{x},t) \cdot \nabla f(\mathrm{x},t) = 0}$$

Ensembles and the Liouville equation

Poisson bracket:

$$\eta(\mathrm{x},t)\cdot\nabla f(\mathrm{x},t)=\sum_{i=1}^{N}\left[\frac{\partial f}{\partial \mathbf{r}_i}\cdot\frac{\partial H}{\partial \mathbf{p}_i}-\frac{\partial f}{\partial \mathbf{p}_i}\cdot\frac{\partial H}{\partial \mathbf{r}_i}\right]=\left\{f(\mathrm{x},t),H(\mathrm{x},t)\right\}$$

Liouville equation in terms of Poisson Bracket:

$$\frac{\partial}{\partial t}f(\mathrm{x},t)+\left\{f(\mathrm{x},t),H(\mathrm{x},t)\right\}=0$$

Equilibrium conditions:

$$\frac{\partial f}{\partial t}=0 \qquad \Rightarrow \qquad \left\{f(\mathrm{x}),H(\mathrm{x})\right\}=0$$

Equilibrium solution:

$$f(\mathrm{x})=F(H(\mathrm{x}))$$

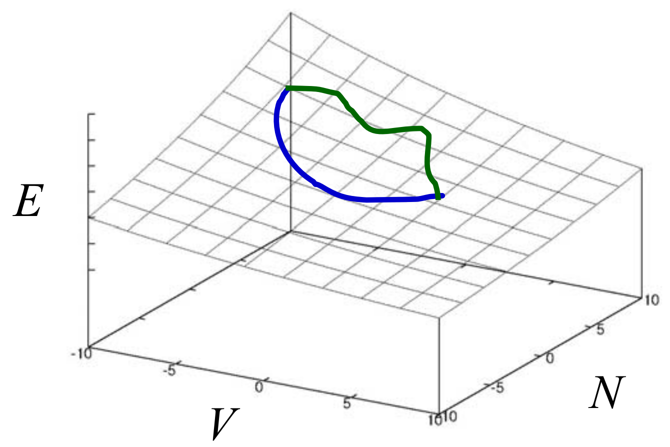
Because of Liouville's Theorem, we can freeze ensemble at any instant in time and compute an observable according to

$$\langle O\rangle=\int d\mathrm{x}\; O(\mathrm{x})F(H(\mathrm{x}))$$

Microcanonical Ensemble

A *microcanonical ensemble* is an ensemble of systems isolated from their surroundings. The evolution of each system is, therefore, governed by Hamilton's equations. The macroscopic variables that are invariant in such an ensemble are the total energy E, the volume V, and total number of particles N.

We first seek to describe the thermodynamics of this ensemble, so we seek a *state function* that depends on N, V, and E. A state function is defined as a thermodynamic function whose change is independent of the path taken in the space of thermodynamic variables.



Microcanonical Ensemble

First law of thermodynamics:

$$E = Q + W$$

$Q =$ Heat absorbed by system

$W =$ Work done on system

Small changes along a reversible path:

$$dE = dQ_{\mathrm{rev}} + dW_{\mathrm{rev}}$$

Heat absorbed related to entropy change at temperature T:

$$dS = \frac{dQ_{\mathrm{rev}}}{T}$$

Work performed by compressing or adding particles:

$$dW_{\mathrm{rev}} = -PdV + \mu dN$$

for a one-component system.

Microcanonical ensemble

Combining work and heat with First Law:

$$dE = TdS - PdV + \mu dN$$

Thus,

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

The entropy $S=S(N,V,E)$ is the state function we seek.

$$dS = \left(\frac{\partial S}{\partial N}\right)_{V,E} dN + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial E}\right)_{N,V} dE$$

Microcanonical Ensemble

Connection to microstates provided by Boltzmann's relation:

$$S(N,V,E) = k \ln \Omega(N,V,E)$$

$\Omega(N,V,E)$ is the number of microstates available to a system.

To find this number, return to equilibrium solutions of Liouville's equation.
For a microcanonical ensemble, the condition $H(\mathrm{x})=E$ must be obeyed.

$$F(H(\mathrm{x})) = \mathcal{N}\delta(H(\mathrm{x}) - E)$$

All points on the constant-energy hypersurface are equally probably, while all points off the surface have zero probability. A microcanonical ensemble is, therefore, one for which all accessible states have equal a priori probability of being accessed, the probability being $1/\Omega(N,V,E)$

$1/\Omega(N,V,E)$ is the normalization, with

$$\Omega(N,V,E) = \frac{E_0}{N!h^{3N}} \int d\mathrm{x}\ \delta(H(\mathrm{x}) - E) \qquad \text{(partition function)}$$

$$= \frac{E_0}{N!h^{3N}} \int d^N\mathbf{p} \int_{D(V)} d^N\mathbf{r}\ \delta(H(\mathbf{p},\mathbf{r}) - E)$$

Microcanonical Ensemble

Thermodynamics:

$$\frac{1}{kT} = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \qquad \frac{P}{kT} = \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} \qquad \frac{\mu}{kT} = \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V,E}$$

Equilibrium observables:

$$\langle O \rangle = \frac{\int d\mathrm{x}\ O(\mathrm{x})\ \delta(H(\mathrm{x}) - E)}{\int d\mathrm{x}\ \delta(H(\mathrm{x}) - E)} = \frac{M_N}{\Omega(N,V,E)} \int d\mathrm{x}\ O(\mathrm{x})\ \delta(H(\mathrm{x}) - E)$$

Now, suppose $S(N,V,E) = CG(\Omega(N,V,E))$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{M_N}{\Omega(N,V,E)} \int d\mathrm{x}\ O_T(\mathrm{x}) \delta(H(\mathrm{x}) - E)$$

$$\frac{\partial S}{\partial E} = CG'(\Omega(N,V,E)) M_N \int d\mathrm{x}\ \delta(H(\mathrm{x}) - E) \frac{\partial \ln \delta(H(\mathrm{x}) - E)}{\partial E}$$

If $A_T(\mathrm{x}) = \partial \ln \delta(H(\mathrm{x}) - E) / \partial E,\ G'(\Omega) = 1/\Omega,\ G(\Omega) = \ln \Omega$

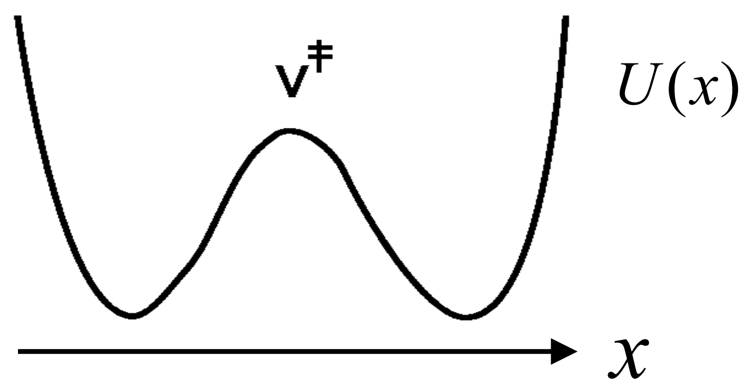
Microcanonical Ensemble

The microcanonical ensemble can be generated by solving Hamilton's equations:

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i} \qquad \dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} = -\frac{\partial U}{\partial \mathrm{r}_i}$$

Phase-space averages computing as time averages:

$$\langle O \rangle = \frac{\int d\mathrm{x}\; O(\mathrm{x})\; \delta(H(\mathrm{x}) - E)}{\int d\mathrm{x}\; \delta(H(\mathrm{x}) - E)} = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\; O(\mathrm{x}_t) = \bar{O}$$



Not ergodic if $E < V^{\ddagger}$

Canonical Ensemble

Using $N, V,$ and E as thermodynamic control variables for an ensemble is not A natural choice, as experiments in the condensed phase are never performed Under these conditions. More natural choices are (N,V,T) or (N,P,T), Corresponding to the canonical and isothermal-isobaric ensembles.

Recall: $S = S(N,V,E) \Rightarrow E = E(N,V,S)$ $\qquad \frac{1}{T} = \frac{\partial S}{\partial E} \Rightarrow T = \frac{\partial E}{\partial S}$

Energy function of N,V,T by Legendre transformation:

$$A(N,V,T) = E(N,V,S(N,V,T)) - S(N,V,T)\frac{\partial E}{\partial S}$$

$$= E - TS$$

$A(N,V,T)$ called the Helmholtz free energy (talk more about tomorrow!)

Canonical Ensemble

Small change in $A(N,V,T)$:

$$dA = dE - SdT - TdS$$

$$= TdS - PdV + \mu dV - SdT - TdS$$

$$= -PdV + \mu dN - SdT$$

Also,

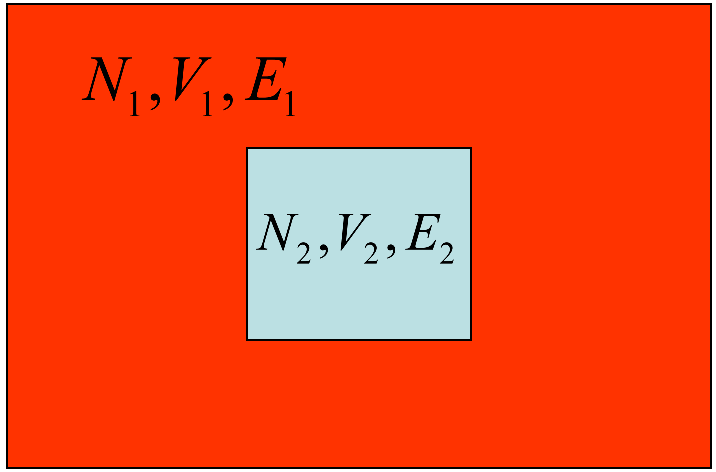
$$dA = \left(\frac{\partial A}{\partial N}\right)_{V,T} dN + \left(\frac{\partial A}{\partial V}\right)_{N,T} dV + \left(\frac{\partial A}{\partial T}\right)_{N,V} dT$$

Thermodynamic relations:

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} \qquad P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \qquad S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

Canonical Ensemble

Microscopic picture:



$$N_1 \gg N_2 \quad V_1 \gg V_2$$

$$E_1 \gg E_2 \quad E = E_1 + E_2$$

$$T_1 = T_2 = T$$

$$H(\mathrm{x}) = H_1(\mathrm{x}_1) + H_2(\mathrm{x}_2)$$

Microcanonical partion function:

$$\Omega(N, V, E) = \int d\mathrm{x}_1 d\mathrm{x}_2 \delta\left(H_1(\mathrm{x}_1) + H_2(\mathrm{x}_2) - E\right) \neq \Omega_1(N_1, V_1, E_1)\Omega_2(N_2, V_2, E_2)$$

Distribution function of system 1:

$$F(H(\mathrm{x}_1)) \propto \int d\mathrm{x}_2 \delta\left(H_1(\mathrm{x}_1) + H_2(\mathrm{x}_2) - E\right)$$

$$\ln F(H(\mathrm{x}_1)) \approx \ln \int d\mathrm{x}_2 \delta(H_2(\mathrm{x}_2) - E) - H_1(\mathrm{x}_1) \frac{\partial}{\partial E} \ln \int d\mathrm{x}_2 \delta(H_2(\mathrm{x}_2) - E)$$

$$= \frac{S_2(N_2, V_2, E)}{k} - \frac{H_1(\mathrm{x}_1)}{kT}$$

Canonical Ensemble

Canonical distribution:

$$F(H(\mathrm{x})) = \frac{1}{Q(N,V,T)} C_N e^{-\beta H(\mathrm{x})} \qquad \beta = \frac{1}{kT}$$

$$Q(N,V,T) = C_N \int d\mathrm{x}\, e^{-\beta H(\mathrm{x})} \qquad C_N = \frac{1}{N!h^{3N}}$$

Thermodynamics:

$$A = E - TS = E + T\frac{\partial A}{\partial T} \;\Rightarrow\; A(N,V,T) = -\frac{1}{\beta}\ln Q(N,V,T)$$

$$\frac{\mu}{kT} = -\left(\frac{\partial \ln Q}{\partial N}\right)_{V,T} \qquad \frac{P}{kT} = \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \qquad S = k\ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

Equilibrium properties:

$$\langle O \rangle = \frac{C_N}{Q(N,V,T)} \int d\mathrm{x}\; O(\mathrm{x}) e^{-\beta H(\mathrm{x})}$$

Canonical Ensemble

In the canonical ensemble, energy is not conserved. Therefore, Hamilton's equations cannot be used to generate a canonical distribution. We need to supplement them with an effect that mimics the thermal reservoir. Many ways to do this!!

Langevin dynamics:

$$d\mathbf{r}_i = \frac{\mathbf{p}_i}{m_i}dt$$

$$d\mathbf{p}_i = -\frac{\partial U}{\partial \mathbf{r}_i}dt - \gamma \mathbf{p}_i dt + \sqrt{2m_i\gamma kT}\,dW$$

Corresponding Fokker-Planck equation:

$$\frac{\partial P(\mathbf{p},\mathbf{r},t)}{\partial t} = \sum_i \left\{ \frac{\partial}{\partial \mathbf{r}_i} \bullet \frac{\mathbf{p}_i}{m_i} + \frac{\partial}{\partial \mathbf{p}_i} \bullet \left[-\gamma \mathbf{p}_i - \frac{\partial U}{\partial \mathbf{r}_i} \right] + \frac{\partial}{\partial \mathbf{p}_i} \bullet \left[\gamma m_i kT \frac{\partial}{\partial \mathbf{p}_i} \right] \right\} P(\mathbf{p},\mathbf{r},t)$$

Stationary solution:

$$P(\mathbf{p},\mathbf{r}) \propto e^{-\beta H(\mathbf{p},\mathbf{r})}$$

Canonical Ensemble

Nosé Hamiltonian: [S. Nosé *J. Chem. Phys*. **81**, 511 (1984)]

Consider a Hamiltonian of the form:

$$H_N(\mathbf{p}, p_s, \mathbf{r}, s) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i s^2} + U(r_1, \ldots, r_N) + \frac{p_s^2}{2Q} + gkT \ln s$$

$$= H\left(\mathbf{p}/s, \mathbf{r}\right) + \frac{p_s^2}{2Q} + gkT \ln s$$

Microcanonical partition function:

$$\Omega(N,V,E) = \int d\mathbf{p} dp_s d\mathbf{r} ds \; \delta\left(H(\mathbf{p}/s, \mathbf{r}) + \frac{p_s^2}{2Q} + gkT \ln s - E \right)$$

Change variables:

$$\mathbf{p}_i' = \frac{\mathbf{p}_i}{s}$$

$$\Omega(N,V,E) = \int d\mathbf{p}' dp_s d\mathbf{r} ds \; s^{3N} \delta\left(H(\mathbf{p}', \mathbf{r}) + \frac{p_s^2}{2Q} + gkT \ln s - E \right)$$

Canonical Ensemble

Delta function identity: $\delta(f(s)) = \frac{\delta(s - s_0)}{\left|f'(s_0)\right|}$

$$\Omega(N,V,E) = \int d\mathbf{p}\,dp_s\,d\mathbf{r}\,e^{(3N+1)(E - H(\mathbf{p},\mathbf{r}) - p_s^2/2Q)/gkT}$$

$$= \frac{e^{E/kT}\sqrt{2\pi QkT}}{(3N+1)kT}\int d\mathbf{p}\,d\mathbf{r}\,e^{-H(\mathbf{p},\mathbf{r})/kT} \propto Q(N,V,T)$$

$$g = 3N+1$$

By solving Hamilton's equations for the extended Hamiltonian, a canonical phase-space average can be computed as a time average:

$$\left\langle O \right\rangle = \frac{\int d\mathrm{x}\; O(\mathrm{x})\; e^{-\beta H(\mathrm{x})}}{\int d\mathrm{x}\; e^{-\beta H(\mathrm{x})}} = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\; O(\mathrm{x}_t) = \overline{O}$$

Classical non-Hamiltonian statistical mechanics

MET, Mundy, Martyna, *Europhys. Lett*. **45**, 149 (1999); MET, Ciccotti, Martyna, Liu, *J. Chem. Phys.* **115**, 1678 (2001).

Equation of motion for Jacobian:

$$\frac{d}{dt}J(\mathrm{x}_t,\mathrm{x}_0)=\kappa(\mathrm{x}_t)J(\mathrm{x}_t,\mathrm{x}_0) \qquad J(\mathrm{x}_0,\mathrm{x}_0)=1$$

Note that for Hamiltonian systems, $\kappa(\mathrm{x})=0 \quad \Rightarrow \quad J(\mathrm{x}_t,\mathrm{x}_0)=1$

$$d\mathrm{x}_t=J(\mathrm{x}_t,\mathrm{x}_0)d\mathrm{x}_0=d\mathrm{x}_0 \qquad \text{(Liouville's Theorem)}$$

If $\kappa(\mathrm{x})\neq 0$, system is non-Hamiltonian, $J(\mathrm{x}_t,\mathrm{x}_0)\neq 1$

Let the non-Hamiltonian phase space be a general Riemannian manifold with a metric tensor $g^{ij}(\mathrm{x},t)$ and determinant $g(\mathrm{x},t)$

Then, Liouville's theorem can be generalized to:

$$\sqrt{g(x_t,t)}dx_t=\sqrt{g(x_0,0)}dx_0$$

Since $\quad J(\mathrm{x}_t,\mathrm{x}_0)=\dfrac{\sqrt{g(\mathrm{x}_0,0)}}{\sqrt{g(\mathrm{x}_t,t)}}$

Classical non-Hamiltonian statistical mechanics

Equation of motion for Jacobian:

$$\frac{d}{dt} J(\mathrm{x}_t, \mathrm{x}_0) = \kappa(\mathrm{x}_t) J(\mathrm{x}_t, \mathrm{x}_0) \qquad J(\mathrm{x}_0, \mathrm{x}_0) = 1$$

Solution:

$$J(\mathrm{x}_t, \mathrm{x}_0) = e^{\int_0^t ds \ \kappa(\mathrm{x}_s)}$$

Define: $\kappa(\mathrm{x}_t) = \frac{d}{dt} w(\mathrm{x}_t, t)$

Then: $J(\mathrm{x}_t, \mathrm{x}_0) = e^{w(\mathrm{x}_t, t) - w(\mathrm{x}_0, 0)}$

Whence: $d\mathrm{x}_t = J(\mathrm{x}_t, \mathrm{x}_0) d\mathrm{x}_0 \implies$

$$e^{-w(\mathrm{x}_t, t)} d\mathrm{x}_t = e^{-w(\mathrm{x}_0, 0)} d\mathrm{x}_0$$

Canonical ensemble

Nosé-Hoover equations:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \qquad \dot{\mathbf{p}}_i = -\frac{\partial U}{\partial \mathrm{r}_i} - \frac{p_\eta}{Q}\mathbf{p}_i$$

$$\dot{\eta} = \frac{p_\eta}{Q} \qquad \dot{p}_\eta = \sum_i \frac{\mathbf{p}_i^2}{m_i} - 3NkT$$

Non-Hamiltonian with compressibility

$$\kappa = \sum_{i=1}^{N}\left[\nabla_{\mathbf{p}_i} \bullet \dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i} \bullet \dot{\mathbf{r}}_i\right] + \frac{\partial \dot{\eta}}{\partial \eta} + \frac{\partial \dot{p}_\eta}{\partial p_\eta} = -3N\frac{p_\eta}{Q} = -3N\dot{\eta}$$

Metric factor: $e^{-w} = e^{3N\eta}$

Conserved energy: $H' = H(\mathbf{p},\mathbf{r}) + \frac{p_\eta^2}{2Q} + 3NkT\eta$

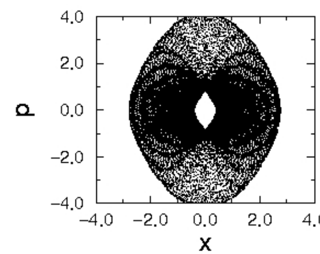
Canonical Ensemble

$$\Omega(N,V,E) = \int d\mathbf{p}\,dp_\eta\,d\mathbf{r}\,d\eta\; e^{3N\eta}\delta\left(H(\mathbf{p},\mathbf{r}) + \frac{p_\eta^2}{2Q} + 3NkT\eta - E \right)$$

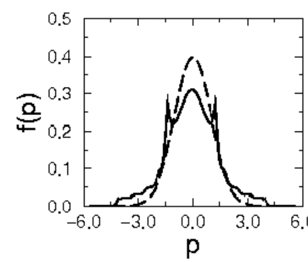
$$\propto \int d\mathbf{p}\; d\mathbf{r}\; e^{-\beta H(\mathbf{p},\mathbf{r})}$$

$$\propto Q(N,V,T)$$

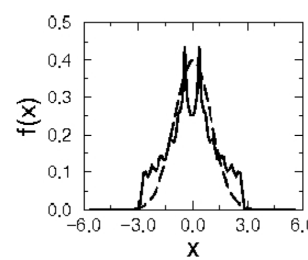
$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$



$$f(p) = \sqrt{\frac{\beta}{2\pi m}}\,e^{-\beta p^2/2m}$$



$$f(x) = \sqrt{\frac{\beta m\omega^2}{2\pi}}\,e^{-\beta m\omega^2 x^2/2}$$



Nosé-Hoover chains: Canonical molecular dynamics

Martyna, Tuckerman, Klein JCP **97**, 2635 (1992)

Thermostatted equations of motion:

Hamilton

↓

Nosé-Hoover

↓

Nosé-Hoover Chains

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_{\eta_1}}{Q_1}\mathbf{p}_i$$

$$\dot{\eta}_k = \frac{p_{\eta_k}}{Q_k} \qquad k = 1, \ldots, M$$

$$\dot{p}_{\eta_1} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - dNkT - \frac{p_{\eta_2}}{Q_2}p_{\eta_1}$$

$$\dot{p}_{\eta_k} = \frac{p_{\eta_{k-1}}^2}{Q_{k-1}} - kT - \frac{p_{\eta_{k+1}}}{Q_{k+1}}p_{\eta_k}$$

$$\dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT$$

Conserved energy:

$$H' = H(\mathbf{p}, \mathbf{r}) + \sum_{k=1}^{M} \frac{p_{\eta_k}^2}{2Q_k} + 3NkT\eta_1 + \sum_{k=2}^{M} kT\eta_k$$

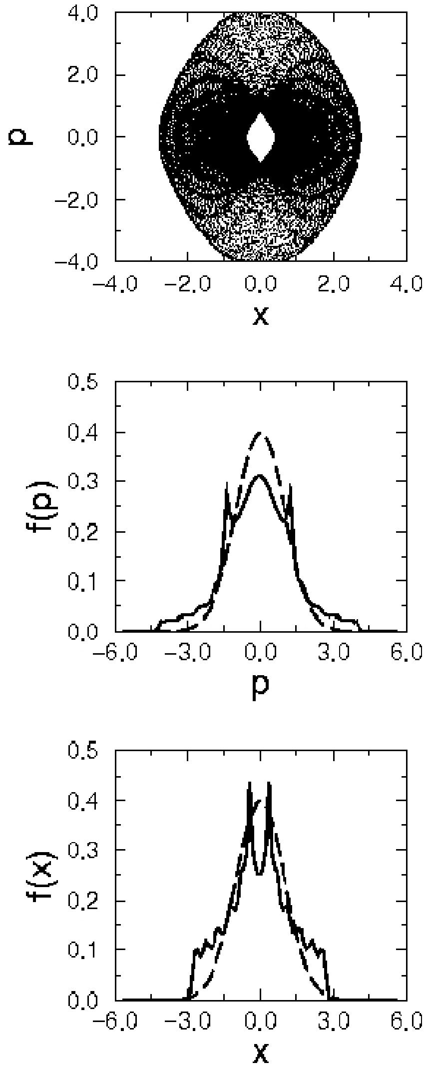
Conserved volume element

$$d\mathrm{x} = e^{3N\eta_1 + \cdots + \eta_M} d^N\mathbf{r}\, d^N\mathbf{p}\, d^M\eta\, d^M p_\eta$$

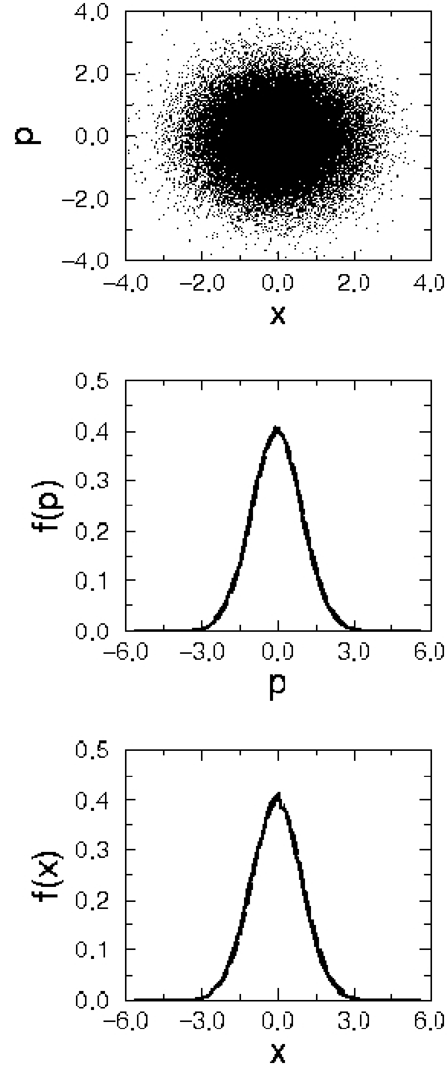
One-dimensional canonical harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \qquad f(p) = \sqrt{\frac{\beta}{2\pi m}} e^{-\beta p^2/2m} \qquad f(x) = \sqrt{\frac{\beta m\omega^2}{2\pi}} e^{-\beta m\omega^2 x^2/2}$$

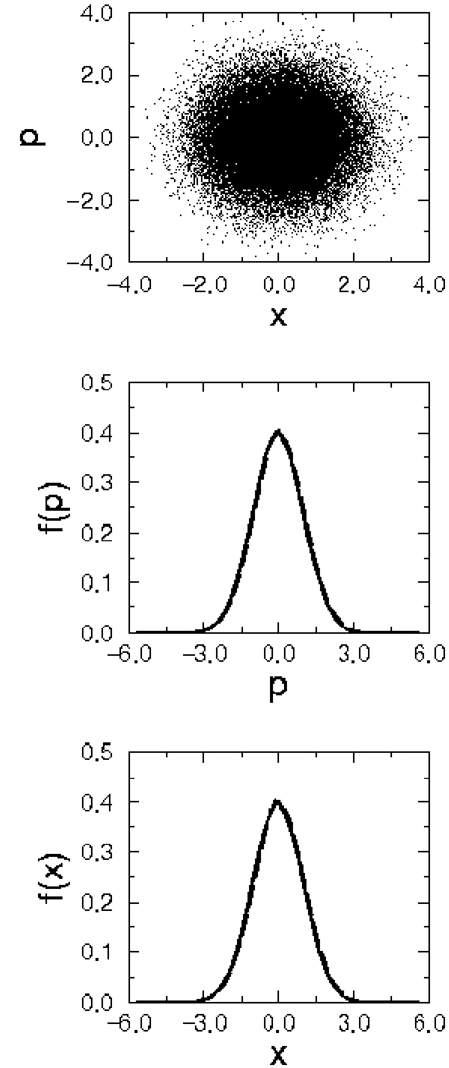
1 chain element



3 chain elements

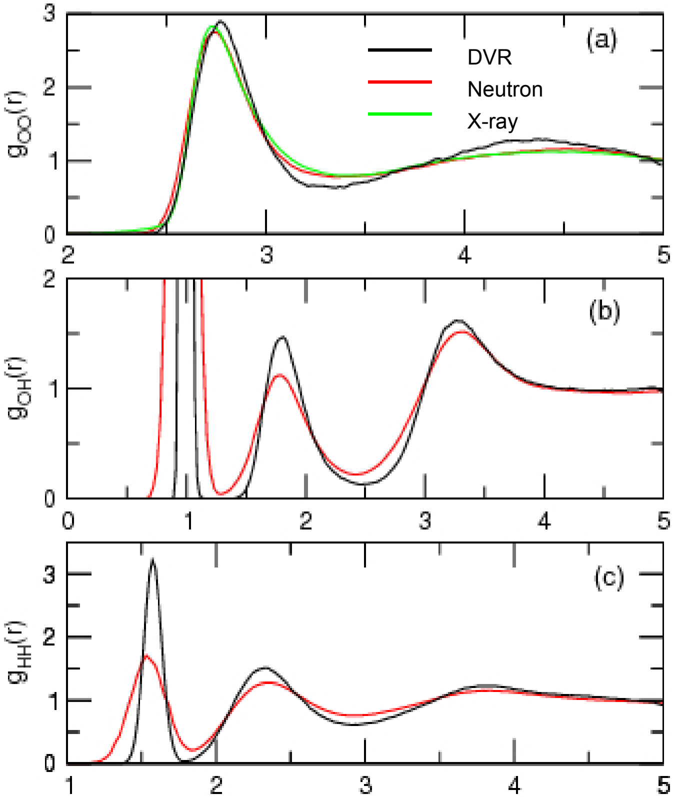


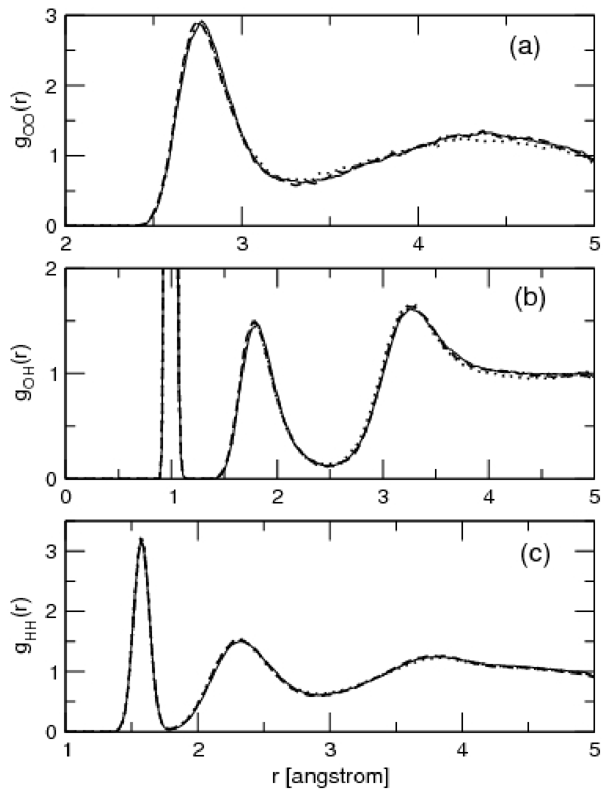
4 chain elements

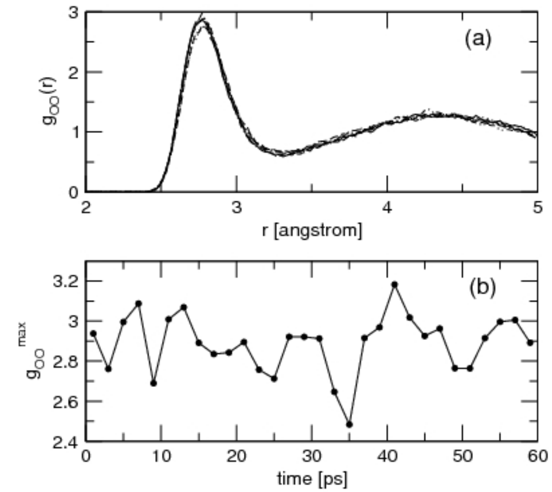


Radial distribution functions of water

CP-BLYP, 75^3 grid, 30 ps, NVT, 300 K, μ = 500 au







H. –S. Lee and MET, JPCA (in press)
Neutron: Soper, et. al. *JCP* **106**, 247 (1997)
X-ray: Hura, et. al. *Chem. Phys*. **113**, 9140 (2000)

NVT fluctuations half those of NVE

Driven dynamics and transport properties

Driven harmonic oscillator:

$$\dot{x} = \frac{p}{m} \qquad \dot{p} = -m\omega^2 x - \gamma \frac{p}{m} + F_0 \cos \Omega t$$

After a short time, transient behavior gives way to steady state behavior that resembles equilibrium in a different region of phase space. The steady state allows transport properties to be computed.

General driven equations of motion:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{C}_i(\mathbf{p},\mathbf{r})F_e(t)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i(\mathbf{p},\mathbf{r})F_e(t)$$

Assume incompressibility:

$$\sum_i \left[\nabla_{\mathbf{p_i}} \bullet \mathbf{D}_i(\mathbf{p},\mathbf{r}) + \nabla_{\mathbf{r_i}} \bullet \mathbf{C}_i(\mathbf{p},\mathbf{r}) \right] = 0$$

Driven dynamics and transport properties

Liouville equation:

$$\frac{\partial}{\partial t} f(\mathrm{x},t) + \dot{\mathrm{x}} \cdot \nabla f(\mathrm{x},t) = \frac{\partial}{\partial t} f(\mathrm{x},t) + iLf(\mathrm{x},t) = 0$$

Linearization scheme:

$$f(\mathrm{x},t) = f_0(H(\mathrm{x})) + \Delta f(\mathrm{x},t)$$

$$iL = iL_0 + i\Delta L(t)$$

Equilibrium condition:

$$iL_0 f_0(H(\mathrm{x})) = 0$$

Linearized Liouville equation:

$$\left(\frac{\partial}{\partial t} + iL_0\right)\Delta f(\mathrm{x},t) = -i\Delta L(t) f_0(H(\mathrm{x}))$$

Driven dynamics and transport properties

Solution:

$$\Delta f(x,t) = -\int_0^t ds\ e^{-iL_0(t-s)} i\Delta L(s) f_0(H(\mathrm{x}))$$

Simplification:

$$i\Delta L(s) f_0(H(\mathrm{x})) = \left(iL(s) - iL_0\right) f_0(H(\mathrm{x})) = iL(s) f_0(H(\mathrm{x}))$$

$$iL(s) f_0(H(\mathrm{x})) = -\frac{\partial f_0}{\partial H(\mathrm{x})} j(\mathrm{x}) F_e(s)$$

$$j(\mathrm{x}) = -\sum_i \left[\mathbf{D}_i(\mathbf{p},\mathbf{r}) \bullet \frac{\partial H}{\partial \mathbf{p}_i} + \mathbf{C}_i(\mathbf{p},\mathbf{r}) \bullet \frac{\partial H}{\partial \mathbf{r}_i} \right]$$ (dissipative flux)

Take equilibrium distribution as a canonical distribution:

$$f_0(H(\mathrm{x})) = \frac{C_N e^{-\beta H(\mathrm{x})}}{Q(N,V,T)}$$

$$iL(s) f_0(H(\mathrm{x})) = \beta f_0(H(\mathrm{x})) j(\mathrm{x}) F_e(s)$$

Driven dynamics and transport properties

Nonequilibrium observable:

$$\langle O \rangle_t = \int d\mathrm{x}\, O(\mathrm{x}) f(\mathrm{x},t) = \int d\mathrm{x}\, O(\mathrm{x}) f_0(H(\mathrm{x})) + \int d\mathrm{x}\, O(\mathrm{x}) \Delta f(\mathrm{x},t)$$

$$= \langle O \rangle_0 + \int d\mathrm{x}\, O(\mathrm{x}) \Delta f(\mathrm{x},t)$$

From linearized solution:

$$\langle O \rangle_t = \langle O \rangle_0 - \beta \int_0^t ds \int d\mathrm{x}\, f_0(H(\mathrm{x})) O(\mathrm{x}) e^{-iL_0(t-s)} j(\mathrm{x}) F_e(s)$$

Let x_t be the unperturbed evolution of the phase-space vector. Evolution of $O(\mathrm{x}_t)$

$$\frac{dO(\mathrm{x}_t)}{dt} = \dot{\mathrm{x}}_t \cdot \nabla_{\mathrm{x}_t} O(\mathrm{x}_t) = iL_0 O(\mathrm{x}_t)$$

$$O(\mathrm{x}_t) = e^{iL_0 t} O(\mathrm{x}_0) = O(\mathrm{x}_0) e^{-iL_0 t}$$

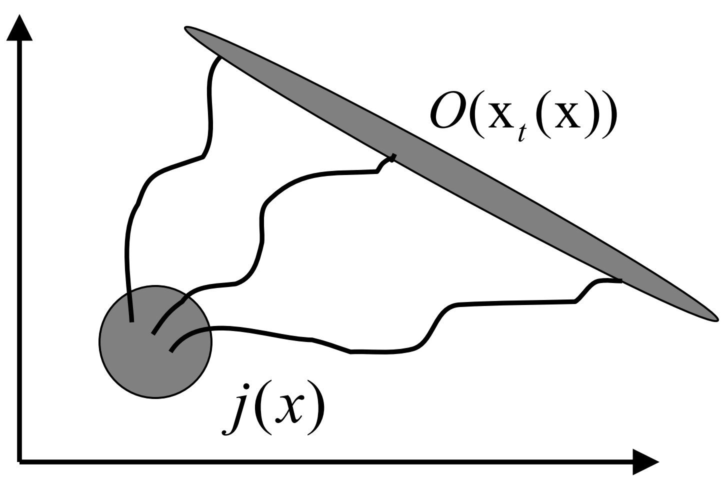
Driven dynamics and transport properties

Nonequilibrium observable:

$$\left\langle O \right\rangle_t = \left\langle O \right\rangle_0 - \beta \int_0^t ds\ F_e(s) \int d\mathrm{x}\, f_0(H(\mathrm{x}))O(\mathrm{x}_{t-s}(\mathrm{x}))\, j(\mathrm{x})$$

$$= \left\langle O \right\rangle_0 - \beta \int_0^t ds\ F_e(s) \left\langle O(t-s)\, j(0) \right\rangle_0$$

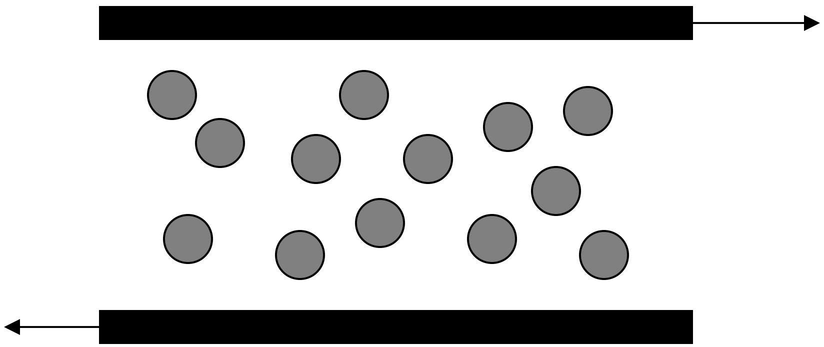
The quantity $\left\langle O(t-s)\, j(0) \right\rangle_0$ is called an *equilibrium time correlation function*

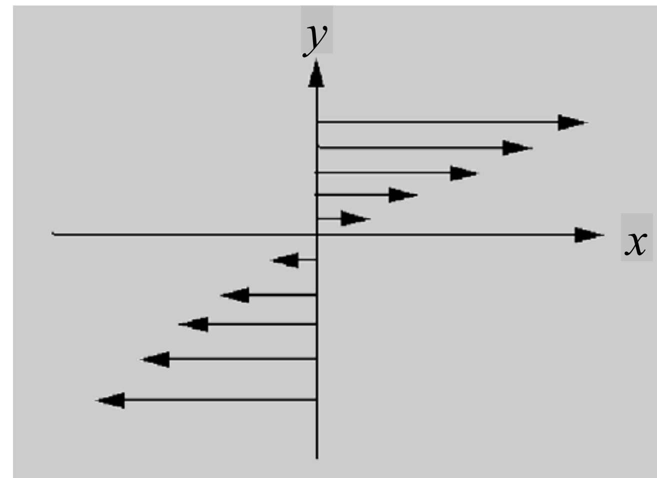


Properties: $\left\langle A(0)B(t) \right\rangle = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} d\tau\ A(\mathrm{x}_\tau)B(\mathrm{x}_{t+\tau})$

Driven dynamics and transport properties

Example: Shear viscosity:





Equations of motion:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \gamma y_i \hat{\mathbf{x}}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \gamma p_{y_i} \hat{\mathbf{x}}$$

Dissipative flux:

$$j(\mathbf{p},\mathbf{r}) = \gamma \sum_i \left[\frac{p_{x_i} p_{y_i}}{m_i} + F_{x_i} y_i \right] = \gamma V P_{xy}$$

Driven dynamics and transport properties

Coefficient of shear viscosity:

$$\eta = -\lim_{t\to\infty} \frac{\langle P_{xy} \rangle_t}{\gamma}$$

From linear response formula:

$$\langle P_{xy} \rangle_t = \cancelto{0}{\langle P_{xy} \rangle_0} - \beta\gamma V \int_0^t ds \langle P_{xy}(0) P_{xy}(t-s) \rangle_0$$

Viscosity:

$$\eta = \beta V \int_0^\infty d\tau \langle P_{xy}(0) P_{xy}(\tau) \rangle_0 \qquad \tau = t - s$$

known as a *Green-Kubo formula*. Transport coefficient related to time integral of an equilibrium autocorrelation function.