

Understanding Molecular Simulation 2010

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Outline

- Statistical Mechanics I: Entropy, Boltzmann distribution, partition function, canonical ensemble [Frenkel Lecture 1, Das Tutorial Lecture 1]
- Statistical Mechanics II: Different ensembles, Dynamics [Frenkel Lecture 2]
- This Tutorial Lecture:
 - Review statistical mechanics covered earlier.
 - Ensembles
 - Fluctuations
 - Dynamics
 - Correlation functions
 - Fluctuation Dissipation Theorem



Statistical Mechanics

- Describes systems with large numbers of particles.
- Large number of particles \Rightarrow large number of states (all positions and velocities).
- However, only small number of properties are of interest (pressure, density, electrical conductivity, compressibility..)
- How to calculate these ‘thermodynamic’ properties??
- Answer: Suitable “Averaging” over micro-states.

Ergodic Hypothesis

- Consider a closed system of N particles, in a volume V , and total energy E .
- How are different microscopic states with the total energy E visited by the system.
- Ergodic Hypothesis: A closed system with energy E is equally likely to be found in any of the microscopic states with total energy E .
- Properties of such a system can be evaluated by uniformly averaging over all such states.
- Statistical Mechanics – Instead of solving for explicit trajectory, we obtain desired properties by averaging over a distribution. Notions of probability and statistics important.

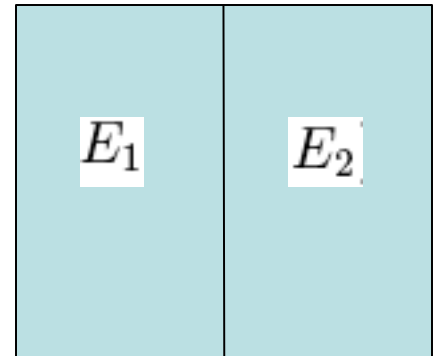
Thermodynamics

- Let total number of states for system with energy E be $\Omega(E)$
- Consider two subsystems with energy E_1 and E_2 , such that $E = E_1 + E_2$
- The total number of states is given by the product

$$\Omega(E_1, E_2) = \Omega_1(E_1) \times \Omega_2(E_2)$$

Or

$$\log \Omega(E_1, E - E_1) = \log \Omega_1(E_1) + \log \Omega_2(E - E_1)$$



What is the most probable value of E_1 ?

That which maximizes $\log \Omega$

$$\left(\frac{\partial \log \Omega(E_1, E - E_1)}{\partial E_1} \right)_{N, V, E} = 0,$$

$$\left(\frac{\partial \log \Omega_1(E_1)}{\partial E_1} \right)_{N_1, V_1} = \left(\frac{\partial \log \Omega_2(E_2)}{\partial E_2} \right)_{N_2, V_2}$$

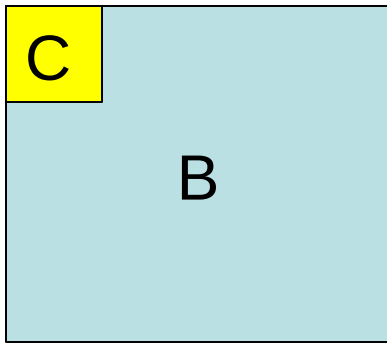
Define $S(N, V, E) \equiv k_B \log \Omega(N, V, E)$

and $\frac{1}{k_B T} \equiv \left(\frac{\partial \log \Omega(E)}{\partial E} \right)_{N, V}$

Conditions above correspond to zeroth and second law of thermodynamics.

Boltzmann Distribution

Consider again a closed system divided into two subsystems, such that they can exchange energy but the total energy of the system being expressible as the sum of the energies of the subsystems.



The probability of a specific microstates with energy E_i is given by the number of states for subsystem B with energy $E - E_i$. Expanding around energy E ,

$$\log \Omega_B(E - E_i) = \log \Omega_B(E) - E_i \frac{\partial \log \Omega_B(E)}{\partial E} + \dots$$

But $\frac{\partial \log \Omega_B(E)}{\partial E} = (k_B T)^{-1}$ which means..

$$\log \Omega_B(E - E_i) = \log \Omega_B(E) - \frac{E_i}{k_B T}$$

The probability of finding subsystem C with energy E_i is:

$$P_i = \frac{\exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)}$$

Writing for energies instead of states: $P(E, T) = \frac{\Omega(E) \exp(-E/k_B T)}{\sum_E \Omega(E) \exp(-E/k_B T)}$

Define the partition function $Q = \sum_j \exp(-E_j/k_B T)$

Contact with thermodynamics: Identify Helmholtz free energy

$$F = -k_B T \log Q$$

Check by calculating average energy, which is given by:

$$U \equiv \langle E \rangle = \sum_j E_j P_j$$

Using thermodynamic relation: $U = \frac{\partial \beta F}{\partial \beta}$ where $\beta \equiv 1/k_B T$

$$\begin{aligned} U &= - \frac{\partial \log \sum_j \exp(-\beta E_j)}{\partial \beta} \\ &= \frac{\sum_j E_j \exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)} \\ &= \sum_j E_j P_j. \end{aligned}$$

We have the same expression as before.

Similarly, for the heat capacity, we derive, using $C_V = \frac{\partial U}{\partial T}$

$$k_B T^2 C_V = \langle E^2 \rangle - \langle E \rangle^2$$

Expression for the response function in terms of fluctuations.

For an atomic system, with energies given in terms of coordinates and momenta (ie, we are treating a classical System), $\sum_j \rightarrow \frac{1}{h^{dN} N!} \int d\mathbf{r}^N d\mathbf{p}^N \exp(-\beta E(\mathbf{r}^N, \mathbf{p}^N))$

d – dimensionality of space. h – Plank's constant.
The factor at front arises from proper counting of phase space volume.

The partition function in this case is:

$$Q(N, V, T) = \frac{1}{h^{dN} N!} \int d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta(\sum_i \frac{p_i^2}{2m} + V(\mathbf{r}^N))]$$

Averages of quantities that are functions of positions and Momenta are evaluated as:

$$\langle A \rangle = \frac{1}{Q} \frac{1}{h^{dN} N!} \int d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta(\sum_i \frac{p_i^2}{2m} + V(\mathbf{r}^N))] A(\mathbf{r}^N, \mathbf{p}^N)$$

Other Ensembles

In analyzing experimental systems, the appropriate ensemble that is appropriate is determined by the nature of contact with the environment:

Isolated system:	Microcanonical	(N, V, E)
Exchange of Energy:	Canonical	(N, V, T)
Exchange of Energy, Volume:	Isothermal, Isobaric	(N, P, T)
Exchange of Energy, Particles:	Grand Canonical	(μ , V, T)

In simulations, the choice of ensemble may also be dictated by accurate determination of properties from finite size simulations, e.g., (N,P,T) rather than (N,V,T) in the presence of a phase transition.

Though equilibrium averages have equivalences between ensembles, fluctuations are different.

Isothermal-Isobaric Ensemble (N,P,T)

In the Isothermal-Isobaric ensemble, the pressure, rather than the volume is kept fixed. The relevant thermodynamic potential is the Gibbs free energy:

$$G = F + PV$$

The volume is given by a derivative of G with respect to pressure:

$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

The Gibbs free energy is given by the partition function $\Delta_N(P,T)$

$$G = -k_B T \log \Delta_N(P, T)$$

$$\Delta_N(P, T) = \int dV d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta PV - \beta E(r^N, p^N)]$$

$$\Delta_N(P, T) = \int dV \exp[-\beta PV] Q_N(V, T)$$

The probability weight here can be derived using the expansion around the total energy and volume of the system+bath as done for the canonical ensemble.

The heat capacity is given by the derivative with respect to T of the enthalpy $H = E + PV$.

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

An evaluation using the partition function yields:

$$C_P = \frac{1}{k_B T^2} \langle (E + PV)^2 \rangle - \langle E + PV \rangle^2$$

The isothermal compressibility is given by the derivative of volume with respect to pressure:

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

An evaluation using the partition function yields:

$$\kappa_T = \frac{1}{k_B T} \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle}$$

As in the canonical ensemble, response functions are obtained in terms of fluctuations of relevant quantities.

Grand Canonical Ensemble (μ, V, T)

In the Grand Canonical ensemble, the chemical potential, rather than the particle number is kept fixed. The relevant thermodynamic potential is the grand potential:

$$\Omega = F - N\mu = G - PV - N\mu$$

The particle number is given by a derivative of the grand potential with respect to μ :

$$N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{V, T}$$

The grand potential is given by the partition function Σ

$$\Omega = -k_B T \log \Sigma \quad \Omega = -PV$$

$$\Sigma = \sum_{N=0}^{\infty} \frac{1}{h^{dN} N!} \exp[\beta \mu N] \int d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta E(\mathbf{r}^N, \mathbf{p}^N)]$$

$$\Sigma = \sum_{N=0}^{\infty} \exp[\beta \mu N] Q_N(V, T)$$

The probability weight here can be derived using the expansion around the total energy and volume of the system+bath as done for the canonical ensemble.

For an isothermal change $VdP = Nd\mu$

$$N \left(\frac{\partial \mu}{\partial N} \right)_{V,T} = V \left(\frac{\partial P}{\partial N} \right)_{V,T} = \frac{1}{\rho \kappa_T}$$

From the partition function we can show:

$$\frac{1}{\langle N \rangle} \left(\frac{\partial \langle N \rangle}{\partial \beta \mu} \right) = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}$$

We then get an expression for the isothermal compressibility in terms of number fluctuations:

$$\rho k_B T \kappa_T = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}$$

This is again a fluctuation formula for the response function, isothermal compressibility.

Time Dependent Phenomena

Time dependent behavior of systems are characterized of in terms of spontaneous fluctuations that arise in the system or response to time dependent perturbations.

The former are described by time correlation functions.
Given quantities A and B,

$$C_{AB}(t, t') = \langle A(t) B(t') \rangle$$

Usually, time correlation functions are stationary, so that

$$C_{AB}(t, t') = \langle A(t) B(t') \rangle = C_{AB}(t'-t) = \langle A(0) B(t'-t) \rangle$$

Normally, variables A and B are defined as deviations from their equilibrium values, so that $\langle A \rangle = 0$ etc.

Linear Response Theory

To consider the response of a system, consider that the system is subjected to a time dependent perturbation that couples to a variable A

$$\Delta H = -f(t)A$$

The time dependent response of a variable $B(t)$ can be written to linear order in f as:

$$\langle B(t) \rangle = \int_{-\infty}^t \chi_{BA}(t, s) f(s) ds$$

This defines the response function $\chi_{BA}(t, s) = \chi_{BA}(t-s)$

Let us consider a constant perturbation f from $t = -\infty$ to 0 which is then switched off. Let $A(0) = A_0$. We can write

$$A_0 = f \int_{-\infty}^0 \chi_{AA}(-s) ds$$

We can write $B(t)$ subject to the condition $A(0) = A_0$:

$$\langle B(t) \rangle_{A_0} = \frac{C_{BA}(t)}{C_{AA}(0)} A_0$$

We have from the expression for the response:

$$A_0 = f \int_{-\infty}^0 \chi_{AA}(-s) ds$$

$$\langle B(t) \rangle_{A_0} = f \int_{-\infty}^0 \chi_{BA}(t-s) ds$$

Thus

$$\frac{\int_{-\infty}^0 \chi_{BA}(t-s) ds}{C_{BA}(t)} = \frac{\int_{-\infty}^0 \chi_{AA}(-s) ds}{C_{AA}(0)}$$

The right hand side is a constant $\frac{\int_{-\infty}^0 \chi_{AA}(-s) ds}{C_{AA}(0)} = \frac{-1}{k_B T}$

Since, to linear order $A_0 = \frac{-1}{k_B T} \langle AA \rangle$

We then get the statement of the **fluctuation-dissipation theorem**:

$$\chi_{BA}(t) = \frac{-1}{k_B T} \frac{dC_{BA}(t)}{dt}$$

Or

$$\langle B(t) \rangle = \beta f C_{BA}(t)$$

Diffusion/Mobility of a tagged particle

Consider a tagged Brownian particle that is subjected to a constant force f from $t = 0$. The corresponding Hamiltonian will be $H = - f x$.

The velocity of the particle as a result can be written following the FDT as:

$$u(t) = \beta f \int_0^t \langle u(t') \dot{x} \rangle dt'$$

Or
$$u(t) = \beta f \int_0^\infty \langle u(t') u(0) \rangle dt'$$

Now, under steady state conditions, the particles will reach a constant drift velocity, given by

$$u = \mu f$$

Thus we have
$$\mu = \lim_{t \rightarrow \infty} \beta \int_0^t \langle u(t') u(0) \rangle dt'$$

Now let us consider a gas of non-interacting Brownian particles, subject to the applied potential V_{ext} . The total current of these particles is given by a diffusion and a drift contribution.

$$j(r, t) = j_{\text{diffusion}} + j_{\text{drift}}$$

The diffusion current is given, as in deriving the diffusion Equation, by

$$j_{\text{diffusion}} = -D \frac{\partial \rho}{\partial x}$$

The current due to drift is given by $j_{\text{drift}} = \mu \rho f$

In the steady state, these two currents cancel out, and we have a steady state distribution:

$$\rho(x) = \rho_0 \exp(-\beta V_{\text{ext}})$$

The applied force is $f = -\frac{\partial V_{ext}}{\partial x}$

Using the above distribution to calculate the diffusion current and equating the two currents, we get

$$D = \mu k_B T$$

the Einstein relation for mobility

Substituting, we get the relation between the diffusion coefficient and the velocity autocorrelation function

$$D = \int_0^\infty \langle u(t)u(0) \rangle dt$$

which can be derived also by other means.