Lecture 3

Other Ensembles

Understanding Molecular Simulations Berend-Smit@Berkeley.edu

Statistical Thermodynamics

Basic assumption

For an isolated system (NVE) any microscopic configuration is equally likely

Consequence

All of statistical thermodynamics and equilibrium thermodynamics







number 1 can be put in M positions, number 2 at M positions, etc

Total number of configurations: M^N with $M = \frac{V}{dr}$

the larger the volume of the gas the more configurations











What is the probability to find this configuration?

exactly equal as to any other configuration!!!!!!

This is reflecting the microscopic reversibility of Newton's equations of motion. A microscopic system has no "sense" of the direction of time

Are we asking the **right question**?

Are we asking the **right question**?

These are microscopic properties; no irreversibility

Thermodynamic is about macroscopic properties:



<u>Measure densities</u>: what is the probability that we have all our N gas particle in the upper half?

N	P(empty)
1	0.5
2	0.5 x 0.5
3	0.5 x 0.5 x 0.5
1000	10 ⁻³⁰¹

Summary

On a microscopic level all configurations are equally likely

On a macroscopic level; as the number of particles is extremely large, the probability that we have a fluctuation from the average value is **extremely** low

$E_1 > E_2$ **Basic assumption**



All micro states will be equally likely!

... but the number of micro states that give an particular energy distribution $(E_1, E-E_1)$ not ...

... so, we observe the most likely one ...

NVE₁

In a macroscopic system we will observe the most likely one $\mathcal{P}(\mathsf{E}_1,\mathsf{E}_2) = \frac{\mathcal{N}_1(\mathsf{E}_1) \times \mathcal{N}_2(\mathsf{E}-\mathsf{E}_1)}{\sum_{\mathsf{E}_1=0}^{\mathsf{E}_1=\mathsf{E}} \mathcal{N}_1(\mathsf{E}_1) \times \mathcal{N}_2(\mathsf{E}-\mathsf{E}_1)}$ The summation only depends on the total energy: $\mathcal{P}(\mathsf{E}_1,\mathsf{E}_2) = \mathsf{C} \times \mathcal{N}_1(\mathsf{E}_1) \times \mathcal{N}_2(\mathsf{E}-\mathsf{E}_1)$ $\ln \mathcal{P}(E_1, E_2) = \ln C + \ln \mathcal{N}_1(E_1) + \ln \mathcal{N}_2(E - E_1)$ We need to find the maximum $\frac{\mathrm{d}\ln\mathcal{P}(\mathsf{E}_1,\mathsf{E}_2)}{\mathrm{d}\mathsf{E}_1} = \frac{\mathrm{d}\ln\mathcal{N}(\mathsf{E}_1,\mathsf{E}_2)}{\mathrm{d}\mathsf{E}_1} = 0$ $d\left[\ln \mathcal{N}_1(\mathsf{E}_1) + \ln \mathcal{N}_2(\mathsf{E} - \mathsf{E}_1)\right] = 0$ dE_1



Let us define a property (almost S, but not quite) :

 $S^* = \ln \mathfrak{N}(E)$

 $\frac{d\ln\mathfrak{N}_1(E_1)}{dE_1} = \frac{d\ln\mathfrak{N}_2(E_2)}{dE_2}$ Equilibrium if: $\left(\frac{\partial S_1^*}{\partial E_1}\right)_{N=V} = \left(\frac{\partial S_2^*}{\partial E_2}\right)_{N=V}$ or

And for the total system: $S^* = S_1^* + S_2^*$

For a system at constant energy, volume and number of particles the **S**^{*} increases until it has reached its **maximum** value at equilibrium

What is this magic property S*?

Canonical Ensemble

The 2nd law

Entropy of an <u>isolated system</u> can only increase; until equilibrium were it takes its maximum value

Most systems are at constant temperature and volume or pressure?

What is the formulation for these systems?



 $T\mathrm{d} S_1 - \mathrm{d} U_1 \geq 0$

fixed volume but can exchange energy



Total system is isolated and the volume is constant Box 1: constant volume and temperature 2^{nd} law: $TdS_1 - dU_1 \ge 0$ $d(U_1 - TS_1) \le 0$ z free energy: A $A \equiv U - TS$

Constant T and V

Let us define the **Helmholtz free energy**: A

For box 1 we can write $dA_1 \leq 0$ Hence, for a system at constant temperature and volume the <u>Helmholtz free energy</u> decreases and takes its <u>minimum value</u> at equilibrium



Thermodynamics What is the average energy of the system? $\langle E \rangle \equiv \sum_{i} E_{i} P(E_{i}) = \frac{\sum_{i} E_{i} \exp(-\beta E_{i})}{\sum_{i} \exp(-\beta E_{i})}$ $= -\frac{\partial \ln \sum_{i} \exp(-\beta E_{i})}{\partial \beta}$ $= -\frac{\partial \ln Q_{N,V,T}}{\partial \beta}$

Compare:

$$\left(\frac{\partial F/T}{\partial 1/T}\right) = E$$

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Thermodynamics First law of thermodynamics dE = TdS - pdVHelmholtz Free energy: $F \equiv E - TS$ $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$ $\left(\frac{\partial F/T}{\partial 1/T}\right) = F + \frac{1}{T} \frac{\partial F}{\partial 1/T} = F - T \frac{\partial F}{\partial T}$ = F + TS = E

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What is the average energy of the system?

$$\langle E \rangle = \sum_{i} E_{i} P(E_{i}) = \frac{\sum_{i} E_{i} \exp(-\beta E_{i})}{\sum_{j} \exp(-\beta E_{j})}$$

$$= -\frac{\partial \ln \sum_{i} \exp(-\beta E_{i})}{\partial \beta}$$

$$= -\frac{\partial \ln Q_{N,V,T}}{\partial \beta}$$
Compare:

$$\left(\frac{\partial F/T}{\partial 1/T}\right) = E$$
Hence:

$$\frac{F}{k_{B}T} = -\ln Q_{N,V,T}$$
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Statistical Thermodynamics:Partition functioncanonical ensemble $Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int dr^N \exp[-\beta U(r^N)]$

Ensemble average

$$\langle A \rangle_{NVT} = \frac{1}{Q_{NVT}} \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta U(\mathbf{r}^N)\right]$$

Probability to find a particular configuration

$$N(\mathbf{r}^{N}) = \frac{1}{Q_{NVT}} \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^{N} \delta(\mathbf{r}^{N} - \mathbf{r}^{N}) \exp\left[-\beta U(\mathbf{r}^{N})\right] \propto \exp\left[-\beta U(\mathbf{r}^{N})\right]$$

Free energy
$$\beta F = -\ln\left(Q_{NVT}\right)$$



Comments to this algorithm:

- 1. Subroutine ener calculates the energy of a particle at the given position.
- 2. Note that, if a configuration is rejected, the old configuration is retained.
- 3. The ranf() is a random number uniform in [0, 1].

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Imposing detailed balance:
$$K(o \rightarrow n) = K(n \rightarrow o)$$

with $K(o \rightarrow n) = \Re(o)\alpha(o \rightarrow n)acc(o \rightarrow n)$
...and for the
reverse move: $K(n \rightarrow o) = \Re(n)\alpha(n \rightarrow o)acc(n \rightarrow o)$
If we sample the canonical ensemble
 $\Re(o) = Ce^{-\beta U(o)}$ and $\Re(n) = Ce^{-\beta U(n)}$
Which gives for the acceptance rules:
 $\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \frac{\Re(n)\alpha(n \rightarrow a)}{\Re(o)\alpha(o \rightarrow n)} = \frac{e^{-\beta U(n)}}{e^{-\beta U(o)}} = e^{-\beta \Delta U}$
Probability to generate state does not depend on n or o

Metropolis acceptance rule

For the canonical ensemble

$$\frac{\operatorname{acc}(o \to n)}{\operatorname{acc}(n \to o)} = \exp\left[-\beta\left(U(n) - U(o)\right)\right]$$

Metropolis rule:

$$\operatorname{acc}(o \to n) = \min\left\{1, \exp\left[-\beta\left(U(n) - U(o)\right)\right]\right\}$$

Assume $\Delta U < 0$ $\alpha(o \rightarrow n) = 1$ and $\alpha(n \rightarrow 0) = \exp\left[-\beta(U(o) - U(n))\right]$ Hence $\frac{\operatorname{acc}(o \rightarrow n)}{\operatorname{acc}(n \rightarrow o)} = \frac{1}{\exp\left[-\beta(U(o) - U(n))\right]}$

Other ensemble



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Example (3): swelling of clays



Deep in the earth clay layers can swell upon adsorption of water:

- How to mimic this in the N,V,T ensemble?
- What is a better ensemble to use?

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NPT ensemble

NPT ensemble

Classical

- Legrendre transformation
- A small system that can exchange heat and volume with a large bath

Statistical

Taylor expansion of a small reservoir

Gibbs free energy

$$dU = TdS - pdV + \sum \mu_i dN_i$$

Required Legrendre transformation:
 $G = U - TS + pV \rightarrow G = G(T, p)$
 $dG = -SdT + Vdp + \sum \mu_i dN_i$
If T,P,N are kept constant, the total Gibbs free
energy is constant and has its minimum value in
equilibrium
Legendre Transformation
The energy is a natural function of the entropy, volume, and number of particles of component i

$$U = U(S, V, N_i)$$
 $dU = TdS - pdV + \sum \mu_i dN_i$
Conjugate variables
 $S: T = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} V: p = -\left(\frac{\partial U}{\partial V}\right)_{S,N_i} N_i: \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j}$
Legendre transformations, to get NPT:
 $G = U - TS + pV \rightarrow G = G(T, p, N)$

Legrencize transformationWe have a function that depends on
and we would like
$$(x_1, x_2, x_3, ..., x_n)$$

 $(x_1, ..., x_r, u_{r+1}, ..., u_n)$ $f = f(x_1, x_2, x_3, ..., x_n)$
 $df = \sum_{i=1}^n u_i dx_i$
 $u_i = \left(\frac{\partial f}{\partial x_i}\right)$ $g = f - \sum_{i=r+1}^n u_i x_i$
 $g = g(x_1, ..., x_r, u_{r+1}, ..., u_n)$

Example: thermodynamics E = E(S, V)dE = TdS - pdVWe prefer to control T: $S \rightarrow T$ Legendre transformation F = U - TS $\mathrm{d}F = \mathrm{d}E - \mathrm{d}\left(TS\right)$ dF = SdT - pdVF = F(T, V)Helmholtz free energy

Legendre transformation I have all my information in L and how can I change my coordinates without loosing any information?

L = L(X)

Suppose I would like to use P $P = \frac{dL(X)}{dX}$

Would this work? L = L(P)

What does work is $P = \frac{dL(X)}{dX}$ with H = L - PXIf we know the slope and the intercept we reconstruct the curve H = H(P)as the envelope of tangent lines (H(P) define all the X lines the "envelope" L)

exchange energy and constant T and p volume We have our box 1 and a bath Total system is isolated and the volume is constant First law dU = dq - pdV = 0Second law dS > 0Box 1: constant pressure and temperature Ist law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$ $dV_1 + dV_b = 0$ or $dV_1 = -dV_b$ The bath is very large and the small changes do not change P or T; in addition the process is reversible $\label{eq:star} \textbf{2^{nd} law:} \quad \mathrm{d}S_1 + \mathrm{d}S_b = \mathrm{d}S_1 + \frac{\mathrm{d}U_b}{\mathsf{T}} + \frac{\mathsf{p}}{\mathsf{T}}\mathrm{d}V_b \geq \mathbf{0}$ $TdS_1 - dU_1 - pdV_1 > 0$

exchange energy and volume



Let us define the Gibbs free energy: G For box 1 we can write $\begin{array}{l} \underline{\text{Total system}} \text{ is isolated and} \\ \text{the volume is constant} \\ \underline{\text{Box 1}} \text{: constant pressure} \\ \text{and temperature} \\ \mathbf{2^{nd}} \text{ law: } TdS_1 - dU_1 - pdV_1 \geq 0 \\ d(U_1 - TS_1 + pV_1) \leq 0 \\ G \equiv U - TS + pV \end{array}$

Constant T and p

Hence, for a system at constant temperature and pressure the <u>Gibbs free energy</u> decreases and takes its minimum value at equilibrium

 $\mathrm{d}G_1 < 0$



$$\ln \Omega (V - V_i, E - E_i) = \ln \Omega (V, E) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V, N} E_i - \left(\frac{\partial \ln \Omega}{\partial V}\right)_{E, N} V_i + \cdots$$
$$\ln \Omega (V - V_i, E - E_i) = \ln \Omega (V, E) - \frac{E_i}{k_B T} - \frac{p}{k_B T} V_i$$
$$\ln \frac{\Omega (E - E_i, V - V_i)}{\Omega (E, V)} = -\frac{E_i}{k_B T} - \frac{pV_i}{k_B T}$$

Hence, the probability to find E_i, V_i :

$$P(E_{i},V_{i}) = \frac{\Omega(E-E_{i},V-V_{i})}{\sum_{j,k} \Omega(E-E_{j},V-V_{k})} = \frac{\exp[-\beta(E_{i}+pV_{i})]}{\sum_{j,k} \exp[-\beta(E_{j}+pV_{k})]}$$

\$\approx \exp[-\beta(E_{i}+pV_{i})]\$





Partition function:

$$\begin{aligned}
\mathcal{P}_{NPT} &= \frac{\beta P}{N!\Lambda^{3N}} \int dV \exp[-\beta PV] \int dr^{N} \exp[-\beta U(r^{N})] \\
\text{Scaled coordinates:} \quad s_{x} &= r_{x}/L_{x} \\
\end{aligned}$$

$$\begin{aligned}
\mathcal{Q}_{NPT} &= \frac{\beta P}{N!\Lambda^{3N}} \int dV \exp[-\beta PV] V^{N} \int ds^{N} \exp[-\beta U(s^{N};L)] \\
\text{Probability to find a particular configuration:} \\
\end{aligned}$$

$$\begin{aligned}
\mathcal{N}_{NPT} \left(V, \mathbf{s}^{N}\right) \approx V^{N} \exp[-\beta PV] \exp[-\beta U(s^{N};L)] \\
\text{Sample a particular configuration:} \\
& \text{Change of volume} \\
& \text{Acceptance rules ??} \\
& \text{Change of reduced coordinates} \\
\end{aligned}$$



$$\begin{split} \text{Imposing detailed balance:} \quad & K(o \to n) = K(n \to o) \\ \text{with} \quad & K(o \to n) = \mathfrak{N}(o)\alpha(o \to n) \operatorname{acc}(o \to n) \\ \text{...and for the} \\ \text{reverse move:} \quad & K(n \to o) = \mathfrak{N}(n)\alpha(n \to o) \operatorname{acc}(n \to o) \\ \text{If we sample the NPT ensemble} \\ & \mathfrak{N}(o) = V_o^N e^{-\beta P V_o} e^{-\beta U(o)} \quad \text{and} \quad & \mathfrak{N}(n) = C V_n^N e^{-\beta P V_n} e^{-\beta U(n)} \\ \text{Suppose we change the position of a} \\ \text{randomly selected particles} \\ & \frac{\operatorname{acc}(o \to n)}{\operatorname{acc}(n \to o)} = \frac{\mathfrak{N}(n)\alpha(n \to o)}{\mathfrak{N}(o)\alpha(o \to n)} = e^{-\beta \Delta U} \end{split}$$

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In the NPT ensemble we also need to sample the volume

$$\Re(o) = V_o^N e^{-\beta P V_o} e^{-\beta U(o)} \text{ and } \Re(n) = C V_n^N e^{-\beta P V_n} e^{-\beta U(n)}$$
The acceptance rule now reads:

$$\frac{\operatorname{acc}(o \to n)}{\operatorname{acc}(n \to o)} = \frac{\Re(n)\alpha(n \to o)}{\Re(o)\alpha(o \to n)} = \frac{V_n^N e^{-\beta P V_n} e^{-\beta U(n)}}{V_o^N e^{-\beta P V_o} e^{-\beta U(o)}}$$

$$= \left(\frac{V_n}{V_o}\right)^N e^{-\beta P \Delta V} e^{-\beta \Delta U}$$

Algorithm: NPT

Randomly change the position of a particle

Randomly change the volume

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Algorithm 10 (Basic NPT-Ensemble Simulation)

```
PROGRAM mc_npt
```

```
do icycl=1,ncycl
  ran=ranf()*(npart+1)+1
  if (ran.le.npart) then
     call mcmove
  else
     call mcvol
```

endif

```
if (mod(icycl,nsamp).eq.0)
```

```
+ call sample
enddo
end
```

basic NPT ensemble simulation

perform neyc1 MC cycles

perform particle displacement

perform volume change

sample averages



Comments to this algorithm:

- 1. Subroutine ener calculates the energy of a particle at the given position.
- 2. Note that, if a configuration is rejected, the old configuration is retained.
- 3. The ranf() is a random number uniform in [0, 1].

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```
SUBROUTINE mcvol
 call toterg(box, eno)
 vo=box**3
 lnvn=log(vo) + (ranf() - 0.5) * vmax
 vn=exp(lnvn)
boxn=vn**(1/3)
 do 1=1, npart
   x(1) = x(1) * boxn/box
 enddo
 call toterg(boxn, enn)
 arg=-beta*((enn-eno)+p*(vn-vo)
+ - (npart+1) * log(vn/vo)/beta)
 if (ranf().gt.exp(arg)) then
   do 1=1, npart
     x(1) = x(1) * box/boxn
   enddo
```

attempts to change the volume total energy old conf. determine old volume perform random walk in ln V

```
new box length
```

rescale center of mass

total energy new conf.

appropriate weight function! acceptance rule (5.2.3) REJECTED restore the old positions

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end1f

end

return



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Adsorption

(and an excuse to do the grand-canonical ensemble)





Thermodynamics of adsorption

What is the thermodynamic language of adsorption?

What are the equilibrium conditions?

Can we make a molecular model of adsorption?



Pressure

In a solid the free energy change to change the volume can be anisotropic

Is described by a stress tensor

Unlike a fluid a solid can resist strain; forces are much larger



Does the adsorption isotherm of a brick change if we stand on it?

 $p = -\left(\frac{\partial F}{\partial V}\right)_{T}$

Pressure in a solid

Let us assume that in the pressure range of the isotherm the solid does not deform

Hence,

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = \infty$$



We cannot change the **volume** of our solid; hence **pressure is not defined** inside the solid.

For these adsorption studies the pressure of the gas phase is not the preferred thermodynamic variable!





Grand-canonical ensemble

Classical

- Legrendre transformation
- A small system that can exchange heat and particles with a large bath

Statistical

Taylor expansion of a small reservoir

Legendre Transformation
The energy is a natural function of the entropy, volume, and number of particles of component i

$$U = U(S,V,N_i)$$
 $dU = TdS - pdV + \sum \mu_i dN_i$
Conjugate variables
 $S: T = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} V: p = -\left(\frac{\partial U}{\partial V}\right)_{S,N_i} N_i: \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j}$
Legendre transformations, to get μ VT:
 $Y \equiv U - TS - \mu N \rightarrow Y = Y(T,V,\mu)$



constant T and µ

Total system is isolated and the volume is constant First law $dU = TdS - pdV + \mu dN = 0$ Second law $dS \ge 0$

Box 1: constant chemical potential and temperature Ist law: $dU_1 + dU_b = 0$ or $dU_1 = -dU_b$ $dN_1 + dN_b = 0$ or $dN_b = -dN_1$ The bath is very large and the small changes do not change μ or T; in addition the process is reversible 2nd law: $dS_1 + dS_b = dS_1 + \frac{1}{T_b} dU_b - \frac{\mu_b}{T_b} dN_b \ge 0$

 $dS_{1} + dS_{b} = dS_{1} + \frac{1}{T_{b}} dU_{b} - \frac{\mu_{b}}{T_{b}} dN_{b} \ge 0$ We can express the changes of the bath in terms of properties of the system $dS_{1} - \frac{1}{T}dU_{1} + \frac{\mu}{T}dN_{1} \ge 0 \qquad d(TS_{1} - U_{1} + \mu N_{1}) \ge 0$ $d(U - TS - \mu N) \le 0$ For the Gibbs free energy we can write: $G \equiv U - TS + pV$ $-pV = U - TS - \mu N$ or $G = \mu N$ Giving: or $d(pV) \ge 0$ $d(-pV) \le 0$ Hence, for a system at constant temperature and chemical potential pV increases and takes its maximum value at equilibrium

$$\mu, V, T \text{ ensemble}$$

$$\lim_{N \to E_{i}} \sum_{N \to N_{i}} \sum_{K \to N_{i}} \sum_{n \to N_{i}} \sum_{k \to N_{i}} Consider a small system that can exchange particles and energy with a big reservoir
$$\ln \Omega \left(E - E_{i}, N - N_{j}\right) = \ln \Omega (E, N) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N} E_{i} - \left(\frac{\partial \ln \Omega}{\partial N}\right)_{E,V} N_{j} + \cdots$$
The terms in the expansion follow from the connection with Thermodynamics: $S = k_{B} \ln \Omega$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$
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$$\ln \Omega (E - E_i, N - N_j,) = \ln \Omega (E, N) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N} E_i - \left(\frac{\partial \ln \Omega}{\partial N}\right)_{E,V} N_j + \cdots$$

$$\ln \Omega (E - E_i, N - N_j) = \ln \Omega (E, N) - \frac{E_i}{k_B T} + \frac{\mu}{k_B T} N_j$$

$$\ln \frac{\Omega (E - E_i, N - N_j)}{\Omega (E, N)} = -\frac{E_i}{k_B T} + \frac{\mu}{k_B T} N_j$$
Hence, the probability to find $E_{i,V}$:
$$P (E_i, N_j) = \frac{\Omega (E - E_i, N - N_j)}{\sum_{k,l} \Omega (E - E_k, N - N_l)} \propto \exp \left[-\frac{E_i}{k_B T} + \frac{\mu N_i}{k_B T} \right]$$


μVTEnsemble

Partition function (scaled coordinates!):

$$Q_{\mu VT} = \sum_{N=0}^{N=\infty} \frac{\exp(\beta \mu N) V^{N}}{\Lambda^{3N} N!} \int ds^{N} \exp\left[-\beta U\left(s^{N};L\right)\right]$$

Probability to find a particular configuration:

$$N_{\mu VT}(N,\mathbf{s}^{N}) \propto \frac{\exp(\beta \mu N) V^{N}}{\Lambda^{3N} N!} \exp\left[-\beta U(\mathbf{s}^{N};L)\right]$$

Sample a particular configuration:

- Change of the number of particles Detailed balance
- Change of reduced coordinates

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In the µVT ensemble we also need to change the number
of particles

$$\mathfrak{N}(o) = \frac{V^{N_o}}{N_o!\Lambda^{3N_o}} e^{\beta\mu N_o} e^{-\beta U(o)} \qquad \mathfrak{N}(n) = C \frac{V^{N_n}}{N_n!\Lambda^{3N_n}} e^{\beta\mu N_n} e^{-\beta U(n)}$$
Imposing detailed balance gives for the acceptance rule

$$\frac{\operatorname{acc}(N \to N+1)}{\operatorname{acc}(N+1 \to N)} = \frac{\mathfrak{N}(N+1)\alpha(N+1 \to N)}{\mathfrak{N}(N)\alpha(N \to N+1)}$$

$$= \frac{\frac{V^{N+1}}{(N+1)!\Lambda^{3N+3}} e^{\beta\mu(N+1)} e^{-\beta U(N+1)}}{\frac{V^N}{(N)!\Lambda^{3N+3}} e^{\beta\mu N} e^{-\beta U(N)}}$$

$$\frac{\operatorname{acc}(N \to N+1)}{\operatorname{acc}(N+1 \to N)} = \frac{V}{(N+1)\Lambda^3} e^{\beta\mu} e^{-\beta[U(N+1)-U(N)]}$$

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A 8

A 8

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A 8

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Comments to this algorithm:

- This algorithm ensures that, after each MC step, detailed balance is obeyed. Per cycle we perform on average npav attempts⁶ to displace particles and nexc attempts to exchange particles with the reservoir.
- Subroutine mcmove attempts to displace a particle (Algorithm 2), subroutine mcexc attempts to exchange a particle with a reservoir (Algorithm 13), and subroutine sample samples quantities every nsamp cycle.

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```
attempt to exchange a particle
 SUBROUTINE mcexc
                                    with a reservoir
                                    decide to remove or add a particle
 if (ranf().lt.0.5) then
                                    test whether there is a particle
   if (npart.eq.0) return
                                    select a particle to be removed
   o=int(npart*ranf())+1
   call ener(x(o), eno)
                                    energy particle o
                                    acceptance rule (5.6.9)
   arg=npart*exp(beta*eno)
      /(zz*vol)
+
   if (ranf().lt.arg) then
                                    accepted: remove particle o
     x(o) = x(npart)
     npart=npart-1
   endif
 else
                                    new particle at a random position
   xn=ranf()*box
   call ener(xn, enn)
                                    energy new particle
                                    acceptance rule (5.6.8)
   arg=zz*vol*exp(-beta*enn)
       /(npart+1)
+
   if (ranf().lt.arg) then
     x(npart+1) = xn
                                    accepted: add new particle
     npart=npart+1
   endif
 endif
 return
 end
```

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Exotic Ensembles



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Model membrane: Lipid bilayer

hydrophilic head group

two hydrophobic tails





Questions

- What is the surface tension of this system?
- What is the surface tension of a biological membrane?
- What to do about this?

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$$\begin{split} \begin{array}{c} \underbrace{A_{j,E_{i}}}_{A_{j,E_{i}}} & \underbrace{E-E_{i}}_{A-A_{j}} \\ \end{array} \end{array} \begin{array}{c} \begin{array}{c} \text{Consider a small system that can} \\ \text{exchange area and energy with a} \\ \text{big reservoir} & I/k_{B}T \\ \end{array} \\ \begin{array}{c} \ln\Omega(E-E_{i,}A-A_{i}) = \ln\Omega(E,A) - \left(\frac{\partial\ln\Omega}{\partial E}\right)_{A}E_{i} - \left(\frac{\partial\ln\Omega}{\partial A}\right)_{E}A_{i} + \cdots \\ \left(\frac{\partial\ln\Omega}{\partial A}\right)_{N} = \left(\frac{\partial S/k_{B}}{\partial A}\right)_{N} = -\frac{\gamma}{k_{B}T} \\ \end{array} \\ \begin{array}{c} \ln\frac{\Omega(E-E_{i},A-A_{j})}{\Omega(E,A)} = -\frac{E_{i}}{k_{B}T} + \frac{\gamma A_{j}}{k_{B}T} \\ P(E_{i},A_{j}) = \frac{\Omega(E-E_{i},A-A_{j})}{\sum_{I,k}\Omega(E-E_{i},A-A_{k})} = \frac{\exp\left[-\beta\left(E_{i}-\gamma A_{k}\right)\right]}{\sum_{I,k}\exp\left[-\beta\left(E_{i}-\gamma A_{k}\right)\right]} \\ \approx \exp\left[-\beta\left(E_{i}-\gamma A_{j}\right)\right] \end{array}$$

Simulations at imposed surface tension

Simulation to a constant surface tension

Simulation box: allow the area of the bilayer to change in such a way that the volume is constant.



$$N_{\gamma VT}(A, \mathbf{s}^{N}) \propto \exp\left[-\beta\left[U(\mathbf{s}^{N}; L) - \gamma A\right]\right]$$
$$\frac{\operatorname{acc}(o \to n)}{\operatorname{acc}(n \to o)} = \frac{N(n)}{N(o)}$$
Suppose we change:
$$L_{o} \to L_{n} \atop A_{o} \to A_{n} \right\} V_{o} = V_{n}$$
$$\frac{\operatorname{acc}(o \to n)}{\operatorname{acc}(n \to o)} = \frac{\exp\left[-\beta\left[U(\mathbf{s}_{n}^{N}; L_{n}) - \gamma A_{n}\right]\right]}{\exp\left[-\beta\left[U(\mathbf{s}_{n}^{N}; L_{o}) - \gamma A_{o}\right]\right]}$$
$$= \exp\left\{-\beta\left[U(n) - U(o)\right] - \beta\gamma(A_{n} - A_{o})\right\}$$



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Non-Boltzmann sampling

$$\langle A \rangle_{NVT_{1}} = \frac{1}{Q_{NVT_{1}}} \frac{1}{\Lambda^{3N} N!} \int dr^{N} A(r^{N}) \exp[-\beta_{1} U(r^{N})]$$

$$= \frac{\int dr^{N} A(r^{N}) \exp[-\beta_{1} U(r^{N})]}{\int dr^{N} \exp[-\beta_{1} U(r^{N})]}$$

$$= \frac{\int dr^{N} A(r^{N}) \exp[-\beta_{1} U(r^{N})]}{\int dr^{N} \exp[-\beta_{1} U(r^{N})] \exp[\beta_{2} U(r^{N}) - \beta_{2} U(r^{N})]}$$

$$= \frac{\int dr^{N} A(r^{N}) \exp[-\beta_{1} U(r^{N})] \exp[\beta_{2} U(r^{N}) - \beta_{2} U(r^{N})]}{\int dr^{N} \exp[-\beta_{1} U(r^{N})] \exp[\beta_{2} U(r^{N}) - \beta_{2} U(r^{N})]}$$

$$= \frac{\int dr^{N} A(r^{N}) \exp[\beta_{2} U(r^{N}) - \beta_{1} U(r^{N})] \exp[-\beta_{2} U(r^{N})]}{\int dr^{N} \exp[\beta_{2} U(r^{N}) - \beta_{1} U(r^{N})] \exp[-\beta_{2} U(r^{N})]}$$

$$= \frac{\langle A \exp[(\beta_{2} - \beta_{1}) U] \rangle_{NVT_{2}}}{\langle \exp[(\beta_{2} - \beta_{1}) U] \rangle_{NVT_{2}}}$$
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$$\langle A \rangle_{NVT_{1}} = \frac{1}{Q_{NVT_{1}}} \frac{1}{\Lambda^{3N}N!} \int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r^{N})\right]$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r^{N})\right]}{\int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r)\right]}{\int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r)\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r)\right]}{\int e^{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[-\beta_{1}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr^{N}A(r^{N}) \exp\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}{\int e^{2}\left[\beta_{2}U(r^{N}) - \beta_{2}U(r^{N})\right]}$$

$$= \frac{\int dr$$



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How to do parallel Monte Carlo



- Is it possible to do Monte Carlo in parallel
 - □ Monte Carlo is sequential!
 - □ We first have to know the fait of the current move before we can continue!

Parallel Monte Carlo

Algorithm (correct?):

- 1. Generate k trial configurations in parallel
- 2. Select out of these the one with the lowest energy

$$P(n) = \frac{\exp\left[-\beta(U_n)\right]}{\sum_{j=1}^{g} \exp\left[-\beta(U_j)\right]}$$

3. Accept and reject using normal Monte Carlo rule: $\operatorname{acc}(o \rightarrow n) = \exp\left[-\beta(U_n - U_o)\right]$

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Detailed balance!

Why the K(o B n) = K(n B o) $K(o \to n) = N(o) \times \alpha (o \to n) \times \operatorname{acc}(o \to n)$ $K(n \to o) = N(n) \times \alpha (n \to o) \times \operatorname{acc}(n \to o)$ $\frac{\operatorname{acc}(o \to n)}{\operatorname{acc}(n \to o)} = \frac{N(n) \times \alpha (n \to o)}{N(o) \times \alpha (o \to n)} = \frac{N(n)}{N(o)}$

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Detailed balance 0 n $K(o \rightarrow n) = K(n \rightarrow o)$ $K(o \rightarrow n) = N(o) \times \alpha(o \rightarrow n) \times \operatorname{acc}(o \rightarrow n)$ $K(n \rightarrow o) = N(n) \times \alpha(n \rightarrow o) \times \operatorname{acc}(n \rightarrow o)$ $\operatorname{acc}(o \to n) \ N(n) \times \alpha(n \to o) \ N(n)$ $\operatorname{acc}(n \to o) = \overline{N(o) \times \alpha(o \to n)} = N(o)$

$$K(o \to n) = N(o) \times \alpha(o \to n) \times \operatorname{acc}(o \to n)$$

$$\alpha(o \to n) = \frac{\exp[-\beta(U_n)]}{\sum_{j=1}^{g} \exp[-\beta(U_j)]}$$

$$\alpha(o \to n) = \frac{\exp[-\beta(U_n)]}{W(n)}$$

$$\alpha(n \to o) = \frac{\exp[-\beta(U_o)]}{\sum_{j=1}^{g} \exp[-\beta(U_j)]}$$

$$\alpha(n \to o) = \frac{\exp[-\beta(U_o)]}{W(o)}$$

$$100$$

$$\frac{\operatorname{acc}(o \to n)}{\operatorname{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$
with
$$\alpha(o \to n) = \frac{\exp[-\beta(U_n)]}{W(n)} \qquad \alpha(n \to o) = \frac{\exp[-\beta(U_o)]}{W(o)}$$

$$\frac{\operatorname{acc}(o \to n)}{\operatorname{acc}(n \to o)} = \frac{N(n) \times \frac{\exp[-\beta(U_o)]}{W(o)}}{N(o) \times \frac{\exp[-\beta(U_n)]}{W(n)}} = \frac{W(n)}{W(o)}$$
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$$Detailed Balance?$$

$$K(o \to n) = K(n \to o)$$

$$K(o \to n) = N(o) \times \alpha(o \to n) \times \operatorname{acc}(o \to n)$$

$$\alpha(o \to n) = \sum_{\{\mathbf{b}\}_{k=1}^{k}} \frac{\exp[-\beta(U_n)]}{\sum_{j=1}^{k} \exp[-\beta(U_j)]} \qquad \{\mathbf{b}_n | \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3, \cdots, \mathbf{b}_k\} = \{\mathbf{b}_n | \{\mathbf{b}\}_{k=1}\}$$

$$\alpha(o \to n) = \sum_{\{\mathbf{b}\}_{k=1}^{k}} \frac{\exp[-\beta(U_n)]}{\sum_{j=1}^{k} \exp[-\beta(U_j)]} \qquad \{\mathbf{b}_n | \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3, \cdots, \mathbf{b}_k\} = \{\mathbf{b}_n | \{\mathbf{b}\}_{k=1}\}$$





Super detailed balance?Summation over all
possible paths
$$K(o \rightarrow n) = \sum_{\{\mathbf{b}\}_{k-1}} K(o \rightarrow n | \{\mathbf{b}\}_{k-1})$$
 $K(n \rightarrow o) = \sum_{\{\mathbf{b}\}_{k-1}} K(n \rightarrow o | \{\mathbf{b}\}_{k-1})$ $K(o \rightarrow n) - K(n \rightarrow o) = \sum_{\{\mathbf{b}\}_{k-1}} K(o \rightarrow n | \{\mathbf{b}\}_{k-1}) - \sum_{\{\mathbf{b}:\}_{k-1}} K(n \rightarrow o | \{\mathbf{b}'\}_{k-1})$ $K(o \rightarrow n) - K(n \rightarrow o) = \sum_{\{\mathbf{b}\}_{k-1}} K(o \rightarrow n | \{\mathbf{b}\}_{k-1}) - \sum_{\{\mathbf{b}:\}_{k-1}} K(n \rightarrow o | \{\mathbf{b}'\}_{k-1})$ Super detailed
balance $K(o \rightarrow n | \{\mathbf{b}\}_{k-1}) = K(n \rightarrow o | \{\mathbf{b}'\}_{k-1})$ Every single term in the first
summation is equal to
any term in the second