Ensembles in Monte Carlo

Ensembles (Chapter 5)
Practical Aspects

Free Energy and Phase Equilibria

Thermodynamic Integration (7.1)
Chemical Potentials (7.2)
Umbrella Sampling (7.4)
(Application: Phase Diagram of Carbon)

Classical and Statistical Thermodynamics

Problem: we have a set of coordinates and velocities -what to do with it?

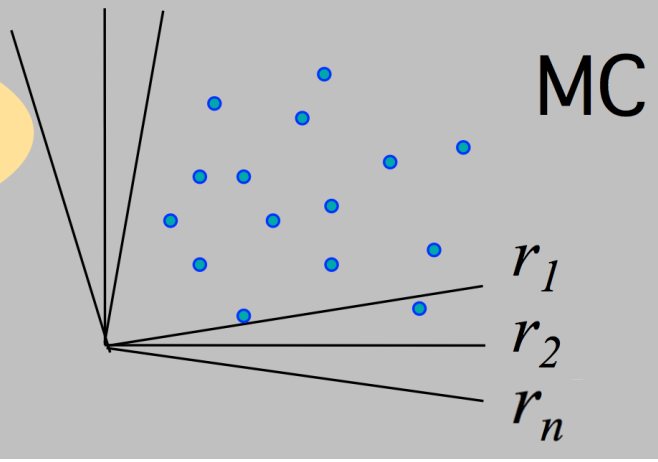
- Statistical Thermodynamics
  - The probability to find a particular configuration
  - Properties are expressed in term of averages
  - Free energies
- Thermodynamics: relation of the free energies to thermodynamic properties

Monte Carlo

What is the correct probability?
Statistical Thermodynamics

- Generate a set of configurations with the *correct* probability
- Compute the thermodynamic and transport properties as averages over all configurations

How to compute these properties from a simulation?



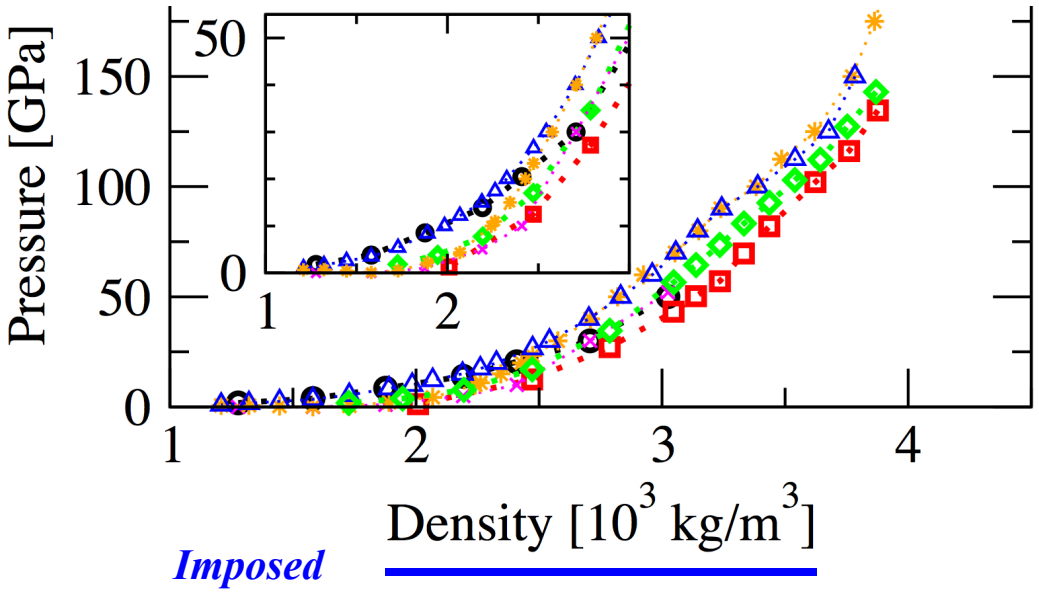
Different Ensembles

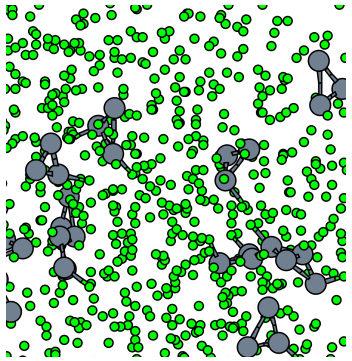
Ensemble	Name	Constant (Imposed)	Fluctuating (Measured)
NVT	Canonical	N,V,T	P
NPT	Isobaric-isothermal	N,P,T	V
μVT	Grand-canonical	μ,V,T	N

NVT

Liquids

Equation of State of Liquid Carbon





Imposed

… if force is difficult to calculate …
e.g. carbon force field

TABLE I. Parameters of the LCBOPII. The units of energy and length are eV and Å, respectively.

Switch	q	q_{min}	q_{max}	p	Switch	q	q_{min}	q_{max}	p	Switch	q	q_{min}	q_{max}	p
S_{sr}^{down}	r_{ij}	1.7	2.2	3.0	S_{mr}^{up}	r_{ij}	1.7	2.2	−2.0	S_{N}^{down}	r_{ij}	1.7	2.2	−3.0
S_{lr}^{down}	r_{ij}	5.5	6.0	0	S_{M}^{up}	N_{ki}	2.0	3.0	0	S_{sat}^{down}	N_{ki}	3.0	4.0	0
S_{db}^{down}	x_{ij}^{db}	0.0	1.0	0	$S_{\gamma,0}^{up}$	γ_{ij}	0.34	0.93	0	$S_{\gamma,2}^{up}$	γ_{ij}	0.30	0.93	0

Short-range potential V^{sr}

V_R $A^{sr}=53026.92614$ $\alpha=6.74750993$

V_A $B_1^{sr}=27618.35706$ $\beta_1=6.34503890$ $B_2^{sr}=34.07142502$ $\beta_2=1.19712839$

G $g_{min}=0.0020588719$ $g_{gr}=0.0831047003$ $g_{max}=16.0$

$g_{1,0}=0.7233666272$ $g_{1,1}=1.7334665088$ $g_{1,2}=1.8701997632$

$g_{2,0}=0.73994527795$ $g_{2,1}=-1.999211817$ $g_{2,2}=-17.43251545$

$g_{2,3}=-33.96127110$ $g_{2,4}=-44.65392079$

$g_{3,0}=-15.19$ $g_{3,1}=-25.6168552398$ $g_{3,2}=-21.51728397$

$g_{3,3}=0.9899080993$ $g_{3,4}=13.66416160$

$A_{y_0}=-0.4$ $B_{y_0}=0.01875$

$A_g=5.6304664723$ $B_g=0.1516943990$ $C_g=0.009832975891$

$D_g=-0.189175977654$ $E_g=0.050977653631$

H $d=0.14$ $C_1=3.335$ $C_4=220.0$ For C_6, L, κ, R_0 and R_1 see text.

F_{ij}^{conj} $F_{ij,0}^{conj}$ $F_{ij,1}^{conj}$

0.0000	0.0207	−0.0046	−0.1278	0.0000	0.0584	0.0416	−0.1278
0.0207	0.0000	−0.0365	−0.1043	0.0584	0.1379	0.0062	−0.1243
−0.0046	−0.0365	0.0000	−0.0273	0.0416	0.0062	0.0936	−0.0393
−0.1278	−0.1043	−0.0273	0.0000	−0.1278	−0.1243	−0.0393	0.0000

A_{ij} $\alpha_0=0.95$

T_{ij} $A_t=-13.152909887$

$B_{t1}=-0.0486839616$ $B_{t2}=3.8$ $B_{t3}=0.62$ $B_{t4}=0.005$

Long-range potential V^{lr}

$\tau_0=3.715735$ $\epsilon_1=0.002827918$ $\lambda_1=1.338162$ $\lambda_2=2.260479$ For ϵ_1, v_1, and v_2 see text.

Middle-range potential V^{mr}

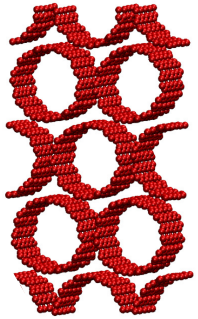
$r_1^{mr}=4.0$ $r_2^{mr}=2.9$ $A_0^{mr}=-0.2345$ $A_1^{mr}=-0.67$ $A_2^{mr}=-4.94$

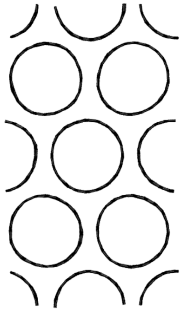
Imp

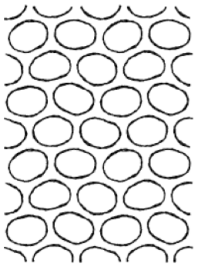
NPT

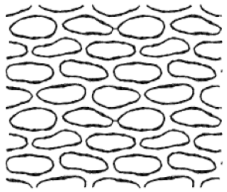
Non-Isotropic Systems
e.g. Solids

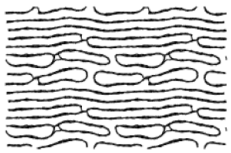
Structure and Transformation of
Carbon Nanotube Arrays

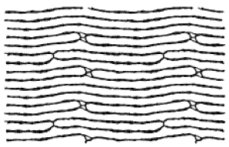


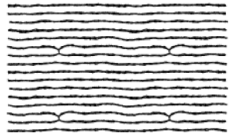








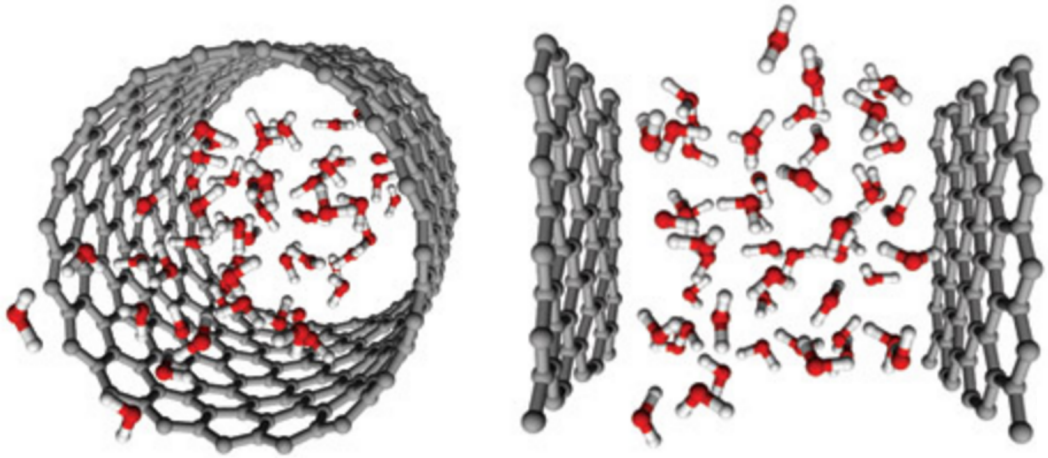




μVT

Adsorption

Adsorption in Carbon Nanostructues



Schwegler et al.

Statistical Thermodynamics

Partition function (NVT)

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

Ensemble average

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

Probability to find a particular configuration

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

Free energy

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

Ensemble average

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

$$= \int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) P(\mathbf{r}^N) \quad = \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) P(\mathbf{r}^N)}{\int \mathrm{d}\mathbf{r}^N P(\mathbf{r}^N)}$$

$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) C \exp[-\beta U(\mathbf{r}^N)]}{\int \mathrm{d}\mathbf{r}^N C \exp[-\beta U(\mathbf{r}^N)]} \quad = \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp[-\beta U(\mathbf{r}^N)]}{\int \mathrm{d}\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]}$$

Generate configuration using MC:

$$\{\mathbf{r}_1^N, \mathbf{r}_2^N, \mathbf{r}_3^N, \mathbf{r}_4^N \cdots, \mathbf{r}_M^N\}$$

Weighted Distribution

$$\overline{A} = \frac{1}{M} \sum_{i=1}^{M} A(\mathbf{r}_i^N) \quad = \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) P^{MC}(\mathbf{r}^N)}{\int \mathrm{d}\mathbf{r}^N P^{MC}(\mathbf{r}^N)}$$

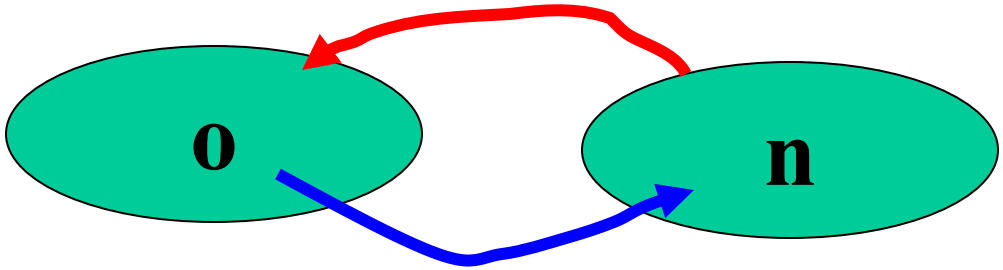
with

$$P^{MC}(\mathbf{r}^N) = C^{MC} \exp[-\beta U(\mathbf{r}^N)]$$

$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) C^{MC} \exp[-\beta U(\mathbf{r}^N)]}{\int \mathrm{d}\mathbf{r}^N C^{MC} \exp[-\beta U(\mathbf{r}^N)]}$$

$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp[-\beta U(\mathbf{r}^N)]}{\int \mathrm{d}\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]}$$

Monte Carlo: Detailed balance



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

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

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

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

- *N(o)* : total number of systems in our ensemble in state o
- *α(o → n)*: a priori probability to generate a move *o → n*
- *acc(o → n)*: probability to accept the move *o → n*

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$

Monte Carlo in NVT-Ensemble

$$N(n) \propto \exp\left[-\beta U(n)\right]$$

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n)}{N(o)}$$

Metropolis, Rosenbluth,Rosenbluth,

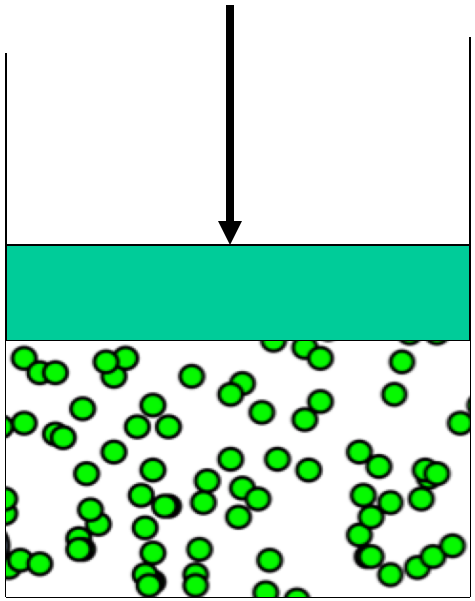
Teller and Teller[#]choice:

[#] J. Chem. Phys. 21, 1087 (1953)

$$\mathrm{acc}(o \to n) = \frac{N(n)}{N(o)} = \exp\left[-\beta(U(n) - U(o))\right] \quad if \quad N(n) < N(o)$$

$$= 1 \qquad if \quad N(n) > N(o)$$

NPT ensemble



We control the

- Temperature (T)
- Pressure (P)
- Number of particles (N)

Scaled coordinates

Partition function

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

Scaled coordinates

$$\mathbf{s}_i = \mathbf{r}_i / L$$

This gives for the partition function

$$Q_{NVT} = \frac{L^{3N}}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]$$

$$= \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]$$

The energy depends on the real coordinates

NPT Ensemble

Partition function:

$$Q_{NPT} = \frac{\beta P}{N!\Lambda^{3N}} \int \mathrm{d}V \exp\left[-\beta PV\right] V^N \int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]$$

Probability to find a particular configuration:

$$N_{NPT}\left(V, \mathbf{s}^N\right) \propto V^N \exp[$$

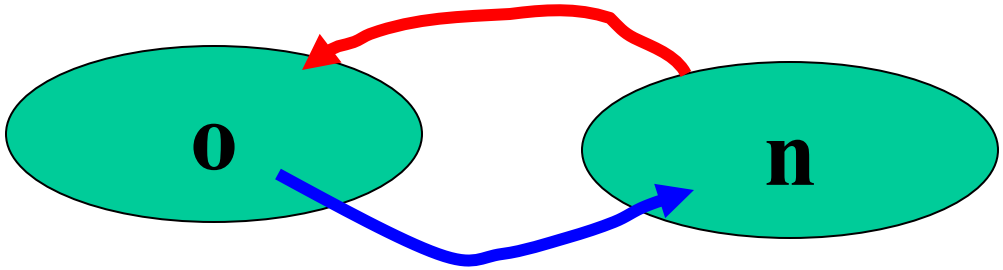
Sample a particular c

- change of volum
- change of reduced

Acceptance rules ??

Detailed balance

Detailed balance



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

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

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

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$

NPT-ensemble

$$N_{NPT}\left(V,\mathbf{s}^N\right) \propto V^N \exp\left[-\beta PV\right]\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n)}{N(o)}$$

Suppose particle

Metropolis, Rosenbluth,Rosenbluth, Teller and Teller[#]choice:

[#] J. Chem. Phys. 21, 1087 (1953)

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \begin{cases} \dfrac{N(n)}{N(o)} & if \quad N(n) < N(o) \\ 1 & if \quad N(n) > N(o) \end{cases}$$

NPT-ensemble

$$N_{NPT}\left(V,\mathbf{s}^N\right) \propto V^N \exp\left[-\beta PV\right]\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} = \frac{N(n)}{N(o)}$$

Suppose we change the ***volume*** of the system

$$\frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} = \frac{V_n^{\,N}\exp\left[-\beta PV_n\right]\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N}};L_n\right)\right]}{V_o^{\,N}\exp\left[-\beta PV_o\right]\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N}};L_o\right)\right]}$$

$$= \left(\frac{V_n}{V_o}\right)^N \exp\left[-\beta P\left(V_n - V_o\right)\right]\exp\left\{-\beta\left[U\left(n\right)-U\left(0\right)\right]\right\}$$

Algorithm: NPT

- Randomly change the position of a particle
- Randomly change the volume

Algorithm 10 (Basic NPT-Ensemble Simulation)

```
 PROGRAM mc_npt                          basic NPT ensemble simulation

 do icycl=1,ncycl                        perform ncycl MC cycles
   ran=ranf()*(npart+1)+1
   if (ran.le.npart) then
     call mcmove                         perform particle displacement
   else
     call mcvol                          perform volume change
   endif
   if (mod(icycl,nsamp).eq.0)
+    call sample                         sample averages
 enddo
 end
```

Algorithm 2 (Attempt to Displace a Particle)

```
   SUBROUTINE mcmove                    attempts to displace a particle

   o=int(ranf()*npart)+1                select a particle at random
   call ener(x(o),eno)                  energy old configuration
   xn=x(o)+(ranf()-0.5)*delx            give particle random displacement
   call ener(xn,enn)                    energy new configuration
   if (ranf().lt.exp(-beta              acceptance rule (3.2.1)
  +    *(enn-eno)) x(o)=xn              accepted: replace x(o) by xn
   return
   end
```

Comments to this algorithm:

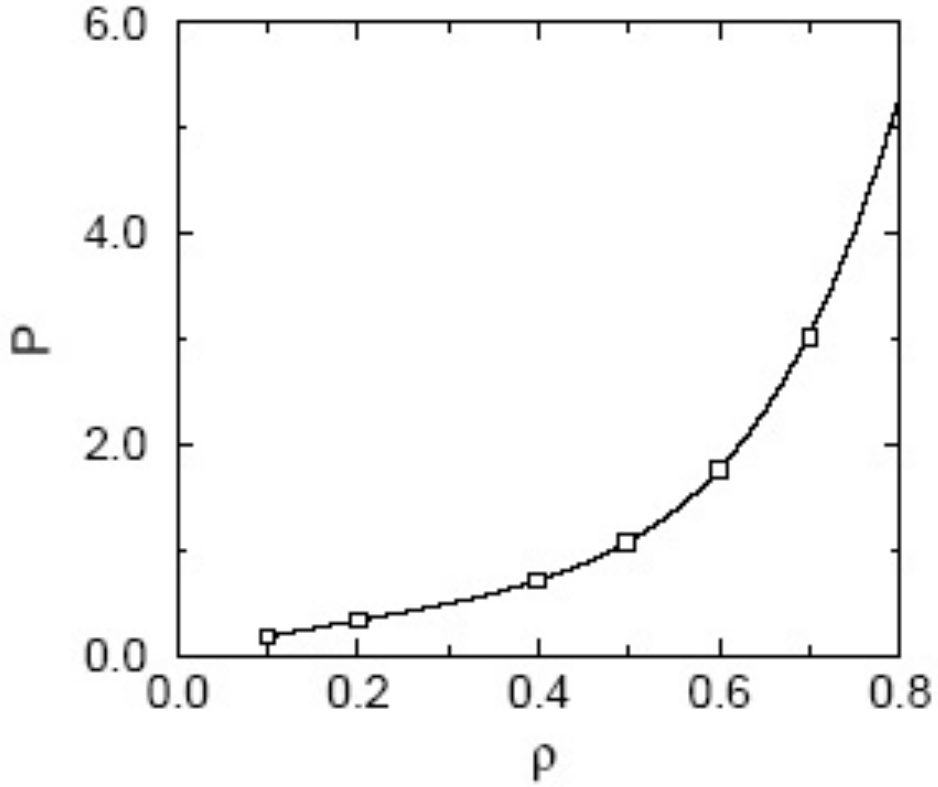
1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

Algorithm 11 (Attempt to Change the Volume)

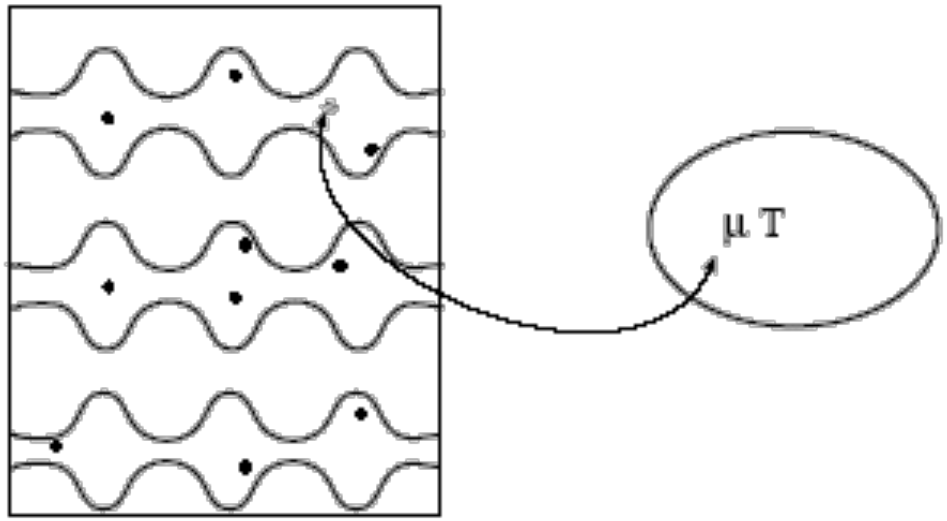
```
SUBROUTINE mcvol                          attempts to change
                                          the volume
call toterg(box,eno)                      total energy old conf.
vo=box**3                                 determine old volume
lnvn=log(vo)+(ranf()-0.5)*vmax            perform random walk in ln V
vn=exp(lnvn)
boxn=vn**(1/3)                            new box length
do i=1,npart
  x(i)=x(i)*boxn/box                      rescale center of mass
enddo
call toterg(boxn,enn)                     total energy new conf.
arg=-beta*((enn-eno)+p*(vn-vo)
+-(npart+1)*log(vn/vo)/beta)              appropriate weight function!
if (ranf().gt.exp(arg)) then              acceptance rule (5.2.3)
  do i=1,npart                            REJECTED
    x(i)=x(i)*box/boxn                    restore the old positions
  enddo
endif
return
end
```

NPT simulations

Equation of State of Lennard Jones System



Grand-canonical ensemble



We impose:

- Temperature (T)
- Chemical potential (μ)
- Volume (V)

- But **NOT** pressure

μVT Ensemble

Partition function:

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

Probability to find a particular configuration:

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

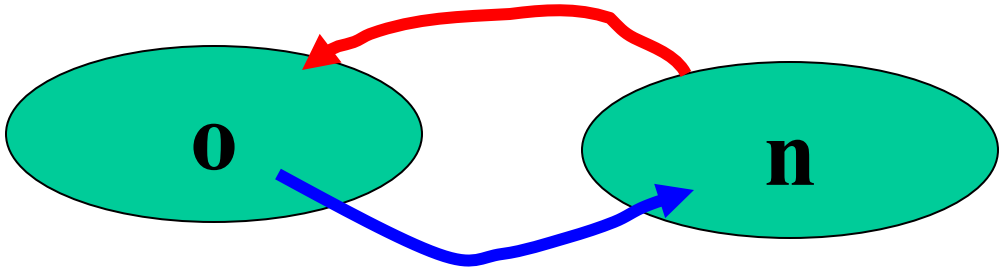
Sample a particular c

- Change of the nu
- Change of reduce

Acceptance rules ??

Detailed balance

Detailed balance



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

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

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

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$

μVT-ensemble

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

$$\frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} = \frac{N(n)}{N(o)}$$

Suppose . particle

Metropolis, Rosenbluth,Rosenbluth,

$\frac{\mathrm{acc}(o -}{\mathrm{acc}(n -}$ Teller and Teller[#]choice:

[#] J. Chem. Phys. 21, 1087 (1953)

$$\mathrm{acc}(o\to n) = \frac{N(n)}{N(o)} \qquad if \quad N(n) < N(o)$$

$$= 1 \qquad if \quad N(n) > N(o)$$

μVT-ensemble

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

$$\frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} = \frac{N(n)}{N(o)}$$

Suppose we change the ***number of particles*** of the system

$$\frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} = \frac{\dfrac{\exp\left(\beta\mu\left(N+1\right)\right)V^{N+1}}{\Lambda^{3N+3}\left(N+1\right)!}\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N+1}};L_n\right)\right]}{\dfrac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N}};L_o\right)\right]}$$

$$= \frac{\exp\left(\beta\mu\right)V}{\Lambda^3\left(N+1\right)}\exp\left[-\beta\Delta U\right]$$

Algorithm 12 (Basic Grand-Canonical Ensemble Simulation)

```
  PROGRAM mc_gc                                  basic μVT ensemble
                                                 simulation
  do icycl=1,ncycl                               perform ncycl MC cycles
   ran=int(ranf()*(npav+nexc))+1
   if (ran.le.npart) then
     call mcmove                                 displace a particle
   else
     call mcexc                                  exchange a particle
   endif                                         with the reservoir
   if (mod(icycl,nsamp).eq.0)
+    call sample                                 sample averages
  enddo
  end
```

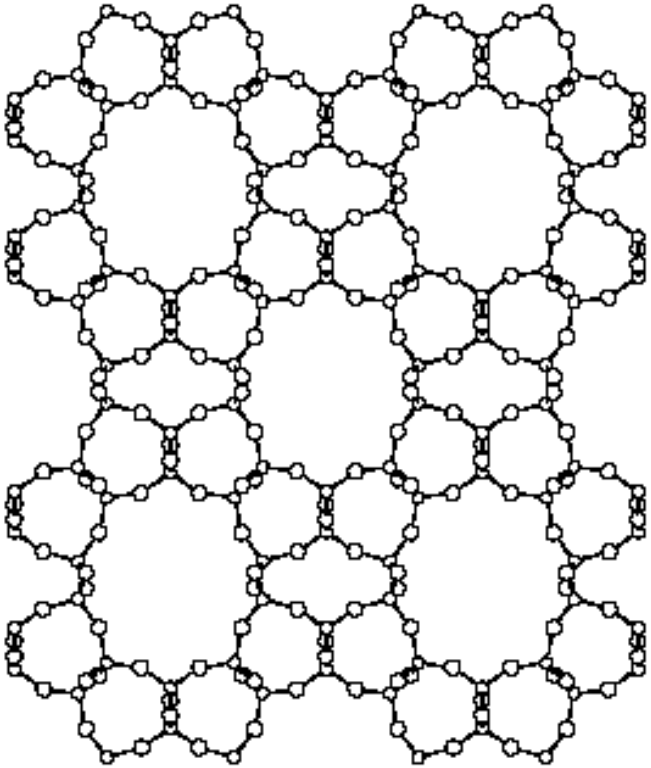
Comments to this algorithm:

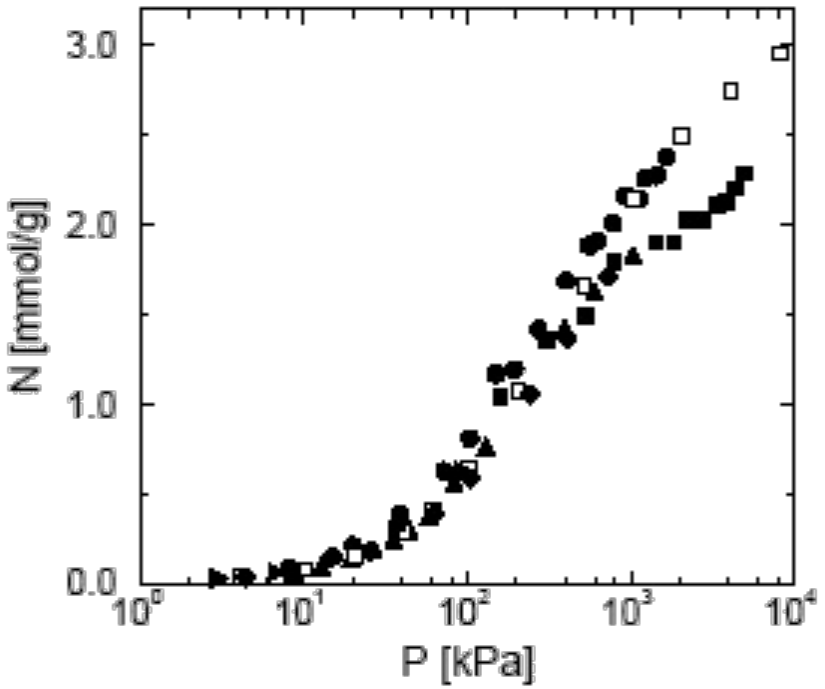
1. *This algorithm ensures that, after each MC step, detailed balance is obeyed. Per cycle we perform on average* `npav` *attempts*[6] *to displace particles and* `nexc` *attempts to exchange particles with the reservoir.*
2. *Subroutine* `mcmove` *attempts to displace a particle (Algorithm 2), subroutine* `mcexc` *attempts to exchange a particle with a reservoir (Algorithm 13), and subroutine* `sample` *samples quantities every* `nsamp` *cycle.*

Algorithm 13 (Attempt to Exchange a Particle with a Reservoir)

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

Application: adsorption in zeolites





Summary

Ensemble	Constant (Imposed)	Fluctuating (Measured)	Function
NVT	N,V,T	P	$\beta F=-\ln Q(N,V,T)$
NPT	N,P,T	V	$\beta G=-\ln Q(N,P,T)$
μVT	μ,V,T	N	$\beta\Omega=-\ln Q(\mu,V,T)=-\beta PV$

Beyond standard MC

$$\langle A \rangle_{NVT} = \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp[-\beta U(\mathbf{r}^N)]}{\int \mathrm{d}\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]}$$

Generate configuration using MC:

$\{\mathbf{r}_1^N, \mathbf{r}_2^N, \mathbf{r}_3^N, \mathbf{r}_4^N \cdots, \mathbf{r}_M^N\}$

$\bar{A} = \frac{1}{M} \sum_{i=1}^{M} A(\mathbf{r}_i^N)$ instead, …

Non-Boltzmann weighted Distribution

Biased Sampling (different T / parallel) – Lecture 2

More to Come

Monday
(**Thijs Vlugt**)

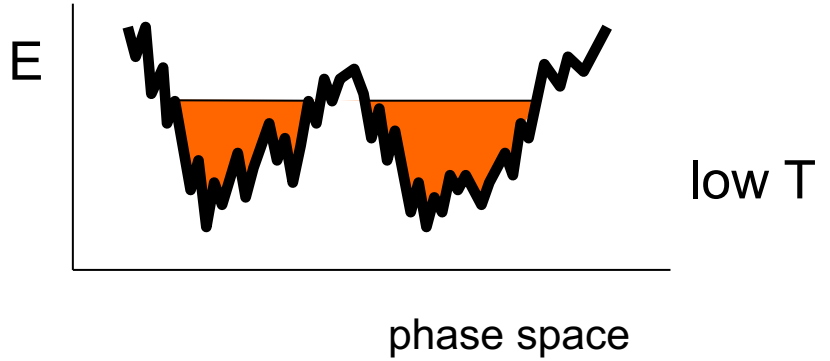
Tuesday
(**Daan Frenkel**)

Parallel tempering/Replica Exchange

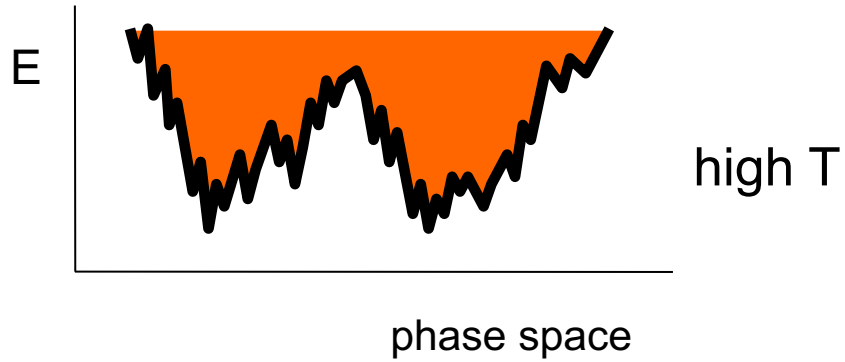
Ergodicity problems can occur, especially in glassy systems: biomolecules, molecular glasses, gels, etc.

The solution: go to high temperature

High barriers in energy landscape: difficult to sample



Barriers effectively low: easy to sample



Parallel tempering/Replica Exchange

Simulate two systems simultaneously

system 1
temperature T_1

system 2
temperature T_2

$$e^{-\beta_1 U_1(r^N)}$$

$$e^{-\beta_2 U_2(r^N)}$$

total Boltzmann weight:

$$e^{-\beta_1 U_1(r^N)} e^{-\beta_2 U_2(r^N)}$$

Swap move

- Allow two systems to swap

system 2
temperature T_1

system 1
temperature T_2

$$e^{-\beta_1 U_2(r^N)}$$

$$e^{-\beta_2 U_1(r^N)}$$

total Boltzmann weight:

$$e^{-\beta_1 U_2(r^N)} e^{-\beta_2 U_1(r^N)}$$

Acceptance rule

The ratio of the new Boltzmann factor over the old one is

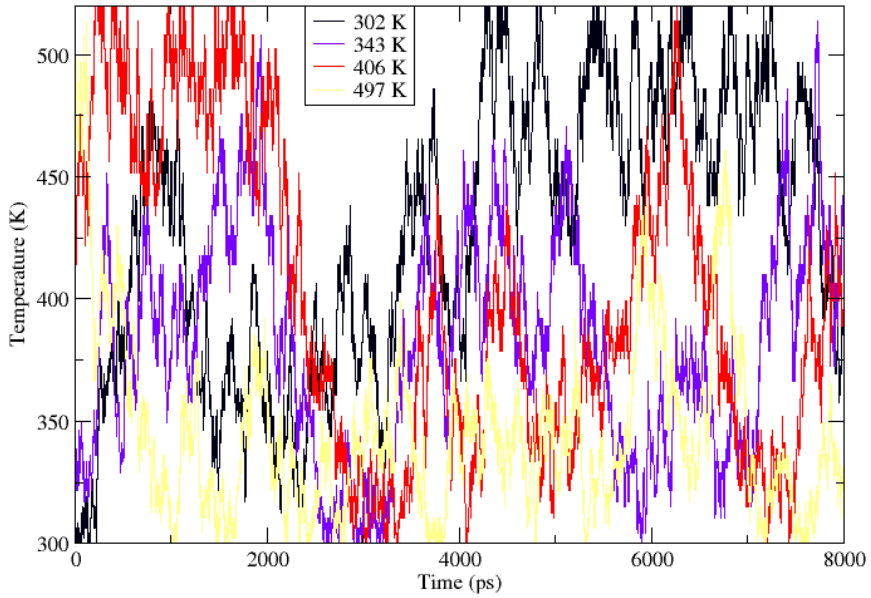
$$\frac{\mathcal{N}(n)}{\mathcal{N}(o)} = e^{(\beta_2-\beta_1)[U_2(r^N)-U_1(r^N)]}$$

The swap acceptance ratio is

$$\mathrm{acc}(1 \leftrightarrow 2) = \min\left(1, e^{(\beta_2-\beta_1)[U_2(r^N)-U_1(r^N)]}\right)$$

More replicas

Consider M replica's in the NVT ensemble at a different temperature.



A swap between two systems of different temperatures (T_i,T_j) is accepted if their potential energies are near.

other parameters can be used: Hamiltonian exchange

Free Energy and Phase Equilibria

Thermodynamic Integration (7.1)
Chemical Potentials (7.2)
Umbrella Sampling (7.4)
(Application: Phase Diagram of Carbon)

Why Free Energies?

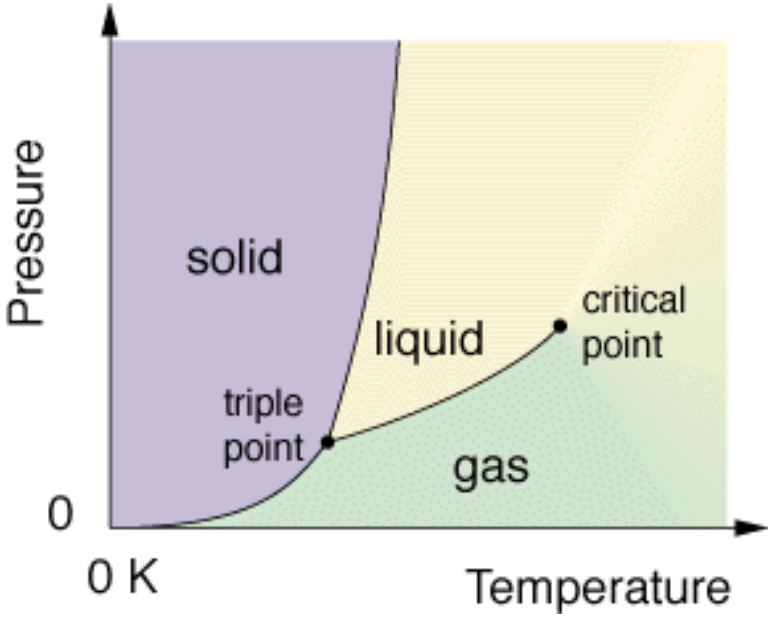
- Reaction equilibrium constants $A \leftrightarrow B$

$$K = \frac{[B]}{[A]} = \frac{p_B}{p_A} = \exp\left[-\beta(G_B - G_A)\right]$$

- Examples:
  - Chemical reactions: e.g. catalysis, etc....
  - Protein folding, binding: free energy gives binding constants

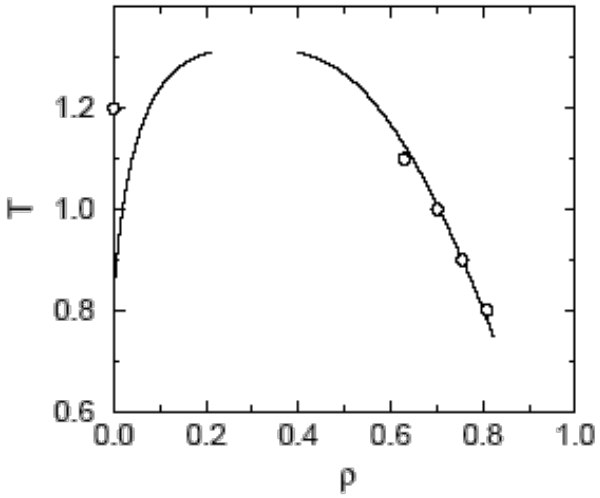
- Phase diagrams
  - Prediction of thermodynamic stability of phases
  - Coexistence lines
  - Critical points
  - Triple points
  - First order/second order phase transitions

Phase diagrams



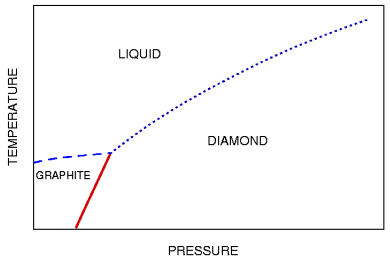
Critical point: no transition between liquid and vapor

Triple point: liquid, vapor and solid in equilibrium.



Along the liquid-gas coexistence line increasing the pressure and temperature at constant volume the liquid density becomes lower and the vapor density higher.

Carbon Phase Diagram



How do we compute these lines?

Phase equilibrium

Criteria for equilibrium (for single component)

$T_I = T_{II}$ $P_I = P_{II}$ $\mu_I = \mu_{II}$

Chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{P,T} = G_m$$

If $\mu_I > \mu_{II}$: transport of particles from phase I to phase II.

Stable phase:

Lowest chemical potential (for single phase: lowest Gibbs free energy)

Relation thermodynamic potentials

Helmholtz free energy: $F = U - TS$

Gibbs free energy: $G = F + PV$

Suppose we have $F(n, V, T)$

Then we can find G from F from:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{n,T} \qquad G = F - \left(\frac{\partial F}{\partial V}\right)_{n,T} V$$

All thermodynamic quantities can be derived from F and its derivatives

We need F (or G)

- We can calculated F(V)

$$F(V) = F(V_0) + \int_{V_0}^{V} \left(\frac{\partial \mathrm{F}}{\partial \mathrm{V}} \right)_{\mathrm{N,T}} \mathrm{dV} = F(V_0) - \int P \mathrm{dV}$$

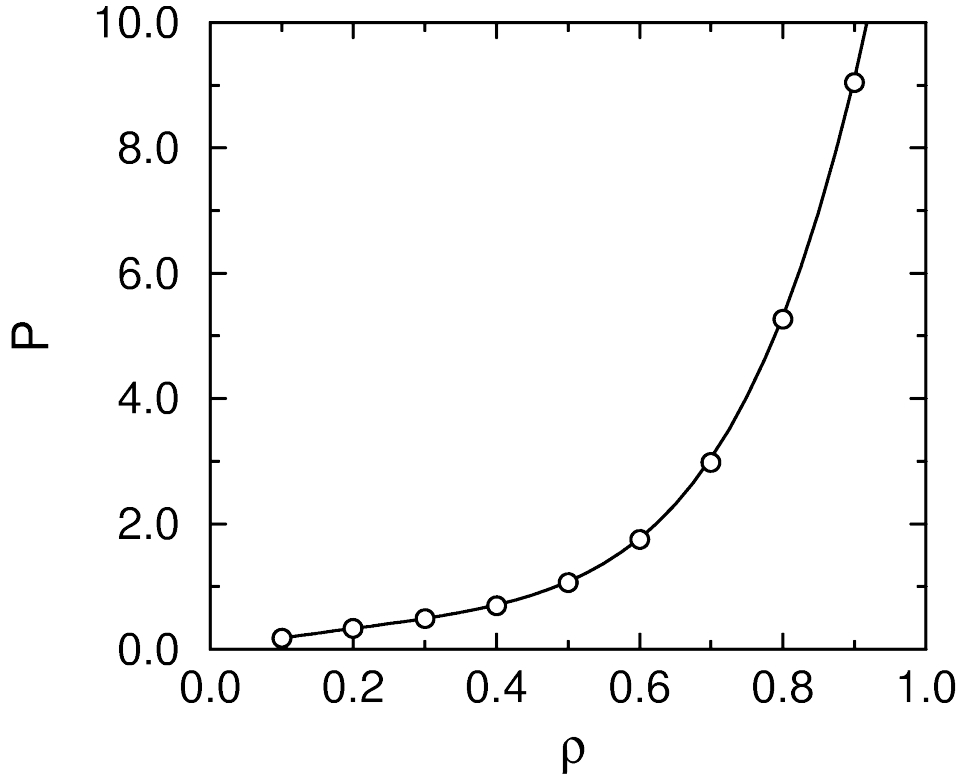
$$F(\rho) = F(\rho_0) + N \int_{\rho_0}^{\rho} \frac{P(\rho')}{\rho^2} \mathrm{d}\rho'$$

- So in fact for only 1 point of the equation of state the F is needed

- For liquid e.o.s even from ideal gas

$$\beta F(\rho)/N = \beta F^{id}(\rho)/N + \int_{0}^{\rho} \frac{\beta P(\rho') - \rho'}{\rho^2} \mathrm{d}\rho'$$

Equation of state



$$P = P(\rho, T)$$

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

$$F(\rho) = F(\rho_0) + N\int_{\rho_0}^{\rho} \frac{P(\rho')}{\rho^2} \mathrm{d}\rho' \qquad F(\rho) = F_{id}(\rho) + (F(\rho) - F_{id}(\rho))$$

$$\beta F(\rho)/N = \beta F^{id}(\rho)/N + \int_0^{\rho} \frac{\beta P(\rho') - \rho'}{\rho^2} \mathrm{d}\rho'$$

Free Energies and Phase Equilibria

General Strategies

- Determine free energy of both phases relative to a reference state

  Free energy difference calculation

  General applicable: Gas, Liquid, Solid, Inhomogeneous systems, …

- Determine free energy difference between two phases

  Gibbs Ensemble

  Specific applicable: Gas, Liquid

Statistical Thermodynamics

Probability to find a particular configuration (NVT)

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

Partition function

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

Free energy

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

Ensemble average

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

Ensemble average versus free energy

Generate configuration using MC: $\left\{\mathrm{r}_1^N, \mathrm{r}_2^N, \mathrm{r}_3^N, \mathrm{r}_4^N \cdots, \mathrm{r}_M^N\right\}$

$$\overline{A} = \frac{1}{M}\sum_{i=1}^{M} A\left(\mathrm{r}_i^N\right) \approx \frac{\int \mathrm{dr}^N A\left(\mathrm{r}^N\right)\exp\left[-\beta U\left(\mathrm{r}^N\right)\right]}{\int \mathrm{dr}^N \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]} = \left\langle A\right\rangle_{NVT}$$

Generate configuration using MD: $\left\{\mathrm{r}_1^N, \mathrm{r}_2^N, \mathrm{r}_3^N, \mathrm{r}_4^N \cdots, \mathrm{r}_M^N\right\}$

$$\overline{A} = \frac{1}{M}\sum_{i=1}^{M} A\left(\mathrm{r}_i^N\right) \approx \frac{1}{T}\int_0^T dt A(t) \int \approx \left\langle A\right\rangle_{NVT}$$

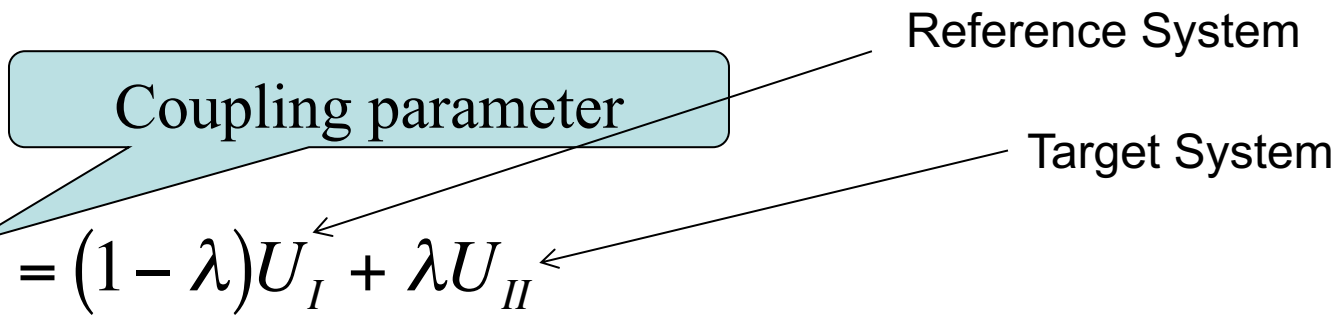
ergodicity

$$\beta F = -\ln Q_{NVT} = -\ln \frac{1}{\Lambda^{3N} N!}\int \mathrm{dr}^N \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]$$

F is difficult, because requires accounting of phase space volume

I - Thermodynamic integration

- Known reference state $\lambda=0$
- Unknown target state $\lambda=1$



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

$$F(\lambda=1) - F(\lambda=0) = \int_{\lambda=0}^{\lambda=1} d\lambda \left(\frac{\partial F(\lambda)}{\partial \lambda} \right)_{N,V,T}$$

Thermodynamic integration

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

$$\left(\frac{\partial F(\lambda)}{\partial \lambda}\right)_{N,T} = -\frac{1}{\beta}\frac{\partial}{\partial \lambda}\ln(Q) = -\frac{1}{\beta}\frac{1}{Q}\frac{\partial Q}{\partial \lambda}$$

$$= \frac{\int \mathrm{d}r^N \left(\partial U(\lambda)/\partial \lambda\right) \exp\left[-\beta U(\lambda)\right]}{\int \mathrm{d}r^N \exp\left[-\beta U(\lambda)\right]}$$

$$= \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

Free-energy difference as ensemble average!

$$F(\lambda=1) - F(\lambda=0) = \int_{\lambda=0}^{\lambda=1} d\lambda \left(\frac{\partial F(\lambda)}{\partial \lambda}\right)_{N,V,T}$$

$$F(\lambda=1) - F(\lambda=0) = \int \mathrm{d}\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

Example

- In general

$$U(\lambda) = (1-\lambda)U_I + \lambda U_{II}$$

$$\left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda = \langle U_{II} - U_I \rangle_\lambda$$

- Specific example

$$U(\lambda) = U^{LJ} + \lambda U^{\text{dipole-dipole}}$$

$$U(0) = U^{LJ}$$ Lennard-Jones

$$U(1) = U^{\text{Stockm}}$$ Stockmayer

$$\left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda = \left\langle U^{dip-dip} \right\rangle_\lambda$$

Free energy of solid

More difficult. What is reference?

Not the ideal gas.

Instead it is the Einstein crystal: harmonic oscillators around r_0

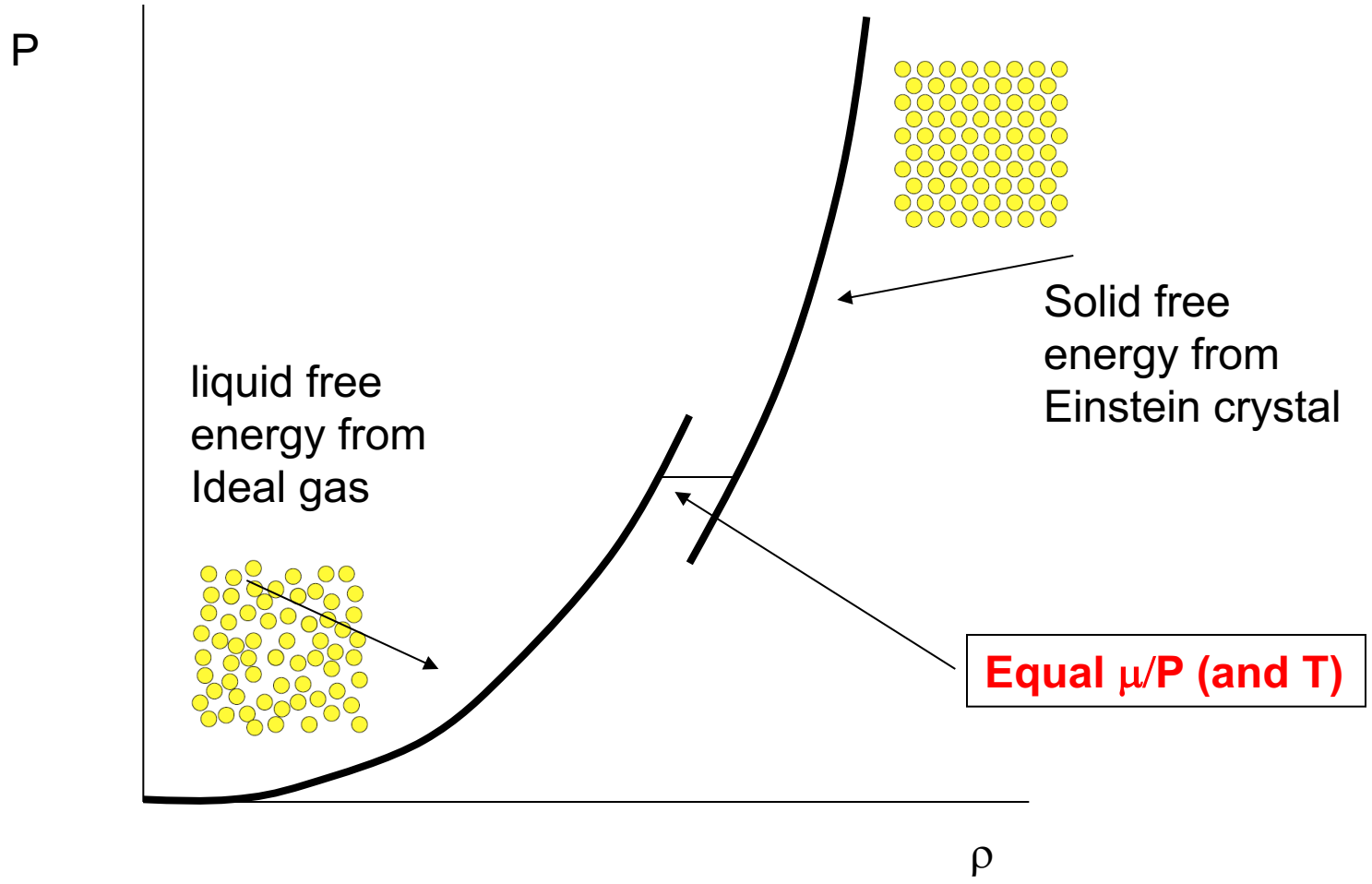
$$U\left(\lambda; r^N\right) = (1-\lambda)U\left(r^N\right) + \lambda U\left(r_0^N\right) + \lambda \sum_{i=1}^{N} \alpha (r_i - r_{0,i})^2$$

$$F = F_{ein} - \int_{\lambda=0}^{\lambda=1} d\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

Note, here:
- $\lambda = 1$ Reference System
- $\lambda = 0$ Target System

$$F = F_{ein} - \int_{\lambda=0}^{\lambda=1} d\lambda \left\langle -U\left(r^N\right) + U\left(r_0{}^N\right) + \sum_{i=1}^{N} \alpha (r_i - r_{0,i})^2 \right\rangle_{\lambda}$$

Hard sphere freezing

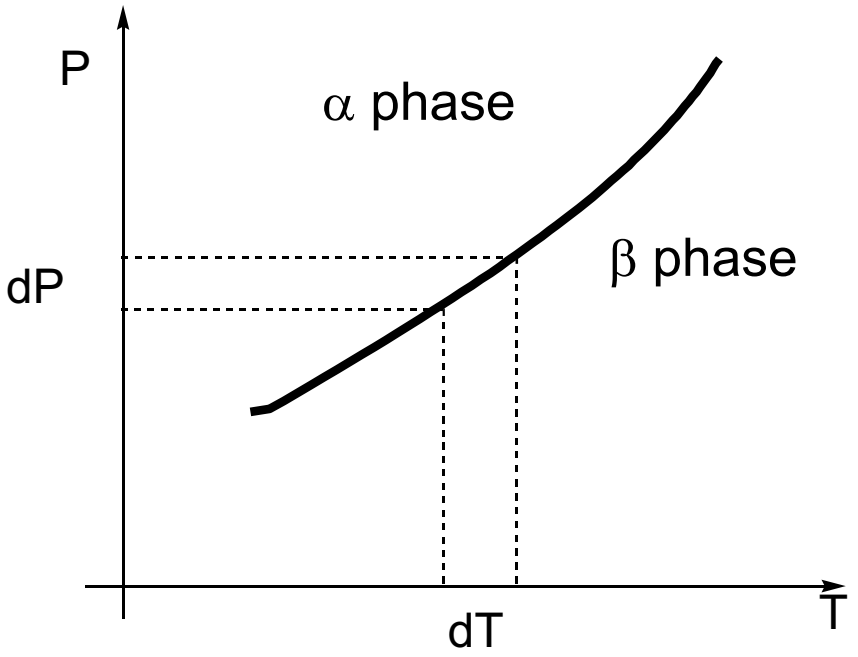


Tracing coexistence curves

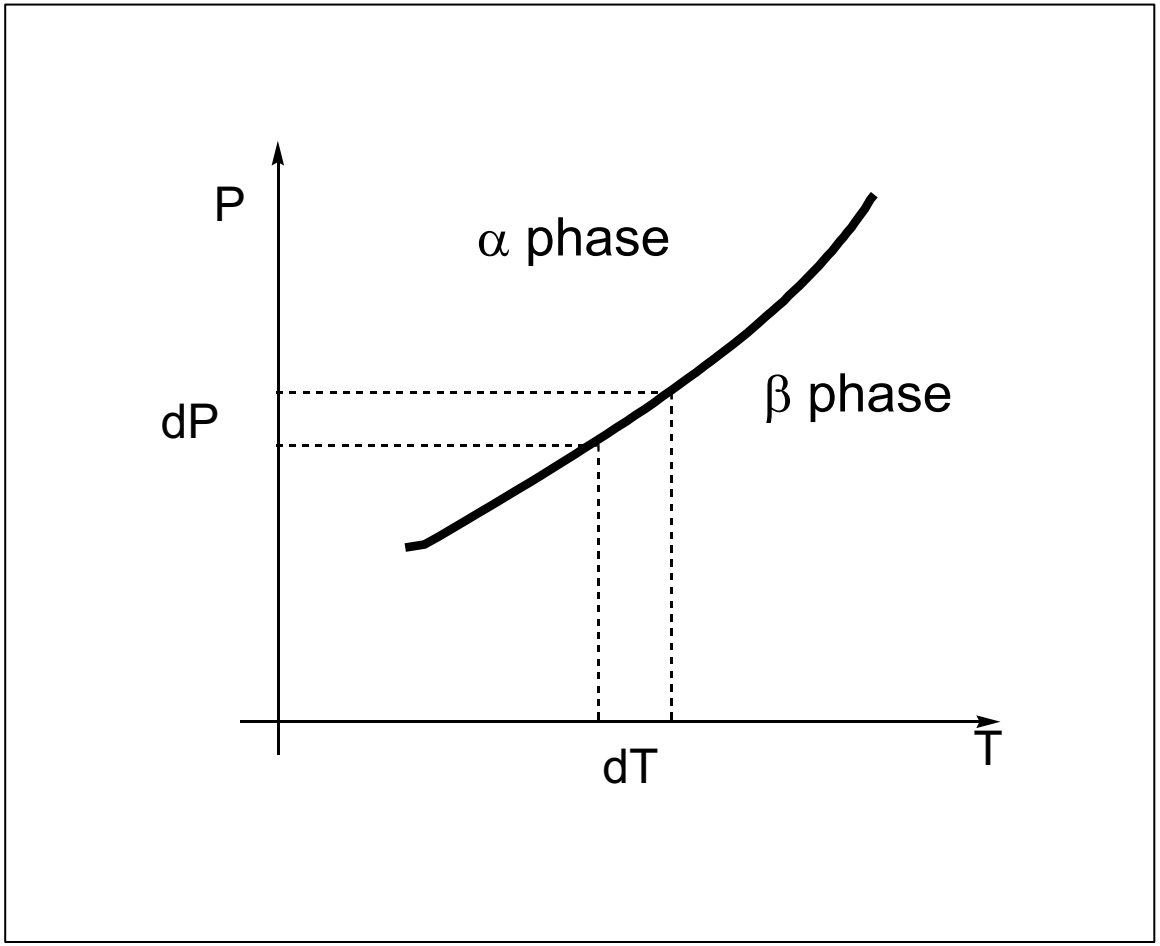
- If we have a coexistence point on the phase diagram we can integrate allong the line while maintaining coexistence.

P en T are equal along coexistence line

$$d\mu_\alpha = d\mu_\beta$$



Tracing coexistence curves



Clapyeron equation

$$\frac{dP}{dT} = \frac{\Delta(U + PV)}{T\Delta V}$$

$$dP = \frac{\Delta(U + PV)}{T\Delta V} dT$$

Particle Insertion Method

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

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

$$= -\ln\left(\frac{V^N}{\Lambda^{3N} N!}\right) - \ln\left(\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]\right)$$

$$= -N \ln\left(\frac{1}{\Lambda^3 \rho}\right) + N - \ln\left(\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]\right)$$

$$\beta F = \beta F^{IG} + \beta F^{ex} \qquad \beta\mu = \beta\mu^{IG} + \beta\mu^{ex}$$

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

$$\beta\mu^{IG} \equiv \left(\frac{\partial \beta F^{IG}}{\partial N}\right)_{V,T} \qquad \beta\mu^{ex} \equiv \left(\frac{\partial \beta F^{ex}}{\partial N}\right)_{V,T}$$

Widom test particle insertion

$$\beta\mu \equiv \left(\frac{\partial \beta F}{\partial N}\right)_{V,T}$$

$$\beta\mu = \frac{\beta F(N+1)) - \beta F(N))}{N+1-N}$$

$$= -\ln \frac{Q(N+1)}{Q(N)}$$

$$= -\ln\left(\frac{\frac{V^{N+1}}{\Lambda^{3N+3}(N+1)!}}{\frac{V^N}{\Lambda^{3N}N!}}\right) - \ln\left(\frac{\int ds^{N+1} \exp\left[-\beta U\left(s^{N+1};L\right)\right]}{\int ds^N \exp\left[-\beta U\left(s^N;L\right)\right]}\right)$$

$$= -\ln\left(\frac{V}{\Lambda^3(N+1)}\right) - \ln\left(\frac{\int ds^{N+1} \exp\left[-\beta U\left(s^{N+1};L\right)\right]}{\int ds^N \exp\left[-\beta U\left(s^N;L\right)\right]}\right)$$

$$\beta\mu = \beta\mu^{IG} + \beta\mu^{ex}$$

$$\beta\mu^{ex} = -\ln\left(\frac{\int ds^{N+1} \exp\left[-\beta U\left(s^{N+1};L\right)\right]}{\int ds^N \exp\left[-\beta U\left(s^N;L\right)\right]}\right)$$

Widom test particle insertion

$$\beta\mu^{ex} = -\ln\left(\frac{\int \mathrm{ds}^{N+1} \exp\left[-\beta U\left(\mathrm{s}^{N+1};L\right)\right]}{\int \mathrm{ds}^{N} \exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]}\right)$$

$$U\left(\mathrm{s}^{N+1};L\right) = \Delta U^{+} + U\left(\mathrm{s}^{N};L\right)$$

$$\beta\mu^{ex} = -\ln\left(\frac{\int \mathrm{ds}^{N} \int \mathrm{ds}_{N+1} \exp\left[-\beta\left(\Delta U^{+} + U\left(\mathrm{s}^{N};L\right)\right)\right]}{\int \mathrm{ds}^{N} \exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]}\right)$$

$$= -\ln\left(\frac{\int \mathrm{ds}_{N+1} \int \mathrm{ds}^{N} \left\{\exp\left[-\beta\Delta U^{+}\right]\right\} \exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]}{\int \mathrm{ds}^{N} \exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]}\right)$$

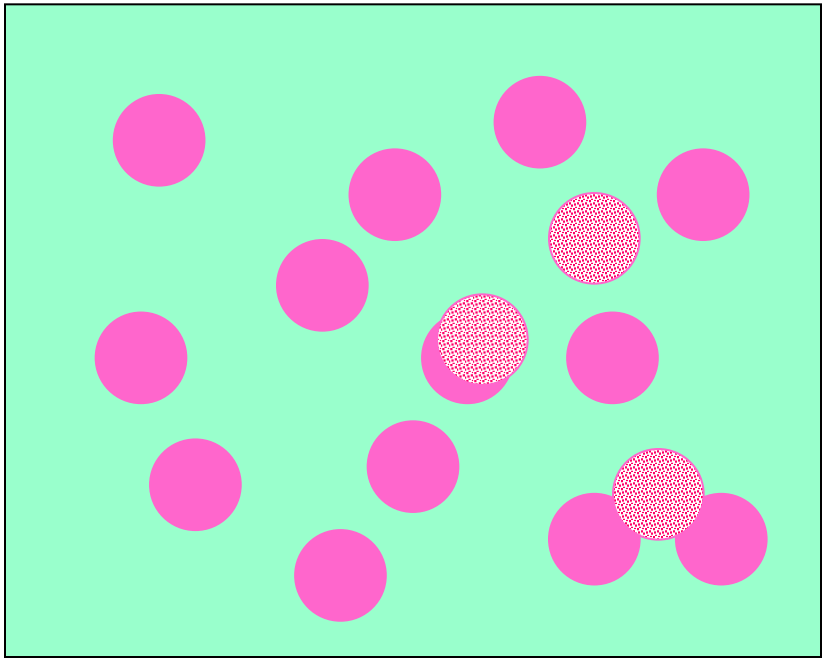
$$= -\ln\left(\int \mathrm{ds}_{N+1} \left\langle \exp\left[-\beta\Delta U^{+}\right]\right\rangle_{NVT}\right)$$

Ghost particle!

Hard spheres

$$\beta\mu^{ex} = -\ln\left(\int \mathrm{ds}_{N+1} \left\langle \exp\left[-\beta\Delta U^{+} \right] \right\rangle_{NVT} \right)$$

$$U(r) = \begin{cases} \infty & r \le \sigma \\ 0 & r > \sigma \end{cases}$$



$$\exp\left[-\beta\Delta U^{+} \right] = \begin{cases} 0 & \text{if overlap} \\ 1 & \text{no overlap} \end{cases}$$

$\left\langle \exp\left[-\beta\Delta U^{+} \right] \right\rangle$ probability to insert a test particle!

But, … may fail at high density

Thermodynamic perturbation – Umbrella Sampling

Two systems:

System 0: N, V, T, U_0

System 1: N, V, T, U_1

$$Q_0 = \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)$$

$$Q_1 = \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_1\right)$$

$$\begin{aligned}
\Delta\beta F &= \beta F_1 - \beta F_0 = -\ln\left(Q_1/Q_0\right) \\
&= -\ln \frac{\int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U_1\right]}{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)} \\
&= -\ln \frac{\int \mathrm{d}\mathbf{s}^N \exp\left[-\beta\left(U_1 - U_0\right)\right]\exp\left[-\beta U_0\right]}{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)}
\end{aligned}$$

$$\Delta\beta F = -\ln\left\langle \exp\left[-\beta\left(U_1 - U_0\right)\right]\right\rangle_0$$

Umbrella sampling

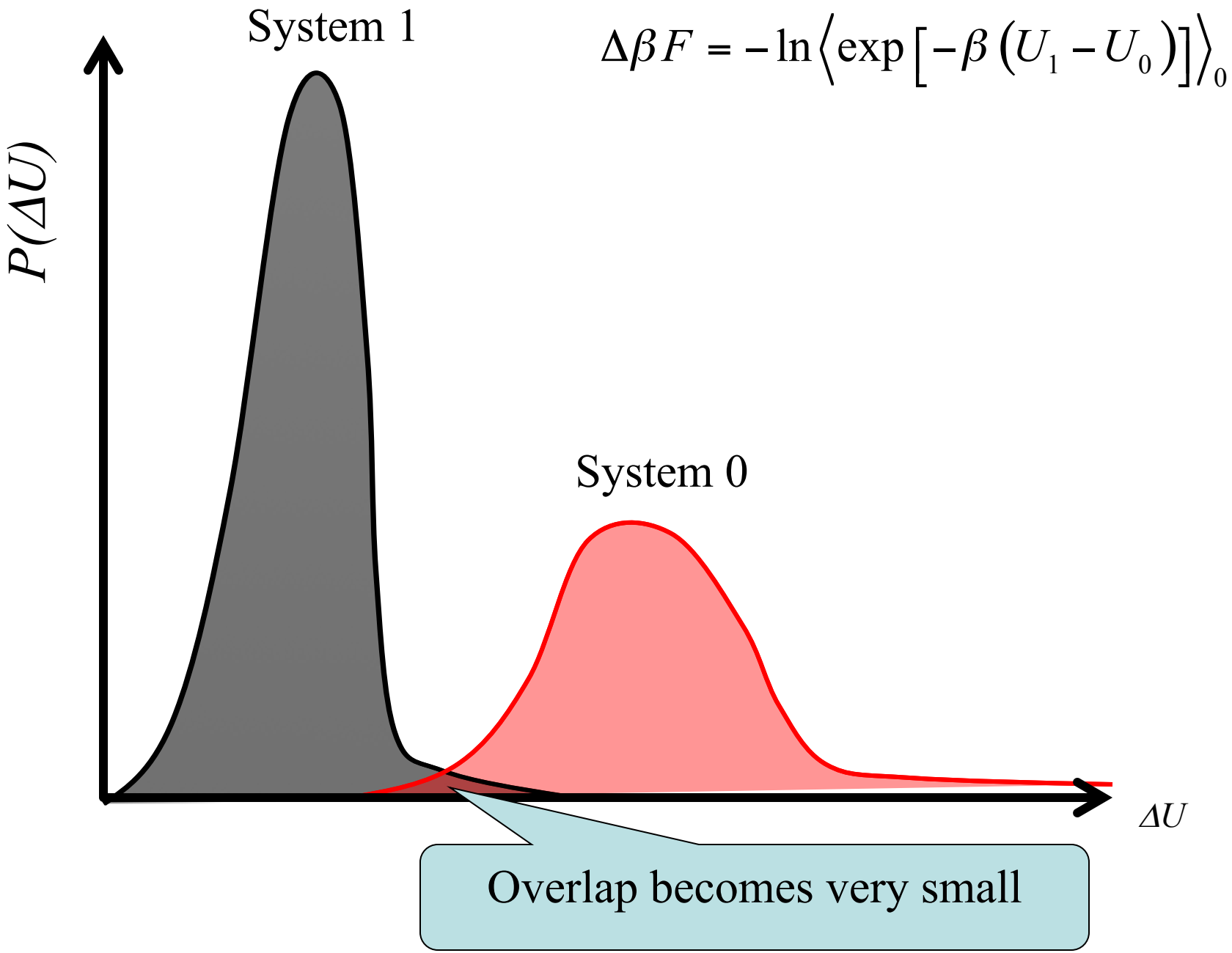
- Start with thermodynamic perturbation

$$\Delta\beta F = -\ln\left(Q_1/Q_0\right) \qquad = -\ln\left(\frac{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_1\right)}{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)}\right)$$

$$\exp\left(-\beta\Delta F\right) = \left(\frac{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)\exp\left(-\beta\Delta U\right)}{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)}\right)$$

$$\exp\left(-\beta\Delta F\right) = \left\langle \exp\left(-\beta\Delta U\right)\right\rangle_0$$

Can we use this for free energy difference between arbitrary systems?


System 1
$\Delta\beta F = -\ln\left\langle \exp\left[-\beta\left(U_1 - U_0\right)\right]\right\rangle_0$
$P(\Delta U)$
System 0
ΔU
Overlap becomes very small

Bridging function

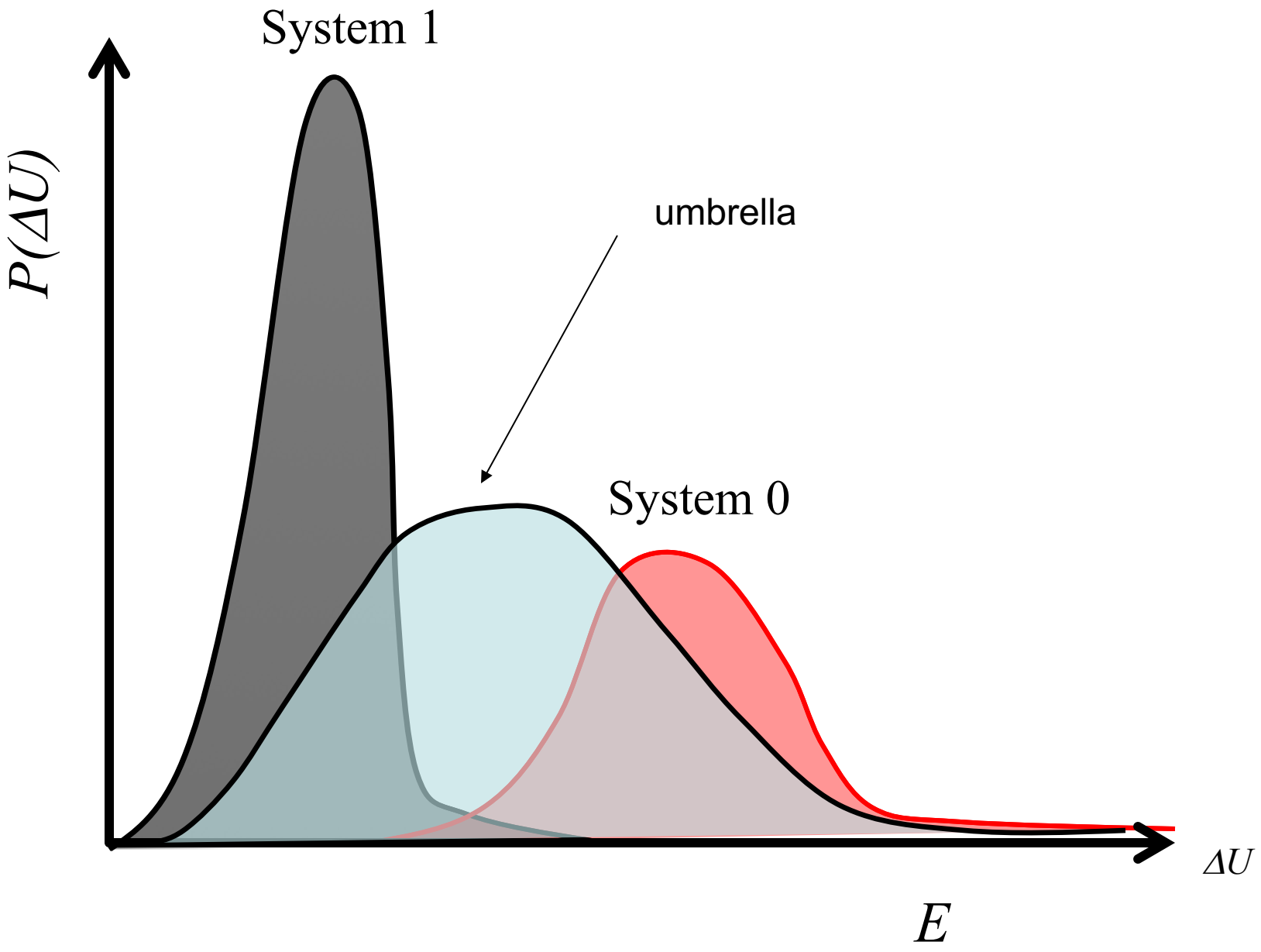
- Introduce function $\pi(s^N)$ altering distribution.

$$\exp\left(-\beta\Delta F\right) = \left(\frac{\int \mathrm{d}\mathbf{s}^N \pi(\mathbf{s}^N) \exp\left(-\beta U_1\right)/\pi(\mathbf{s}^N)}{\int \mathrm{d}\mathbf{s}^N \pi(\mathbf{s}^N) \exp\left(-\beta U_0\right)/\pi(\mathbf{s}^N)} \right)$$

$$\exp\left(-\beta\Delta F\right) = \langle \exp\left(-\beta\Delta U\right)) \rangle_0$$

$$= \frac{\left\langle \exp\left(-\beta U_1\right)/\pi \right\rangle_\pi}{\left\langle \exp\left(-\beta U_0\right)/\pi \right\rangle_\pi}$$

- This approach is called umbrella sampling


System 1
umbrella
System 0
P(ΔU)
ΔU
E

III - Overlapping Distribution Method

Two systems:

System 0: $N,\ V,T,\ U_0$ System 1: $N,\ V,T,\ U_1$

$$Q_0 = \frac{V^N}{\Lambda^{3N} N!}\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right) \qquad Q_1 = \frac{V^N}{\Lambda^{3N} N!}\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_1\right)$$

$$\Delta\beta F = \beta F_1 - \beta F_0 = -\ln\left(Q_1/Q_0\right) = -\ln\left(\frac{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_1\right)}{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)}\right) = -\ln\left(\frac{Q_1}{Q_0}\right)$$

$=\Delta U$ (δ function)

$$p_0(\Delta U) = \frac{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)\delta\left(U_1 - U_0 - \Delta U\right)}{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_0\right)} \qquad p_1(\Delta U) = \frac{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_1\right)\delta\left(U_1 - U_0 - \Delta U\right)}{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_1\right)}$$

$$p_1(\Delta U) = \frac{\int \mathrm{d}\mathbf{s}^N \exp\left[-\beta\left(U_1 - U_0\right)\right]\exp\left[-\beta U_0\right]\delta\left(U_1 - U_0 - \Delta U\right)}{\int \mathrm{d}\mathbf{s}^N \exp\left(-\beta U_1\right)}$$

$$= \frac{1}{Q_1} = \frac{Q_0}{Q_1}\frac{1}{Q_0}$$

$$\frac{Q_0}{Q_1} = \exp\left(\beta\Delta F\right) = \frac{Q_0}{Q_1}\exp\left(-\beta\Delta U\right)\frac{\int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U_0\right]\delta\left(U_1 - U_0 - \Delta U\right)}{Q_0}$$

$$p_1\left(\Delta U\right) = \frac{Q_0}{Q_1}\exp\left(-\beta\Delta U\right)p_0\left(\Delta U\right)$$

$$\ln p_1\left(\Delta U\right) = \beta\left(\Delta F - \Delta U\right) + \ln p_0\left(\Delta U\right)$$

Overlapping Distribution Method

$$\ln p_1(\Delta U) = \beta(\Delta F - \Delta U) + \ln p_0(\Delta U)$$

$$f_0(\Delta U) \equiv \ln p_0(\Delta U) - 0.5\beta\Delta U$$

$$f_1(\Delta U) \equiv \ln p_1(\Delta U) + 0.5\beta\Delta U$$

Simulate system 0: compute f_0
Simulate system 1: compute f_1

$$\beta\Delta F = f_1(\Delta U) - f_0(\Delta U)$$

Chemical potential

System 0: *N-1, V, T, U* + 1 ideal gas

System 1: *N, V, T, U*

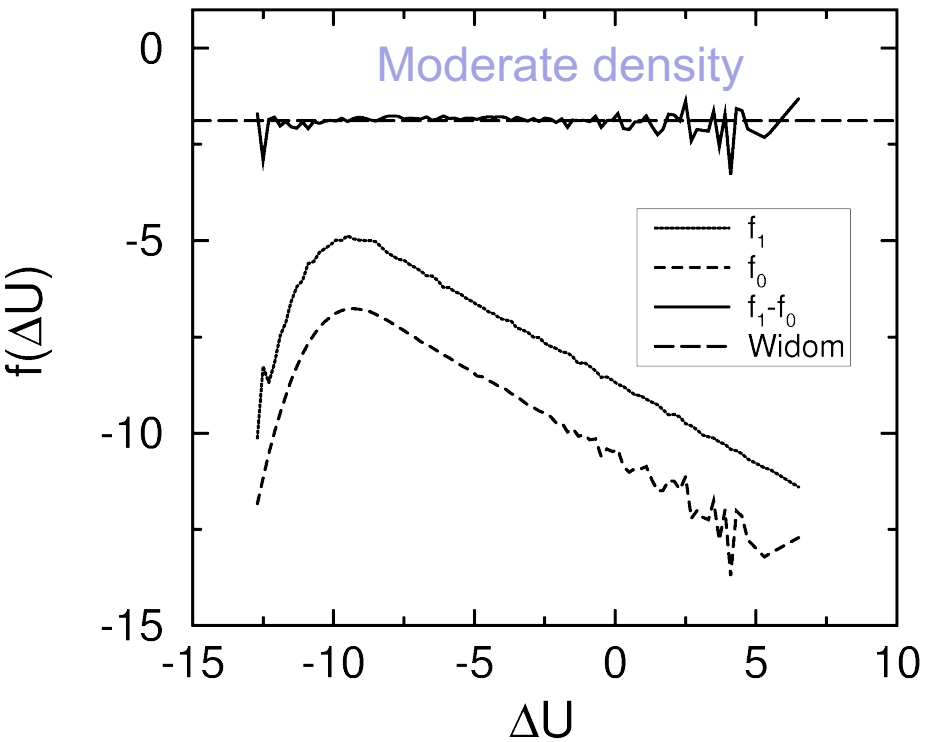
$$\Delta\beta F = \beta F_1 - \beta F_0 \equiv \beta\mu^{ex}$$

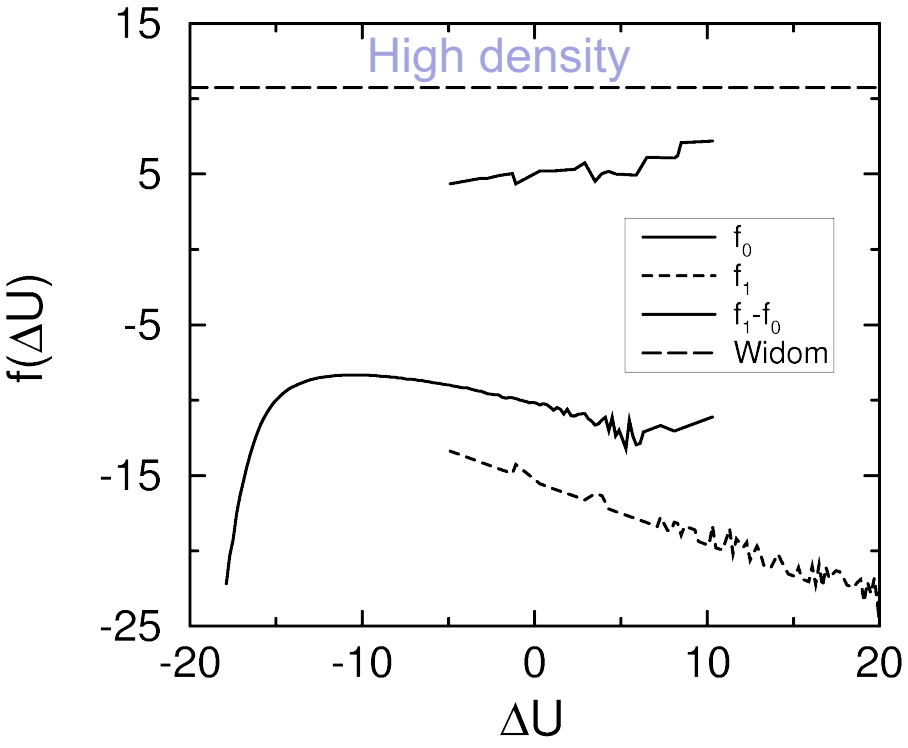
$$\Delta U = U_1 - U_0$$

System 0: test particle energy

System 1: real particle energy

$$\beta\mu^{ex} = f_1(\Delta U) - f_0(\Delta U)$$





IV - Non-Boltzmann sampling

T_1 is arbitrary!

$$\langle A \rangle_{NVT_1} = \frac{1}{Q_{NVT_1}} \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta_1 U(\mathbf{r}^N)\right]$$

$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta_1 U(\mathbf{r}^N)\right]}{\int \mathrm{d}\mathbf{r}^N \exp\left[-\beta_1 U(\mathbf{r}^N)\right]}$$

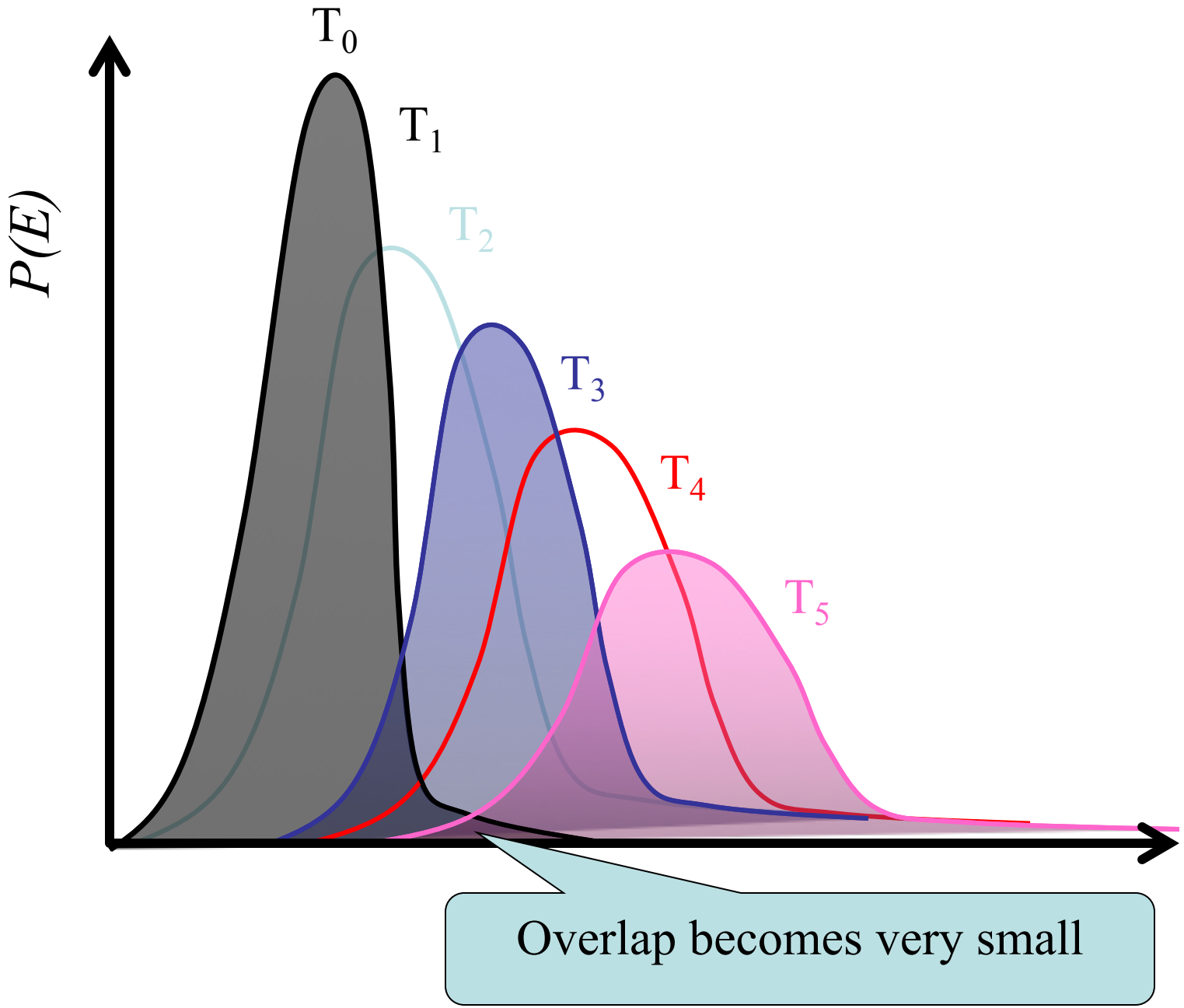
$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta_1 U(\mathbf{r}^N)\right] \exp\left[\beta_2 U(\mathbf{r}^N) - \beta_2 U(\mathbf{r}^N)\right]}{\int \mathrm{d}\mathbf{r}^N \exp\left[-\beta_1 U(\mathbf{r}^N)\right] \exp\left[\beta_2 U(\mathbf{r}^N) - \beta_2 U(\mathbf{r}^N)\right]}$$

$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp\left[\beta_2 U(\mathbf{r}^N) - \beta_1 U(\mathbf{r}^N)\right] \exp\left[-\beta_2 U(\mathbf{r}^N)\right]}{\int \mathrm{d}\mathbf{r}^N \exp\left[\beta_2 U(\mathbf{r}^N) - \beta_1 U(\mathbf{r}^N)\right] \exp\left[-\beta_2 U(\mathbf{r}^N)\right]}$$

We only need a *single* simulation!

$$= \frac{\left\langle A \exp\left[(\beta_2 - \beta_1) U\right]\right\rangle_{NVT_2}}{\left\langle \exp\left[(\beta_2 - \beta_1) U\right]\right\rangle_{NVT_2}}$$

We perform a simulation at $T=T_2$ and we determine A at $T=T_1$


T0
T1
T2
T3
T4
T5
P(E)
Overlap becomes very small