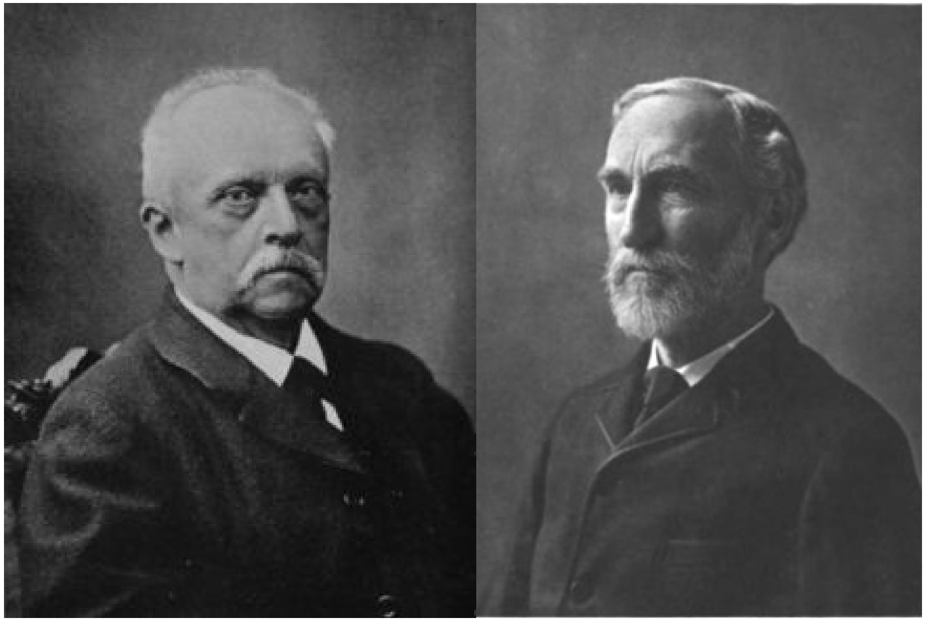
Free energies and phase transitions



Why Free Energies?

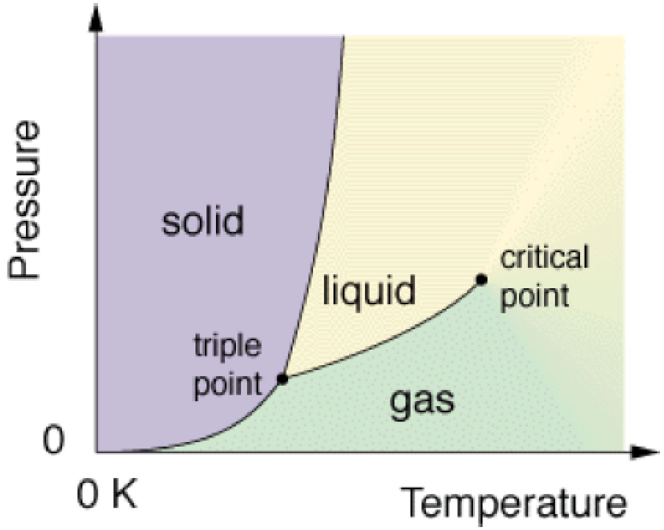
- Reaction equilibrium constants $A \leftrightarrow B$

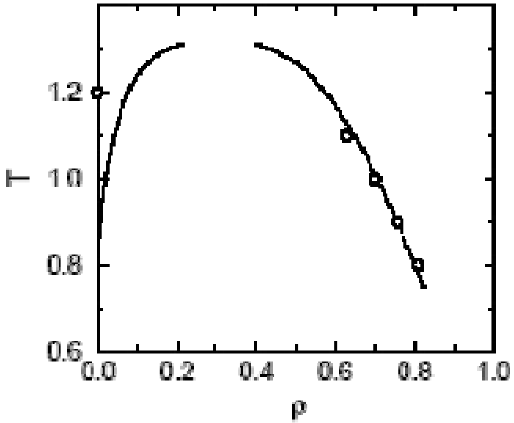
$$K = \frac{[B]}{[A]} = \frac{p_B}{p_A} = \exp[-\beta(G_B - G_A)]$$

- Examples:
  - Chemical reactions, 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





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

Critical point: no difference between liquid and vapor
Triple point: liquid, vapor and solid in equilibrium.

How do we compute these lines?

Condition for phase coexistence in a one-component system:

$$T_1 = T_2$$

$$P_1 = P_2$$

$$\mu_1 = \mu_2$$

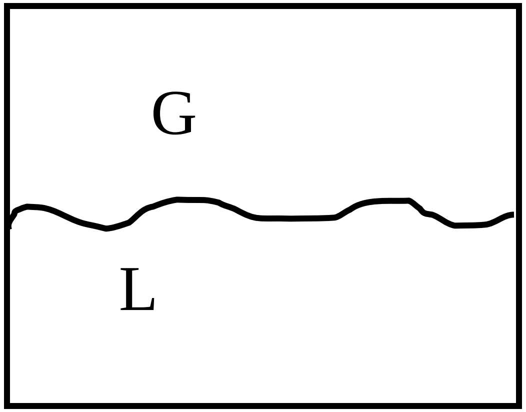
The Gibbs “Ensemble”

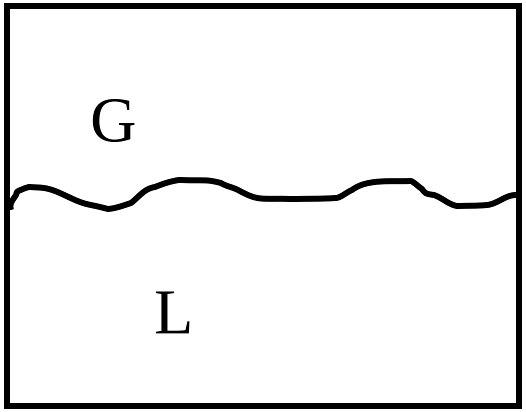
NVT Ensemble

Fluid

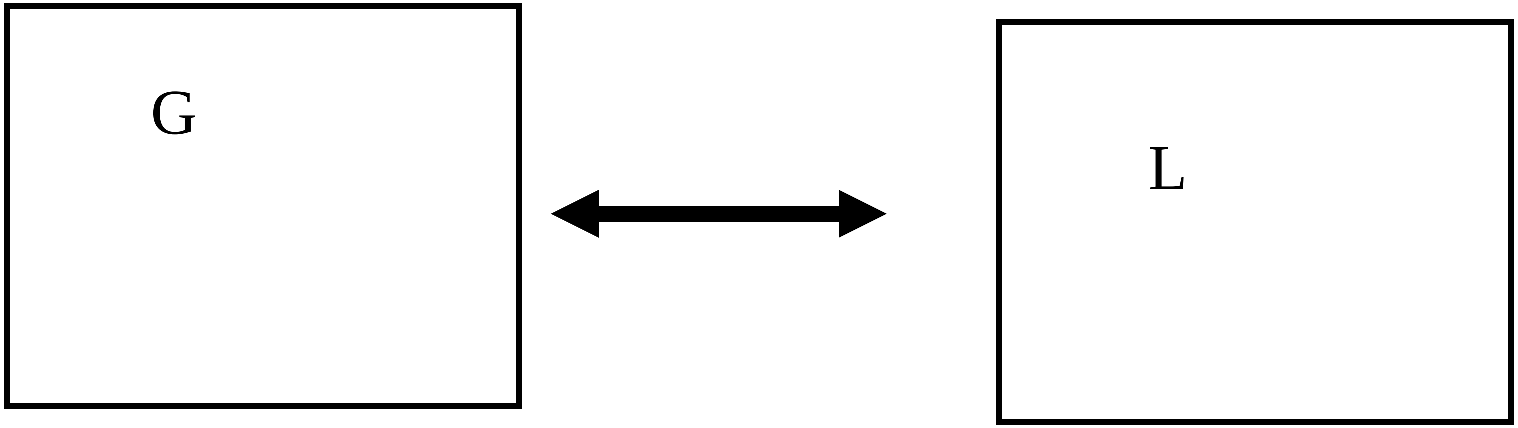
Fluid

NVT Ensemble





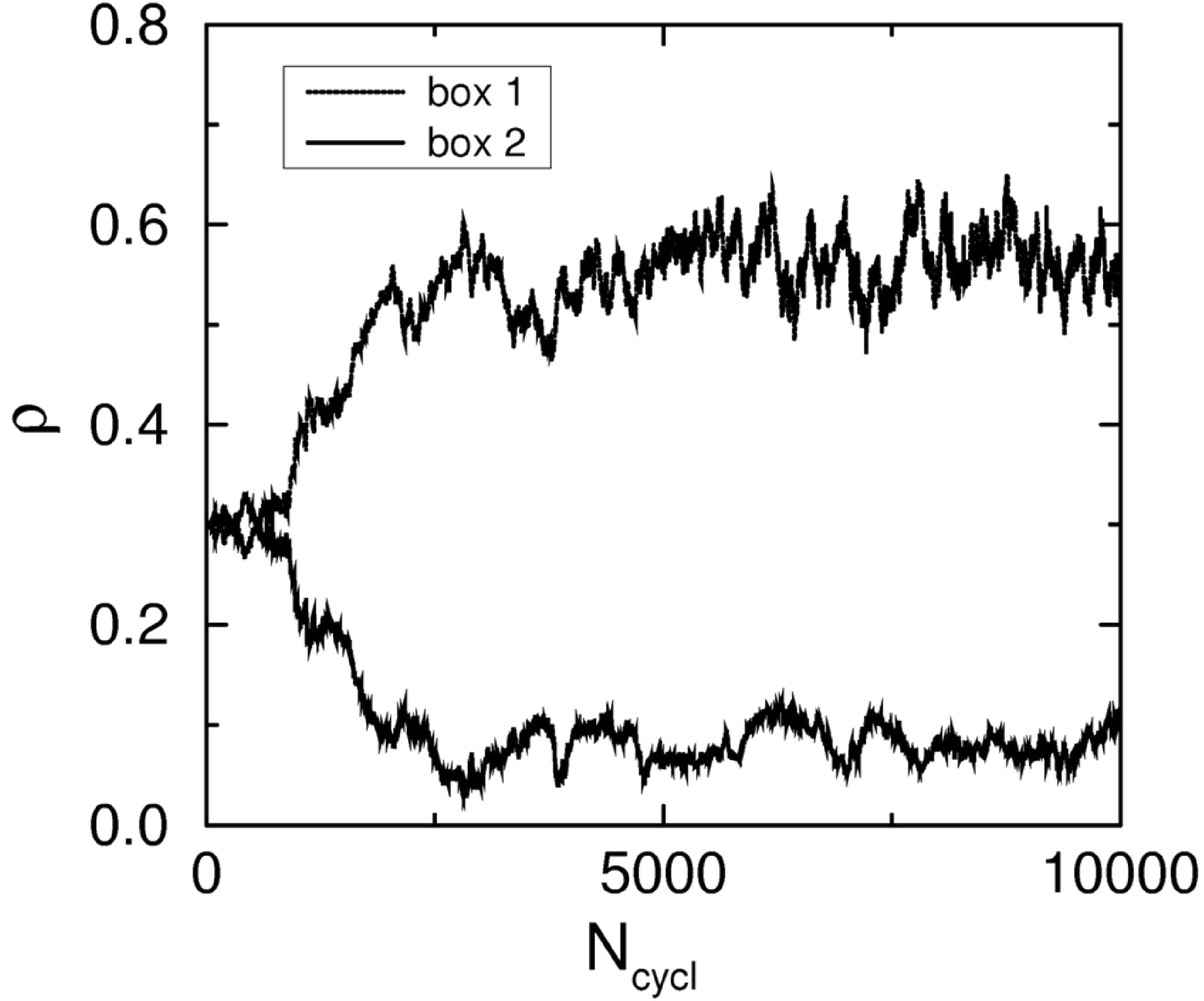
Gibbs Ensemble

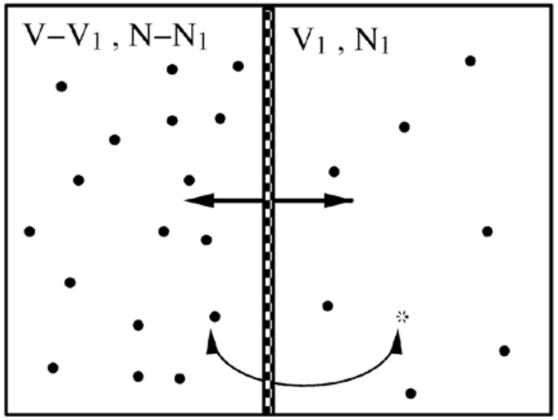


G

L

Equilibrium!

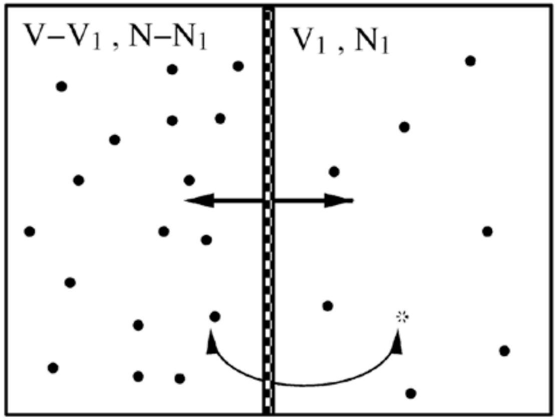

box 1
box 2
ρ
0.0
0.2
0.4
0.6
0.8
0
5000
10000
N_{cycl}



- Distribute n_1 particles over two volumes
- Change the volume V_1
- Displace the particles

$$Q_{\mathrm{G}}(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1\, V_1^{n_1} (V-V_1)^{N-n_1}$$

$$\int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

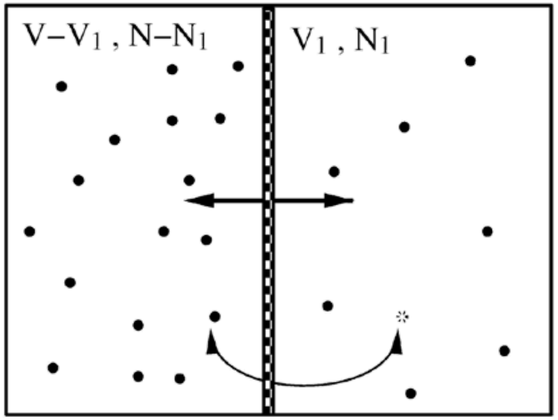


$$Q_G(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1\, V_1^{n_1} (V-V_1)^{N-n_1}$$

$$\int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

Distribute n_1 particles over two volumes:

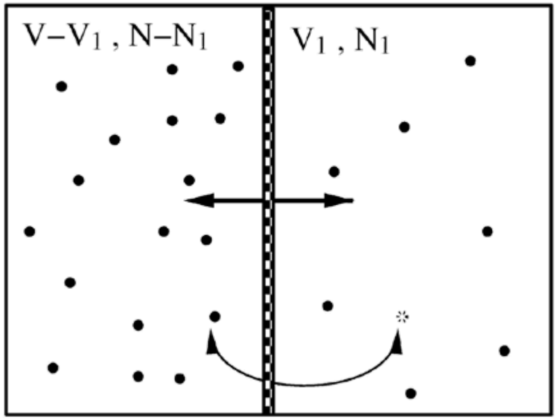
$$\binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!}$$



$$Q_{\mathrm{G}}(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1\, V_1^{n_1} (V-V_1)^{N-n_1}$$

$$\int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

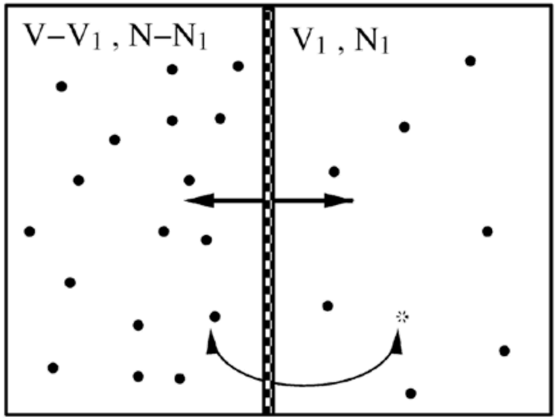
Integrate volume V_1



$$Q_{\mathrm{G}}(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1\, V_1^{n_1} (V-V_1)^{N-n_1}$$

$$\int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

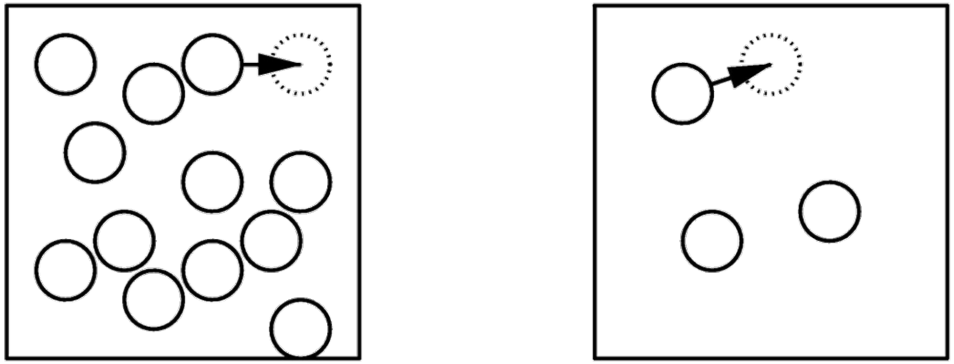
Displace the particles in box 1 and box2



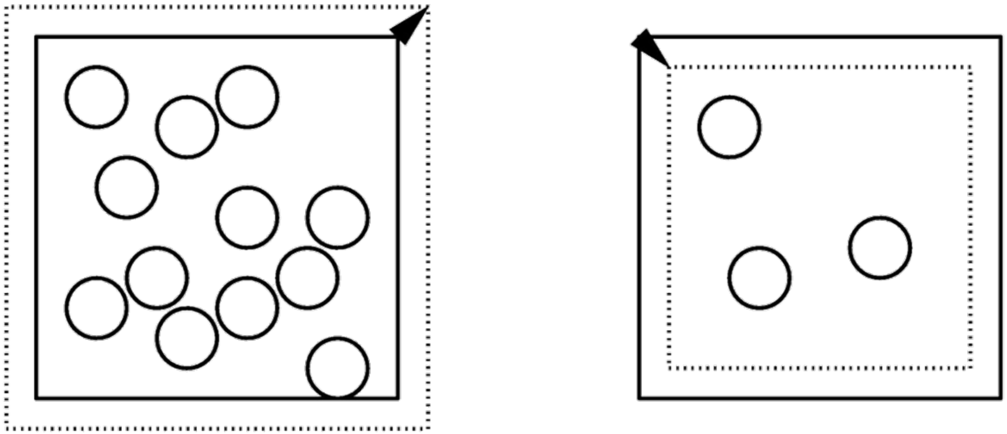
$$Q_{\mathrm{G}}(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1\, V_1^{n_1} (V-V_1)^{N-n_1} \int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

Probability distribution

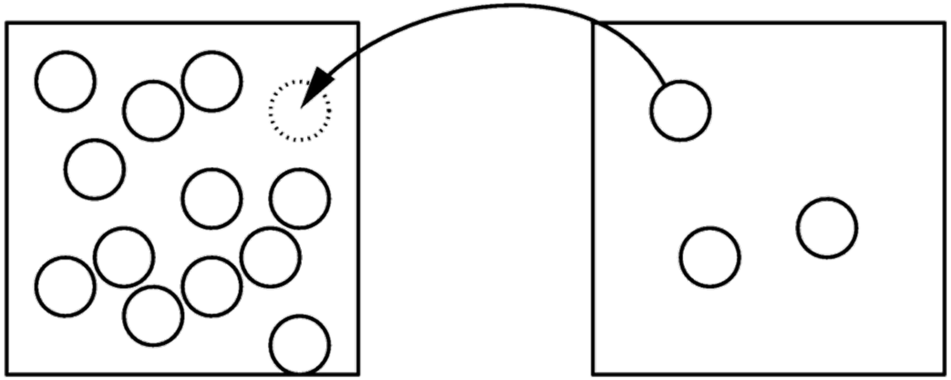
$$N(n_1, V_1, \mathbf{s}_1^{n_1}, \mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U(\mathbf{s}_1^{n_1}) + U(\mathbf{s}_2^{N-n_1})]\right\}.$$



Particle displacement



Volume change



Particle exchange

Acceptance rules

$$N(n_1,V_1,\mathbf{s}_1^{n_1},\mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U(\mathbf{s}_1^{n_1})+U(\mathbf{s}_2^{N-n_1})]\right\}.$$

Detailed Balance:

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

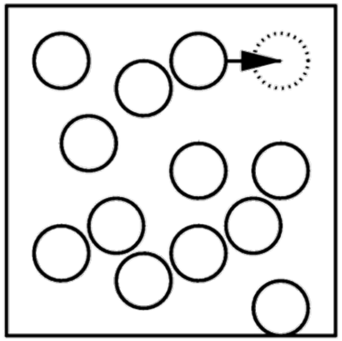
$$N(o)\times\alpha(o\to n)\times\mathrm{acc}(o\to n) = N(n)\times\alpha(n\to o)\times\mathrm{acc}(n\to o)$$

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

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

Displacement of a particle in box 1

$$N(n_1,V_1,\mathbf{s}_1^{n_1},\mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U(\mathbf{s}_1^{n_1})+U(\mathbf{s}_2^{N-n_1})]\right\}.$$



$$N(n) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(n)+U(\mathbf{s}_2^{N-n_1})]\right\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U(\mathbf{s}_2^{N-n_1})]\right\}$$

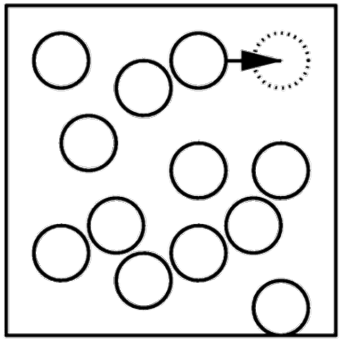
$$\frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} = \frac{\cancel{\dfrac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}}\exp\left\{-\beta[U_1(n)+\cancel{U(\mathbf{s}_2^{N-n_1})}]\right\}}{\cancel{\dfrac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}}\exp\left\{-\beta[U_1(o)+\cancel{U(\mathbf{s}_2^{N-n_1})}]\right\}}$$

Displacement of a particle in box 1

$$N(n_1, V_1, \mathbf{s}_1^{n_1}, \mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U(\mathbf{s}_1^{n_1}) + U(\mathbf{s}_2^{N-n_1})]\right\}.$$

$$N(n) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U_1(n) + U(\mathbf{s}_2^{N-n_1})]\right\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U_1(o) + U(\mathbf{s}_2^{N-n_1})]\right\}$$



$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{\exp\left\{-\beta[U_1(n)]\right\}}{\exp\left\{-\beta[U_1(o)]\right\}}$$

Acceptance rules

$$N(n_1,V_1,\mathbf{s}_1^{n_1},\mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U(\mathbf{s}_1^{n_1})+U(\mathbf{s}_2^{N-n_1})]\right\}.$$

Adding a particle to box 2

$$N(n) \propto \frac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\big(N-(n_1-1)\big)!}\exp\left\{-\beta[U_1(n)+U_2(n)]\right\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U_2(o)]\right\}$$

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

Moving a particle from box 1 to box 2

$$N(n) \propto \frac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\big(N-(n_1-1)\big)!}\exp\{-\beta[U_1(n)+U_2(n)]\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\{-\beta[U_1(o)+U_2(o)]\}$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)} = \frac{\dfrac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\big(N-(n_1-1)\big)!}\exp\{-\beta[U_1(n)+U_2(n)]\}}{\dfrac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\{-\beta[U_1(o)+U_2(o)]\}}$$

Moving a particle from box 1 to box 2

$$N(n) \propto \frac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!}\exp\{-\beta[U_1(n)+U_2(n)]\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\{-\beta[U_1(o)+U_2(o)]\}$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)} = \frac{\dfrac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{\cancel{(n_1-1)!}\left(N-(n_1-1)\right)\cancel{!}}\exp\{-\beta[U_1(n)+U_2(n)]\}}{\dfrac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1\cancel{!}\cancel{(N-n_1)}!}\exp\{-\beta[U_1(o)+U_2(o)]\}}$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)} = \frac{\dfrac{V_2}{n_2+1}}{\dfrac{V_1}{n_1}}\exp\{-\beta[\Delta U_1+\Delta U_2]\}$$

Algorithm 17 (Basic Gibbs Ensemble Simulation)

```
PROGRAM mc_Gibbs                          Gibbs ensemble simulation

do icycl=1,ncycl                          perform ncycl MC cycles
  ran=ranf()*(npart+nvol+nswap)
  if (ran.le.npart) then
    call mcmove                           attempt to displace a particle
  else if (ran.le.(npart+nvol))
    call mcvol                            attempt to change the volume
  else
    call mcswap                           attempt to swap a particle
  endif
  call sample                             sample averages
enddo
end
```

Algorithm 18 (Attempt to Change the Volume in the Gibbs Ensemble)

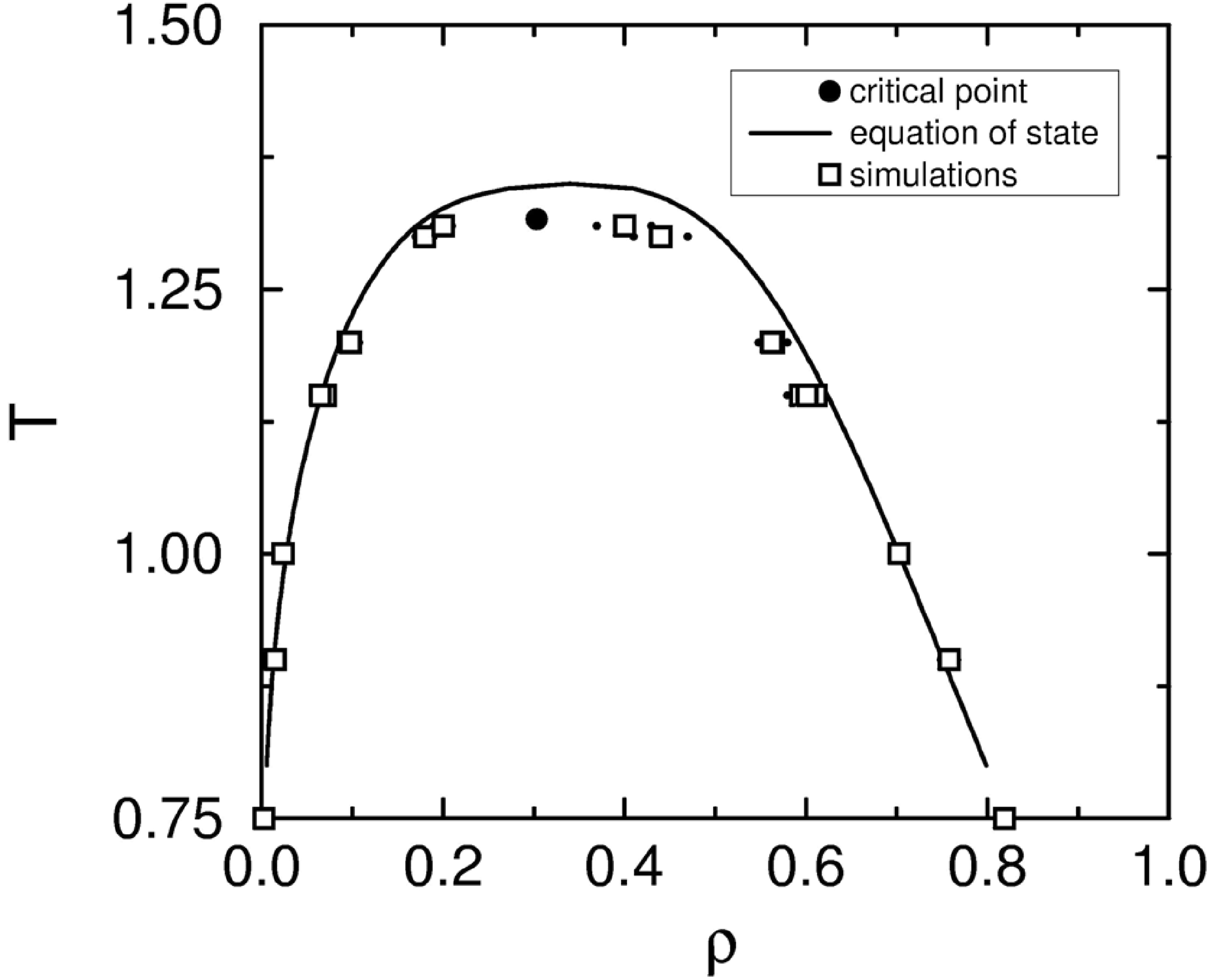
```
 SUBROUTINE mcvol                     attempt to change
                                      the volume
 call toterg(box1,en1o)               energy old conf. box 1
 call toterg(box2,en2o)               and 2 (box1: box length)
 vo1=box1**3                          old volume box 1 and 2
 vo2=v-vo1
 lnvn=log(vo1/vol2)+                  random walk in ln V1/V2
+    (ranf()-0.5)*vmax
 v1n=v*exp(lnvn)/(1+exp(lnvn))        new volume box 1 and 2
 v2n=v-v1n
 box1n=v1n**(1/3)                     new box length box 1
 box2n=v2n**(1/3)                     new box length box 2
 do i=1,npart
   if (ibox(i).eq.1) then             determine which box
     fact=box1n/box1o
   else
     fact=box2n/box2o
   endif
   x(i)=x(i)*fact                     rescale positions
 enddo
 call toterg(box1n,en1n)              total energy box 1
 call toterg(box2n,en2n)              total energy box 2
 arg1=-beta*((en1n-en1o)+
```

```
      box1n=v1n**(1/3)                      new box length box 1
      box2n=v2n**(1/3)                      new box length box 2
      do i=1,npart
        if (ibox(i).eq.1) then              determine which box
          fact=box1n/box1o
        else
          fact=box2n/box2o
        endif
        x(i)=x(i)*fact                      rescale positions
      enddo
      call toterg(box1n,en1n)               total energy box 1
      call toterg(box2n,en2n)               total energy box 2
      arg1=-beta*((en1n-en1o)+
     + (npbox(1)+1)*log(v1n/v1o)/beta)      appropriate weight function
      arg2=-beta*((en2n-en2o)+              acceptance rule (8.3.3)
     + (npbox(2)+1)*log(v2n/v2o)/beta)
      if (ranf().gt.exp(arg1+arg2)) then
        do i=1,npart                        REJECTED
          if (ibox(i).eq.)  then            determine which box
            fact=box1o/box1n
          else
            fact=box2o/box2n
          endif
          x(i)=x(i)*fact                    restore old configuration
        enddo
      endif
      return
      end
```

Algorithm 19 (Attempt to Swap a Particle between the Two Boxes)

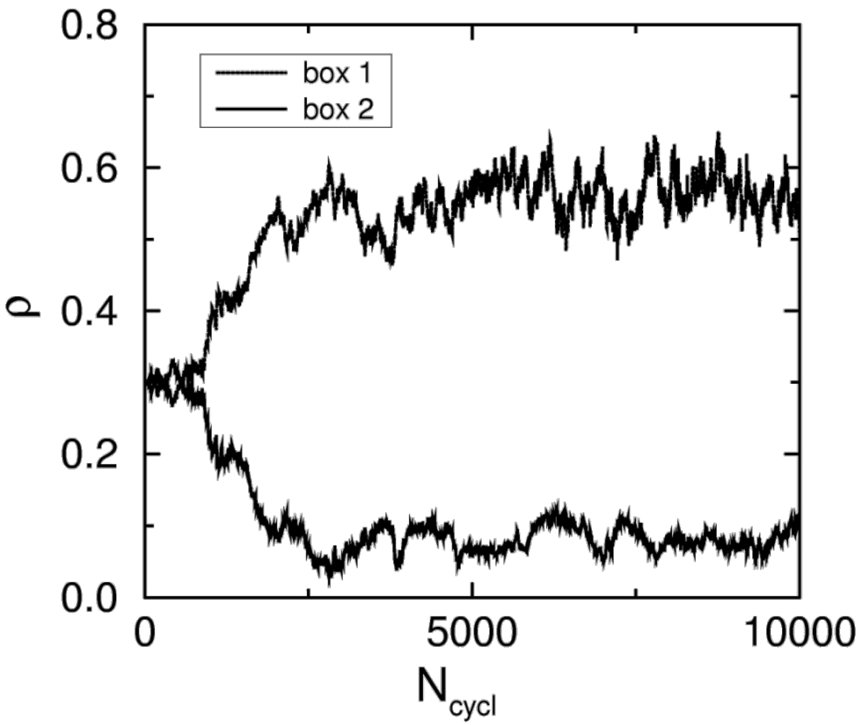
```
 SUBROUTINE mcswap                       attempts to swap a particle
                                         between the two boxes
 if (ranf().lt.0.5) then                 which box to add or remove
   in=1
   out=2
 else
   in=2
   out=1
 endif
 xn=ranf()*box(in)                       new particle at a random position
 call ener(xn,enn,in)                    energy new particle in box in
 w(in)=w(in)+vol(in)*                    update chemical potential (8.3.5)
+ exp(-beta*enn)/(npbox(in)+1)
 if (npbox(out).eq.0) return             if box empty return
 ido=0                                   find a particle to be removed
 do while (ido.ne.out)
    o=int(npart*ranf())+1
    ido=ibox(o)
 enddo
 call ener(x(o),eno,out)                 energy particle o in box out
 arg=exp(-beta*(enn-eno +
+ log(vol(out)*(npbox(in)+1)/            acceptance rule (8.3.4)
+ (vol(in)*npbox(out)))/beta))
```

```
      in=2
      out=1
    endif
    xn=ranf()*box(in)                   new particle at a random position
    call ener(xn,enn,in)                energy new particle in box in
    w(in)=w(in)+vol(in)*                update chemical potential (8.3.5)
   + exp(-beta*enn)/(npbox(in)+1)
    if (npbox(out).eq.0) return         if box empty return
    ido=0                               find a particle to be removed
    do while (ido.ne.out)
       o=int(npart*ranf())+1
       ido=ibox(o)
    enddo
    call ener(x(o),eno,out)             energy particle o in box out
    arg=exp(-beta*(enn-eno +
   + log(vol(out)*(npbox(in)+1)/        acceptance rule (8.3.4)
   + (vol(in)*npbox(out)))/beta))
    if (ranf().lt.arg) then
      x(o)=xn                           add new particle to box in
      ibox(o)=in
      nbox(out)=npbox(out)-1
      nbox(in)=npbox(in)+1
    endif
    return
    end
```

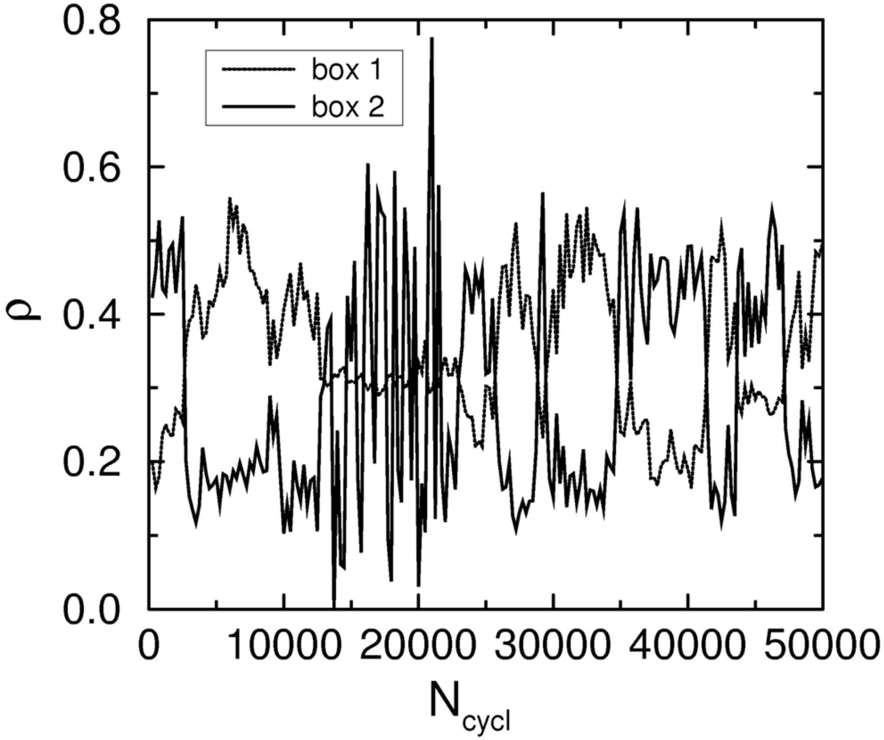


critical point
equation of state
simulations
T
ρ
1.50
1.25
1.00
0.75
0.0
0.2
0.4
0.6
0.8
1.0

Analyzing the results (1)

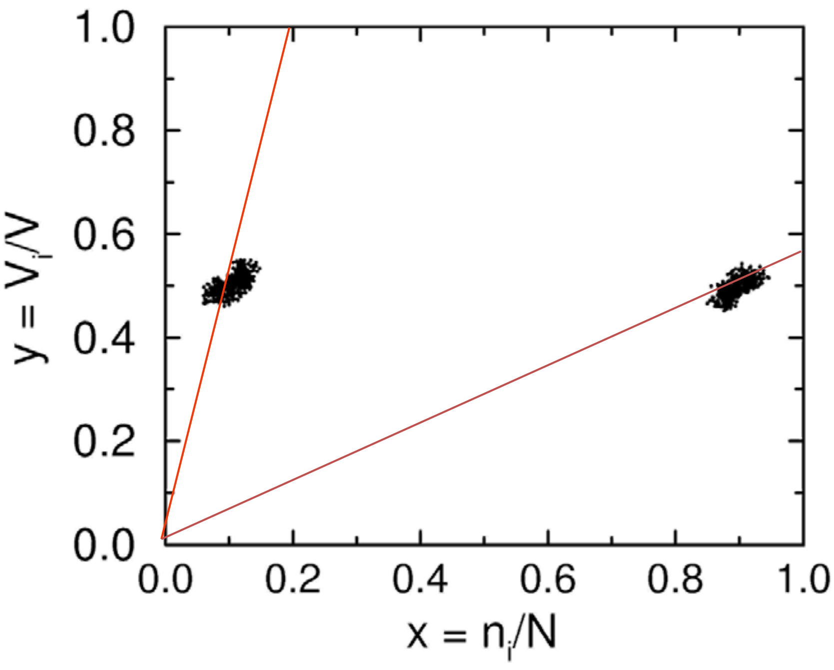


Well below T_c

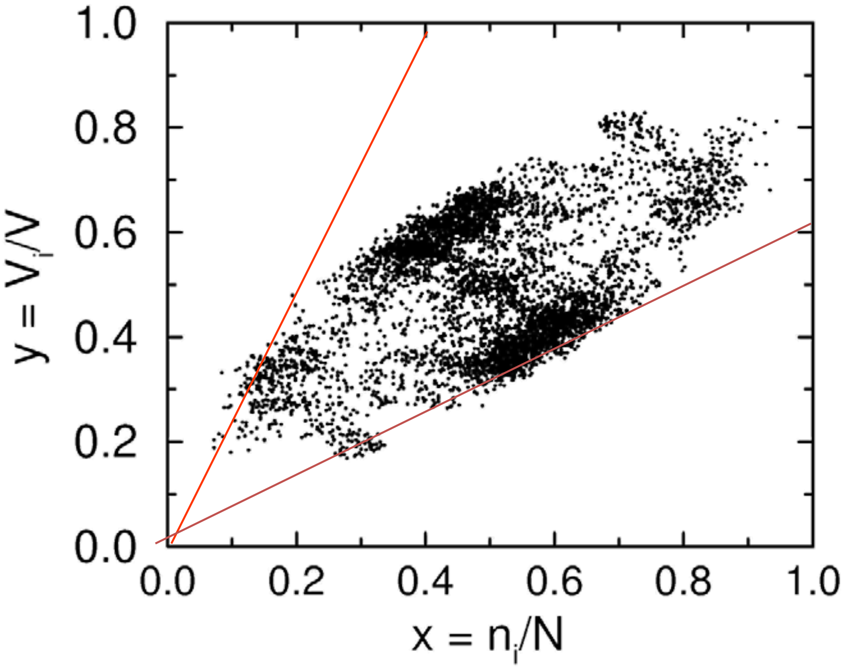


Approaching T_c

Analyzing the results (2)

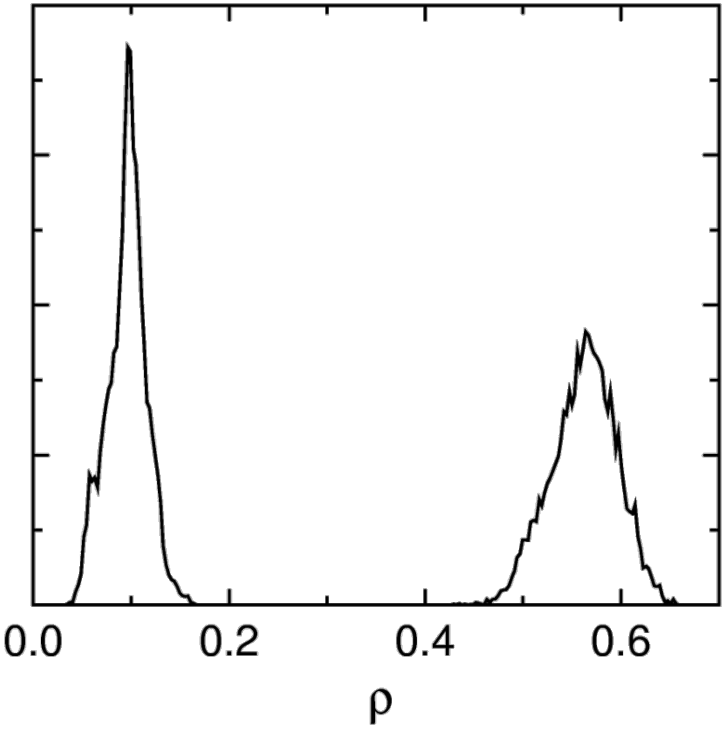


Well below T_c

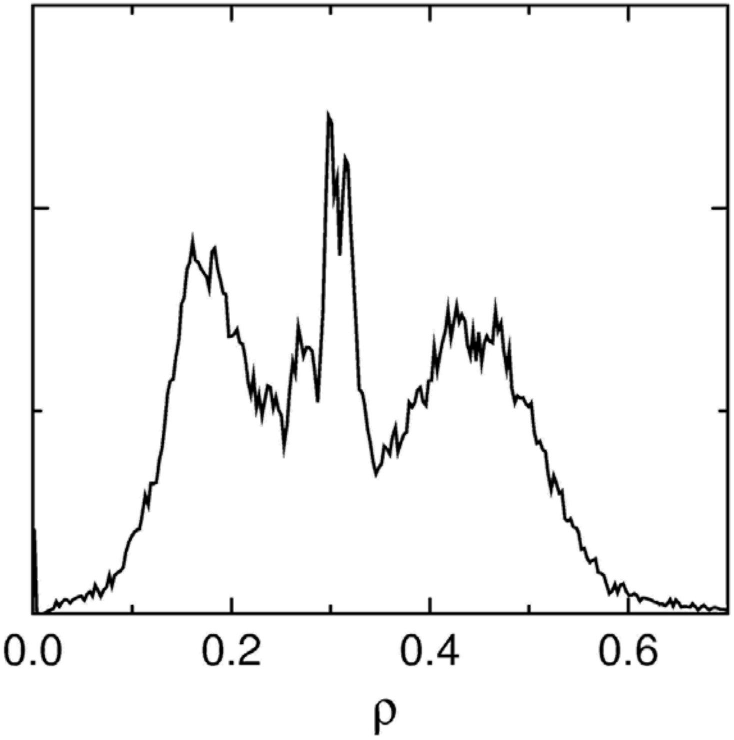


Approaching T_c

Analyzing the results (3)



Well below T_c



Approaching T_c

Condition for phase coexistence in a one-component system:

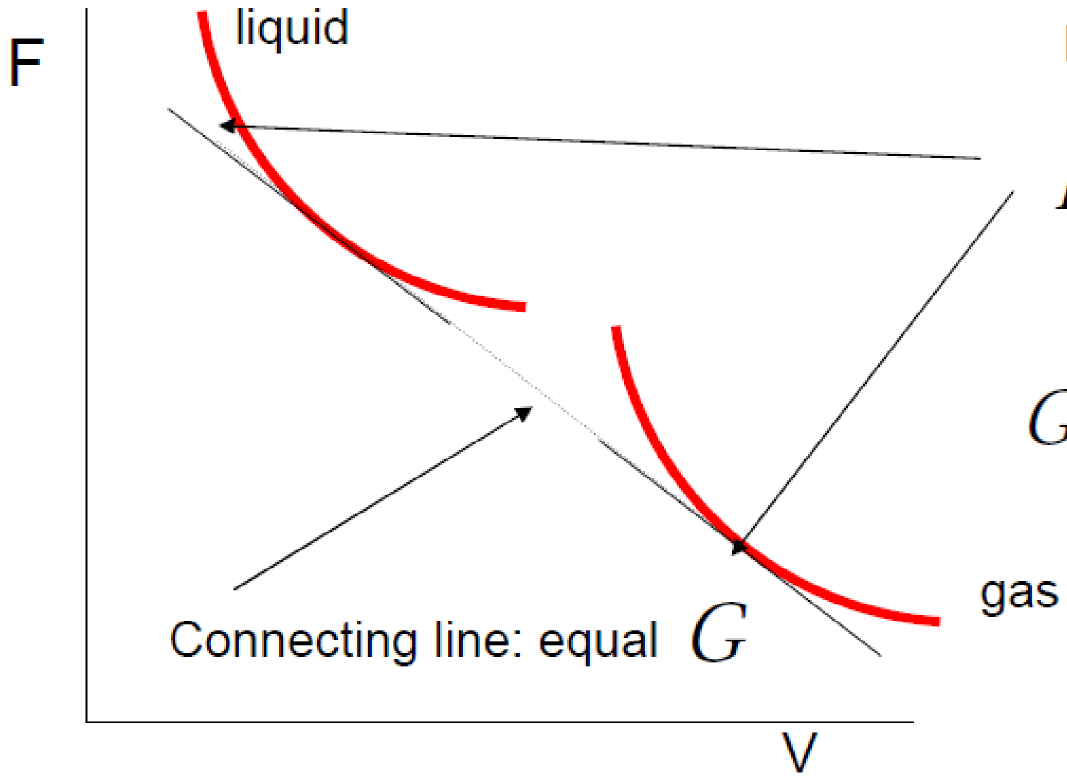
$$T_1 = T_2$$

$$P_1 = P_2$$

$$\mu_1 = \mu_2$$

Phase equilibria from F(V,T)

Common tangent construction



Connecting line: equal G

Equal tangents

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

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

With normal Monte Carlo simulations, we cannot compute “thermal” quantities, such as S, F and G, because they depend on the **total volume of accessible phase space**.

For example:

$$F = -kT \ln Q$$

and

$$Q = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp[-\mathcal{U}(\mathbf{r}^N)/k_B T]$$

F cannot be computed with importance sampling

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

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

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

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

Generate configuration using MC:

$$\left\{ \mathrm{r}_1^N, \mathrm{r}_2^N, \mathrm{r}_3^N, \mathrm{r}_4^N \cdots, \mathrm{r}_M^N \right\}$$

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

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

with

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

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

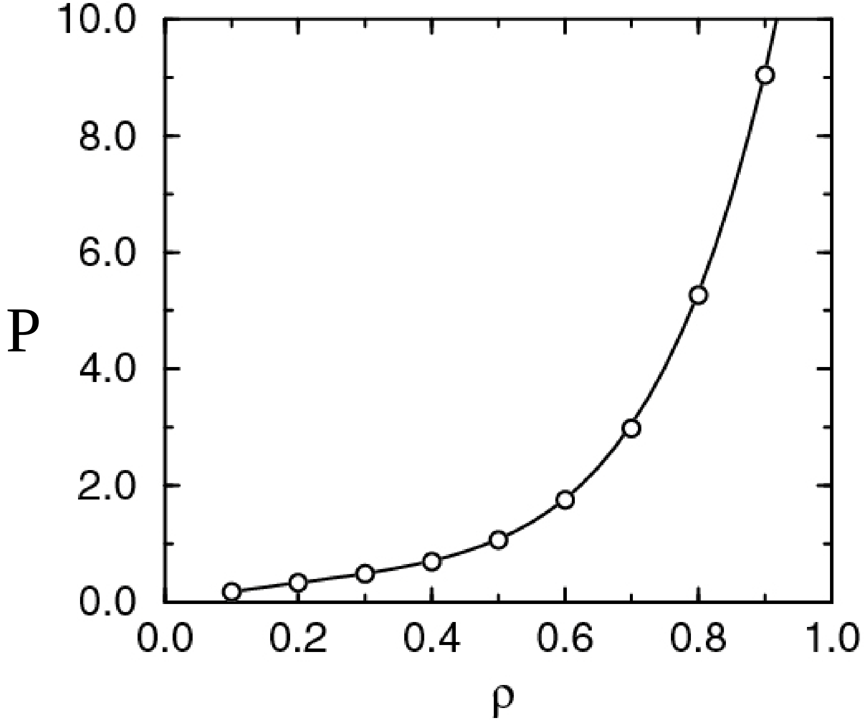
Solutions:

1. “normal” thermodynamic integration
2. “artificial” thermodynamic integration
3. “particle-insertion” method

How are free energies measured experimentally?

$$\frac{\partial F}{\partial V} = -P$$

$$\frac{\partial F/T}{\partial 1/T} = E$$



$$F(V) = F(V_0) + \int_{V_0}^{V} (-P)\,dV$$

Then take the limit $V_0 \Rightarrow \infty$.

Not so convenient because of divergences.
Better:

$$F^{ex}(V) = F(V) - F_{\text{id.gas}}(V)$$

$$= F^{ex}(V_0) + \int_{V_0}^{V} (-P^{ex})\, dV$$

$\Rightarrow 0$, as $V_0 \Rightarrow \infty$

This approach works if we can integrate from a known reference state - Ideal gas (“T=∞”), Harmonic crystal (“T=0”),

Otherwise: use “artificial” thermodynamic integration (Kirkwood)

Suppose we know F(N,V,T) for a system with a simple potential energy function U_0: F_0(N,V,T).

We wish to know F_1(N,V,T) for a system with a potential energy function U_1.

Consider a system with a mixed potential energy function (1-λ)U_0+ λ U_1: F_λ(N,V,T).

$$F_\lambda(N,V,T) = \mathrm{const} - kT \ln \int d\mathbf{r}^N \exp(-\beta(\lambda U_1 + (1-\lambda)U_0)$$

hence

$$\frac{\partial F_\lambda(N,V,T)}{\partial\lambda} = \frac{\int d\mathbf{r}^N (U_1 - U_0) \exp(-\beta(\lambda U_1 + (1-\lambda)U_0)}{\int d\mathbf{r}^N \exp(-\beta(\lambda U_1 + (1-\lambda)U_0)}$$

Or:

$$\frac{\partial F_\lambda(N,V,T)}{\partial\lambda} = \langle U_1 - U_0 \rangle_\lambda$$

And therefore

$$F_1(N,V,T) = F_0(N,V,T) + \int_0^1 \langle U_1 - U_0 \rangle_\lambda d\lambda$$

Free Enegy of Solids

More difficult. What is reference?

Not the ideal gas.

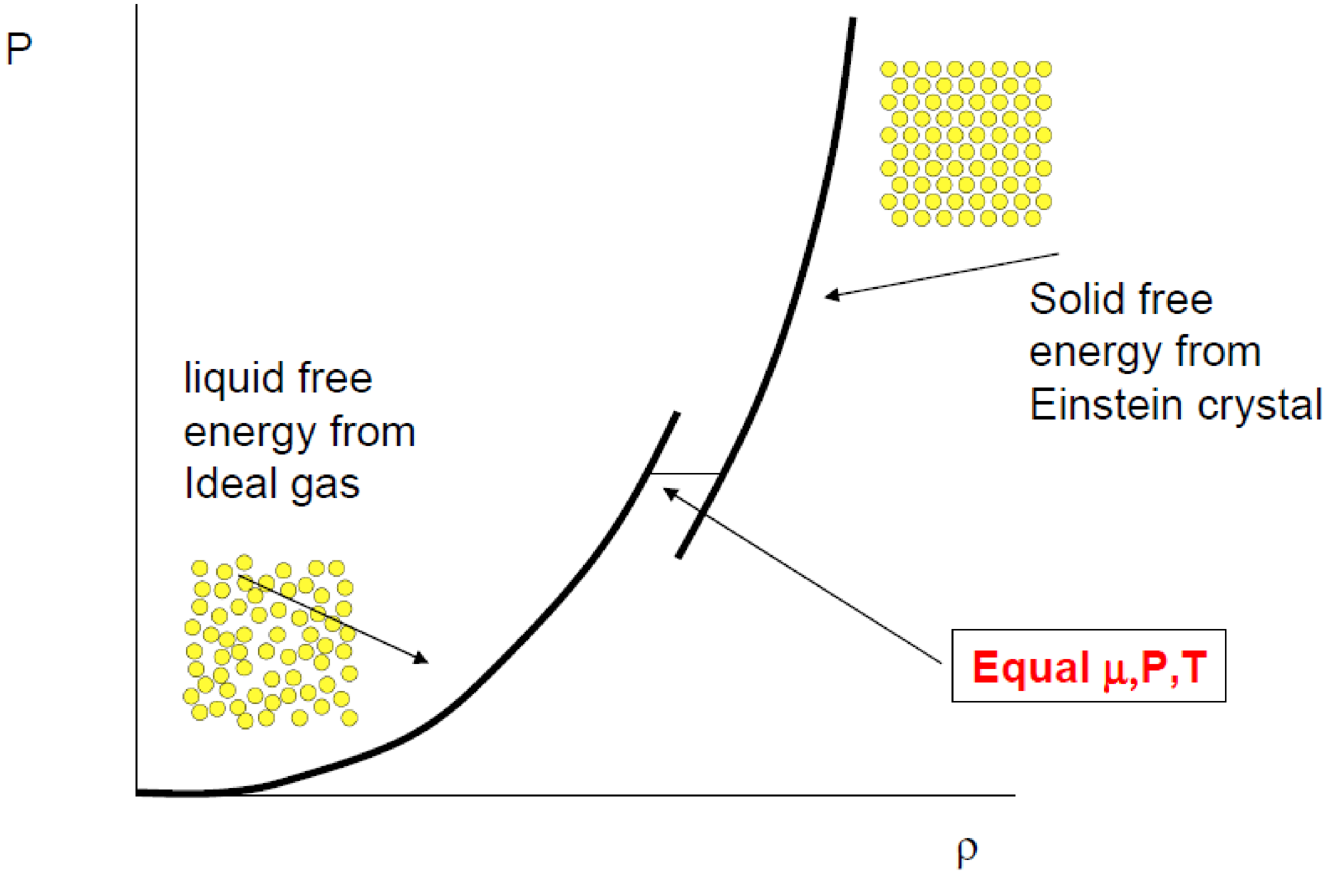
Instead it is the Einstein crystal: harmonic oscillators around r$_0$

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

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

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

Example: Hard Sphere Freezing



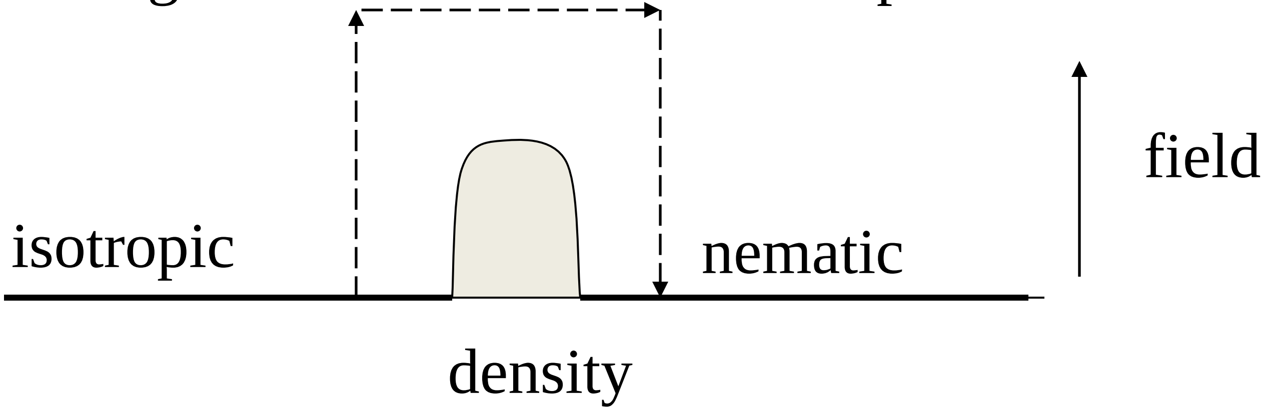
liquid free energy from Ideal gas

Solid free energy from Einstein crystal

Equal μ,P,T

1. Nematic liquid crystal:

   Start from isotropic phase. Switch on “magnetic field” and integrate around the I-N critical point



2. Modulated Phases (microphases):

   Start from an oscillating field at the modulation of interest. Switch off the “magnetic field” while turning on the interaction.

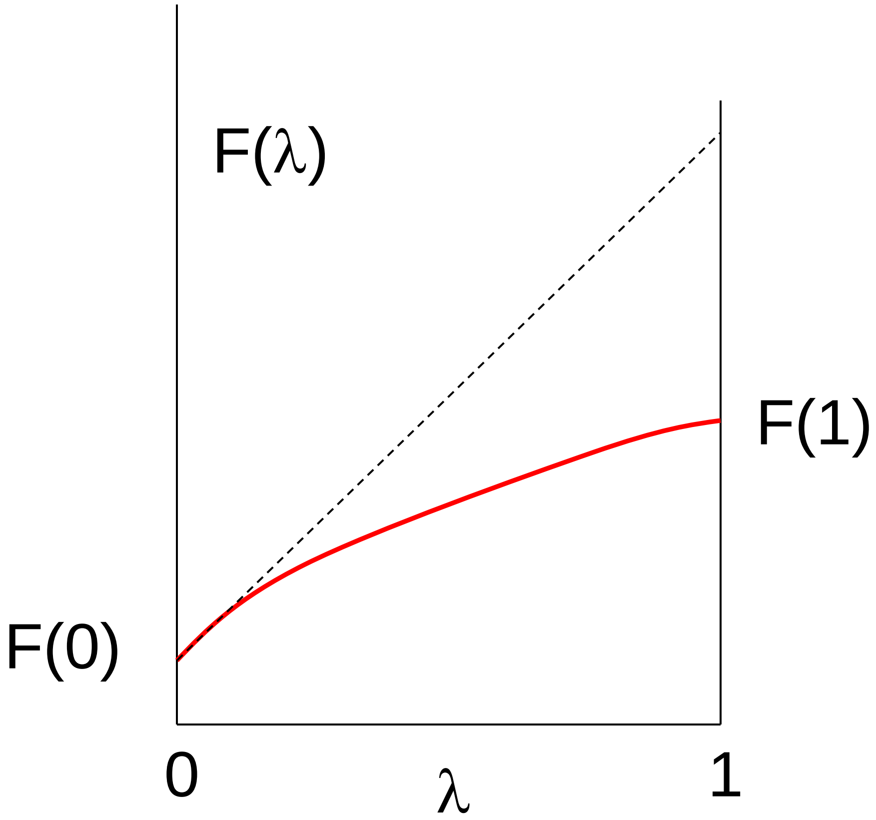
The second derivative is ALWAYS negative:

$$\left(\frac{\partial^2 F}{\partial \lambda^2}\right)_{NVT\lambda} = -\beta\left(\left\langle (U_1 - U_0)^2 \right\rangle_{NVT\lambda} - \langle (U_1 - U_0)\rangle^2_{NVT\lambda}\right) \leq 0$$

Therefore:

$$\left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda=0} \geq \left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda}$$

Good test of simulation results…

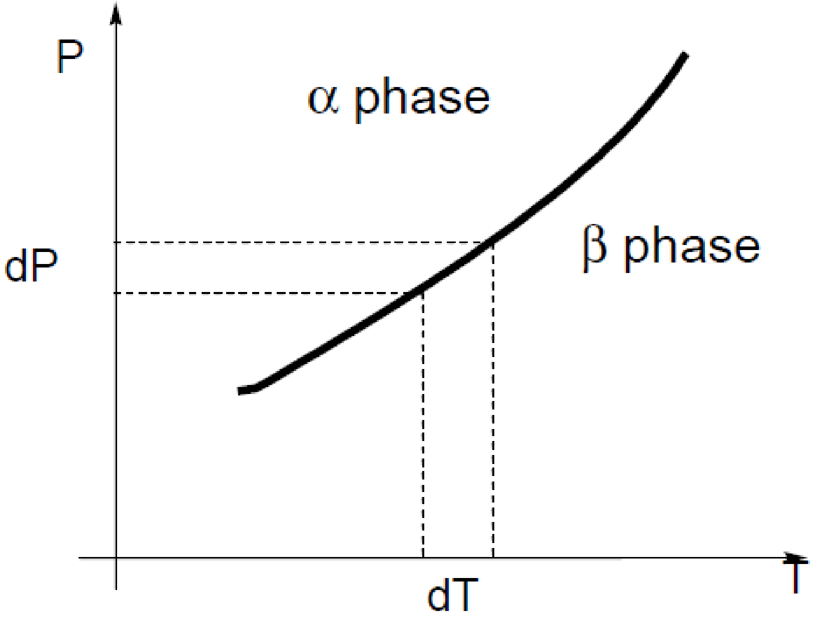


Tracing Coexistence Curves

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

P en T are equal along coexistence line

$$\boxed{d\mu_\alpha = d\mu_\beta}$$



Tracing Coexistence Curves

$$d\mu = dg = -sdT + vdP$$

$$-s_\alpha dT + v_\alpha dp = -s_\beta dT + v_\beta dP$$

$$\frac{dP}{dT} = \frac{s_\beta - s_\alpha}{v_\beta - v_\alpha}$$

Clapeyron equation

$$\boxed{\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T\Delta v}}$$

$$\frac{dP}{dT} = \frac{\Delta(u + Pv)}{T\Delta v}$$

Chemical Potentials

Particle insertion method to compute chemical potentials

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

But N is not a continuous variable.
Therefore

$$\mu \approx \left(\frac{F(N+1,V,T) - F(N,V,T)}{(N+1) - N}\right)$$

$$F(N+1,V,T)-F(N,V,T) = -kT \ln \frac{Q(N+1,V,T)}{Q(N,V,T)}$$

Does that help?

Yes: rewrite

$$\begin{aligned} Q(N,V,T) &= \frac{1}{N!\Lambda^{3N}} \int d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N)) \\ &= \frac{V^N}{N!\Lambda^{3N}} \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N; L)) \end{aligned}$$

s is a scaled coordinate: $0 \leq \mathbf{s} < 1$

$\mathbf{r} = L\,\mathbf{s}$ (is box size)

$$\frac{Q(N+1,V,T)}{Q(N,V,T)} =$$

$$\frac{V}{(N+1)\Lambda^3}\frac{\int d\mathrm{s}^{N+1}\exp(-\beta U(\mathrm{s}^{N+1}))}{\int d\mathrm{s}^{N}\exp(-\beta U(\mathrm{s}^{N}))}$$

Now write

$$U(\mathrm{s}^{N+1}) \equiv U(\mathrm{s}^N) + \Delta U(\mathrm{s}_{N+1};\mathrm{s}^N)$$

then

$$\frac{Q(N+1,V,T)}{Q(N,V,T)} =$$

$$\frac{V}{(N+1)\Lambda^3}\int d\mathrm{s}_{N+1}\langle\exp(-\beta\Delta U(\mathrm{s}_{N+1};\mathrm{s}^N))\rangle$$

And therefore

$$\mu \approx \left(\frac{F(N+1,V,T) - F(N,V,T)}{(N+1) - N} \right)$$

$$\mu = -kT \ln \left(\frac{V}{(N+1)\Lambda^3} \int d\mathrm{s}_{N+1} \langle \exp(-\beta \Delta U(\mathrm{s}_{N+1}, \mathrm{s}^N)) \rangle \right)$$

but

$$-kT \ln \left(\frac{V}{(N+1)\Lambda^3} \right) = kT \ln(\rho \Lambda^3) = \mu^{\text{id.gas}}$$

So, finally, we get:

$$\mu = \mu^{\text{id.gas}} - kT \ln\left(\int d\mathbf{s}_{N+1} \langle \exp(-\beta \Delta U(\mathbf{s}_{N+1}, \mathbf{s}^N)) \rangle \right) \equiv \mu^{\text{id.gas}} + \mu^{\text{ex}}$$

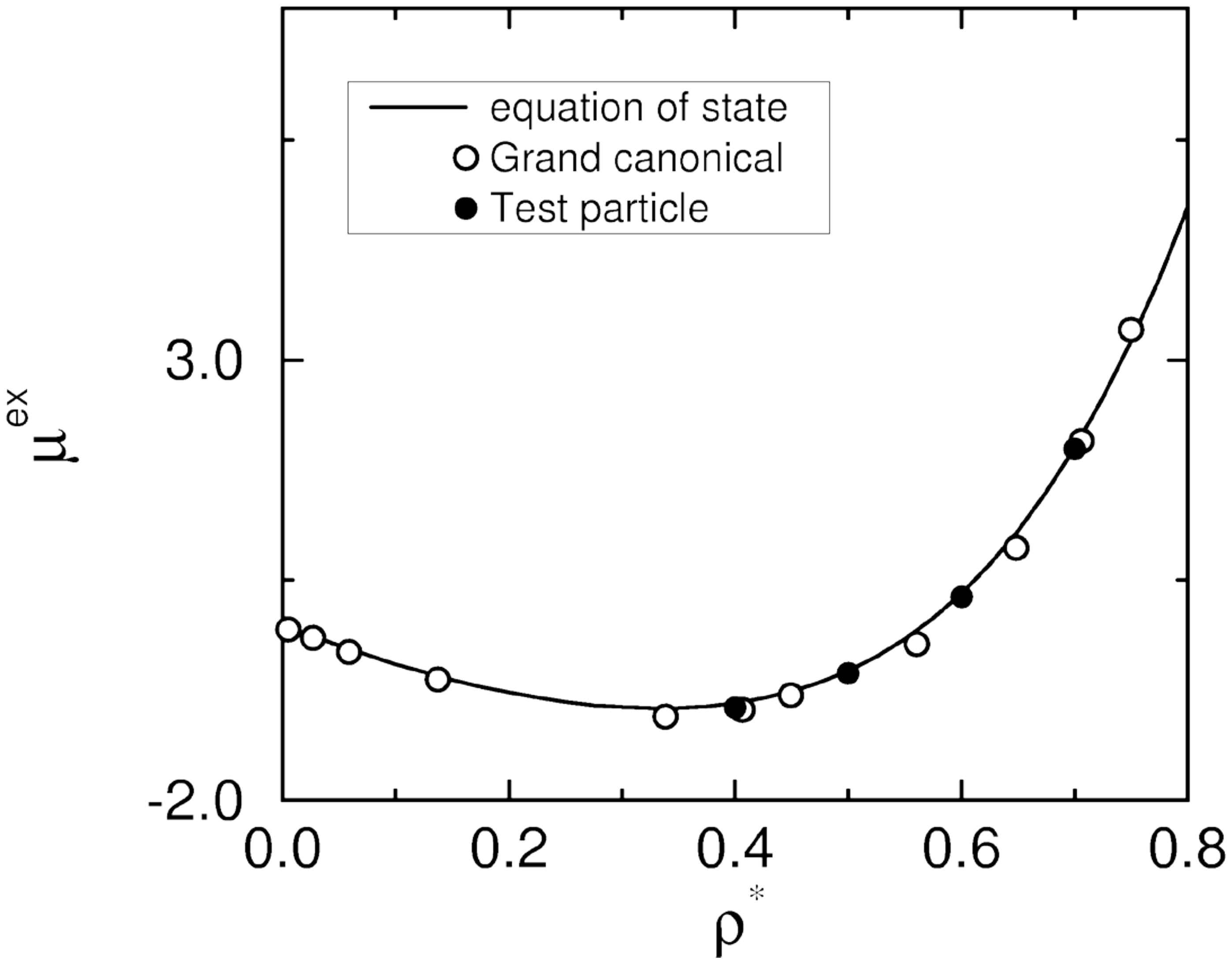
Interpretation:

1. Evaluate ΔU for a random insertion of a molecule in a system containing N molecule.
2. Compute $\exp(-\beta \Delta U)$
3. Repeat M times and compute the average “Boltzmann factor” $\langle \exp(-\beta \Delta U) \rangle$
4. Then $\mu^{\text{ex}} = -kT \ln \langle \exp(-\beta \Delta U) \rangle$

Algorithm 16 (Widom Test Particle Insertion)

```
      subroutine Widom                   excess chemical potential
                                         via the addition of test particles
      xtest=box*ranf()                   generate a random position
      call ener(xtest,entest)            determine energy
      wtest=wtest                        update Boltzmann factor in (7.2.5)
     +      +exp(-beta*entest)
      return
      end
```

Lennard-Jones fluid



Other ensembles: NPT

NVT: Helmholtz free energy

NPT: Gibbs free energy

NVT:

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

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

NPT:

$$\beta\mu = \ln\left(\Lambda^{3}\beta P\right) - \ln\left\langle \frac{\beta PV}{N+1}\int \mathrm{ds}_{N+1}\exp\left(-\beta\Delta U^{+}\right) \right\rangle$$

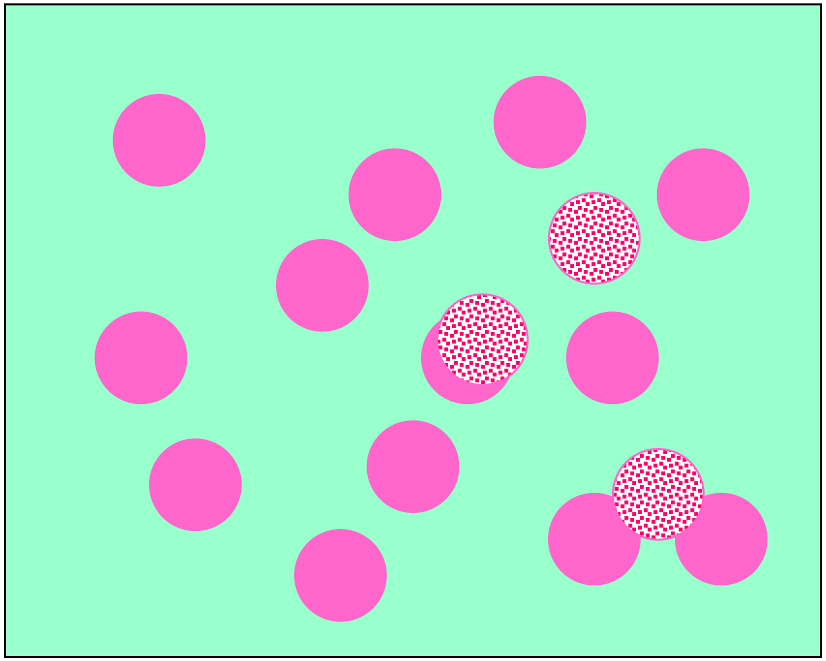
$$\beta\mu = \ln\left(\Lambda^{3}\beta P\right) - \ln\left\langle \frac{\beta PV}{N+1}\int \mathrm{ds}_{N+1}\exp\left(-\beta\Delta U^{+}\right) \right\rangle$$

Hard spheres

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

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

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



Probability to insert a test particle!

Problems with Widom method:

Low insertion probability yields poor statistics.

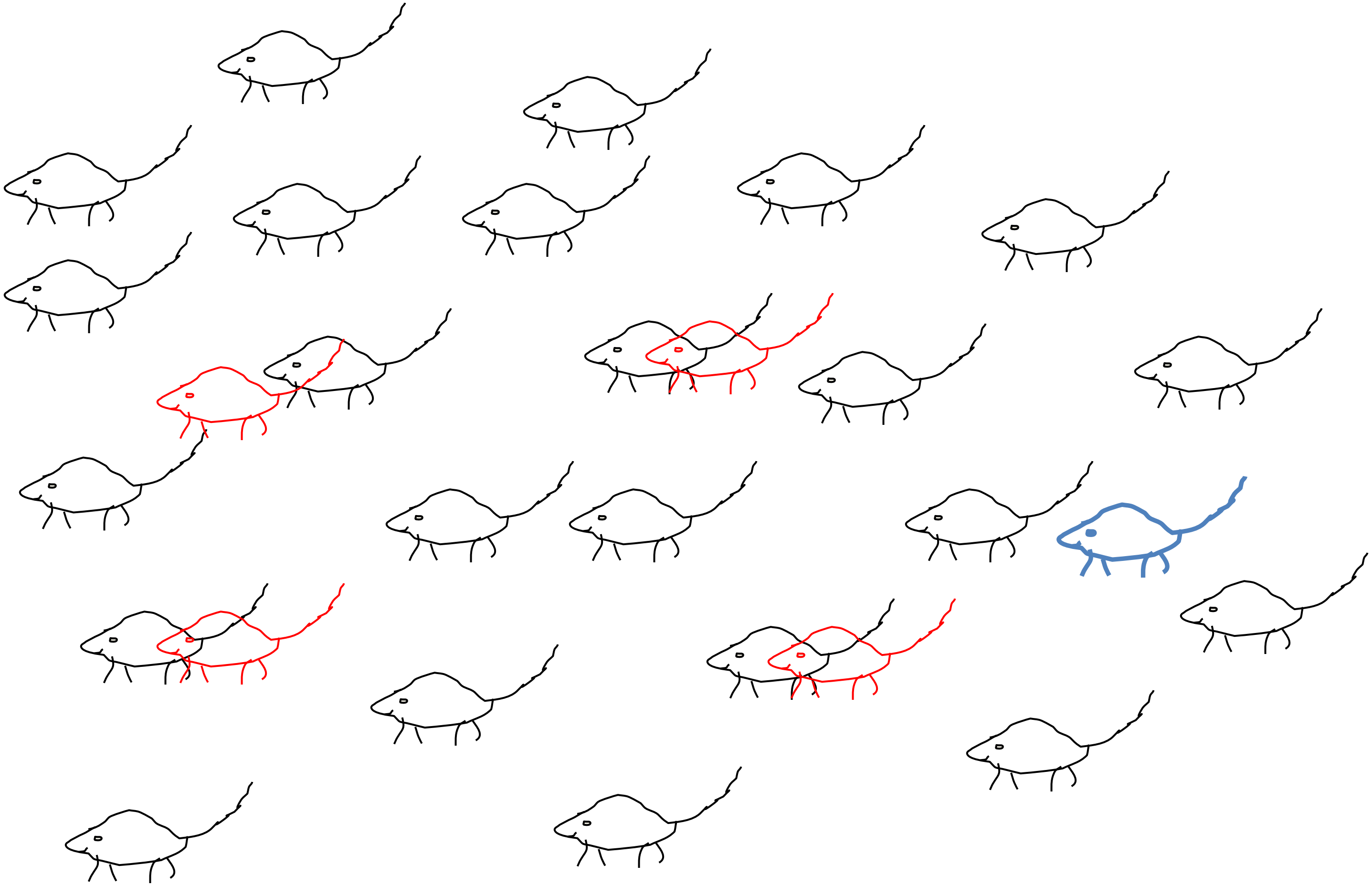
For instance:

Trial insertions that consist of a sequence of intermediate steps.

Examples: changing polymer conformations, moving groups of atoms, …

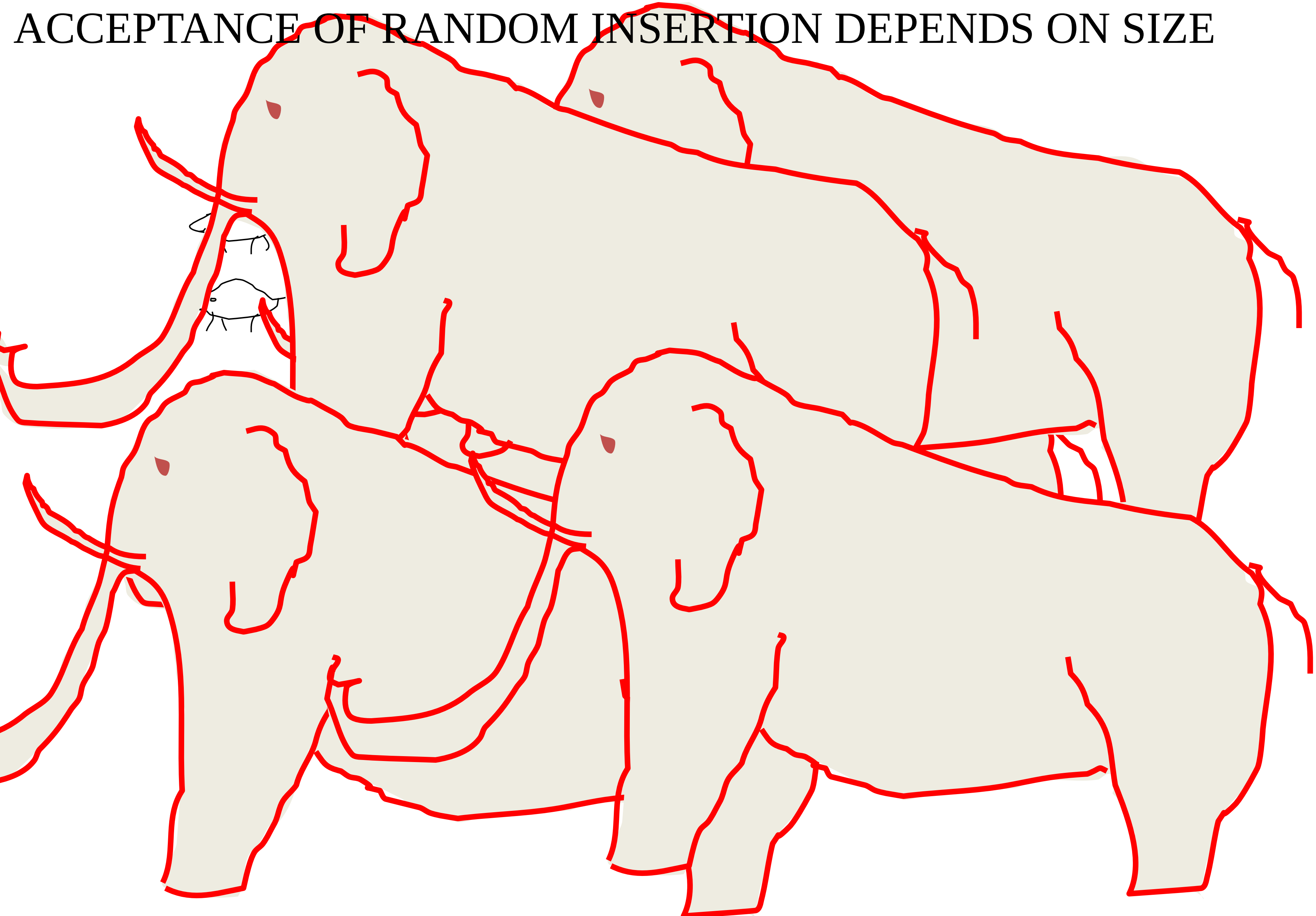
What is the problem with polymer simulations?

ACCEPTANCE OF RANDOM INSERTION DEPENDS ON SIZE



What is the problem with polymer simulations?

ACCEPTANCE OF RANDOM INSERTION DEPENDS ON SIZE



ANALOGY:

Finding a seat in a crowded restaurant.

Next: consider the random inserti
molecule (polymer).

Waiter! Can you seat 100 persons… together please!

Random insertions of polymers in dense liquids usually fail completely…

(Partial) Solution: Biased insertion.

Thijs Vlugt’s lecture later this week…

Interpretation:

1. Evaluate ΔU for a random **REMOVAL** of a molecule in a system containing N+1 molecule.

$(+\beta\Delta U)$

d compute the ave

”

$T \ln\langle \exp(+\beta\Delta U)\rangle$

What is wrong?

$\exp(+\beta \Delta U)$ is not bounded. The average that we compute can be dominated by INFINITE contributions from points that are NEVER sampled.

What to do?

Consider:

$$p_0(\Delta U) \equiv \frac{\int \exp(-\beta U_N)\delta(\Delta U - U_{N+1} + U_N)}{\int \exp(-\beta U_N)}$$
$$= \frac{\int \exp(-\beta U_N)\delta(\Delta U - U_{N+1} + U_N)}{Q_N}$$

And also consider the distribution

$$p_1(\Delta U) \equiv \frac{\int \exp(-\beta U_{N+1})\delta(\Delta U - U_{N+1} + U_N)}{\int \exp(-\beta U_{N+1})}$$

p_0 and p_1 are related:

$$\begin{aligned}
p_1(\Delta U) &= \frac{\int \exp(-\beta(U_N + \Delta U))\delta(\Delta U - U_{N+1} + U_N)}{Q_{N+1}} \\
&= \exp(-\beta\Delta U)\frac{\int \exp(-\beta U_N)\delta(\Delta U - U_{N+1} + U_N)}{Q_{N+1}} \\
&= \exp(-\beta\Delta U)\frac{p_0(\Delta U)Q_N}{Q_{N+1}}
\end{aligned}$$

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

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

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

Fit f_0 and f_1 to two polynomials that only differ by a constant.

$$\beta\Delta$$

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

$$f_1(\Delta U) \equiv C_1$$

$$f_0(\Delta U) \equiv C_0 + a\Delta U + b\Delta U^2 + c\Delta U^3$$

$$\beta\Delta F = C_1 - C_0$$

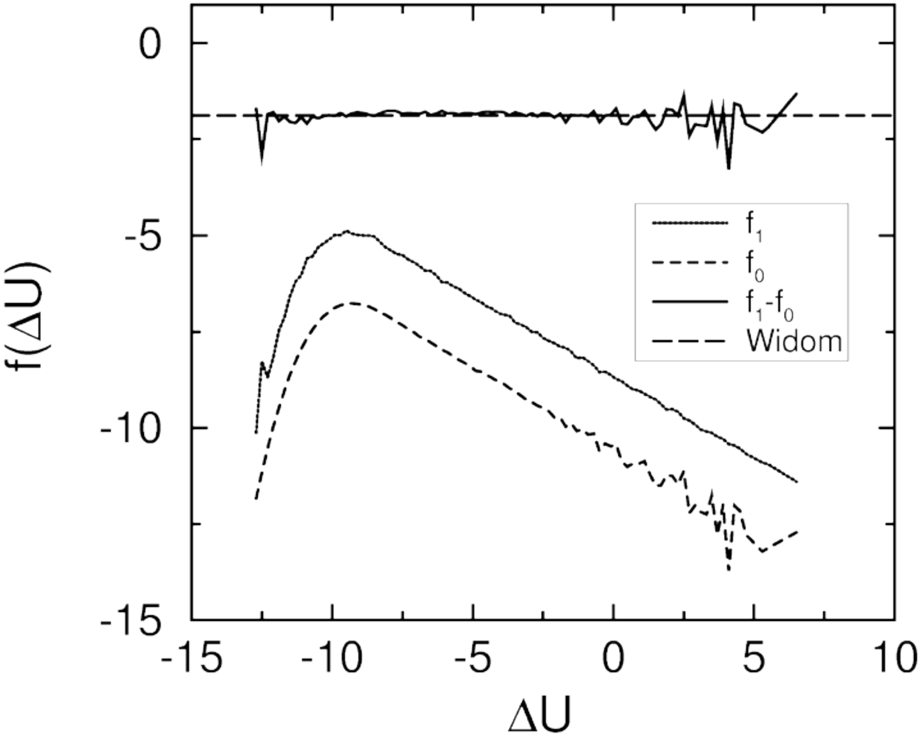
Chemical potential

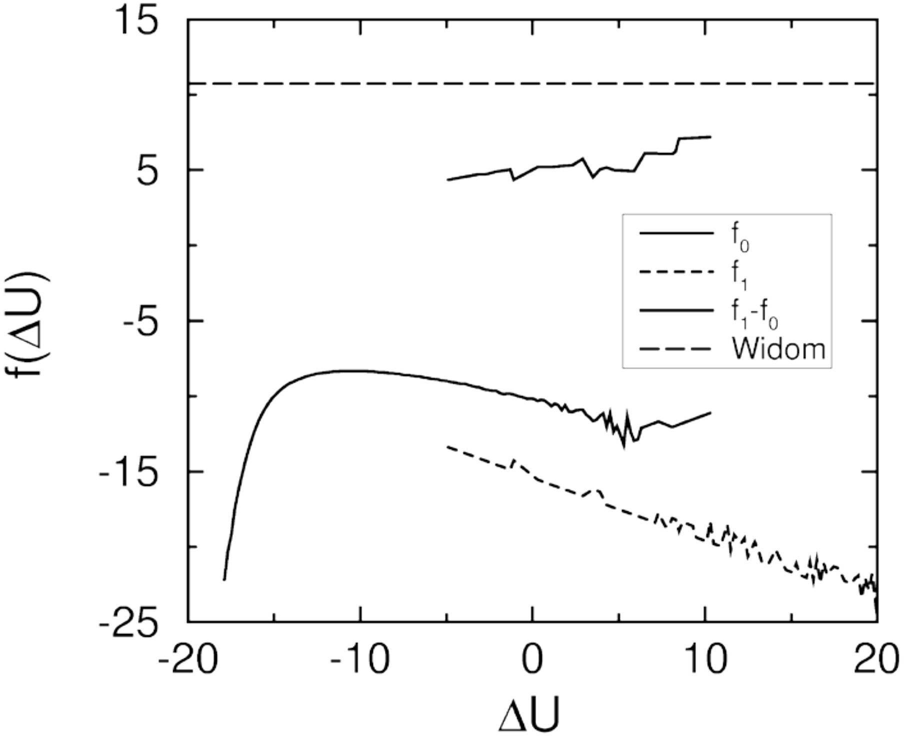
System 0: *N-1, V, T, U* + 1 ideal gas System 1: *N, V, T, U*

$$\Delta\beta F = \beta F_1 - \beta F_0 \equiv \beta\mu^{ex} \qquad \Delta U = U_1 - U_0$$

System 0: test particle energy System 1: real particle energy

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





Does it work for hard spheres?

consider ΔU=0

$$f_1(0) = f_0(0) + \beta\mu$$

$$f_1(0) = \ln(1) + (constant)$$

$$f_0(0) = \ln(P_{acc}) + (constant)$$

$$\beta\mu = -\ln(P_{acc})$$

Non-Boltzmann sampling

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

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

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

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

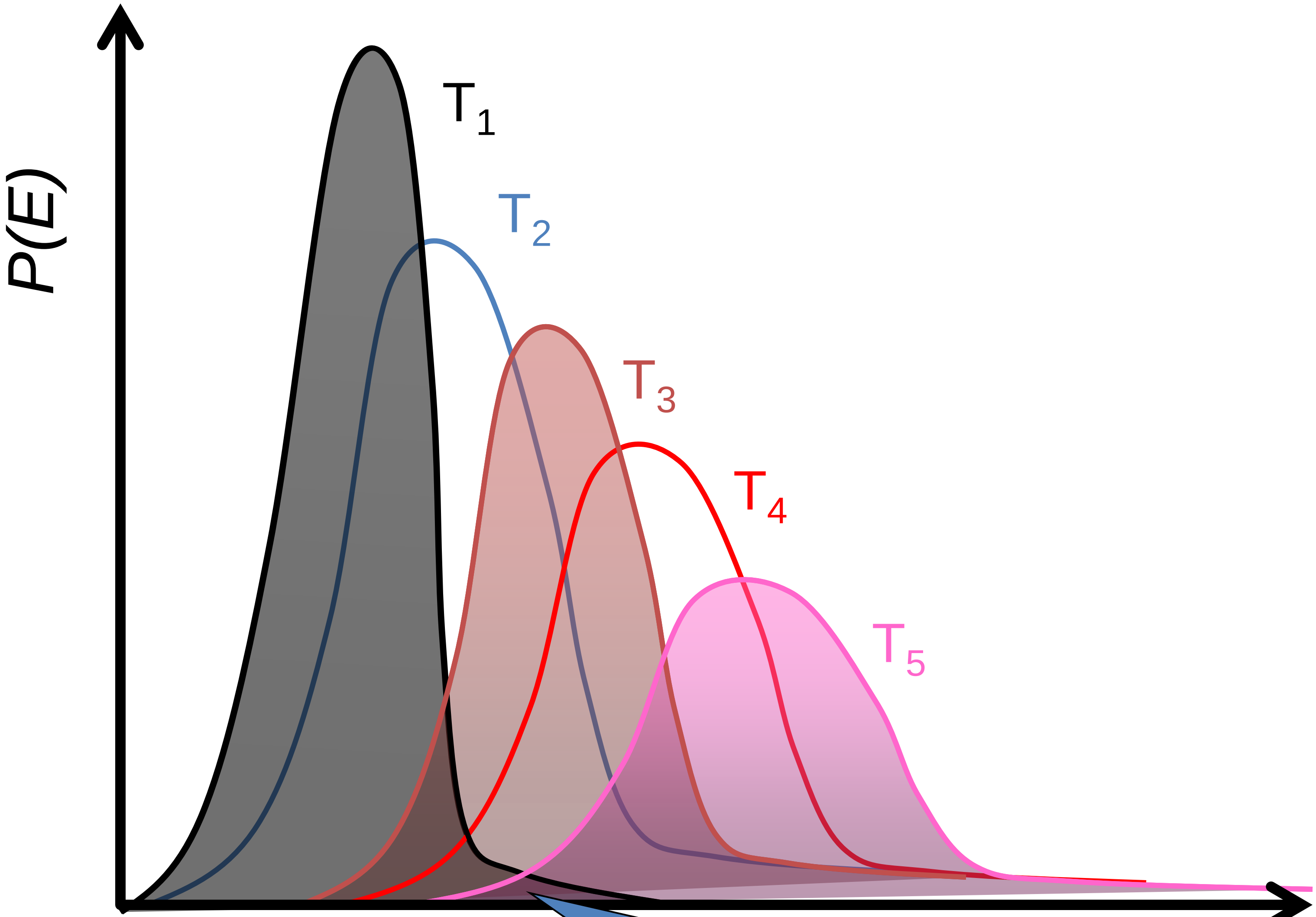
$$= \frac{\langle A\exp[(\beta_2-\beta_1)U]\rangle_{NVT_2}}{\langle \exp[(\beta_2-\beta_1)U]\rangle_{NVT_2}}$$

T_1 is arbitrary!

Why are we not using this?

We only need a *single* simulation!

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



Overlap becomes very small

Umbrella Sampling

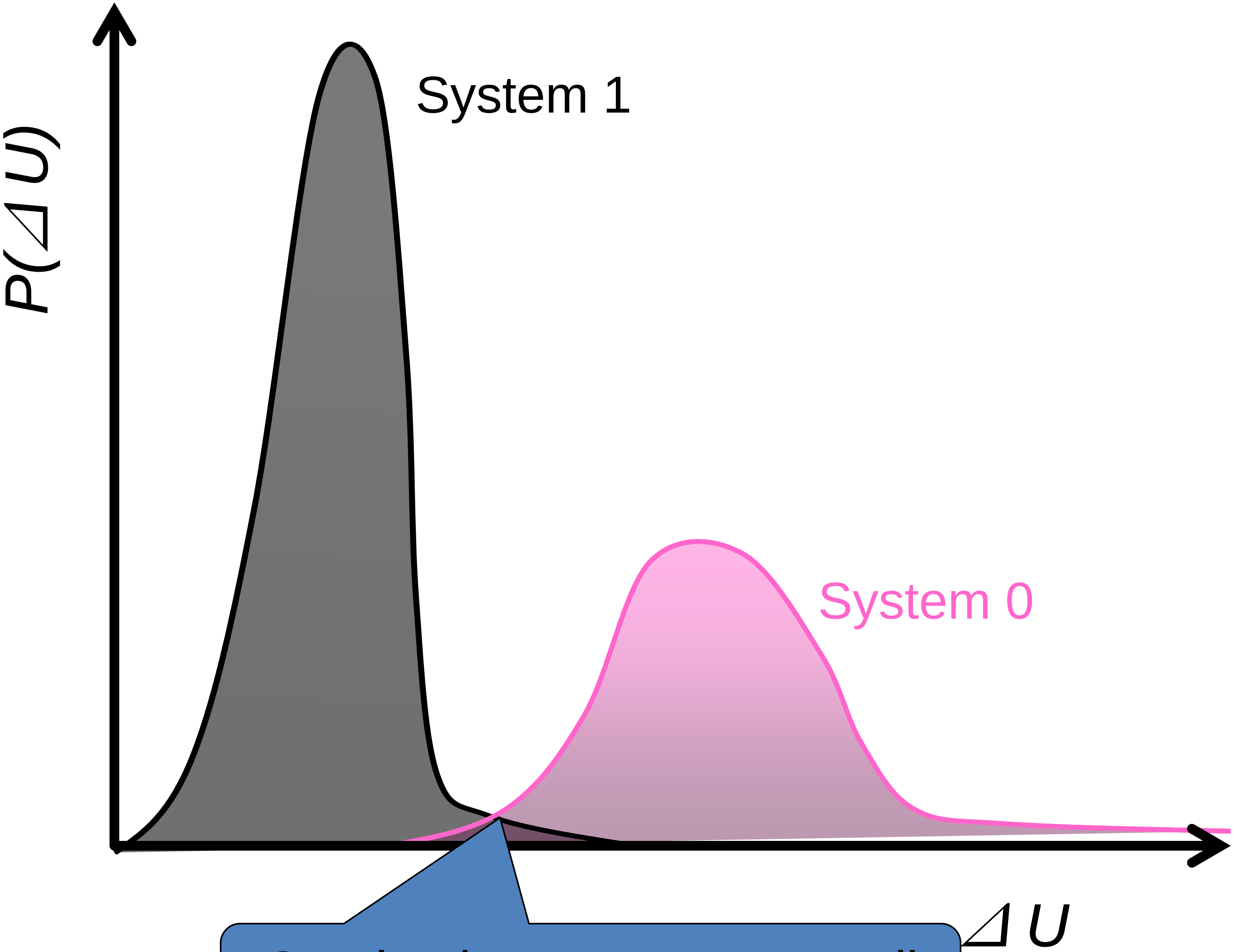
- Start with thermodynamic perturbation.

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

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

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

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



Overlap becomes very small

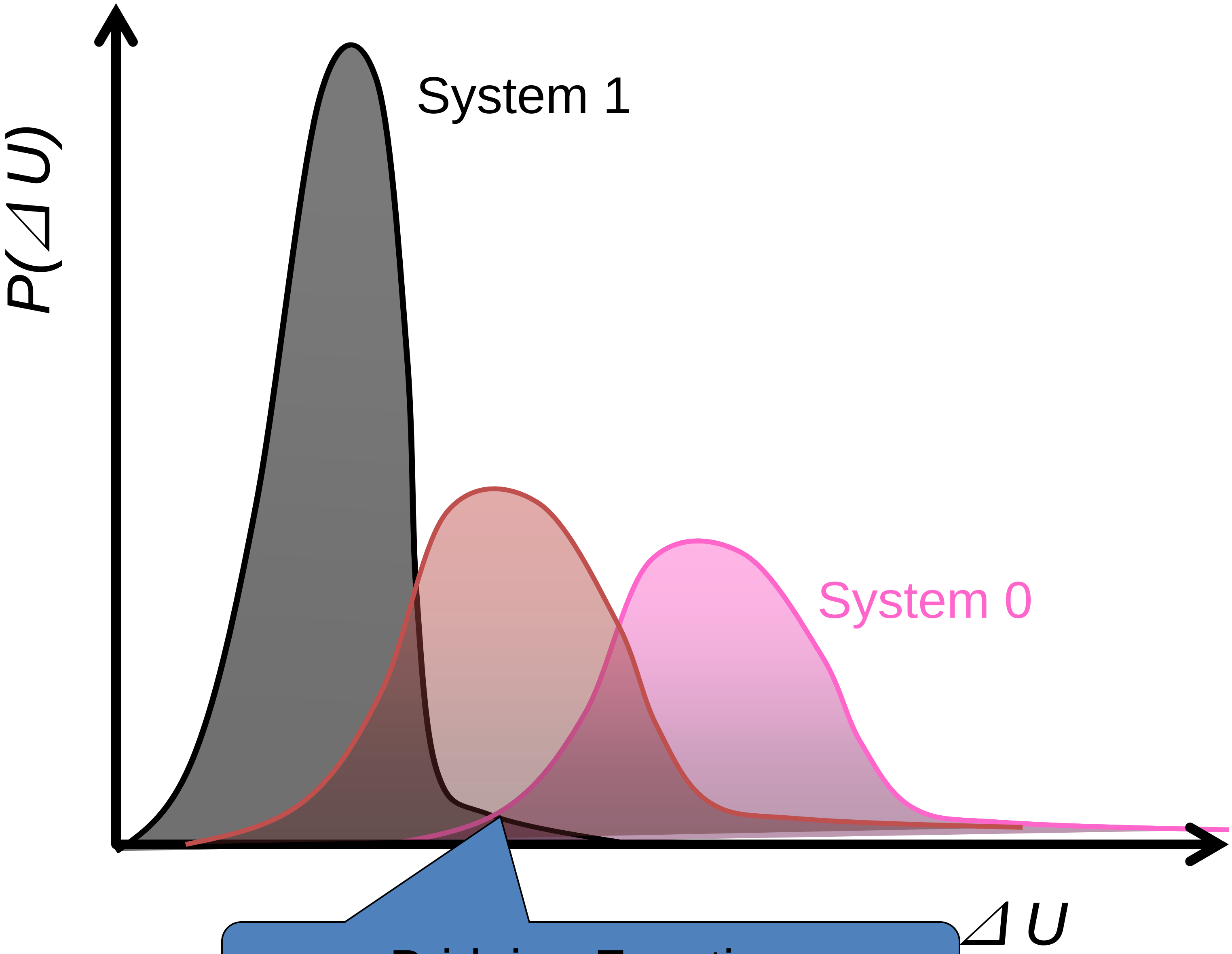
Bridging Function

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

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

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

This approach is called umbrella sampling



Bridging Function

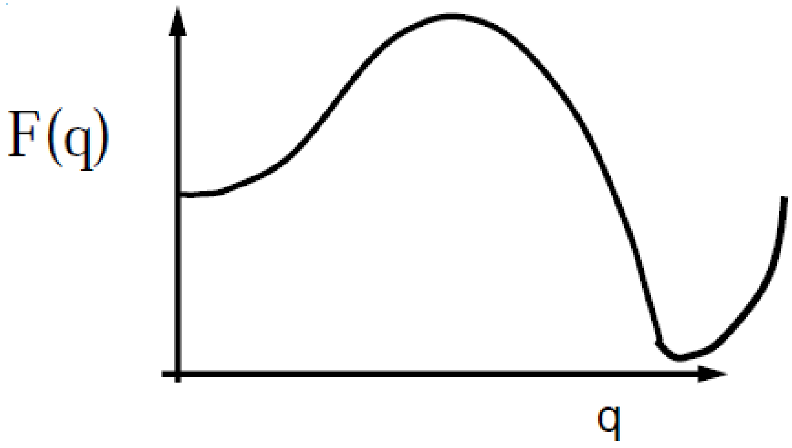
Landau Free Energy

Often the free energy is needed as a function of a certain order parameter q

$$\beta F = -\ln \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N))$$

$$\beta F(q) = -\ln \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \delta(q'(\mathbf{r}^N) - q) \exp(-\beta U(\mathbf{r}^N))$$

$$\beta F(q) = -\ln P(q)$$



Umbrella Sampling

Add and subtract bias potential w(q) to U

$$P(q) = \frac{\int d\mathbf{r}^N \delta\left(q'(\mathbf{r}^N) - q\right) \exp\left[-\beta(U(\mathbf{r}^N) + w(q') - w(q'))\right]}{\int d\mathbf{r}^N \exp\left[-\beta(U(\mathbf{r}^N + w(q') - w(q'))\right]}$$

$$P(q) = \frac{\int d\mathbf{r}^N \delta\left(q'(\mathbf{r}^N) - q\right) \exp\left[-\beta(U(\mathbf{r}^N) + w(q'))\right] \exp\left(\beta w(q')\right)}{\int d\mathbf{r}^N \exp\left[-\beta(U(\mathbf{r}^N + w(q'))\right) \exp\left(\beta w(q')\right]}$$

$$P(q) = \frac{\left\langle \delta\left(q'(\mathbf{r}^N) - q\right) \exp\left(\beta w(q')\right)\right\rangle_{\text{biased}}}{\left\langle \exp\left(\beta w(q')\right)\right\rangle_{\text{biased}}}$$

$$P(q) = \frac{\exp\left(\beta w(q)\right)}{\left\langle \exp\left(\beta w(q')\right)\right\rangle_{\text{biased}}} P_{\text{biased}}(q)$$

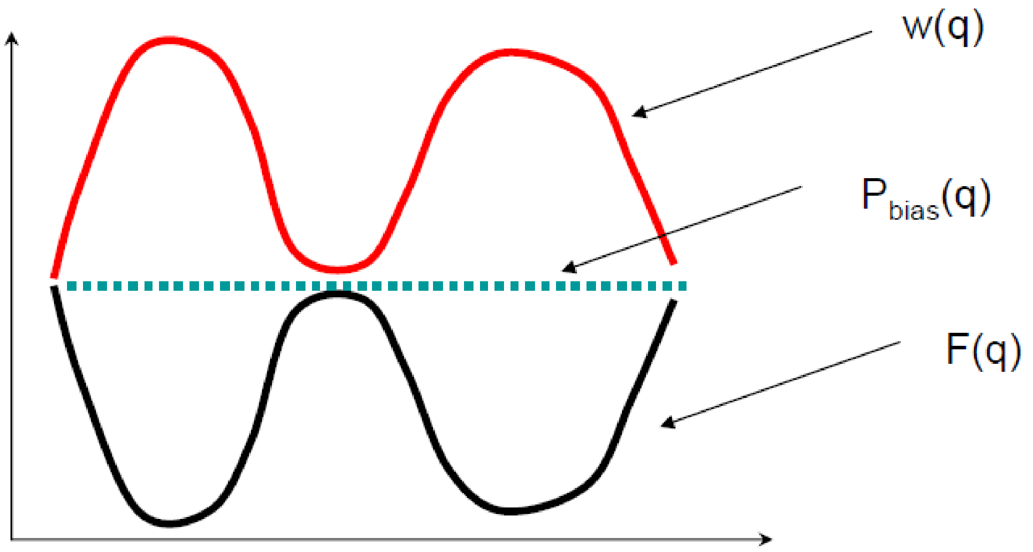
$$\beta F(q) = -\ln P(q) = -\ln P_{\text{biased}}(q) - \beta w(q) + \text{const}$$

Umbrella Sampling

$$\beta F(q) = -\ln P(q) = -\ln P_{\text{biased}}(q) - \beta w(q) + \text{const}$$

Best choice w(q)=-F(q)

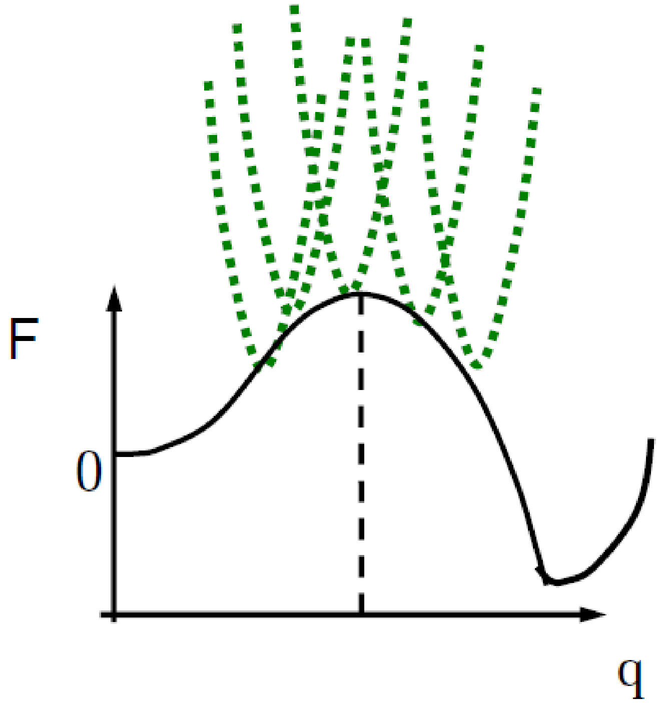
Means P_{biased} = constant: entire q-range is equally sampled.



Usually w(q) is difficult to guess: windows

Umbrella Sampling

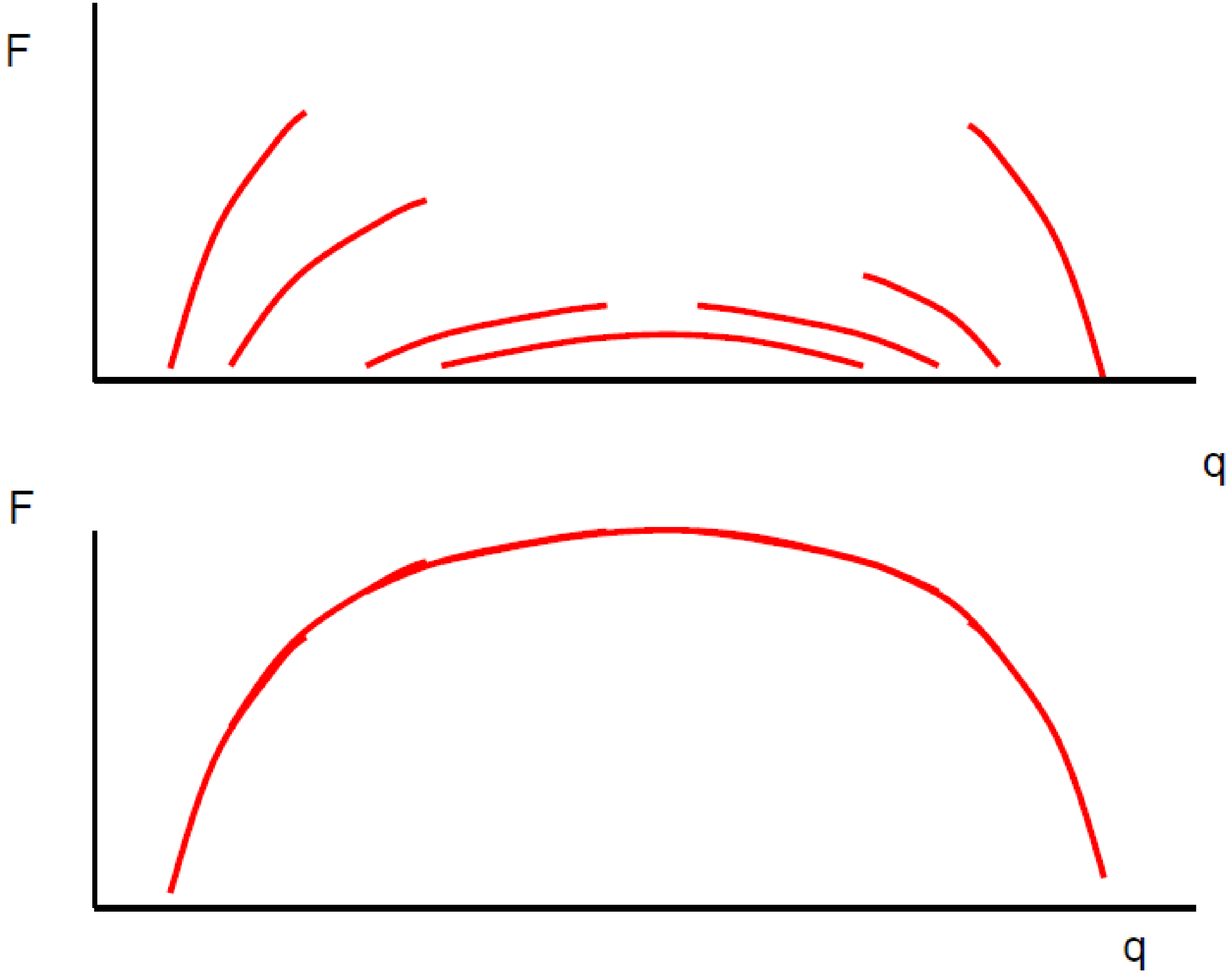
Different windows have different potential $w_i(q)$



Boltzmann : $\exp[-\beta\,(U + w(q))]$

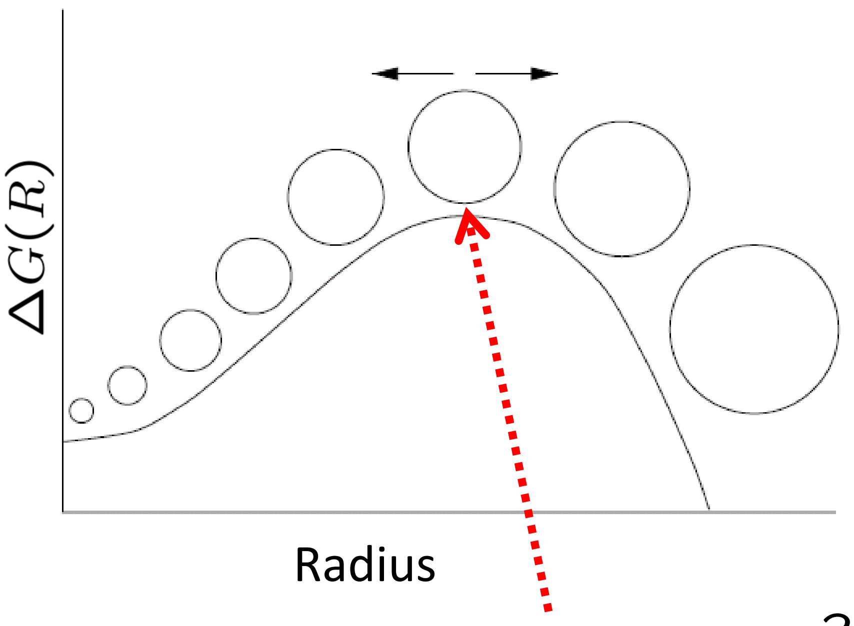
$$\beta F(q) = -\ln P_{\mathrm{biased}}(q) - \beta w(q) + \mathrm{const}$$

Reconstructing the Free Energy

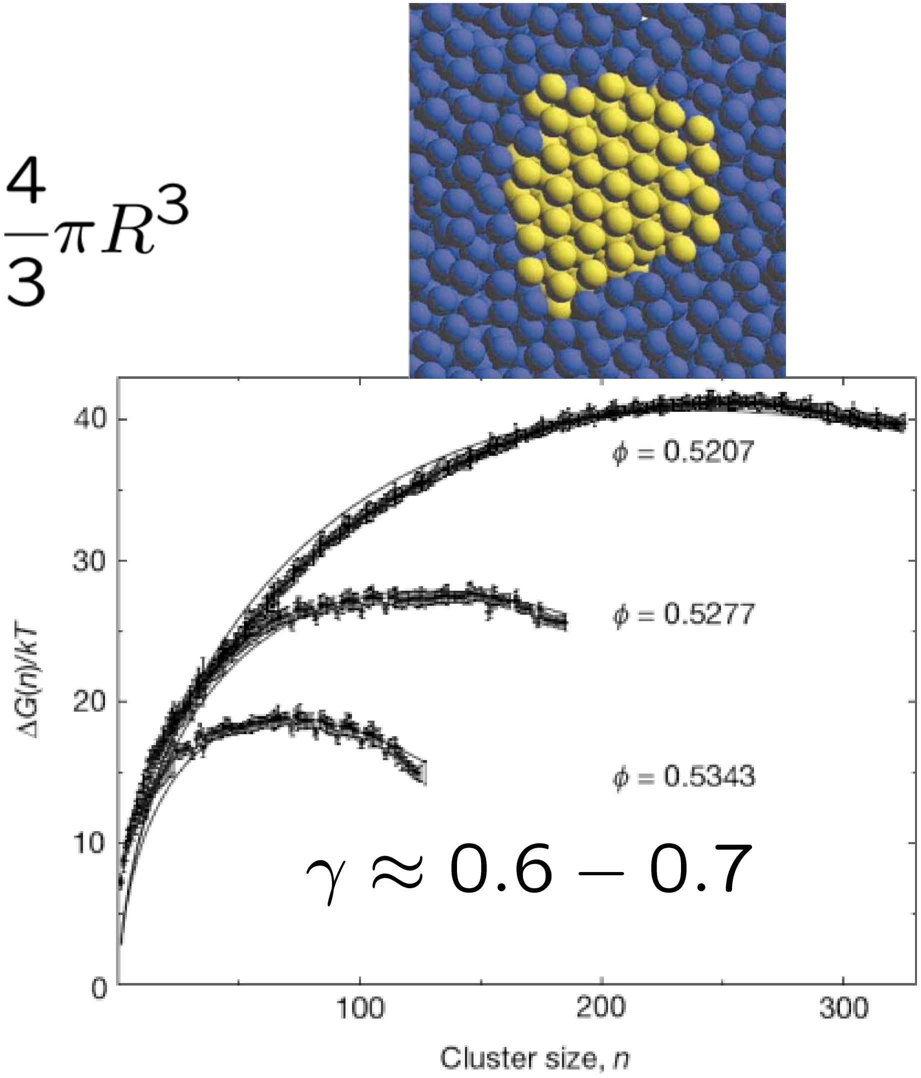


Crystal Nucleation

$$\Delta G(R) = \gamma 4\pi R^2 - \Delta\mu\rho_s\frac{4}{3}\pi R^3$$



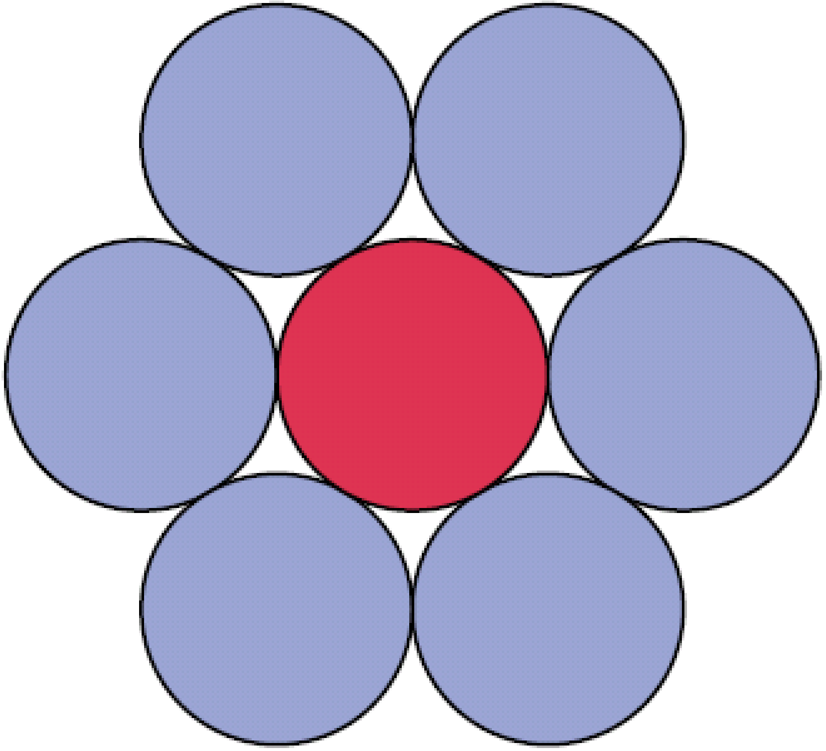
$$\Delta G^{\dagger}(R^*) = \frac{16\pi\gamma^3}{3(\Delta\mu)^2}$$



$$\gamma \approx 0.6 - 0.7$$

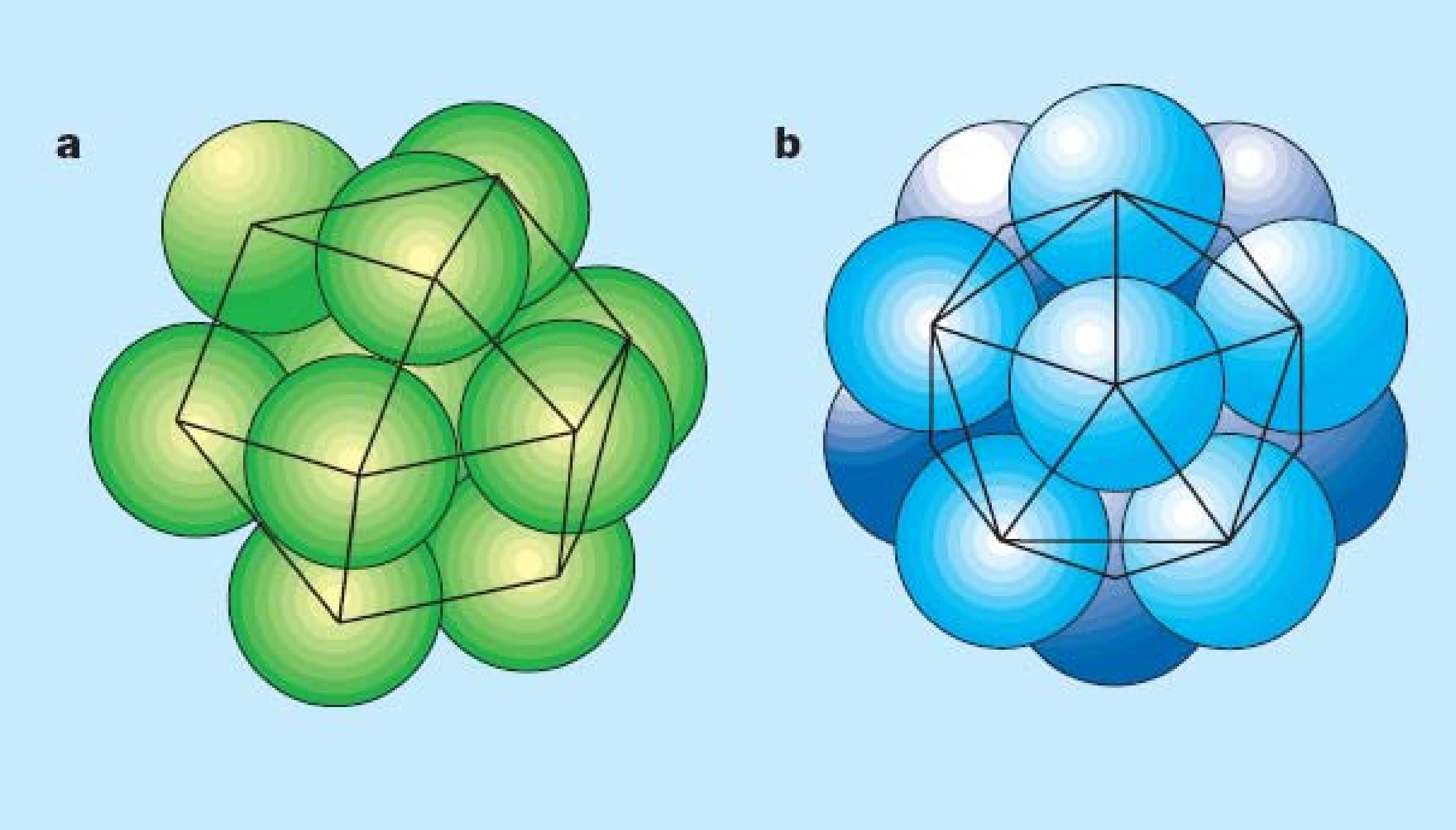
Auer and Frenkel (2002)

2D Local and Global Packing



Perfect Hexagon

3D Global vs. Local Packing

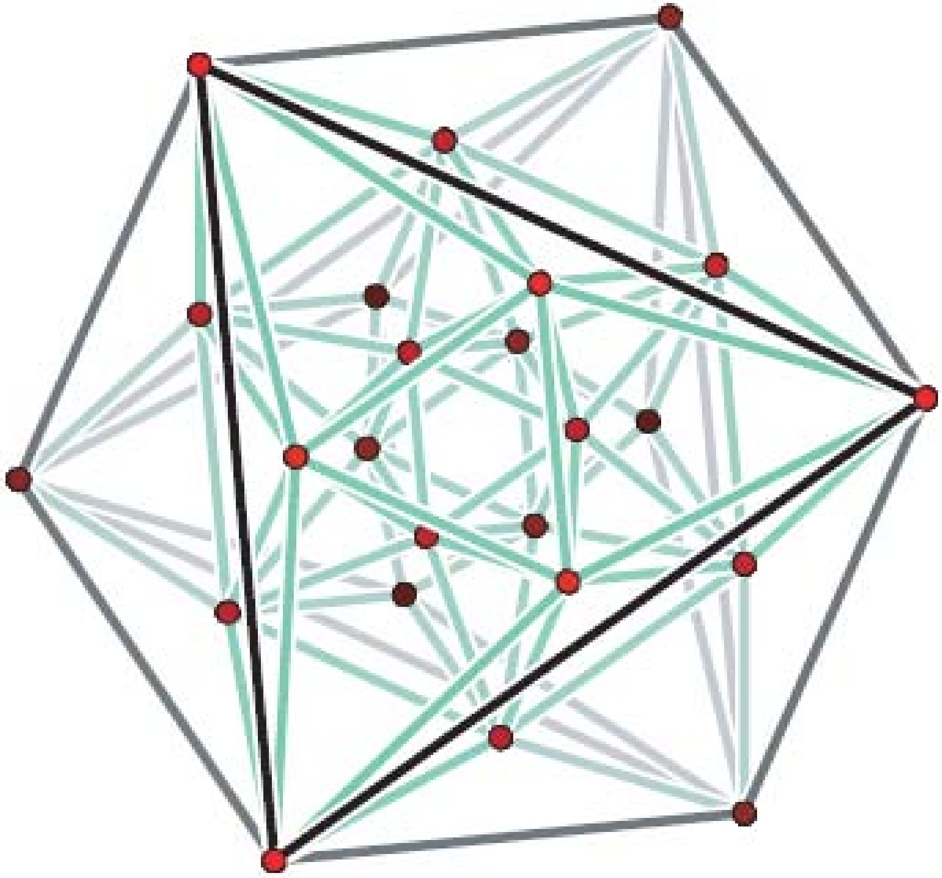


FCC Unit Cell

Perfect Icosahedron

Spaepen (2000)

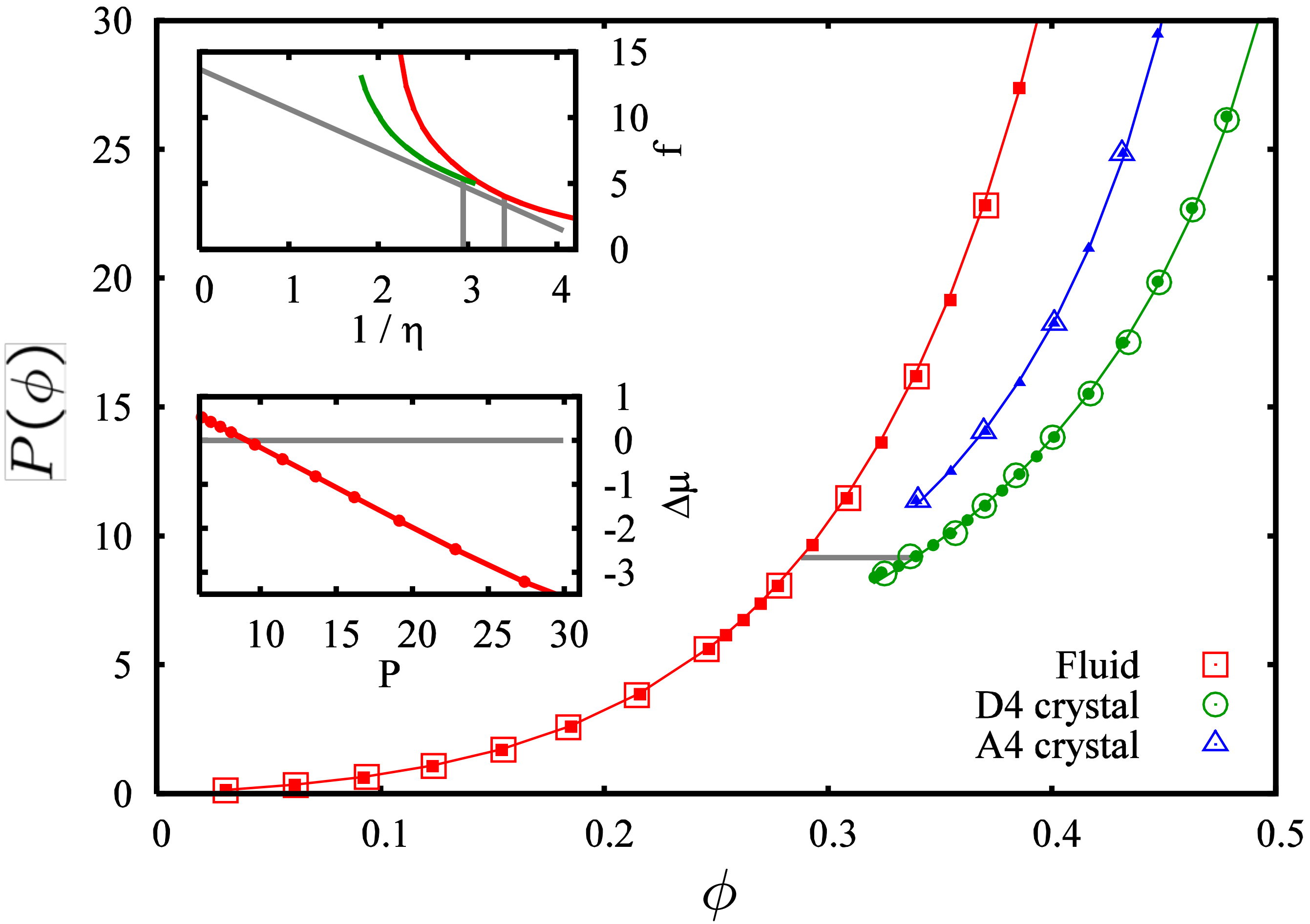
4D Local and Global Packing



24-cell (24 vertices)

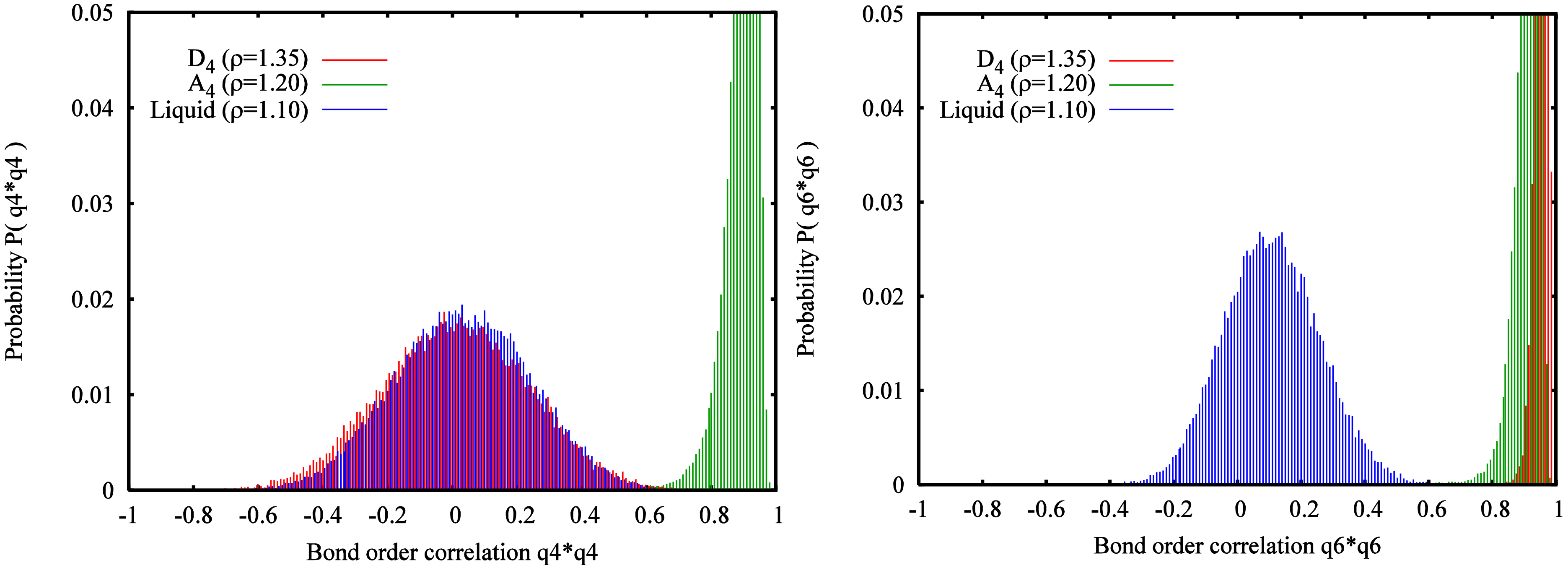
Musin (2003)

4D Hard Sphere Phase Diagram

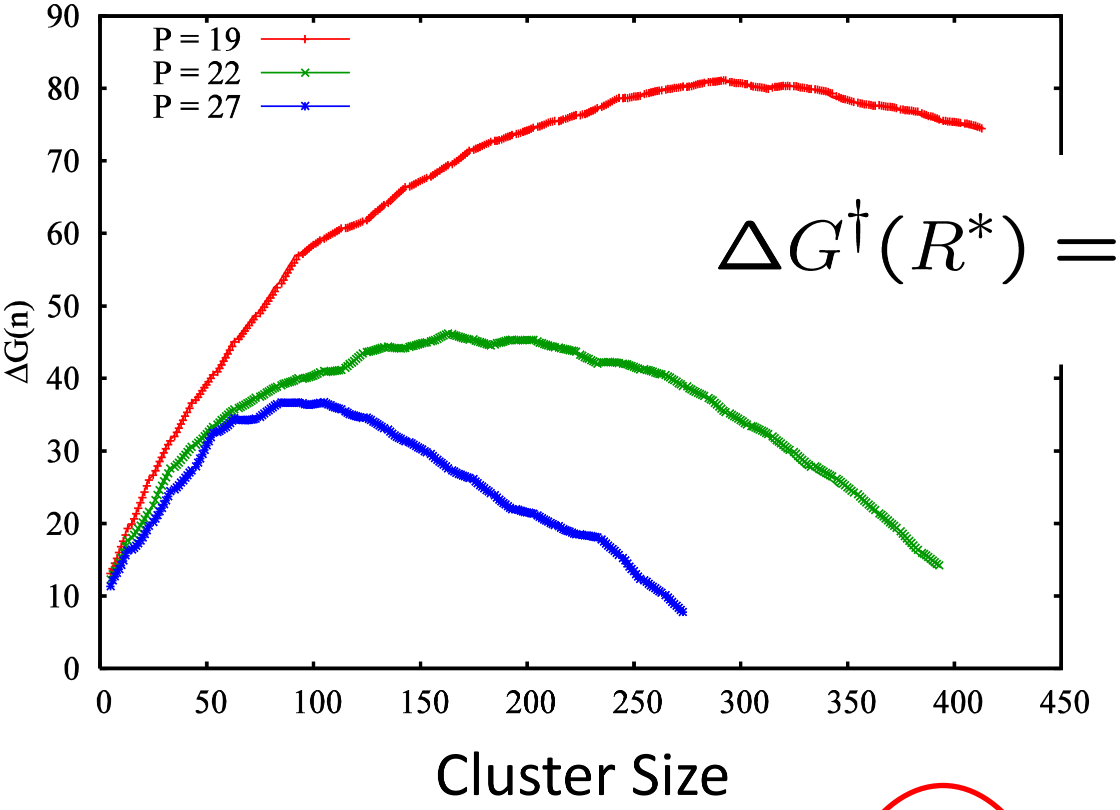


van Meel *et al.* (2009)

Order Parameter

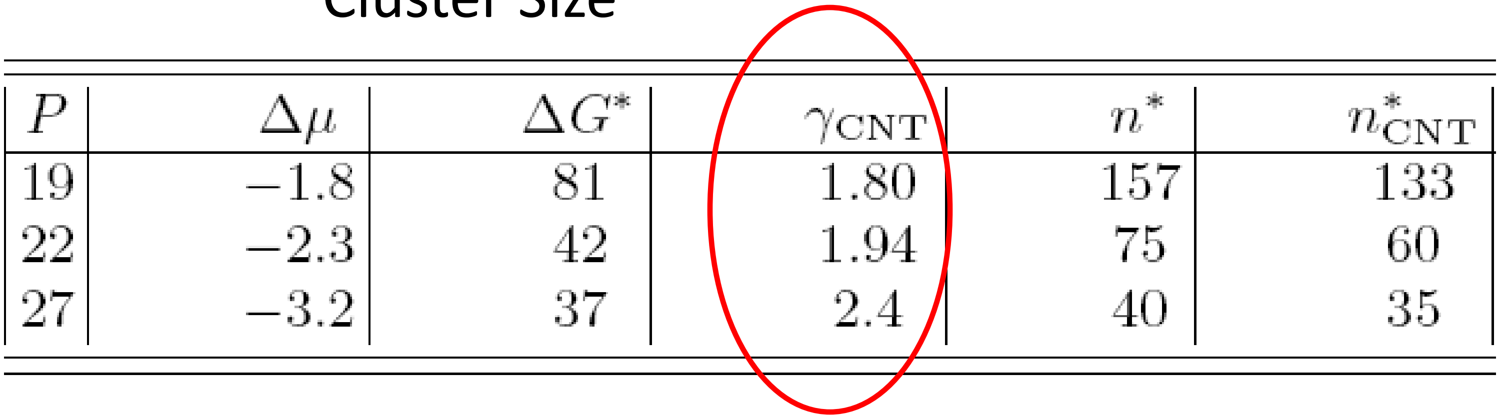


Nucleation Barrier



$$\Delta G^{\dagger}(R^{*}) = \frac{27\pi^{2}\gamma^{4}}{2\rho_{D_4}^{3}\Delta\mu^{3}}$$

In 3D, the surface tension is 2-3 times smaller for similar supersaturations!



P	$\Delta\mu$	ΔG^{*}	γ_{CNT}	n^{*}	n^{*}_{CNT}
19	-1.8	81	1.80	157	133
22	-2.3	42	1.94	75	60
27	-3.2	37	2.4	40	35