Lecture 2

D. Frenkel, Boulder, July 6, 2006

Lecture 2+3: Simulations of Soft Matter

1. Why Lecture 1 was irrelevant…
2. Coarse graining
3. Phase equilibria
4. Applications

An atom	3Å	1 atom
A Colloid	300nm	10^9 atoms
A cell	30 μm	10^{15} atoms
A pebble	3cm	10^{23} atoms

Don't try atomistic simulations

What distinguishes Colloids from atoms or pebbles?

Size?   (1 nm – 1 μm)
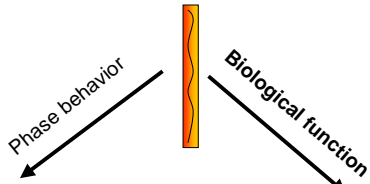
No: distinguish through properties

Distinction between small molecules and colloids:

To understand the behavior of colloids we do NOT need to know their structure in atomic detail.

Consequence:

Molecules may behave like colloids in **SOME** respects, but not in others…

Example: TMV

Phase behavior

Biological function

Colloid

Only overall shape, charge and flexibility matter

Not a colloid…

Precise sequence matters…

Question: Is a Pebble a colloid?

Colloids can be described by statistical mechanics:

Relevant energies $\mathbf{O}(k_B T)$

Example: barometric height distribution

colloids

pebbles

$P(h) = \exp(-mgh/kT)$

$\langle h \rangle = kT/mg$

Should be larger than particle size.

For colloids:

$\langle h \rangle = kT/mg = kT/(4\pi/3 \, \rho \, R^3 \, g)$

Must be of order R.

$kT/(4\pi/3 \, \rho \, R^3 \, g) = R$

$kT/(4\pi/3 \, \rho \, g) = R^4$

$\Rightarrow 2R = \sigma \approx 1\mu$

on earth…

Experiment

For pebbles (e.g. 50 g)

$\langle h \rangle = kT/mg = 10^{-18}$ cm

on earth…

For colloids:

$\langle h \rangle = kT/mg = kT/(4\pi/3 \, \rho \, R^3 \, g)$

Must be of order R.

$kT/(4\pi/3 \, \rho \, R^3 \, g) = R$

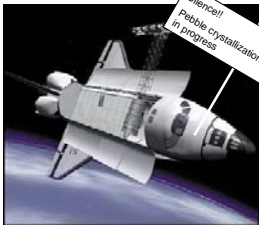$kT/(4\pi/3 \, \rho \, g) = R^4$

$\Rightarrow 2R = \sigma \approx 1\mu$

on earth…

For pebbles (e.g. 50 g)

$\langle h \rangle = kT/mg = 10^{-18}$ cm

on earth…

Is a pebble in space a colloid?

Silence!!
Pebble crystallization experiment in progress

To explore possible structures, the colloids must diffuse at least their own radius during an experiment:

2D $t_{exp} = R^2$, but $D = kT/(6\pi\eta R)$. Therefore:
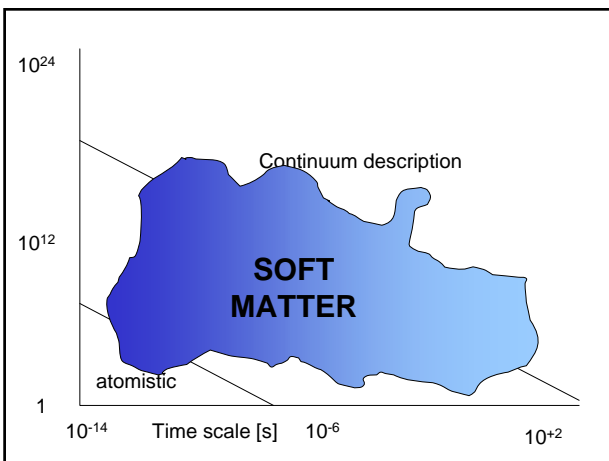

$t_{exp} \approx 3\pi\eta R^3/kT$

For 1 μ colloids in water:

$t_{exp} \approx 1$ sec

But

For 1 cm pebbles in water:

$t_{exp} \approx 10^{12}$ sec !!!

10^{24}

Continuum description

10^{12}

SOFT MATTER

atomistic

1

10^{-14} Time scale [s] 10^{-6} 10^{+2}

Most simulations of soft matter use coarse grained models:

1. Lattice models ("Be wise –discretize")
2. Pseudo-atomistic models (pearl-necklace polymers, polymers as soft spheres, dissipative particle dynamics etc etc etc
3. Quasi continuum models (particles + (charge)density fields, particles + hydrodynamic fields, etc etc etc)

The models for dynamics are all different

(# of models ≈ # of researchers)

But there are some general classifications:

1. Models with Newtonian dynamics on coarse-grained objects.
2. Stochastic dynamics WITH momentum conservation (yields hydrodynamics)
3. Stochastic dynamics WITHOUT momentum conservation (does not reproduce hydrodynamics)

Simulations of soft matter are time consuming:

1. Because of the large number of degrees of freedom (**solution: coarse graining**)
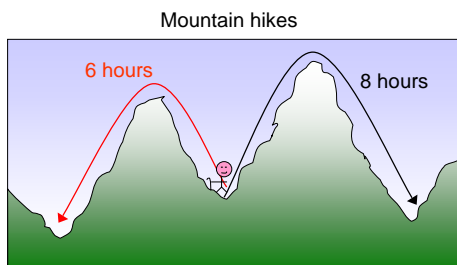2. Because the dynamics is intrinsically slow. Examples:
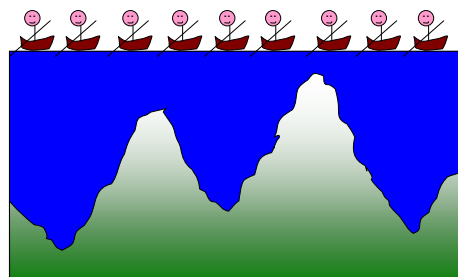
   1. Polymer dynamics $\quad \tau \sim N^3$

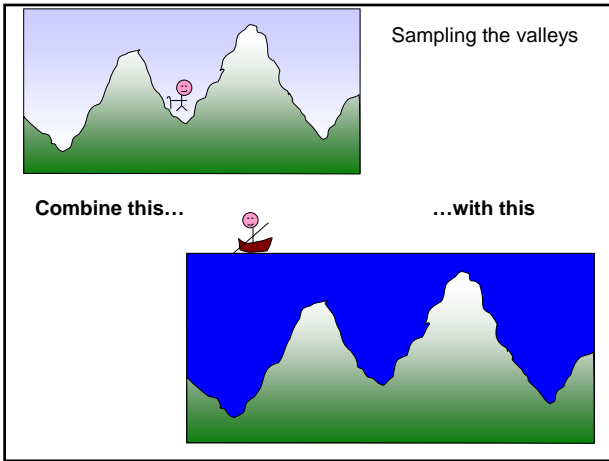   2. Hydrodynamics $\quad \tau \sim L^2/\nu$

   3. Activated dynamics $\quad \tau \sim e^{-\Delta G/kT}$

Slow dynamics implies slow equilibration. This is particularly serious for glassy systems.

Mountain hikes

6 hours

8 hours

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20 minutes

Sampling the valleys

Combine this…   **…with this**

Parallel Tempering

COMBINE Low-temperature and high-temperature runs in a SINGLE Parallel simulation

In practice:

System 1 at temperature T_1

System 2 at temperature T_2

Boltzmann factor
$$\exp(-\beta_1 U_1(r^N))$$

Boltzmann factor
$$\exp(-\beta_2 U_2(r^N))$$

Total Boltzmann factor

$$\exp(-\beta_1 U_1(r^N))\exp(-\beta_2 U_2(r^N))$$

SWAP move

System 1 at temperature T_2
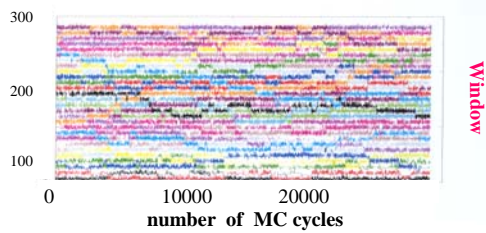
System 2 at temperature T_1

Boltzmann factor
$$\exp(-\beta_2 U_1(r^N))$$

Boltzmann factor
$$\exp(-\beta_1 U_2(r^N))$$

Total Boltzmann factor

$$\exp(-\beta_2 U_1(r^N))\exp(-\beta_1 U_2(r^N))$$

Ratio

$$\frac{\text{new Boltzmann weight}}{\text{old Boltzmann weight}}$$

$$=$$

$$\exp\{-(\beta_1 - \beta_2)[\mathcal{U}_2(\mathbf{r}^N) - \mathcal{U}_1(\mathbf{r}^N)]$$

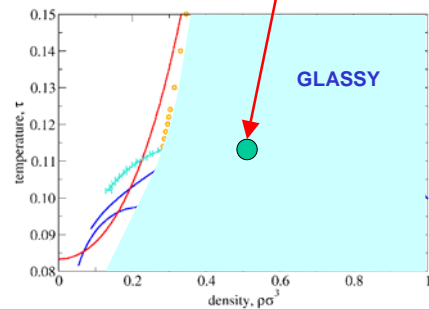Systems may swap temperature if their combined Boltzmann factor allows it.

$$\mathrm{acc(swap)}$$

$$=$$

$$\min\left(1, \exp\{-(\beta_1 - \beta_2)[\mathcal{U}_2(\mathbf{r}^N) - \mathcal{U}_1(\mathbf{r}^N)]\}\right)$$

number of MC cycles

Window

NOTES:

1. One can run MANY systems in parallel
2. The control parameter need not be temperature

Application: computation of a critical point INSIDE the glassy phase of "sticky spheres":

GLASSY

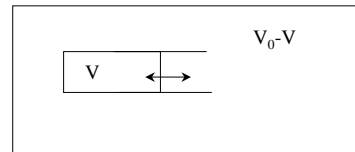Most experiments are not performed at constant Volume, but at constant pressure.

Can we do simulations at constant pressure?

Start from partition function Q(N,V,T):

Constant-pressure Monte Carlo

$$Q_{tot}(M,N,V_0,V,T) = Q(N,V,T) \times Q(M,V_0-V,T)$$

$$\mathcal{P}(V) = \frac{Q(N,V,T)Q(M,V_0-V,T)}{\int dV\, Q(M,N,V_0,V,T)}$$

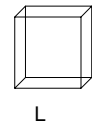$$\boxed{\mathcal{P}(V) = \frac{Q(N,V,T)Q(M,V_0-V,T)}{\int dV\, Q(M,N,V_0,V,T)}}$$

$$Q(M,V_0-V,T) = \exp(-F(M,V_0-V,T)/kT)$$

$$
\begin{aligned}
F(M,V_0-V,T) &\approx F(M,V_0,T) - V\left(\frac{\partial F}{\partial V}\right) \\
&= F(M,V_0,T) + PV
\end{aligned}
$$

$$\mathcal{P}(V) = \frac{Q(N,V,T)e^{-PV/kT}}{\int dV\, Q(N,V,T)e^{-PV/kT}}$$

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

Introduce "scaled" coordinates:

$$\mathbf{r} \equiv L\mathbf{s}$$

L

$$Q(N,V,T) = \frac{V^N}{\Lambda^{3N}N!}\int d\mathbf{s}^N \exp[-\beta\mathcal{U}(\mathbf{s}^N,V)]$$

$$\mathcal{P}(V, \mathbf{s}^N) = c \, \exp[-\beta \mathcal{U}(\mathbf{s}^N, V)] V^N e^{-\beta P V}$$

(c = normalisation constant)

Write this as:

$$\mathcal{P}(V, \mathbf{s}^N) = c \, e^{-\beta[\mathcal{U}(\mathbf{s}^N, V) + PV - NkT \ln V]}$$
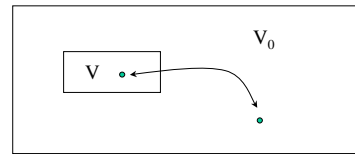
Looks like a Boltzmann weight.

Now we can do standard Metropolis sampling on the scaled coordinates $\mathbf{s}^N$ … AND the volume **V**.

$$P_{acc}(V \to V') = \min\{1, e^{-\beta[\mathcal{U}(\mathbf{s}^N, V') - \mathcal{U}(\mathbf{s}^N, V) + P(V'-V) - NkT \ln(V'/V)]}\}$$

Similarly: Grand-Canonical Monte Carlo

$$\mathcal{P}(N, \mathbf{s}^N) = c \, \frac{V^N}{N! \Lambda^{3N}} e^{-\beta \mathcal{U}(\mathbf{s}^N)} e^{N\beta\mu}$$

$$P_{acc}(N \to N+1) = \min\{1, \frac{V}{(N+1)\Lambda^3} e^{-\beta[\mathcal{U}(\mathbf{s}^{N+1}) - \mathcal{U}(\mathbf{s}^N) - \mu]}\}$$

V_0

V

Condition for phase coexistence in a one-component system:

$$T_1 = T_2$$

$$P_1 = P_2$$

$$\mu_1 = \mu_2$$

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

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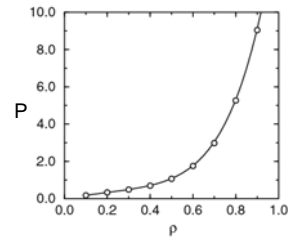
Solutions:

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:

$$F_{excess}(V) = F(V) - F_{id.gas}(V)$$

$$= F_{excess}(V_0) + \int_{V_0}^{V} (-P_{excess})dV$$

$\Rightarrow 0$, 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 $(1-\lambda)U_0 + \lambda\, U_1$: $F_\lambda(N,V,T)$.

$$F_\lambda(N,V,T) = \text{constant}-$$

$$kT \ln \int dr^N \exp(-\beta(\lambda U_1 + (1-\lambda)U_0))$$

hence

$$\frac{\partial F_\lambda(N,V,T)}{\partial \lambda} =$$

$$\frac{\int dr^N (U_1 - U_0)\exp(-\beta(\lambda U_1 + (1-\lambda)U_0))}{\int dr^N \exp(-\beta(\lambda U_1 + (1-\lambda)U_0))}$$

Or:

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

And therefore

$$F_1(N,V,T) = F_0(N,V,T) + \int_0^1 \langle U_1 - U_0 \rangle_\lambda d\lambda$$
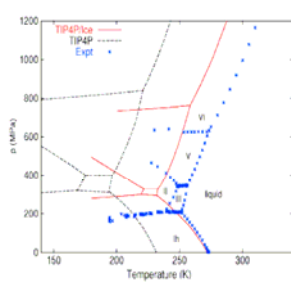
Example of application: testing models for water

FIG. 1. The phase diagram of TIP4P Ice (full lines) and TIP4P (dashed) compared to the experiment (stars). The labels mark the domain of stability of the ice phases in the experimental phase diagram.

J. L. F. Abascal, E. Sanz, R. García Fernández, and C. Vega, J.C.P. **122**, 234511 (2005)

You can think up your own thermodynamic integration schemes…

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

$$Q(N,V,T) = \frac{1}{N!\Lambda^{3N}} \int dr^N \exp(-\beta U(r^N)) =$$

$$\frac{1}{N!\Lambda^{3N}} V^N \int ds^N \exp(-\beta U(s^N; L)$$

s is a scaled coordinate: 0≤**s**<1

r = L **s**   (**L** is box size)

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

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

Now write

$$U((s^{N+1}) \equiv U(s^N) + \Delta U(s_{N+1}, s^N)$$

then

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

$$\frac{V}{(N+1)\Lambda^3} \int ds_{N+1} \langle \exp(-\beta \Delta U(s_{N+1}, s^N)) \rangle$$

And therefore

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

$$-kT \ln \left(\frac{V}{(N+1)\Lambda^3} \right) =$$

but

$$kT \ln(\rho \Lambda^3) = \mu_{id.gas}$$

So, finally, we get:

$$\mu = \mu_{id.gas} - kT \ln \left(\int ds_{N+1} \langle \exp(-\beta \Delta U(s_{N+1}, s^N)) \rangle \right)$$

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" $< \exp(-\beta \Delta U) >$

4. Then:

$$\mu_{excess} = -kT \ln < \exp(-\beta \Delta U) >$$

$$\mu_{excess} = -kT \ln < \exp(-\beta \Delta U) >$$

For repulsive interactions:
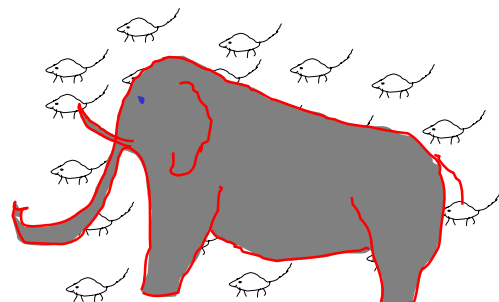
$$< \exp(-\beta \Delta U) > = \text{Acceptance Probability}$$

Intuitive interpretation:

Excess chemical potential measures how difficult it is to insert a particle at random without creating overlaps.

ACCEPTANCE OF RANDOM INSERTION DEPENDS ON SIZE
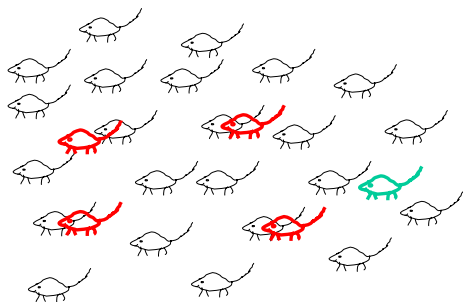
ACCEPTANCE OF RANDOM INSERTION DEPENDS ON SIZE

Particle insertion continued....

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

therefore

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

But also

$$\mu \approx +kT \ln \frac{Q(N,V,T)}{Q(N+1,V,T)}$$

As before:

$$Q(N,V,T) = \frac{1}{N!\Lambda^{3N}} \int dr^N \exp(-\beta U(r^N)) =$$

$$\frac{1}{N!\Lambda^{3N}} V^N \int ds^N \exp(-\beta U(s^N; L))$$

With **s** a scaled coordinate: $0 \leq$ **s** < 1

r = L **s**   (L is box size)

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

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

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

Now write

$$U((s^N) \equiv U(s^{N+1}) - \Delta U(s_{N+1}, s^N)$$

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

$$\frac{(N+1)\Lambda^3}{V} \langle \exp(+\beta \Delta U(s_{N+1}, s^N)) \rangle_{N+1}$$

And therefore

$$\mu = \mu_{id.gas} + kT \ln \left(\langle \exp(+\beta \Delta U(s_{N+1}, s^N)) \rangle_{N+1} \right)$$

Interpretation:

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

2. Compute $\exp(+\beta\Delta U)$

3. Repeat M times and compute the average "Boltzmann factor"

4. Then

$$\mu_{excess} = +kT \ln < \exp(+\beta\Delta U) >$$

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:

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

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:

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

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

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

so

$$p_1(\Delta U) = \exp(-\beta\Delta U)\frac{Q_N}{Q_{N+1}}p_0(\Delta U)$$

but $\frac{Q_N}{Q_{N+1}} = \exp(+\beta\mu)$ hence

$$p_1(\Delta U) = \exp(-\beta\Delta U)\exp(\beta\mu)p_0(\Delta U)$$

Rewrite:

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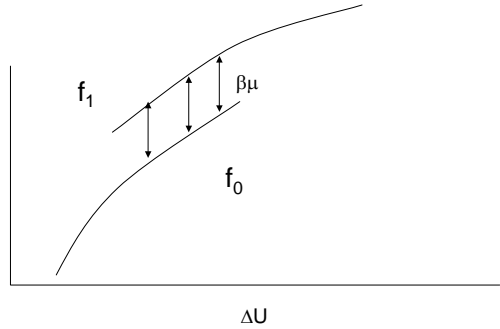
define

$$f_1(\Delta U) \equiv \ln(p_1(\Delta U)) + \beta \Delta U/2$$

$$f_0(\Delta U) \equiv \ln(p_0(\Delta U)) - \beta \Delta U/2$$

Then:

$$f_1(\Delta U) = f_0(\Delta U) + \beta \mu$$

For **ALL** ΔU

Diagnostic test:

If the distributions do not overlap, **don't trust your results for μ**

Does it work for hard spheres?

consider $\Delta U = 0$

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

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

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

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