Free Energy and Phase Equilibria

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

Why Free Energies?

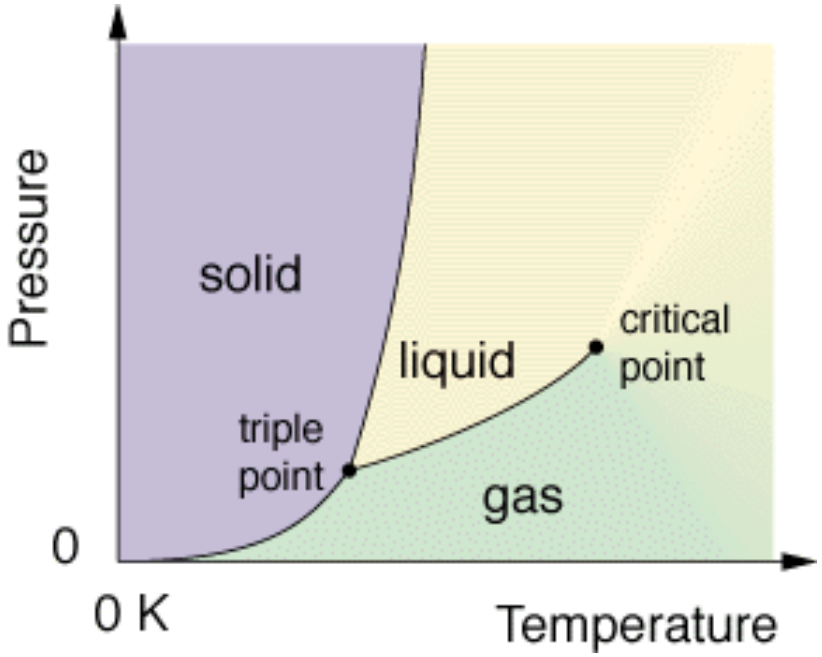
- Reaction equilibrium constants $A \leftrightarrow B$

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

- 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

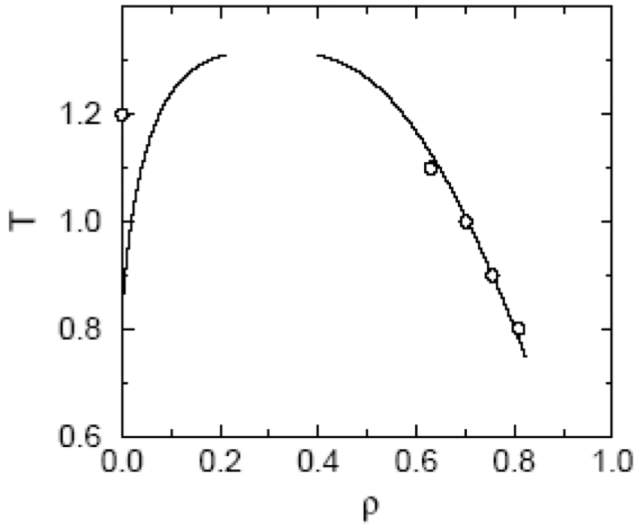
Phase diagrams



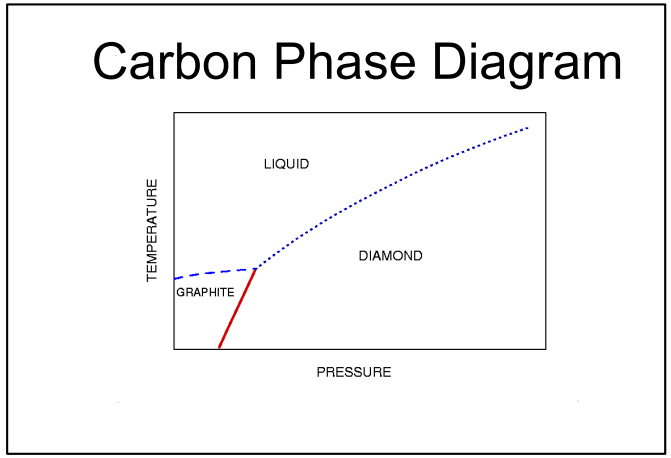
Critical point: no transition between liquid and vapor

Triple point: liquid, vapor and solid in equilibrium.

How do we compute these lines?



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



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 one-component system: 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:

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

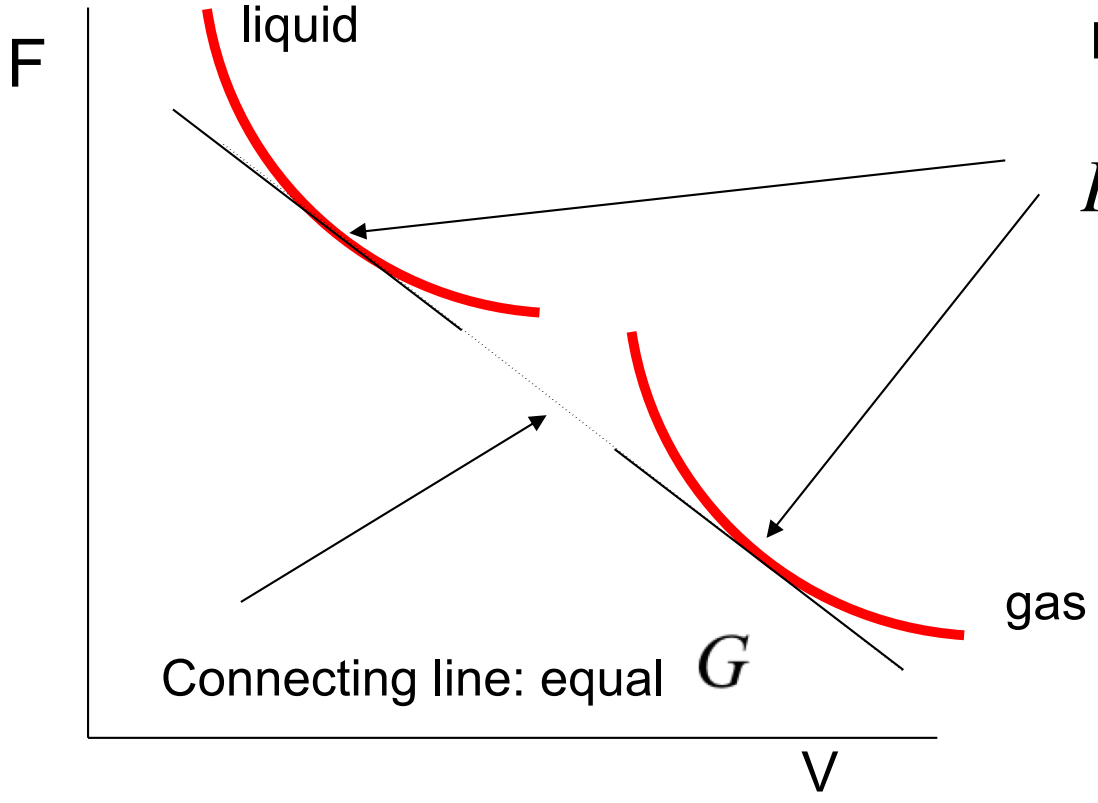
All thermodynamic quantities can be derived from F and its derivatives

Phase equilibria from F(V,T)

Common tangent construction

$$0 = \Delta G = \Delta F + P\Delta V$$

$$\boxed{\Delta F = -P\Delta V}$$



Equal tangents

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

We need F (or G)

- We can calculated F(V), using equation of state $P(V)$

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

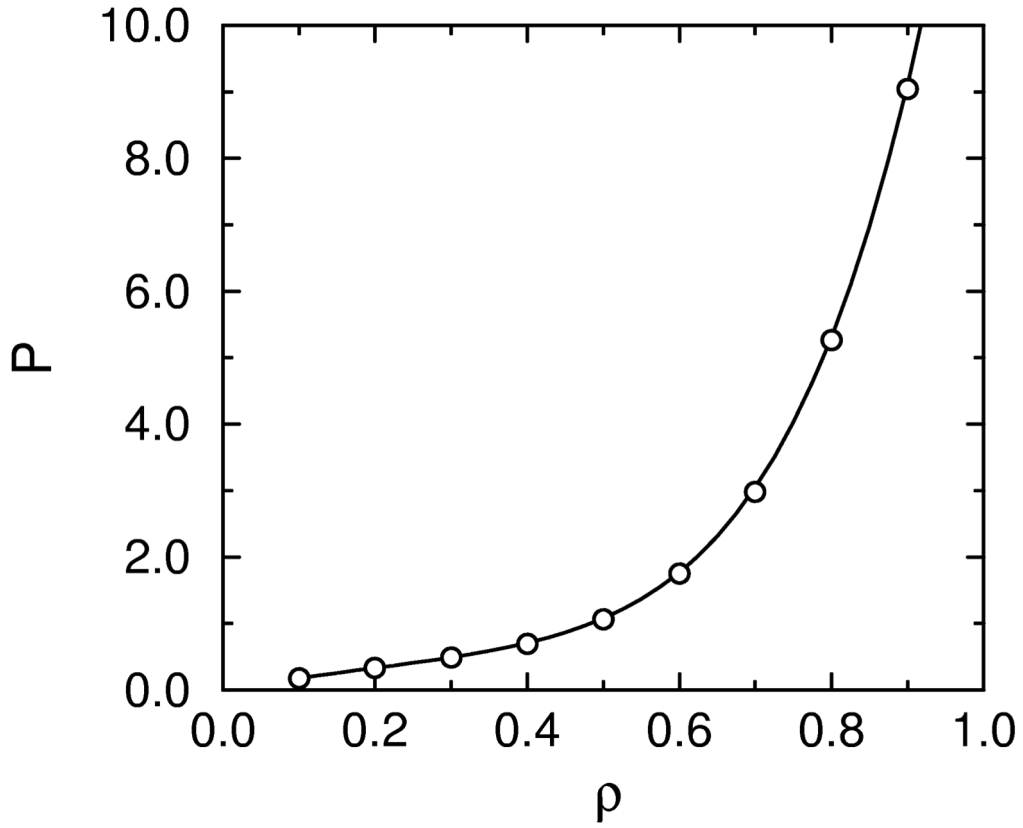
$$F(\rho) = F(\rho_0) + N \int_{\rho_0}^{\rho} \frac{P(\rho')}{\rho^2} \mathrm{d}\rho' \qquad (V = N/\rho)$$

- Note: for only 1 point of the equation of state F must be known

- 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



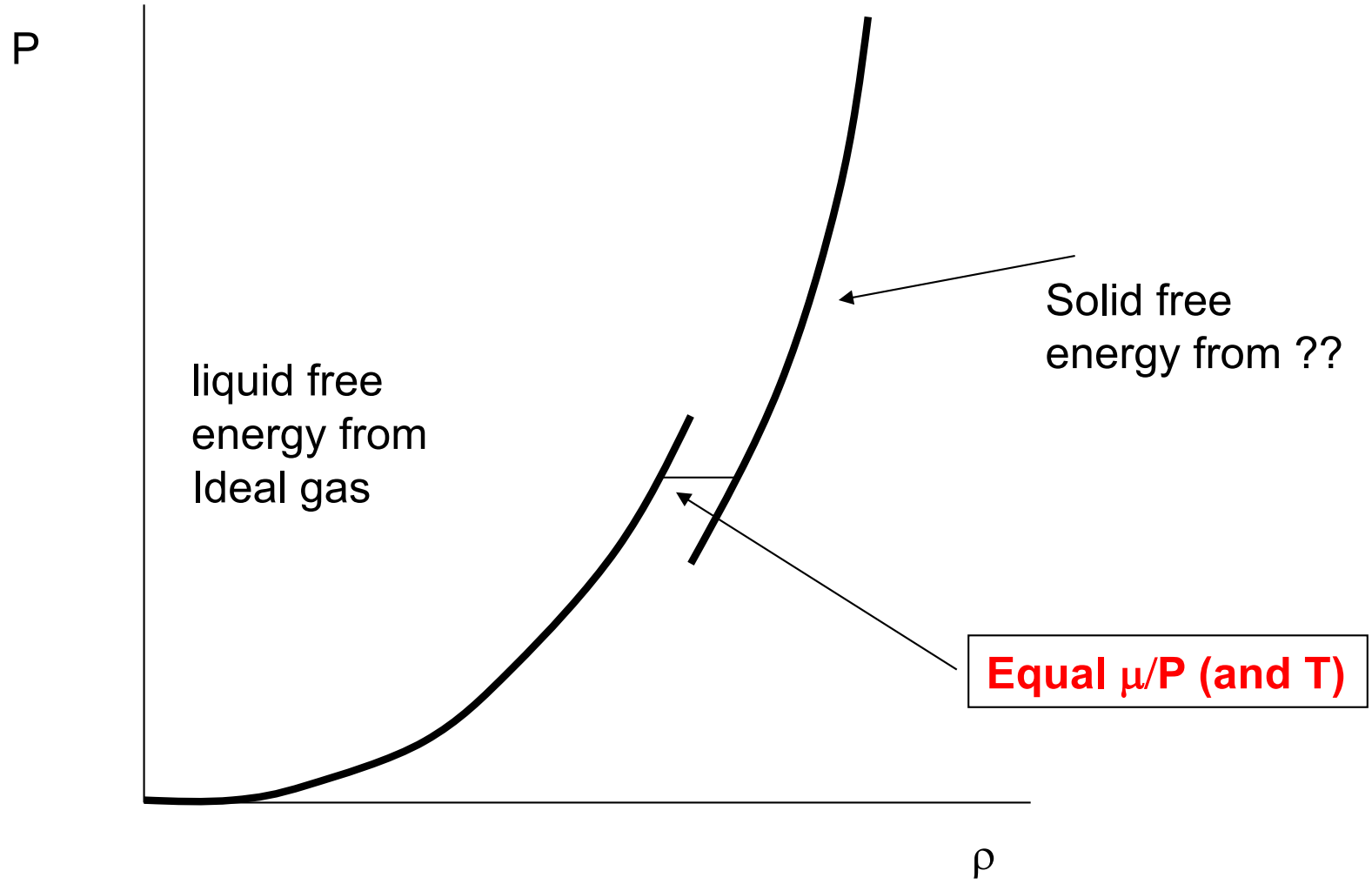
$$P = P(\rho, T)$$

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

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

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

Phase Equilibrium
Free Energy Liquid and Solid



Free Energies and Phase Equilibria

General Strategies

- Determine free energy of both phases separately, 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)

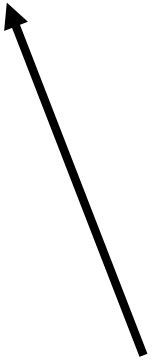
$$P\left(\mathrm{r}^N\right) = \frac{1}{Q_{NVT}} \frac{1}{\Lambda^{3N} N!} \int \mathrm{dr}'^N \delta\left(\mathrm{r}'^N - \mathrm{r}^N\right) \exp\left[-\beta U\left(\mathrm{r}'^N\right)\right] \propto \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]$$

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

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

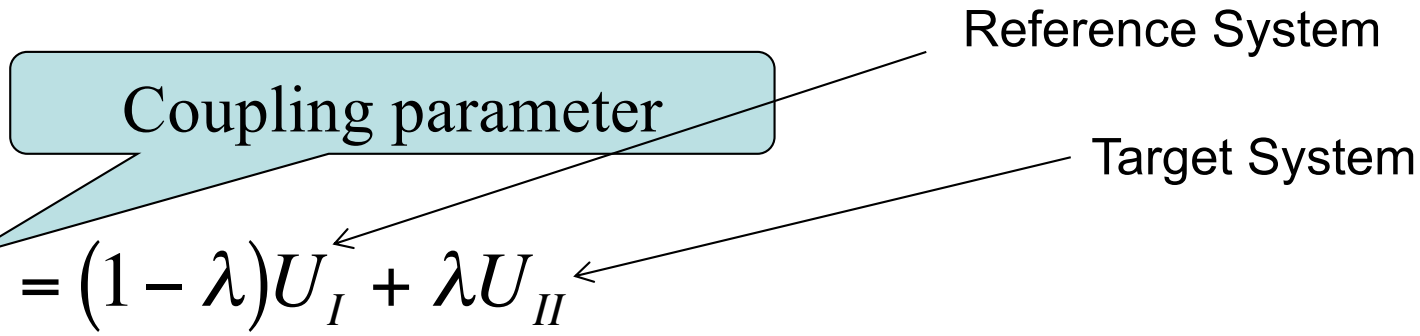


F is difficult, because requires measuring the phase space volume

This is **not** a weighted average … this is **not** sampling

I - Thermodynamic integration

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



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

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

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

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!

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

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

Examples

- 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 different example

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

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

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

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

Free energy of solid

More difficult. What is reference?

Not the ideal gas … but a system that has a “similar” spatial ordering

One (natural) choice is an **Einstein crystal**: harmonic oscillators around r_0

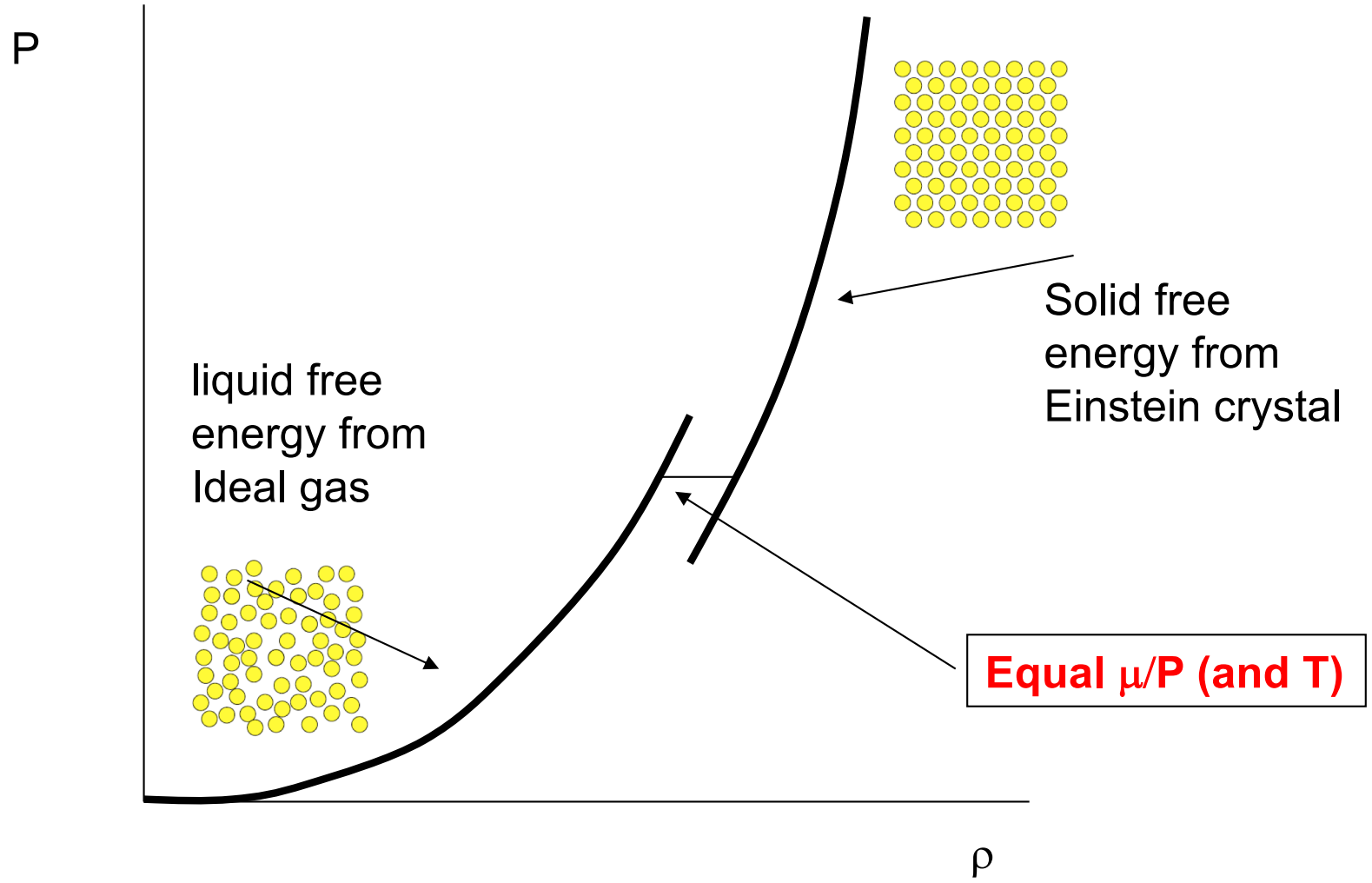
$$U\left(\lambda; r^N\right) = (1-\lambda)U\left(r^N\right) + \lambda U\left(r_0^N\right) + \lambda \sum_{i=1}^{N} \alpha (r_i - r_{0,i})^2$$

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

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



II - Thermodynamic perturbation

Two systems:

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

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

$$\Delta\beta F = \beta F_1 - \beta F_0 = -\ln\left(Q_1/Q_0\right)$$

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

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

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

Particle Insertion Method

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

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

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

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

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

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

$$\left.\begin{array}{l} \beta\mu = \beta\mu^{IG} + \beta\mu^{ex} \\ \beta\mu^{IG} \equiv \left(\dfrac{\partial \beta F^{IG}}{\partial N}\right)_{V,T} \quad \beta\mu^{ex} \equiv \left(\dfrac{\partial \beta F^{ex}}{\partial N}\right)_{V,T} \end{array}\right\}$$

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

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

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

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

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

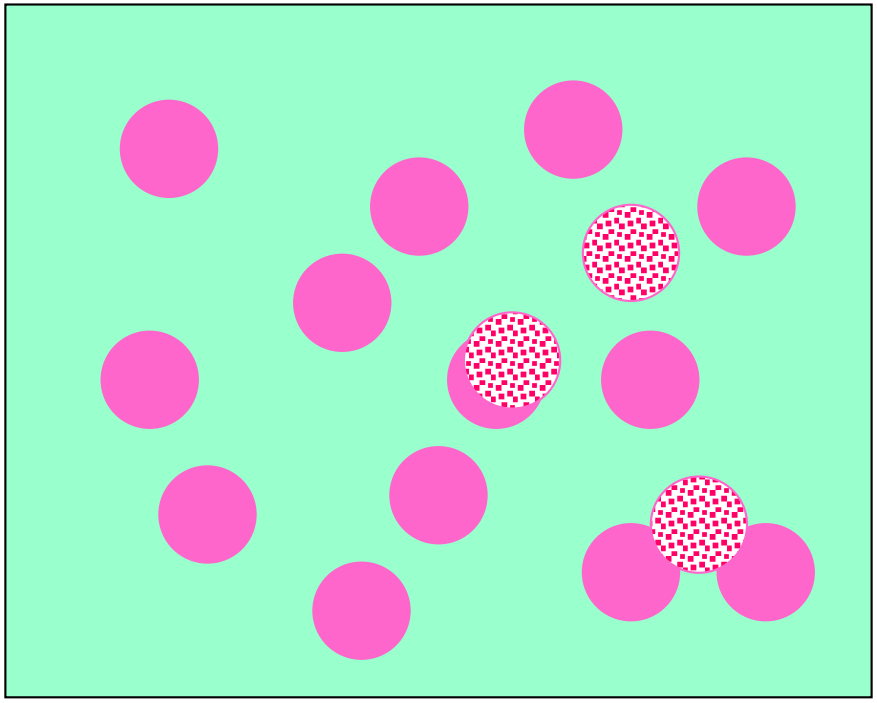
$$= -\ln\left(\int ds_{N+1} \left\langle \exp\left[-\beta\Delta U^{+}\right]\right\rangle_{NVT}\right)$$

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

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

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

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

Umbrella sampling

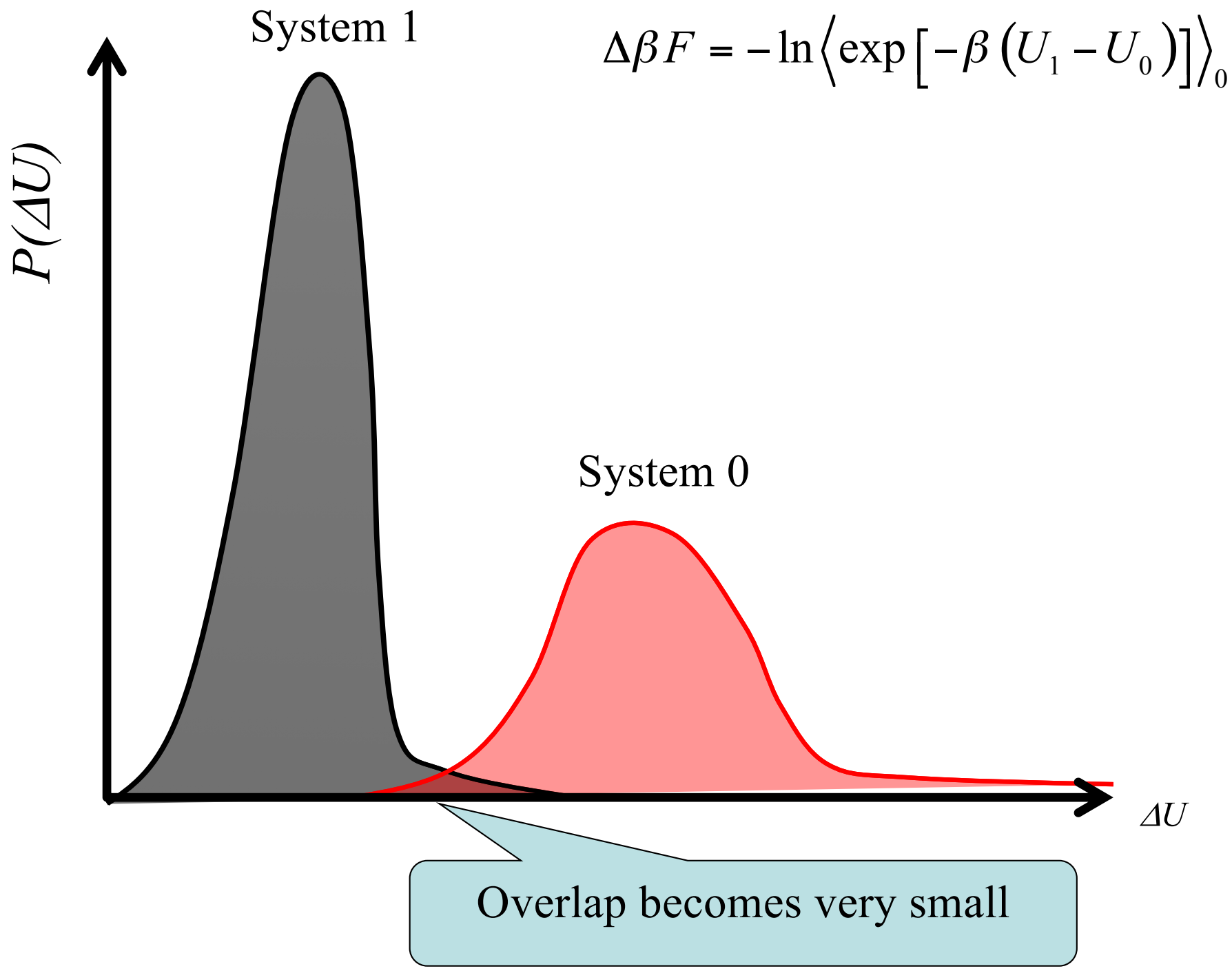
- Start with thermodynamic perturbation

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

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

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

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

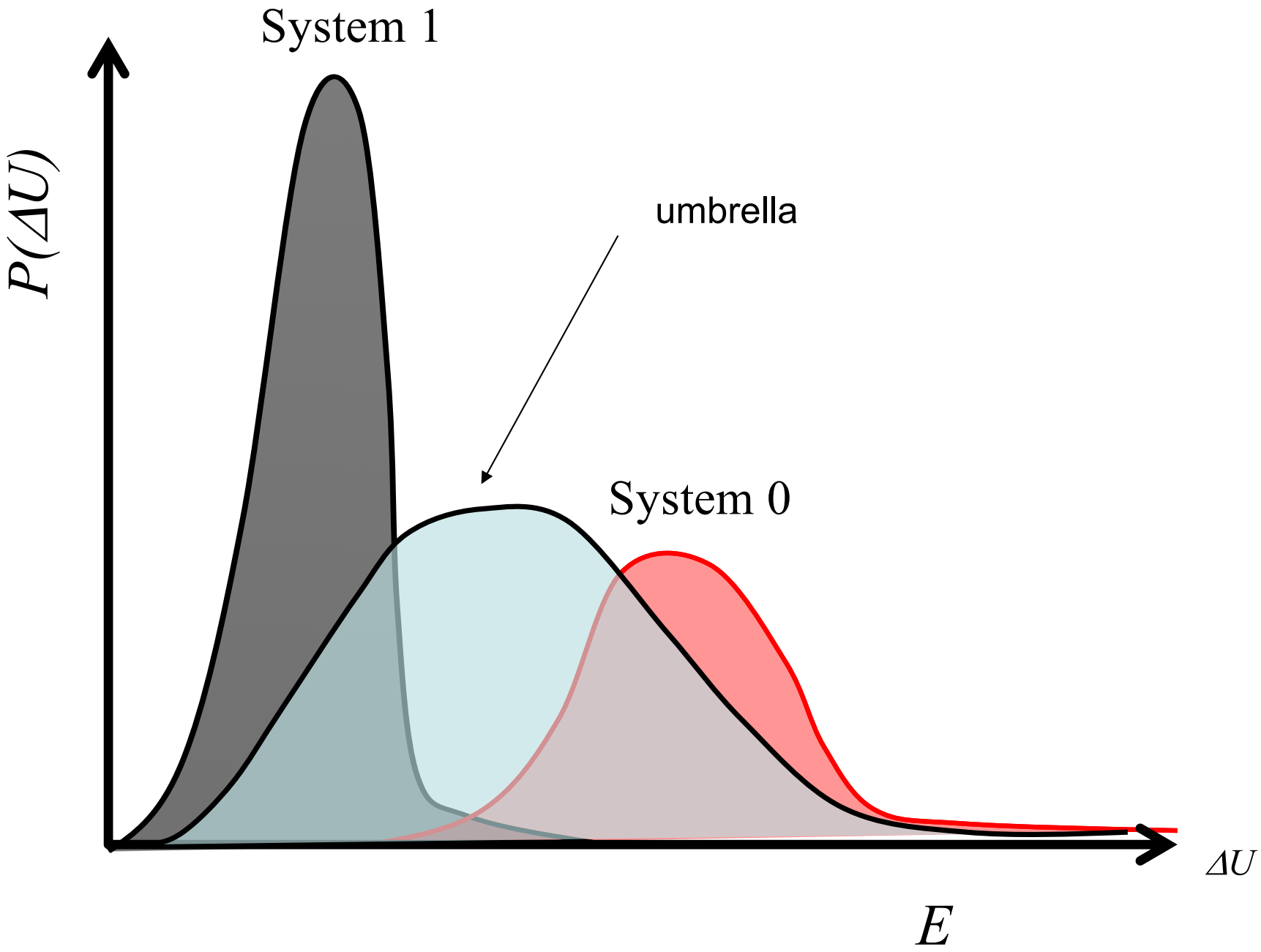
- Introduce function $\pi(s^N)$ altering distribution.

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

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

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

- 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 (LJ fluid)

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

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

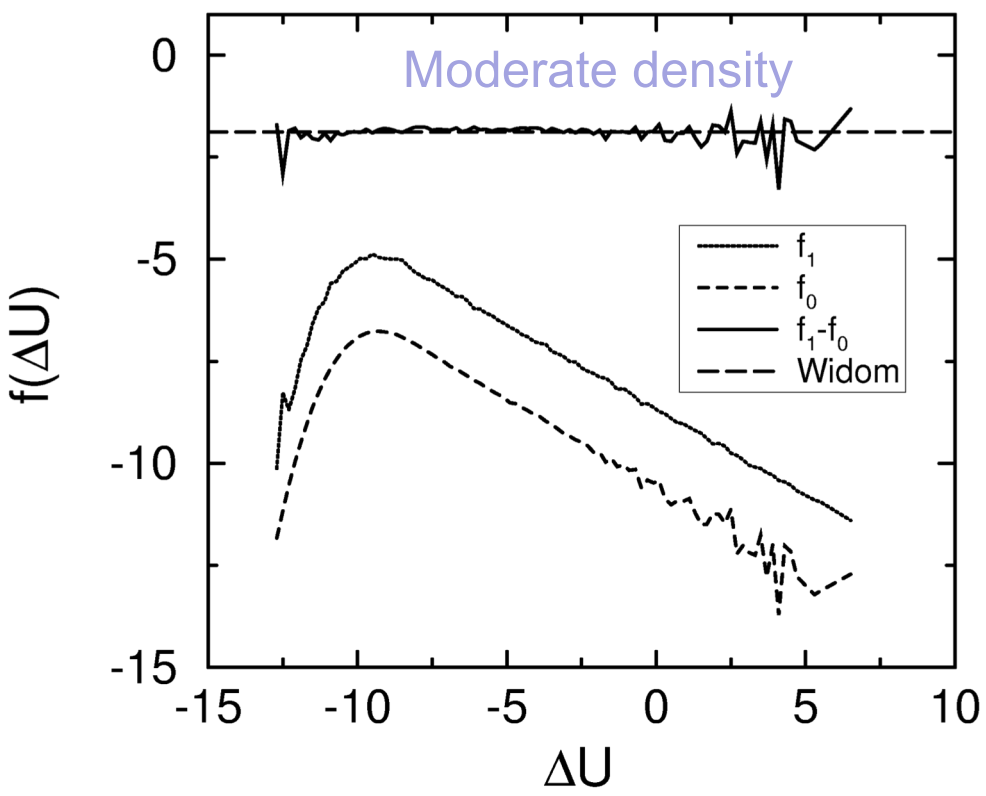
$$\Delta\beta F = \beta F_1 - \beta F_0 \equiv \beta\mu^{ex}$$

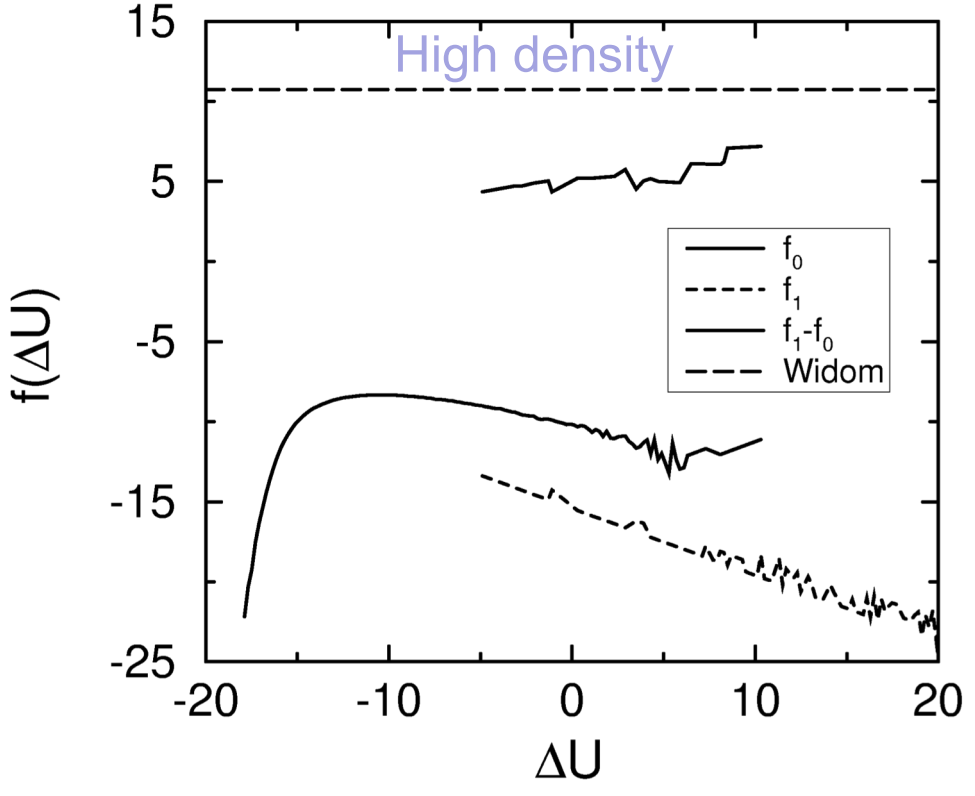
$$\Delta U = U_1 - U_0$$

System 0: test particle energy

System 1: real particle energy

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



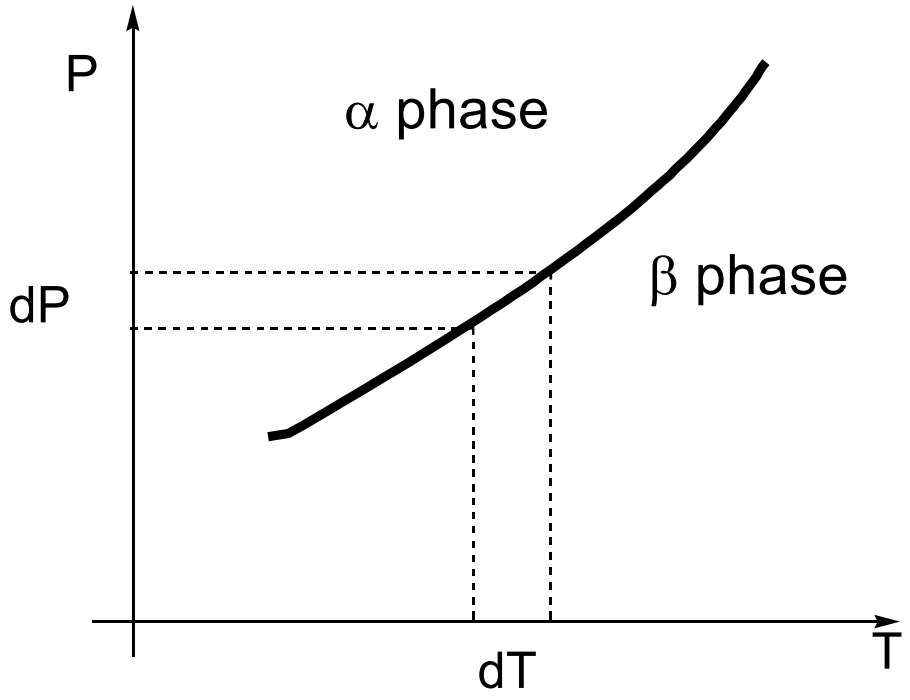


Tracing coexistence curves

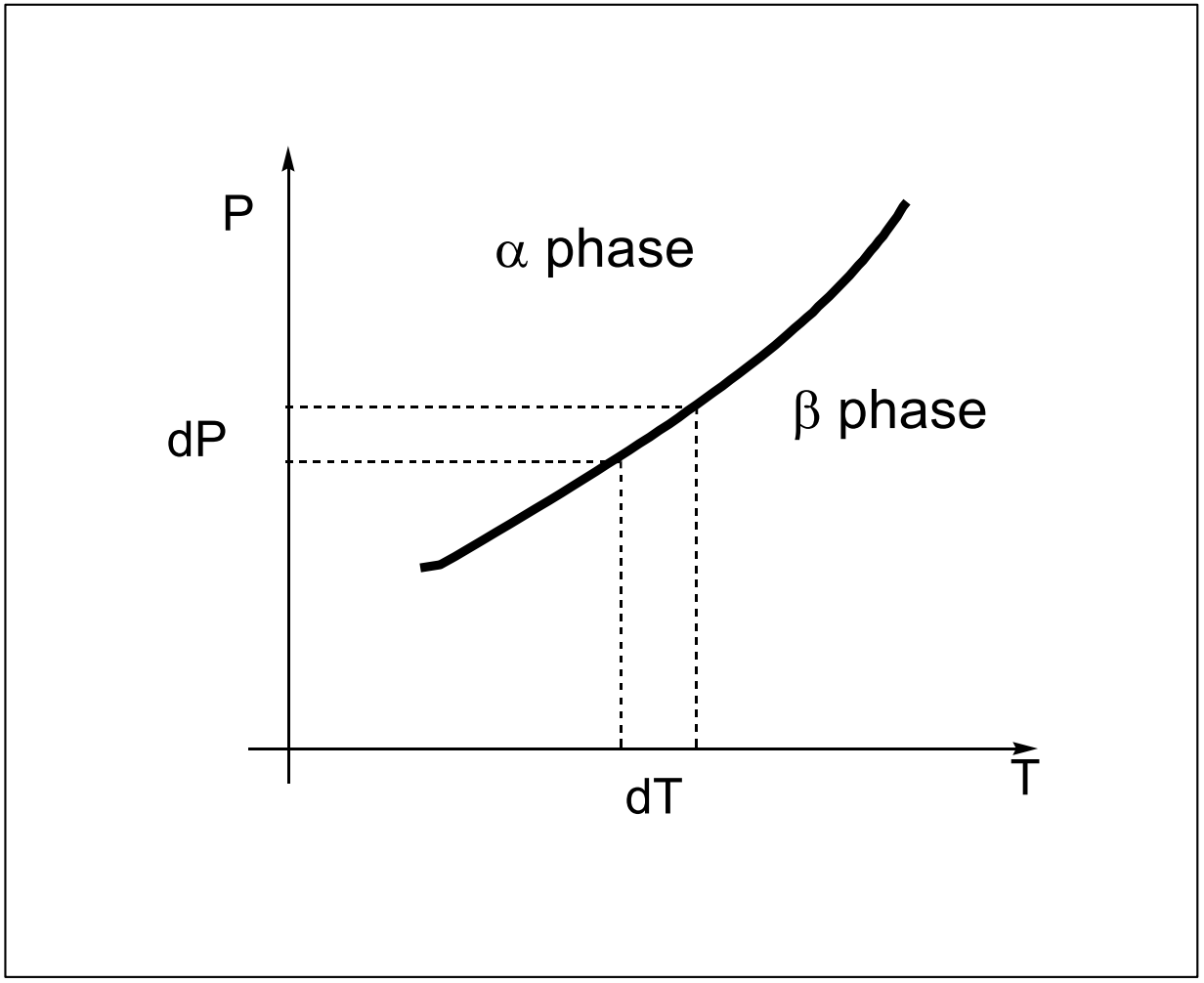
- If we have a coexistence point on the phase diagram we can integrate allong the line while maintaining coexistence.

P en T are equal along coexistence line

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



Tracing coexistence curves



Clapyeron equation

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

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

Example:
Carbon Phase Diagram