Free Energy and Phase equilibria

Thermodynamic integration 7.1
Chemical potentials 7.2
Overlapping distributions 7.2
Umbrella sampling 7.4

Why free energies?

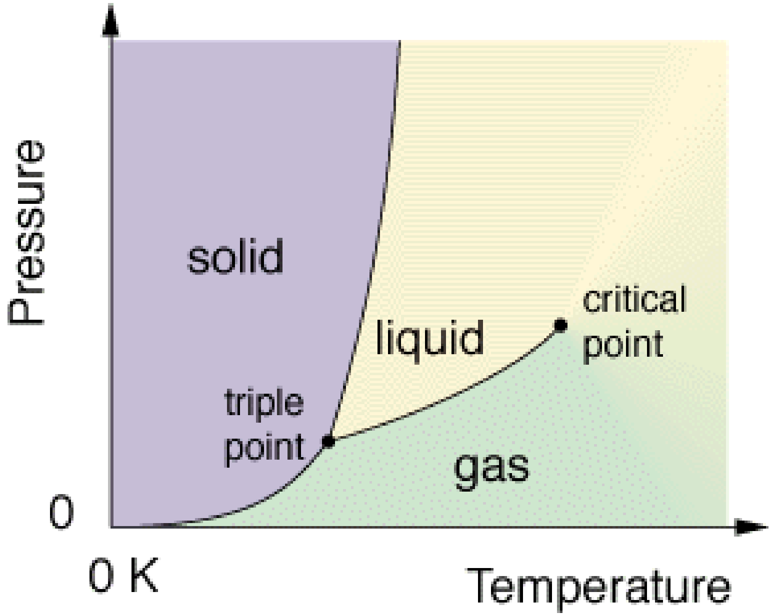
- Reaction equilibrium constants $A \leftrightarrow B$

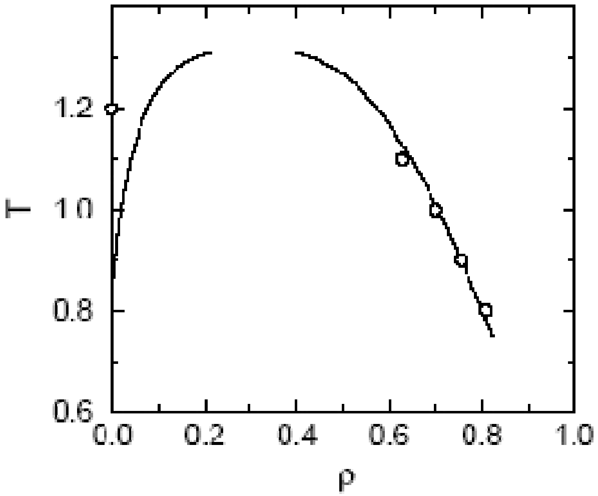
$$K = \frac{[B]}{[A]} = \frac{p_B}{p_A} = \exp[-\beta(G_B - G_A)]$$

- 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?

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)

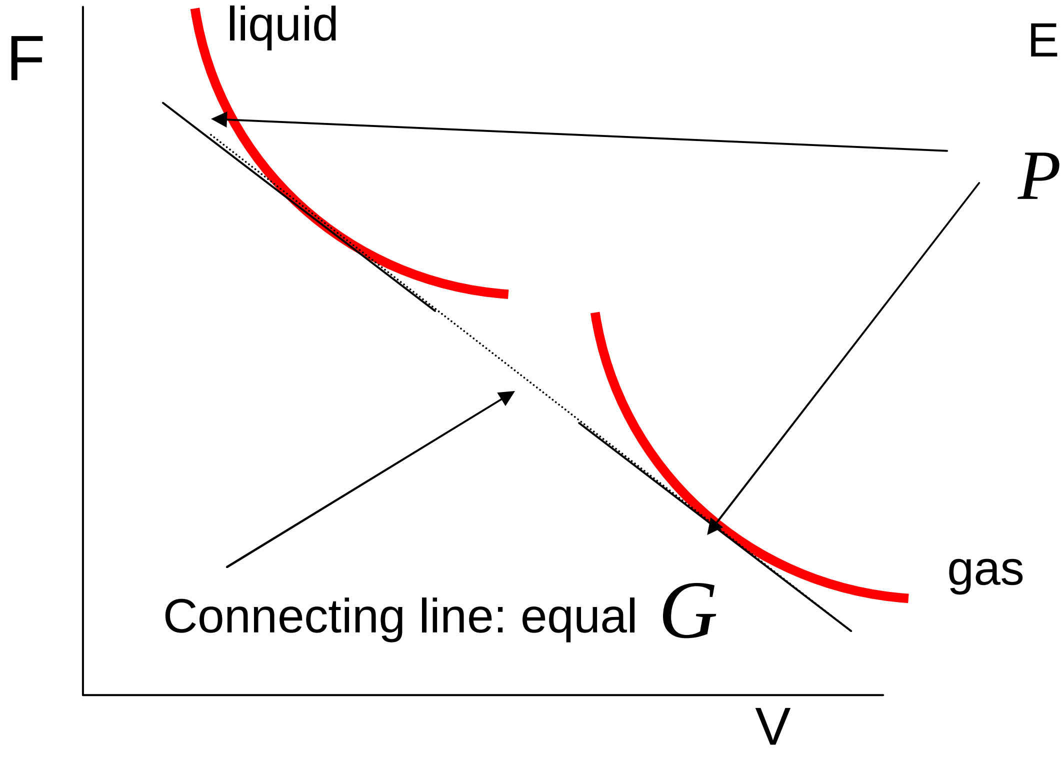
Then we can find G from F from:

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

All thermodynamic quantities can be derived from F and its derivatives

Phase equilibria from F(V,T)

Common tangent construction



Equal tangents

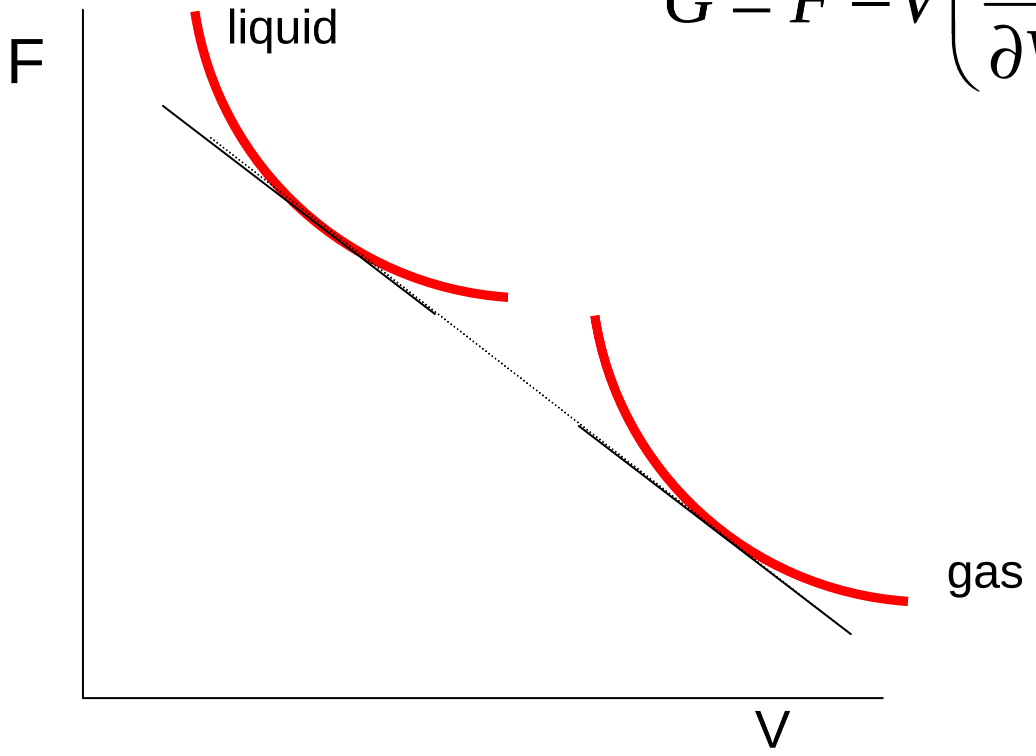
$$P = -\left(\frac{\partial F}{\partial V}\right)_{n,T}$$

Connecting line: equal G

Common tangent construction

Helmholtz Free Energy Perspective

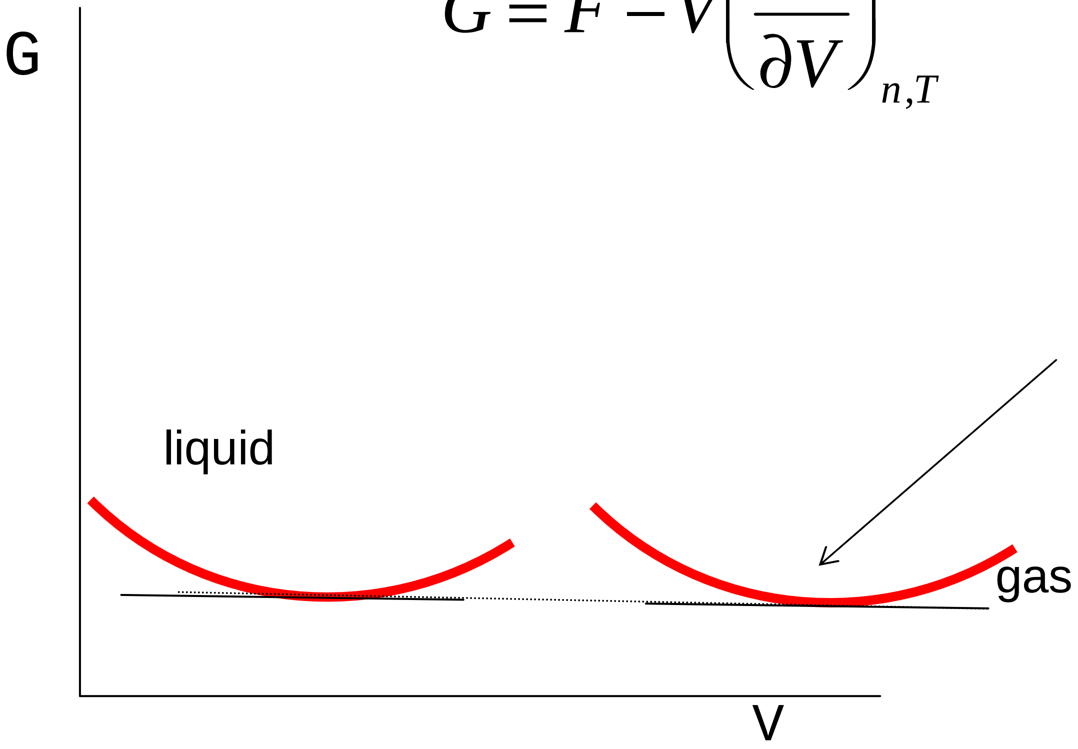
$$G = F - V\left(\frac{\partial F}{\partial V}\right)_{n,T}$$



Common tangent construction

Gibbs Free Energy Perspective

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



Both liquid and vapor G equal and minimal

Only equilibrium when P,T is on coexistence line.

We need F or μ

- So equilibrium from F(V) alone or from P and μ

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

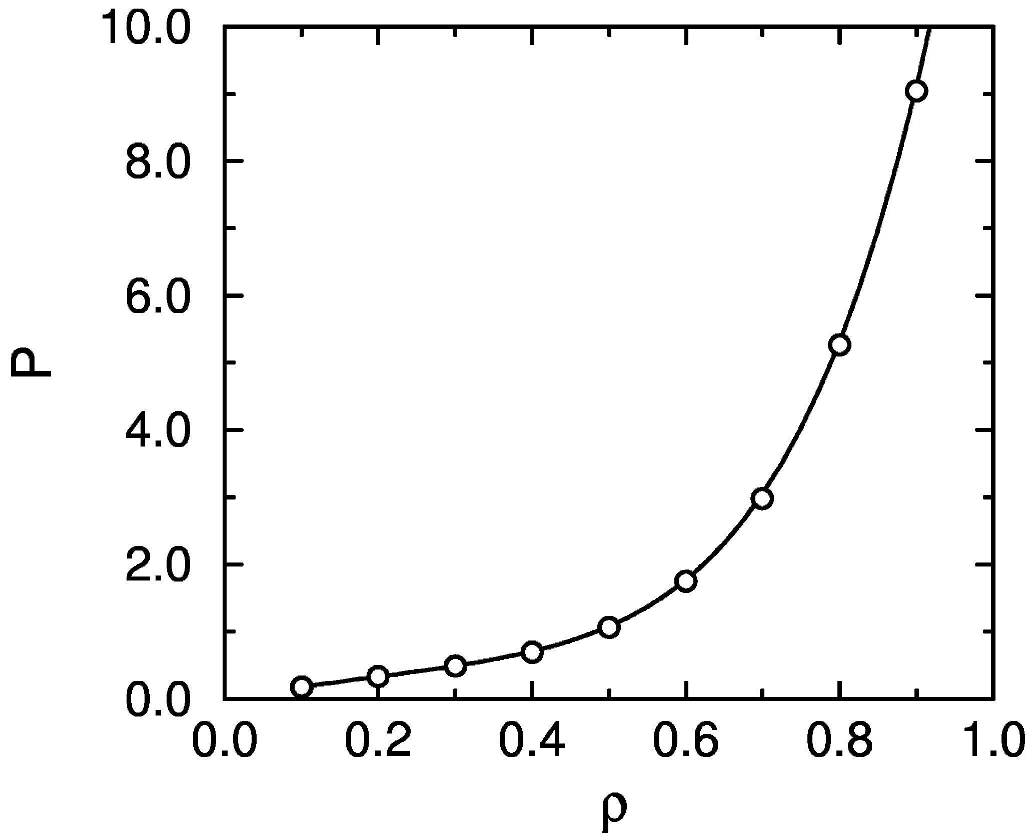
$$F(\rho) = F(\rho_0) + N\int_{\rho_0}^{\rho} \frac{P(\rho')}{\rho^2}\mathrm{d}\rho'$$

- 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

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

Equation of state



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

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

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

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

Statistical Thermodynamics

Partition function

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

Ensemble average

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

Probability to find a particular configuration

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

Free energy

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

Ensemble average versus free energy

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

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

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

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

ergodicity

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

F is difficult, because requires accounting of phase space volume

More general integration method from known state: TI

Thermodynamic integration

- Known reference state λ=0
- unkown target state λ=1

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

Coupling parameter

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

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

Thermodynamic integration

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

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

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

Free energy as ensemble average!

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

Example

- In general

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

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

- 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.

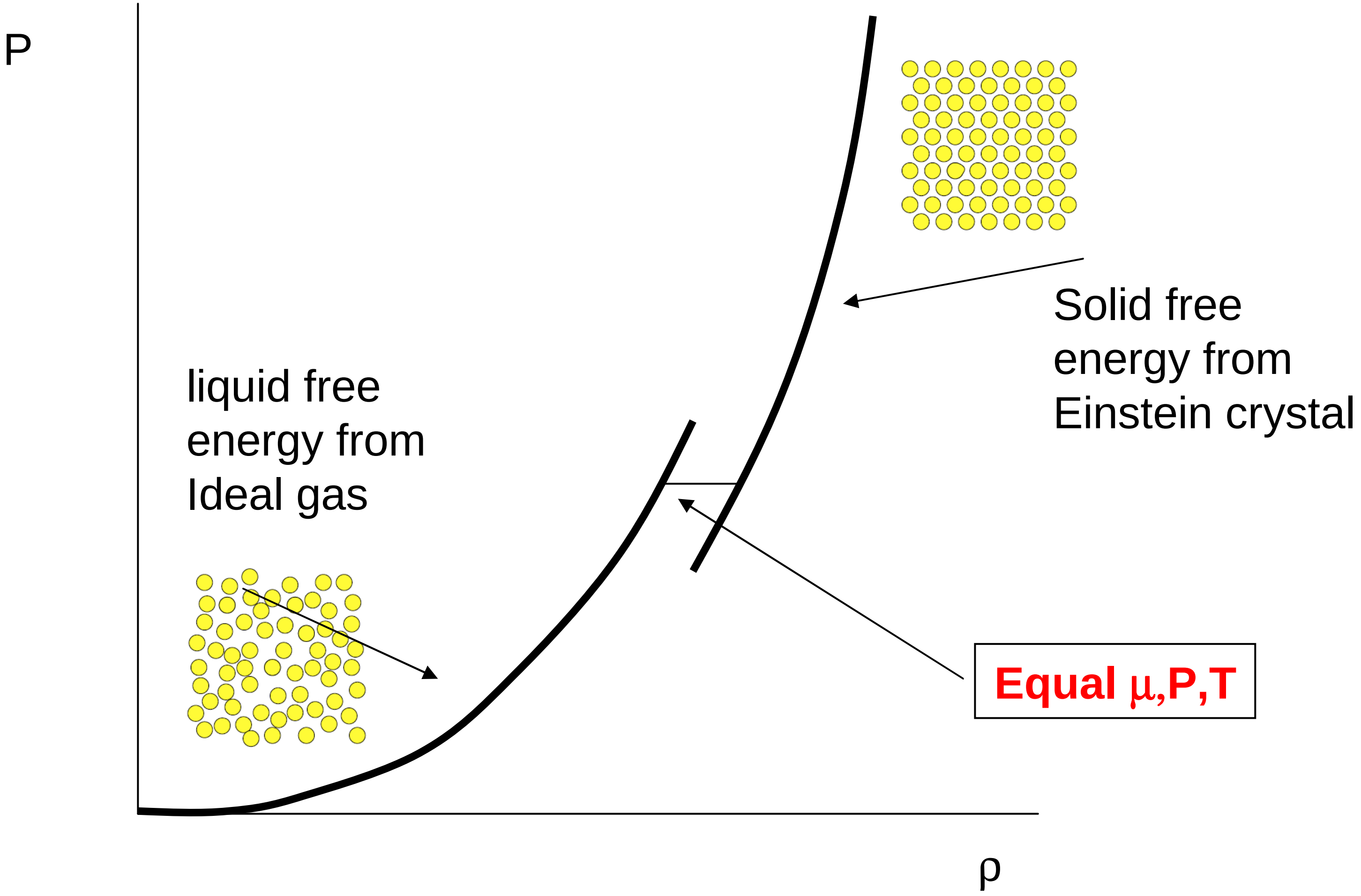
Instead it is the Einstein crystal: harmonic oscillators around r_0

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

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

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

Hard sphere freezing



liquid free
energy from
Ideal gas

Solid free
energy from
Einstein crystal

Equal μ,P,T

Thermodynamic perturbation

Two systems:

System 0: N, V, T, U_0

System 1: N, V, T, U_1

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

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

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

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

Chemical potential

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

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

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

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

$$\left.\begin{aligned} &\beta F = \beta F^{IG} + \beta F^{ex} \\ &\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{V,T} \end{aligned}\right\}$$

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

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

Widom test particle insertion

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

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

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

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

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

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

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

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!

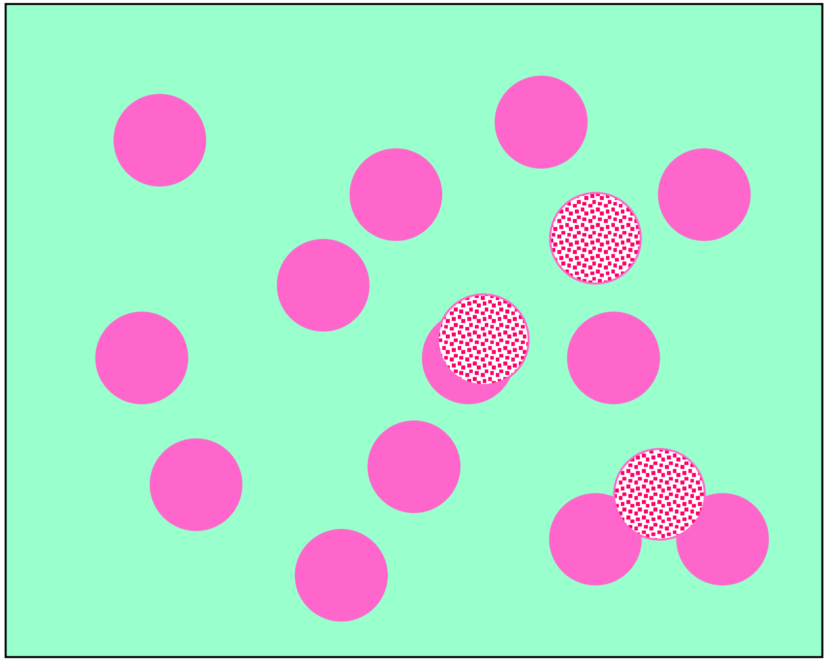
Algorithm 16 (Widom Test Particle Insertion)

```
 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
```

Hard spheres

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

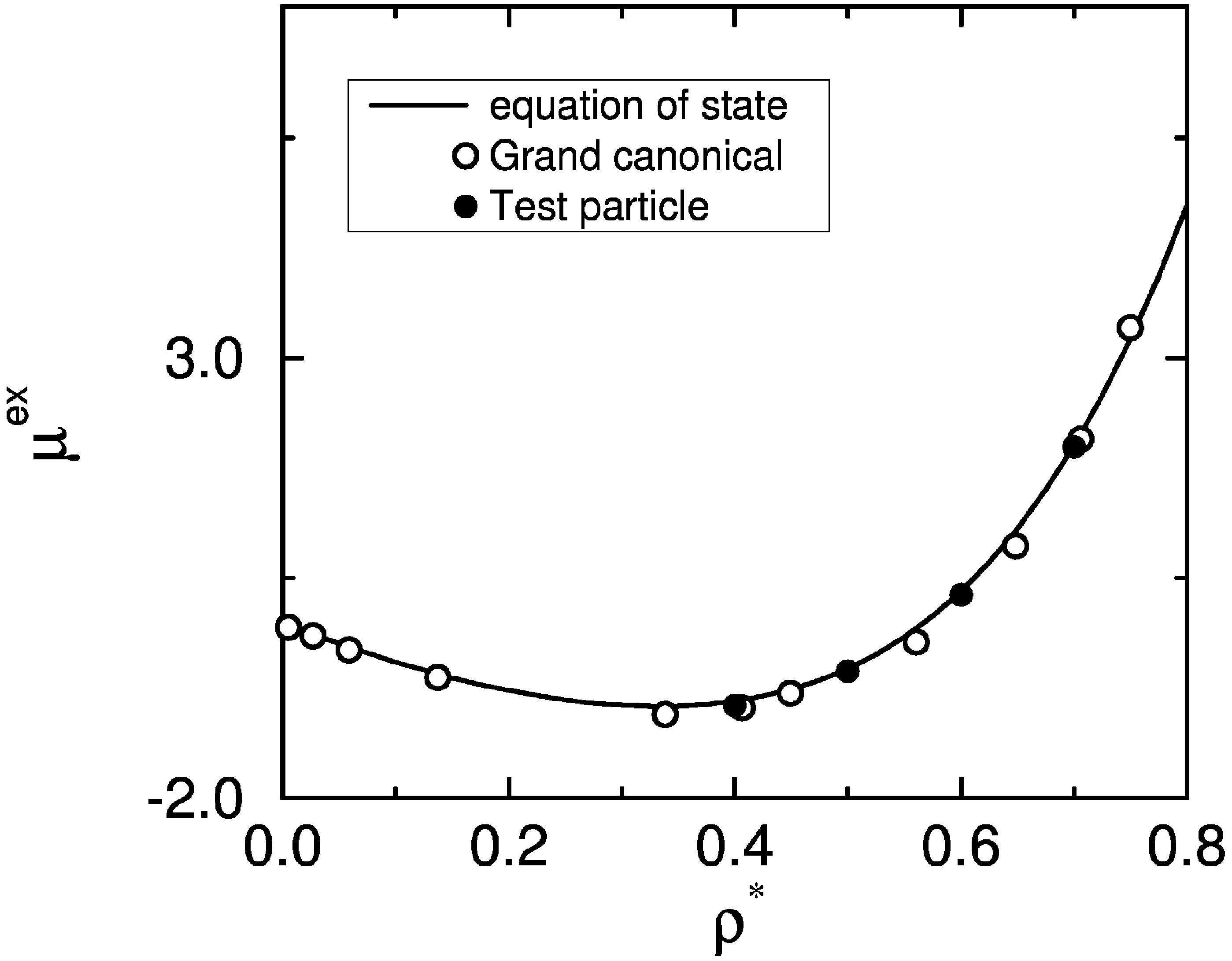
$$U(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$



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

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

Lennard-Jones fluid



Overlapping Distribution Method

Two systems:

System 0: N, V, T, U_0

System 1: N, V, T, U_1

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

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

$$\Delta\beta F = \beta F_1 - \beta F_0 = -\ln(Q_1/Q_0) = -\ln\left(\frac{\int d\mathbf{s}^N \exp(-\beta U_1)}{\int d\mathbf{s}^N \exp(-\beta U_0)}\right) = -\ln\left(\frac{q_1}{q_0}\right)$$

$=\Delta U$ (δ function)

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

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

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

$$= \frac{1}{q_1} = \frac{q_0}{q_1}\frac{1}{q_0}$$

$$\frac{q_0}{q_1} = \exp(\beta\Delta F)$$

$$= \frac{q_0}{q_1}\exp(-\beta\Delta U)\frac{\int d\mathbf{s}^N \exp[-\beta U_0]\delta(U_1 - U_0 - \Delta U)}{q_0}$$

$$p_1(\Delta U) = \frac{q_0}{q_1}\exp(-\beta\Delta U)p_0(\Delta U)$$

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

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

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

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

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

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

$$f_1(\Delta U) \equiv C_1 + a\Delta U + b\Delta U^2 + c\Delta U^3$$

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

Fit f_0 and f_1 to two polynomials that only differ by the offset

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

Chemical potential

System 0: $N\text{-}1, V, T, U$ + 1 ideal gas

System 1: N, V, T, U

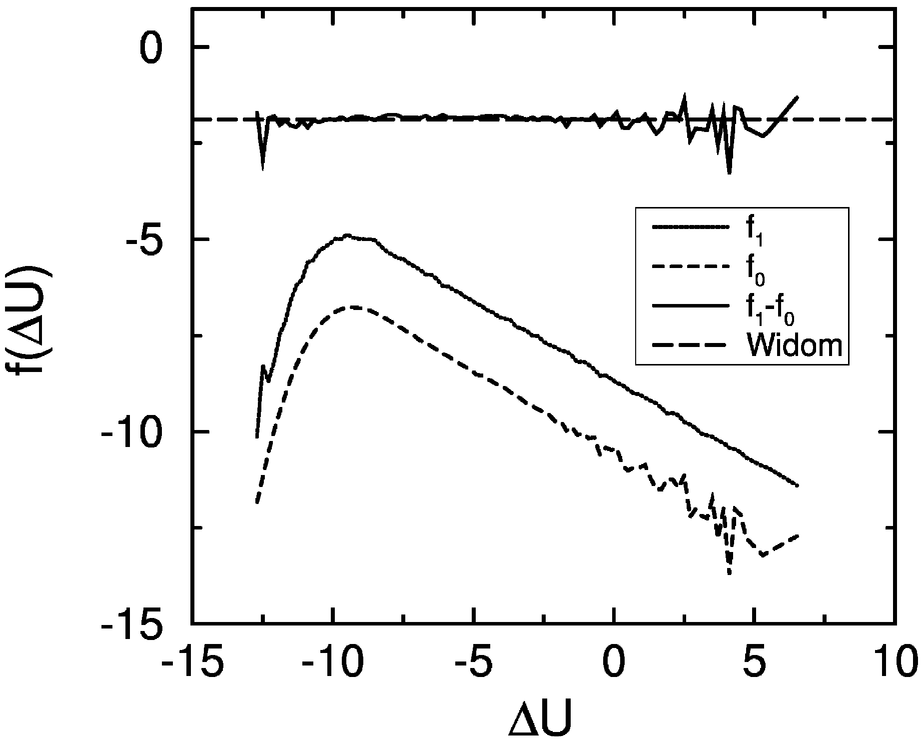
$$\Delta\beta F = \beta F_1 - \beta F_0 \equiv \beta\mu^{ex}$$

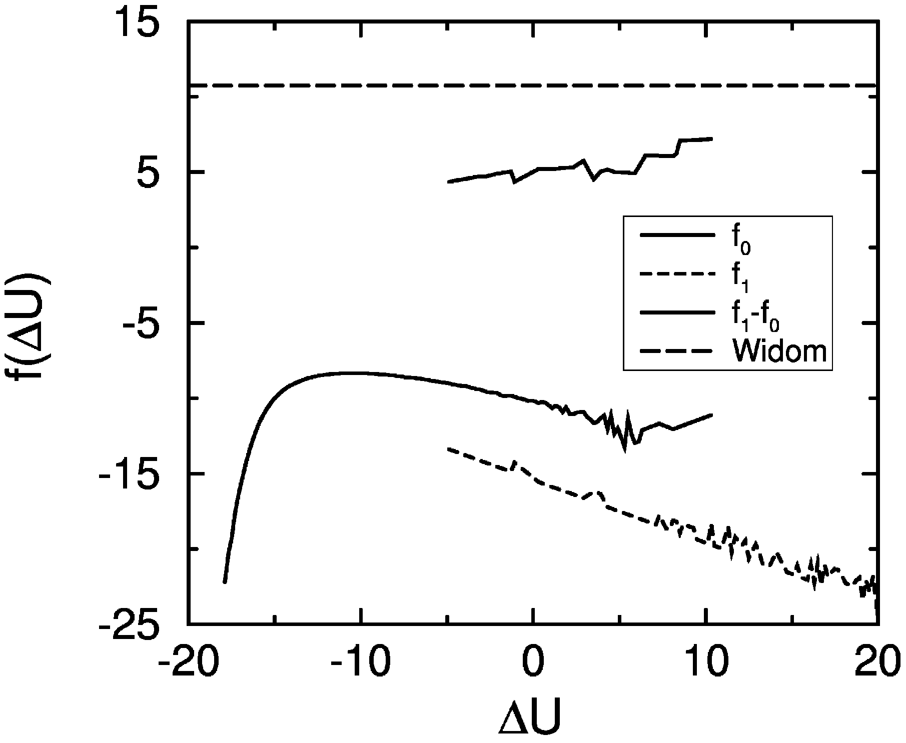
$$\Delta U = U_1 - U_0$$

System 0: test particle energy

System 1: real particle energy

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





Non-Boltzmann sampling

T_1 is arbitrary!

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

Why are we not using this?

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

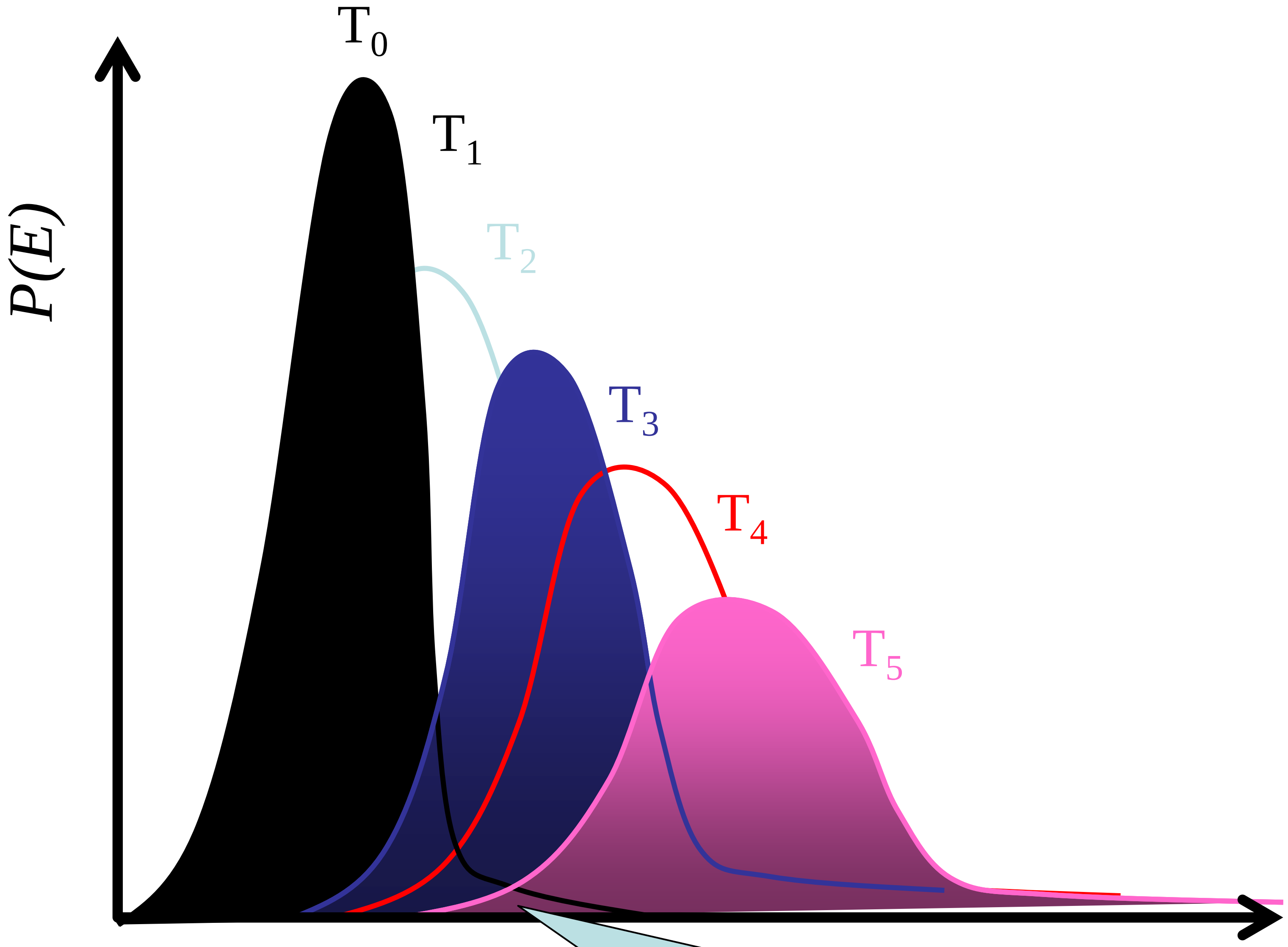
$$= \frac{\int \mathrm{d}\mathrm{r}^N A\left(\mathrm{r}^N\right)\exp\left[-\beta_1 U\left(\mathrm{r}^N\right)\right]\exp\left[\beta_2 U\left(\mathrm{r}^N\right)-\beta_2 U\left(\mathrm{r}^N\right)\right]}{\int \mathrm{d}\mathrm{r}^N \exp\left[-\beta_1 U\left(\mathrm{r}^N\right)\right]\exp\left[\beta_2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

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

We only need
a *single*
simulation!

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

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



Overlap becomes very small

Umbrella sampling

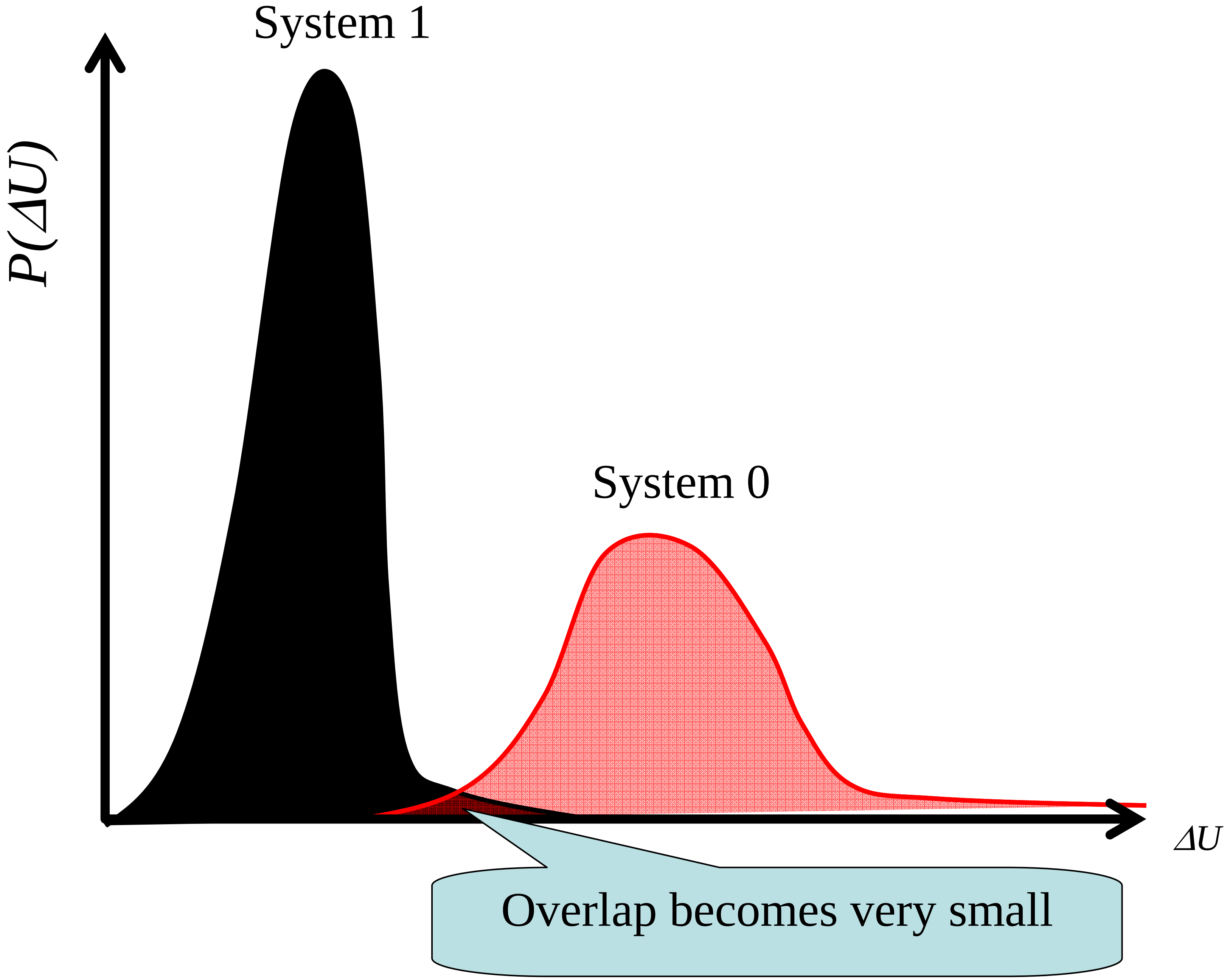
- Start with thermodynamic perturbation

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

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

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

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



Overlap becomes very small

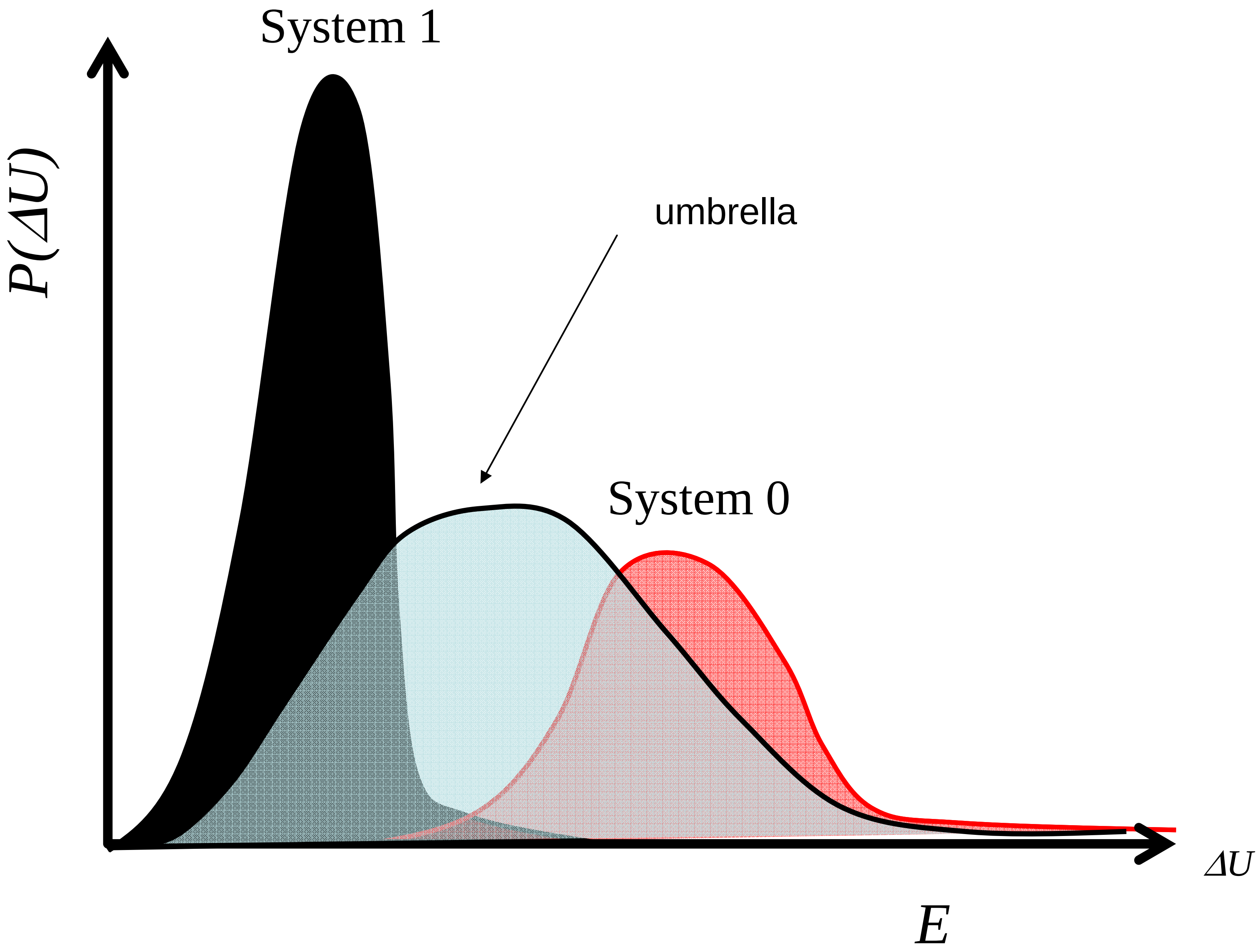
Bridging function

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

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

$$\exp\left(-\beta\Delta F\right)=\frac{\left\langle\exp\left(-\beta U_1\right)/\pi\right\rangle_\pi}{\left\langle\exp\left(-\beta U_{01}\right)/\pi\right\rangle_\pi}$$

- This approach is called umbrella sampling


System 1
$P(\Delta U)$
umbrella
System 0
ΔU
E

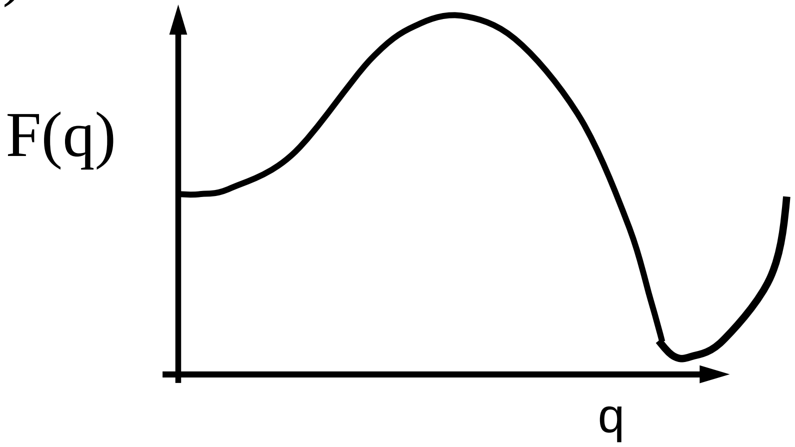
Landau free energy

Many times free energy is needed as a function of a certain order paramter q

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

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

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



Umbrella sampling

- Add and subtract bias potential w(q) to U

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

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

$$P(q) = \frac{\left\langle \delta(q - q') \exp(+\beta w(q')) \right\rangle_{biassystem}}{\left\langle \exp(+\beta w(q')) \right\rangle_{biassystem}}$$

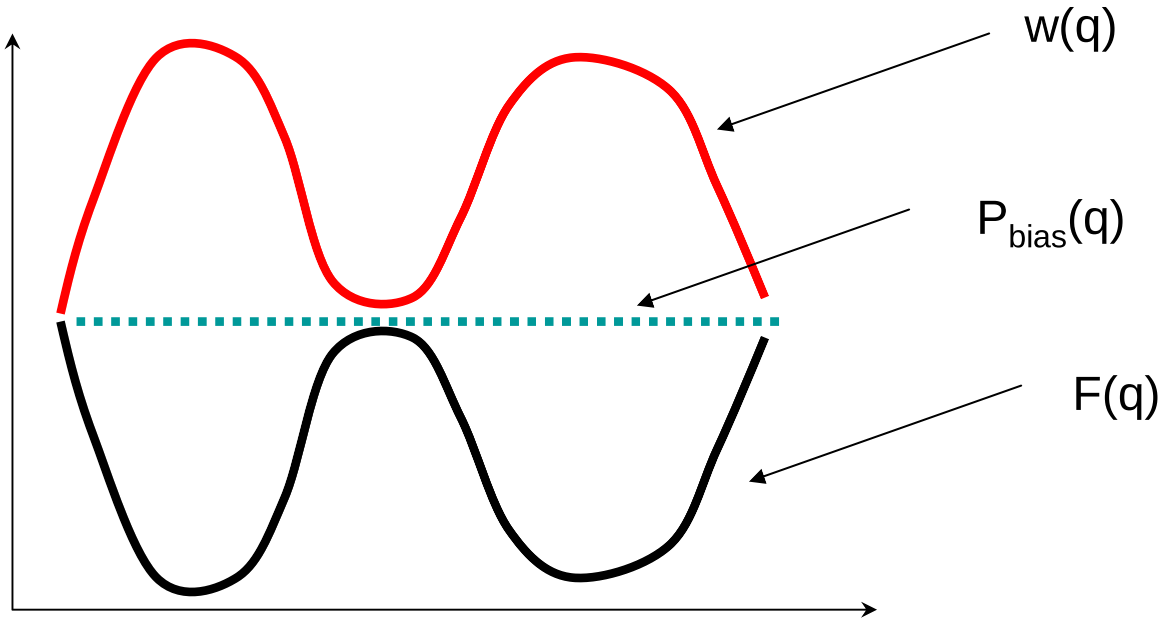
$$P(q) = \frac{\exp(+\beta w(q))}{\left\langle \exp(+\beta w(q')) \right\rangle_{bias}} P_{bias}(q)$$

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

Umbrella sampling

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

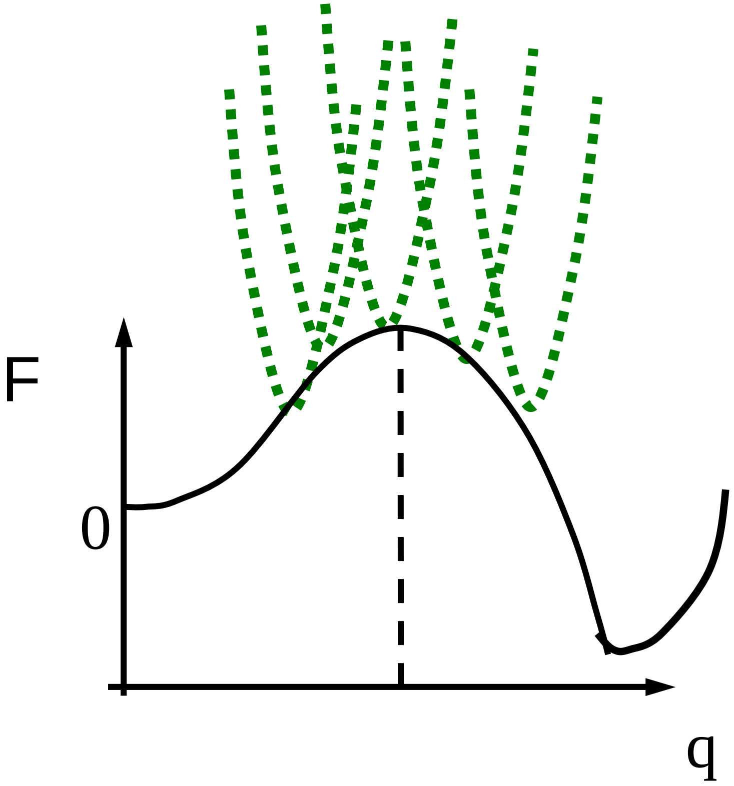
- Best choice w(q)=-F(q)
- Means P_{bias} = constant: entire q-range is equally sampled.



Usually w(q) difficult to guess: windows

Umbrella sampling

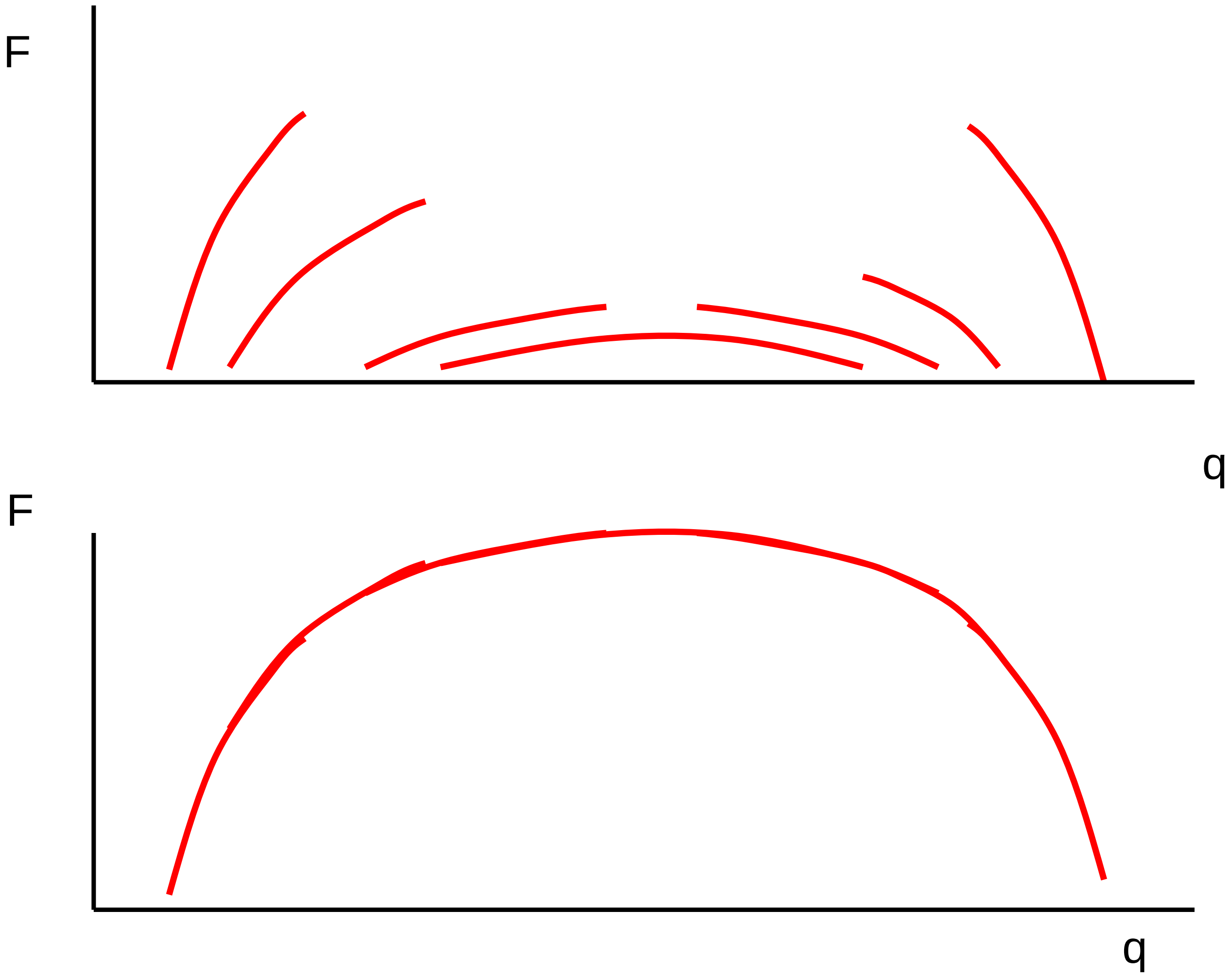
- Different windows have different potential $w_i(q)$



$$\text{Boltzmann} : \exp\left(-\beta(U + w(q))\right)$$

$$F(q) = -kT \ln P_{bias}(q) - w_{bias}(Q)$$

Reconstructing the free energy

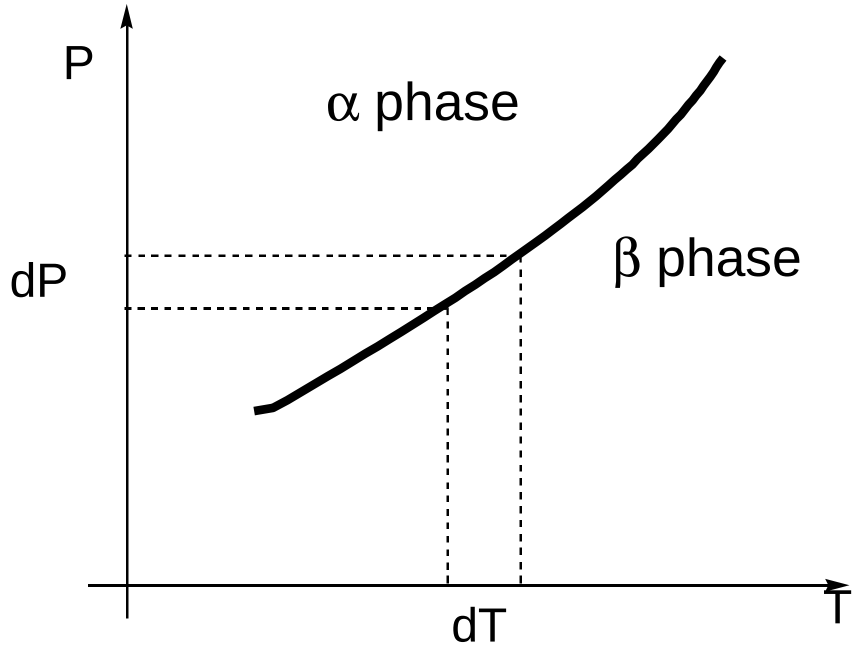


Tracing coexistence curves

- 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

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



Tracing coexistence curves

$$d\mu = dG_m = -S_m dT + V_m dP$$

$$-S_{m,\alpha} dT + V_{m,\alpha} dP = -S_{m,\beta} dT + V_{m,\beta} dP$$

$$\frac{dP}{dT} = \frac{S_{m,\beta} - S_{m,\alpha}}{V_{m,\beta} - V_{m,\alpha}}$$

Clapeyron equation

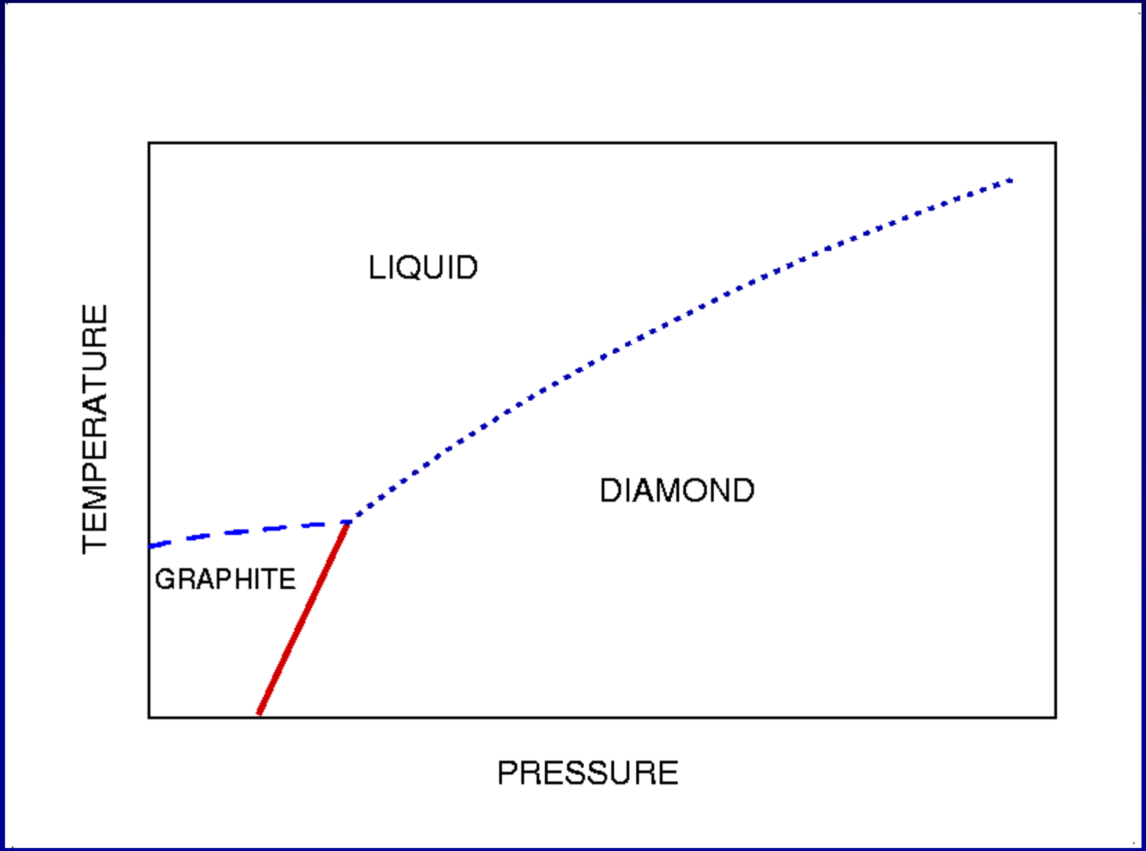
$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\Delta V_m}$$

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

Free Energy Calculations

Application to Carbon

Phase Transitions, Nucleation, and Planet Interiors



Carbon Phase Diagram

Why Carbon Phase Diagram?

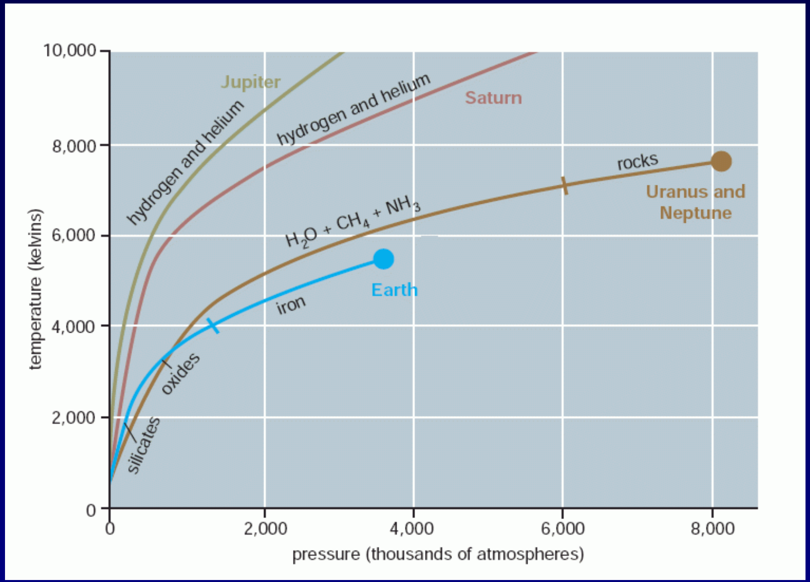
Diamonds in the Sky!

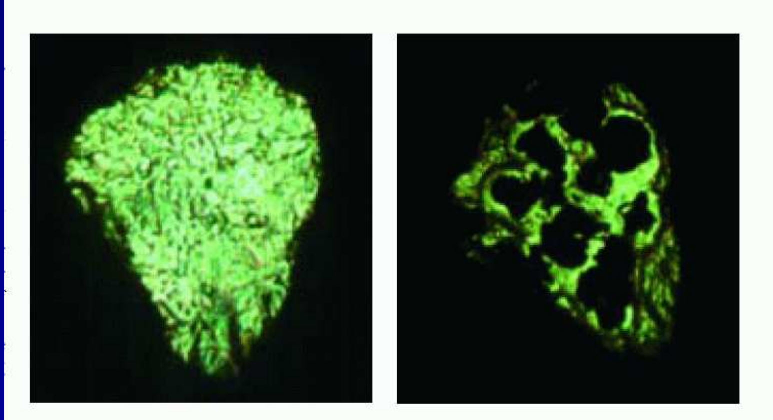
Uranus, Neptune

Interior rich in carbon

Temperature and Pressures extreme

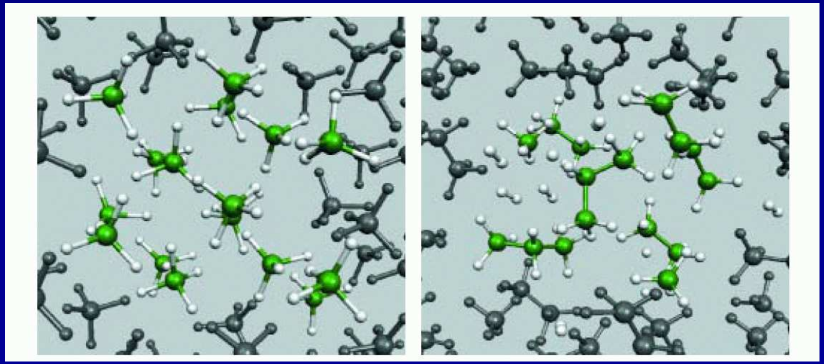
5000 K , 1 GPa





CH4: Laser heating in diamond- anvil cell

(Bennedetti et al, Science 1999)



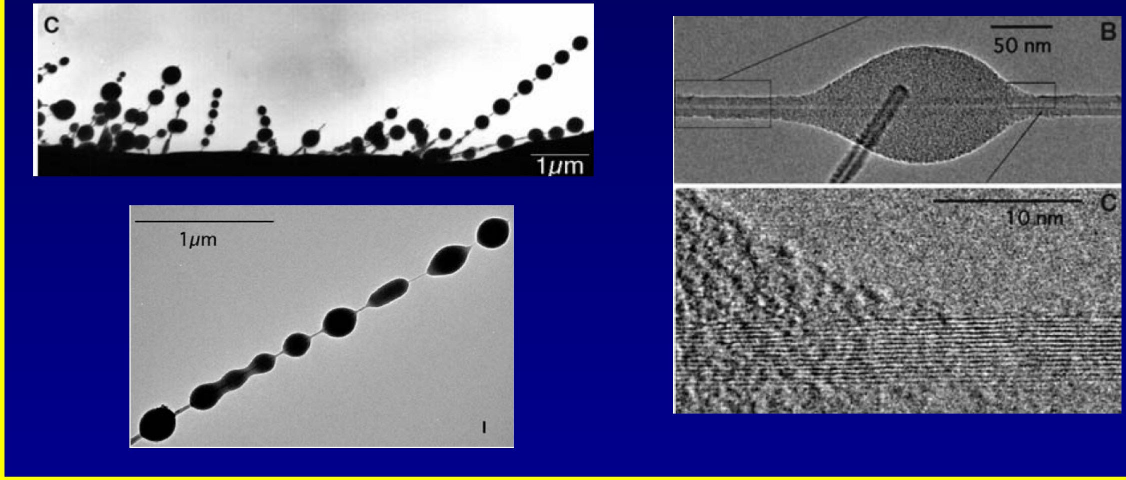
CH4: heating and pressuring in simulation (Scandolo,2003)

Why Carbon Phase Diagram?

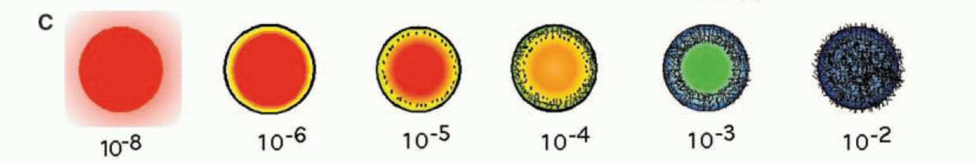
de Heer et al, Science 2005:

Multi Wall Nanotubes from liquid carbon drops

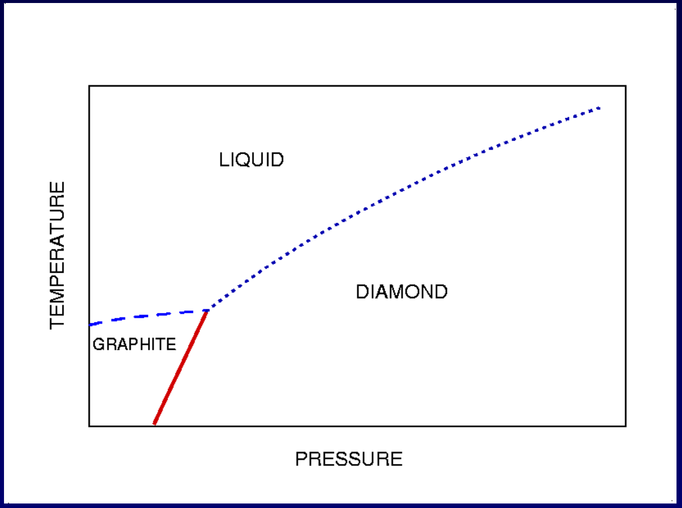
Microscopy Observations



Hypothesized Model



“State” of Carbon Phase Diagram



Graphite-Diamond: Well Established

Graphite-Liquid : Significant Spread

Possibly maximum in PT plane

LLPT in Brenner potential

LLPT in DFT-PBE/BP absent (Galli et al, 2003, Ghiring. et al, 2004)

Diamond-Liquid : Large uncertainty

Few experiments reported show positive PT slope

Modeling of Carbon

~1990: DFT-MD of liquid structure (Galli et al)

~1990: Brenner potential (Brenner)

~1999: Phase diagram with Brenner potential (Ree et al)

~2004: DFT-MD of liquid EOS (Galli et al, Ghiringhelli et al)

1990-2005: Improvement of empirical potentials

LCBOP

Emperical Bond-Order Potential

Los and Fasolino (PRB 2003);

Improvement by Los et al. PRB 2004: LCBOPI; PRB 2005: LCBOPII

Validated by crystal structures, clusters, defect energies, liquid structure

Determining Coexistence Points (I)

Free-energy changes using

$$U_\lambda = (1-\lambda)U^* + \lambda U^{\mathrm{ref}}$$

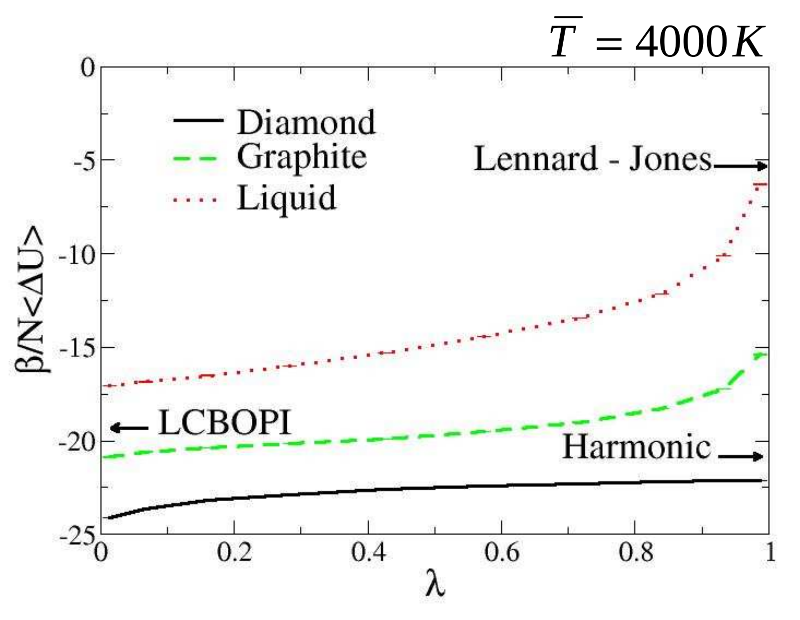
$$F^* = F^{\mathrm{ref}} + \int_0^1 \mathrm{d}\lambda \left\langle U^{\mathrm{ref}} - U^* \right\rangle_\lambda$$

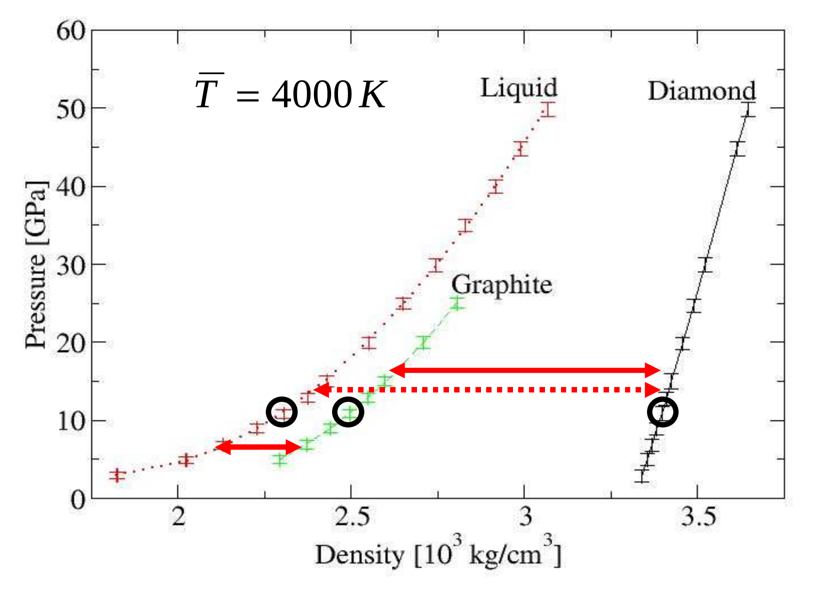
Free energy of initial state point (P=10 GPa, T=4000K)

Liquid: change LCBOP into LJ: $U^{ref} = U_{LJ}$

Graphite & Diamond: change LCBOP into Einstein Crystal

Determining Coexistence Points (I)





Free energy along isotherm T=4000K

$$\beta\mu(\rho) = \frac{\beta F^*}{N} + \beta\left(\frac{a}{\rho^*} + b\,\ln\frac{\rho}{\rho^*} + b + c\,(2\rho - \rho^*)\right)$$

Liquid-Graphite: P_{coex} = 6.7 +/- 0.6 GPa
Diamond-Liquid: P_{coex} = 12.8 +/- 0.2 GPa (Metastable)
Graphite-Diamond: P_{coex} = 15.1 +/- 0.3 GPa

Tracing Coexistence Lines

Use Clausius-Clapeyron from initial coexistince point

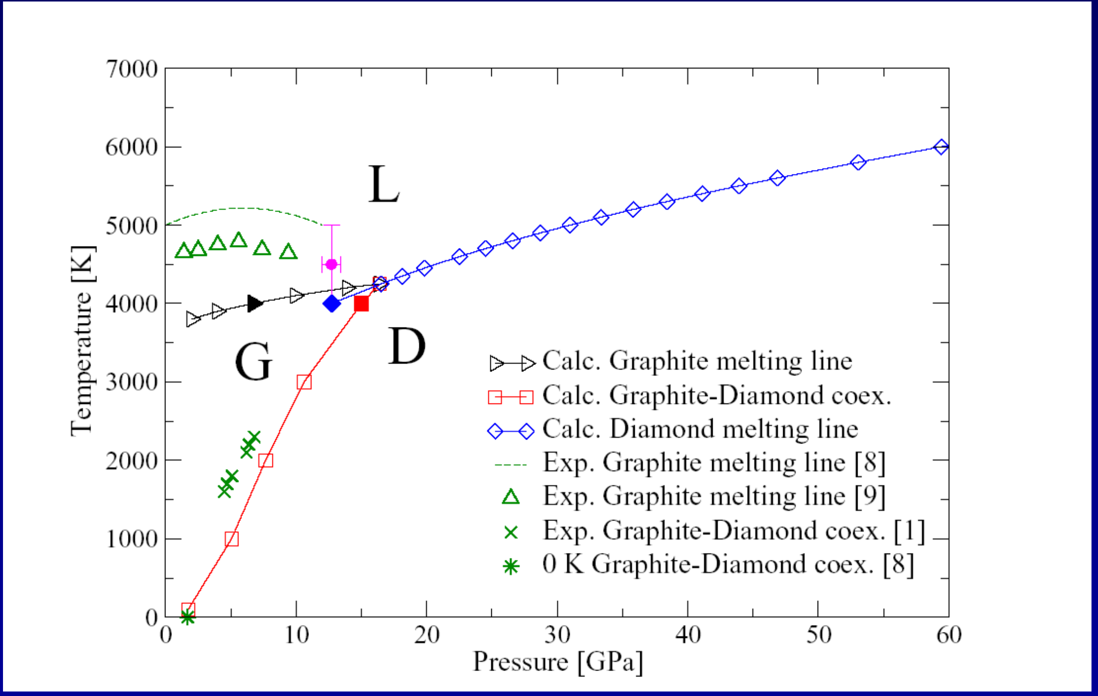
$$\mathrm{d}T/\mathrm{d}P = T\Delta v/\Delta h$$

Integration by higher-order predictor-corrector scheme

Calculated LCBOPI phase diagram

Low-pressure range

Comparison with experiment



Calculated LCBOPI phase diagram

High-pressure range

Comparison with experiment and calculations