Free Energy and Phase equilibria

Thermodynamic integration 7.1
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Application: Phase diagram of Carbon

Why free energies?

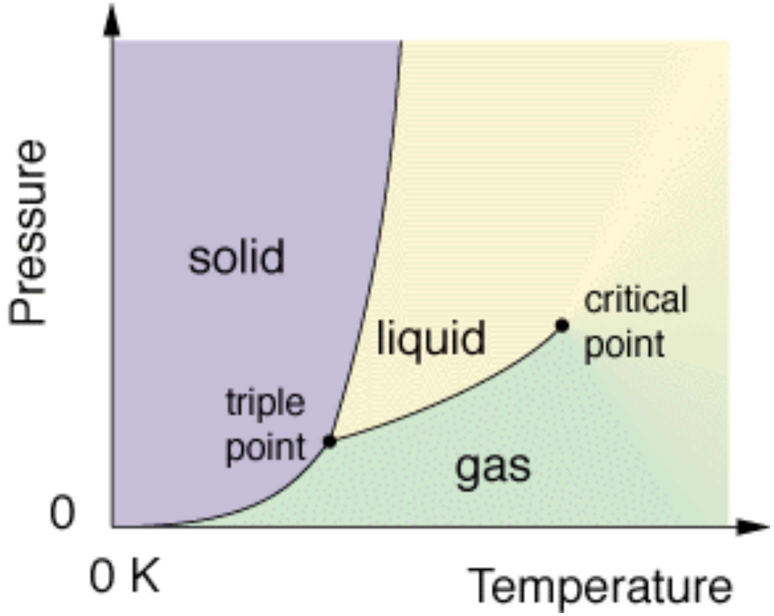
- Reaction equilibrium constants $A \leftrightarrow B$

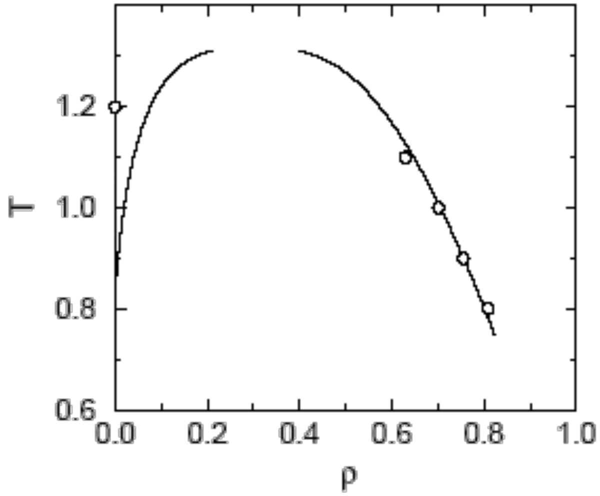
$$K = \frac{[B]}{[A]} = \frac{p_B}{p_A} = \exp\left[-\beta(G_B - G_A)\right]$$

- Examples:
  - Chemical reactions, 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

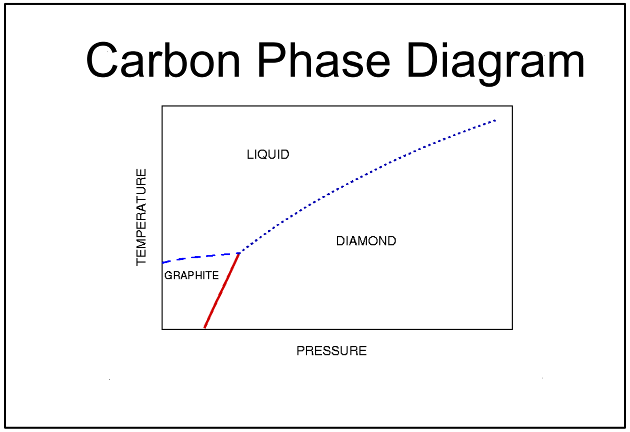
Phase diagrams





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

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


Carbon Phase Diagram

How do we compute these lines?

Phase equilibrium

Criteria for equilibrium (for single component)

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

Chemical potential

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

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

Stable phase:

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

Relation thermodynamic potentials

Helmholtz free energy: $F = U - TS$

Gibbs free energy: $G = F + PV$

Suppose we have F(n,V,T)

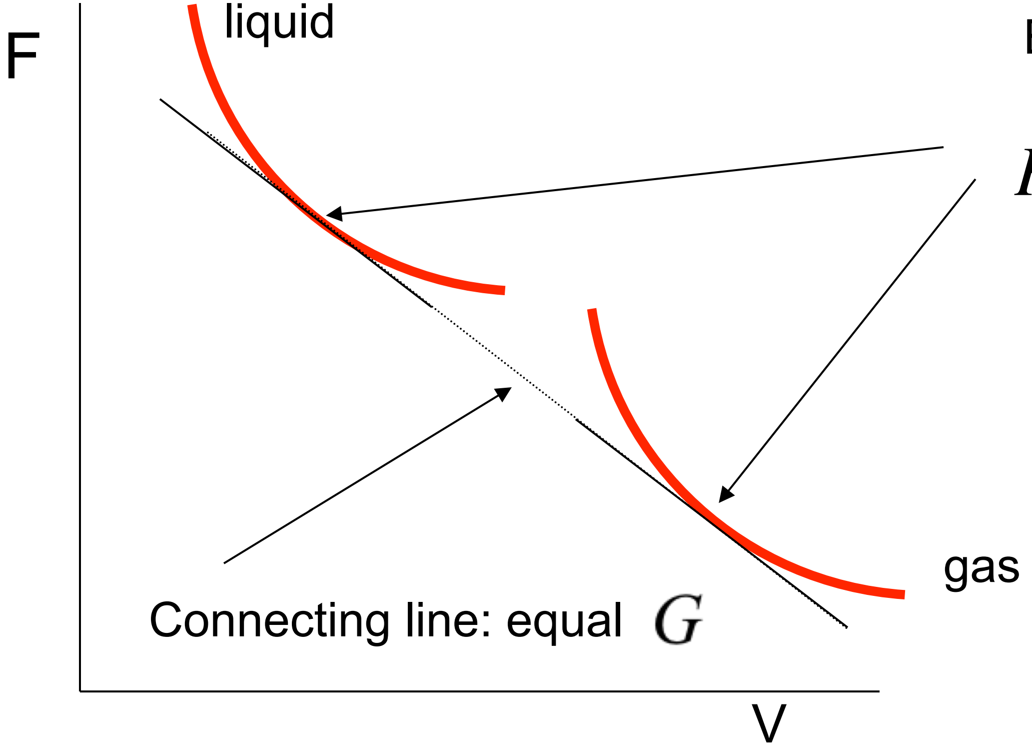
Then we can find G from F from:

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

All thermodynamic quantities can be derived from F and its derivatives

Phase equilibria from F(V,T)

Common tangent construction



Equal tangents

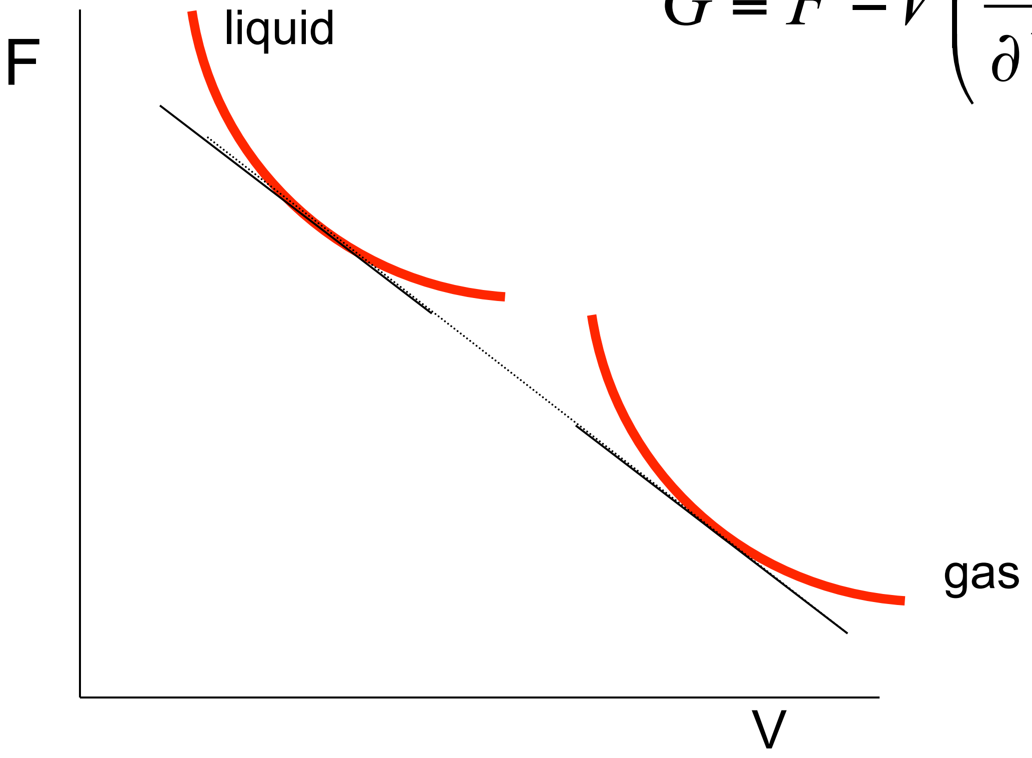
$$P = -\left(\frac{\partial F}{\partial V}\right)_{n,T}$$

Connecting line: equal G

Common tangent construction

Helmholtz Free Energy Perspective

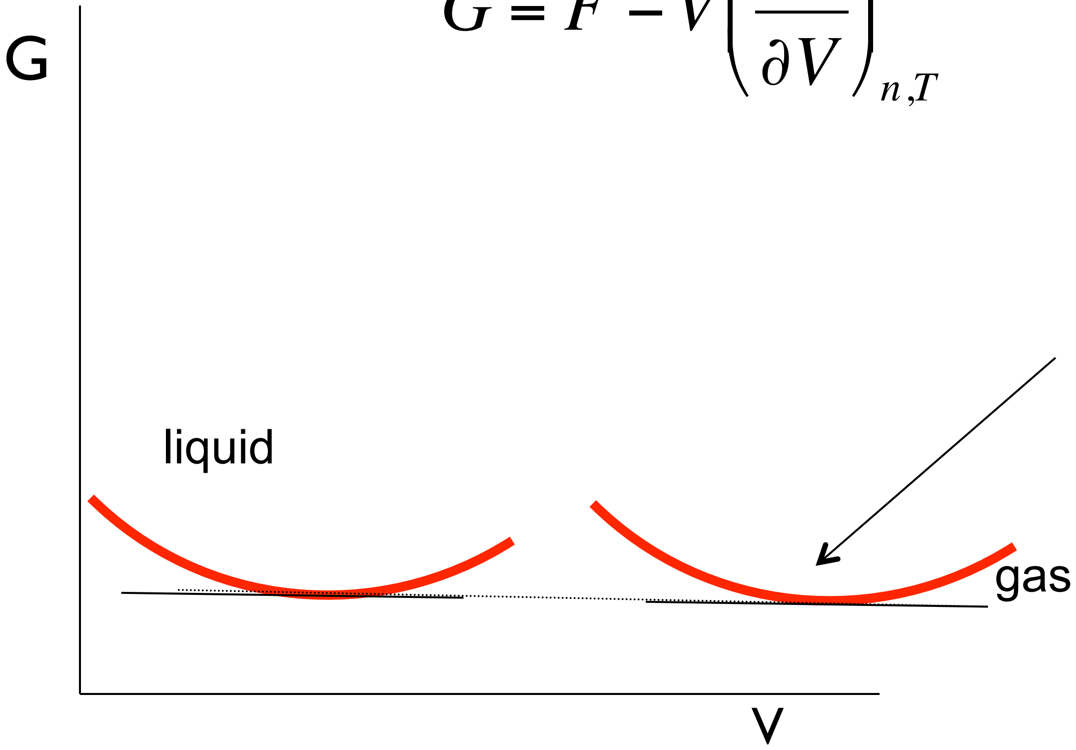
$$G = F - V\left(\frac{\partial F}{\partial V}\right)_{n,T}$$



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

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

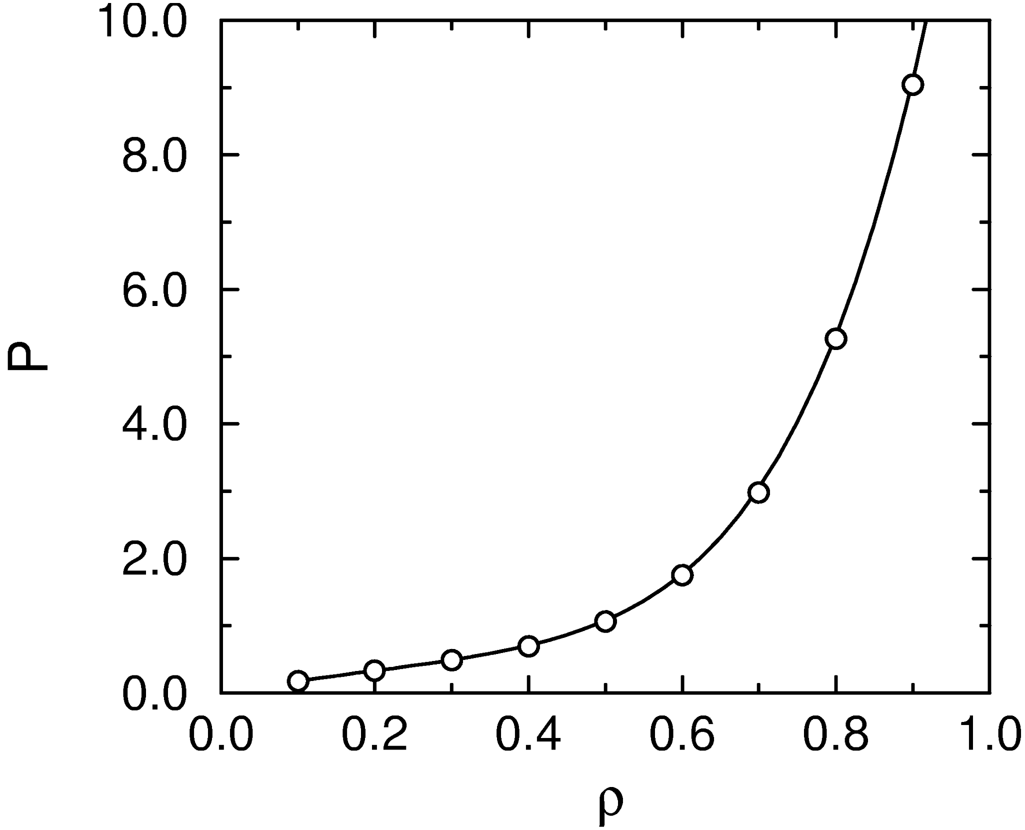
$$F(\rho) = F(\rho_0) + N\int_{\rho_0}^{\rho} \frac{P(\rho')}{\rho^2} \mathrm{d}\rho'$$

- 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

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

Equation of state



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

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

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

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

Free Energies and Phase Equilibria

General Strategies

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

  Free energy difference calculation

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

- Determine free energy difference between two phases

  Gibbs Ensemble (Lecture Thijs Vlugt)

  Specific applicable: Gas, Liquid

Statistical Thermodynamics

Probability to find a particular configuration

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

Partition function

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

Free energy

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

Ensemble average

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

Ensemble average versus free energy

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

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

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

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

ergodicity

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

F is difficult, because requires accounting of phase space volume

I - Thermodynamic integration

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

Reference System

Coupling parameter

Target System

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

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

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

Thermodynamic integration

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

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

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

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

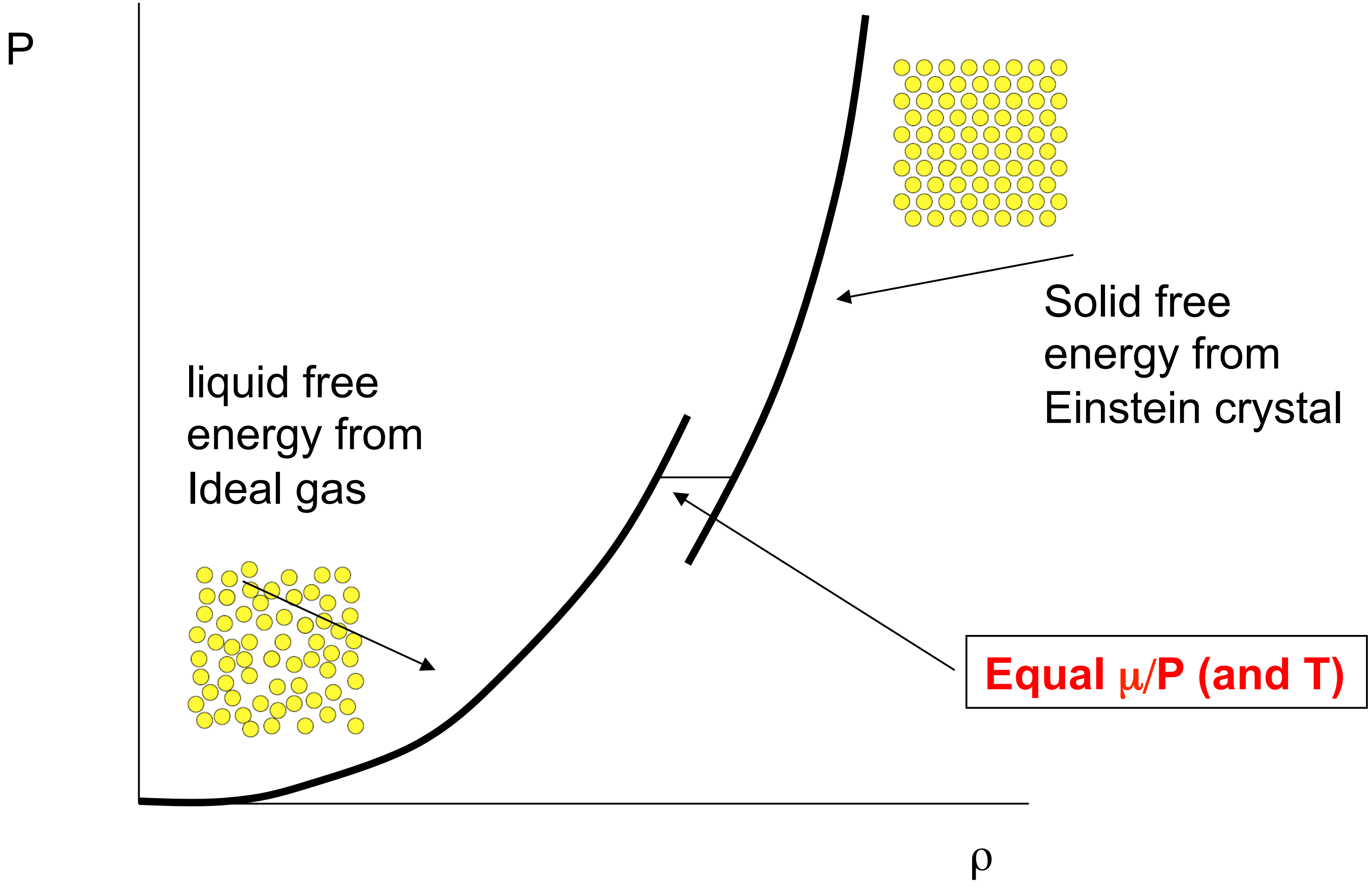
$$U\left(\lambda; r^N\right) = (1-\lambda)U\left(r^N\right) + \lambda U\left(r_0^N\right) + \lambda \sum_{i=1}^{N} \alpha(r_i - r_i)^2$$

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

Note, here:
λ = 1 Reference System
λ = 0 Target System

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

Hard sphere freezing



liquid free
energy from
Ideal gas

Solid free
energy from
Einstein crystal

Equal μ/P (and T)

II - Thermodynamic perturbation

Two systems:

System 0: N, V, T, U_0

System 1: N, V, T, U_1

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

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

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

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

Chemical potential

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

$$\begin{aligned} \beta F &= -\ln\left(Q_{NVT}\right) \\ &= -\ln\left(\frac{V^N}{\Lambda^{3N} N!}\right) - \ln\left(\int \mathrm{d}\mathrm{s}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]\right) \\ &= -N \ln\left(\frac{1}{\Lambda^3 \rho}\right) + N - \ln\left(\int \mathrm{d}\mathrm{s}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]\right) \end{aligned}$$

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

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

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

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

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

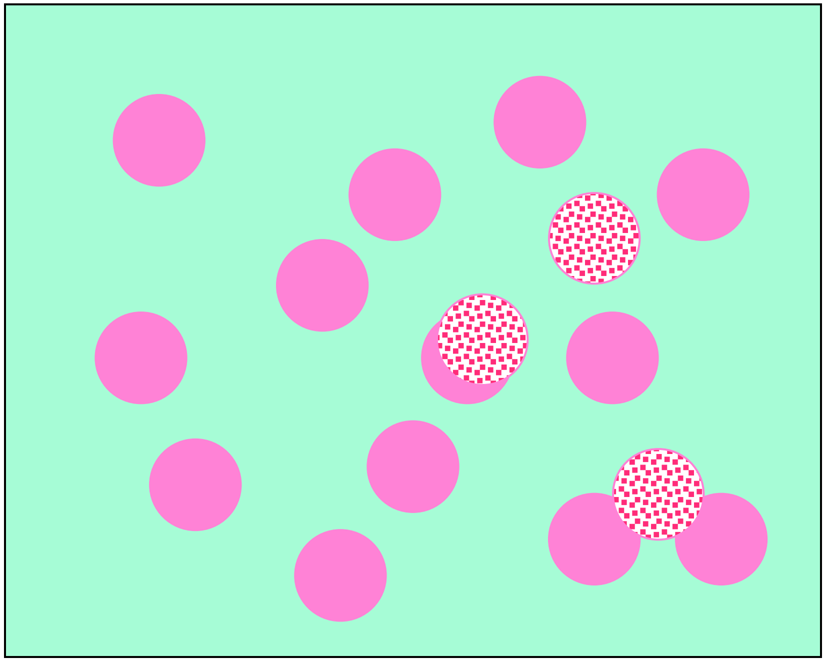
$$= -\ln\left(\frac{\int \mathrm{ds}_{N+1}\int \mathrm{ds}^{N}\left\{\exp\left[-\beta\Delta U^{+}\right]\right\}\exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]}{\int \mathrm{ds}^{N}\exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]}\right)$$

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

Ghost particle!

Hard spheres

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



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

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

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

But, … may fail at high density

III - Overlapping Distribution Method

Two systems:

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

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

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

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

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

=ΔU (δ function)

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

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

$$\frac{Q_0}{Q_1} = \exp\left(\beta\Delta F\right)$$

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

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

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

Overlapping Distribution Method

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

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

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

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

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

Chemical potential

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

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

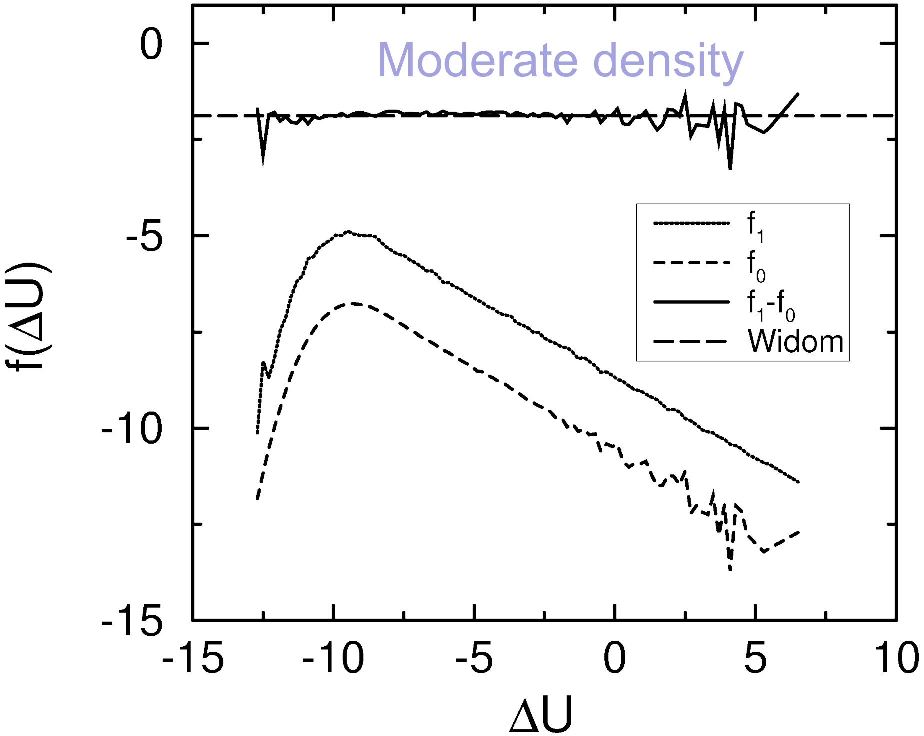
$$\Delta\beta F = \beta F_1 - \beta F_0 \equiv \beta\mu^{ex}$$

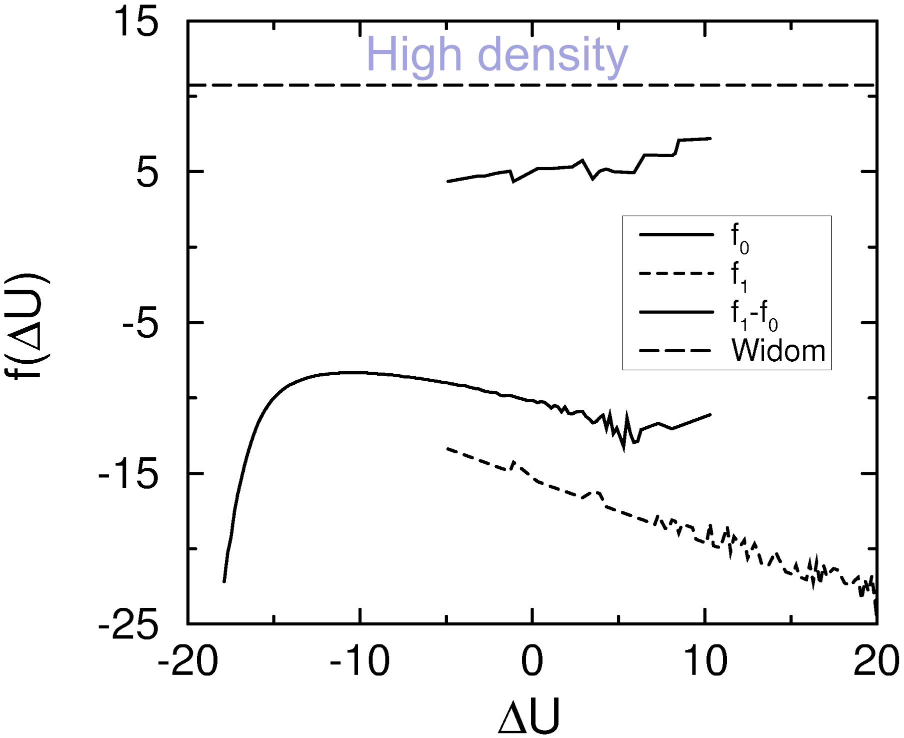
$$\Delta U = U_1 - U_0$$

System 0: test particle energy

System 1: real particle energy

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





IV - Non-Boltzmann sampling

T_1 is arbitrary!

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

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

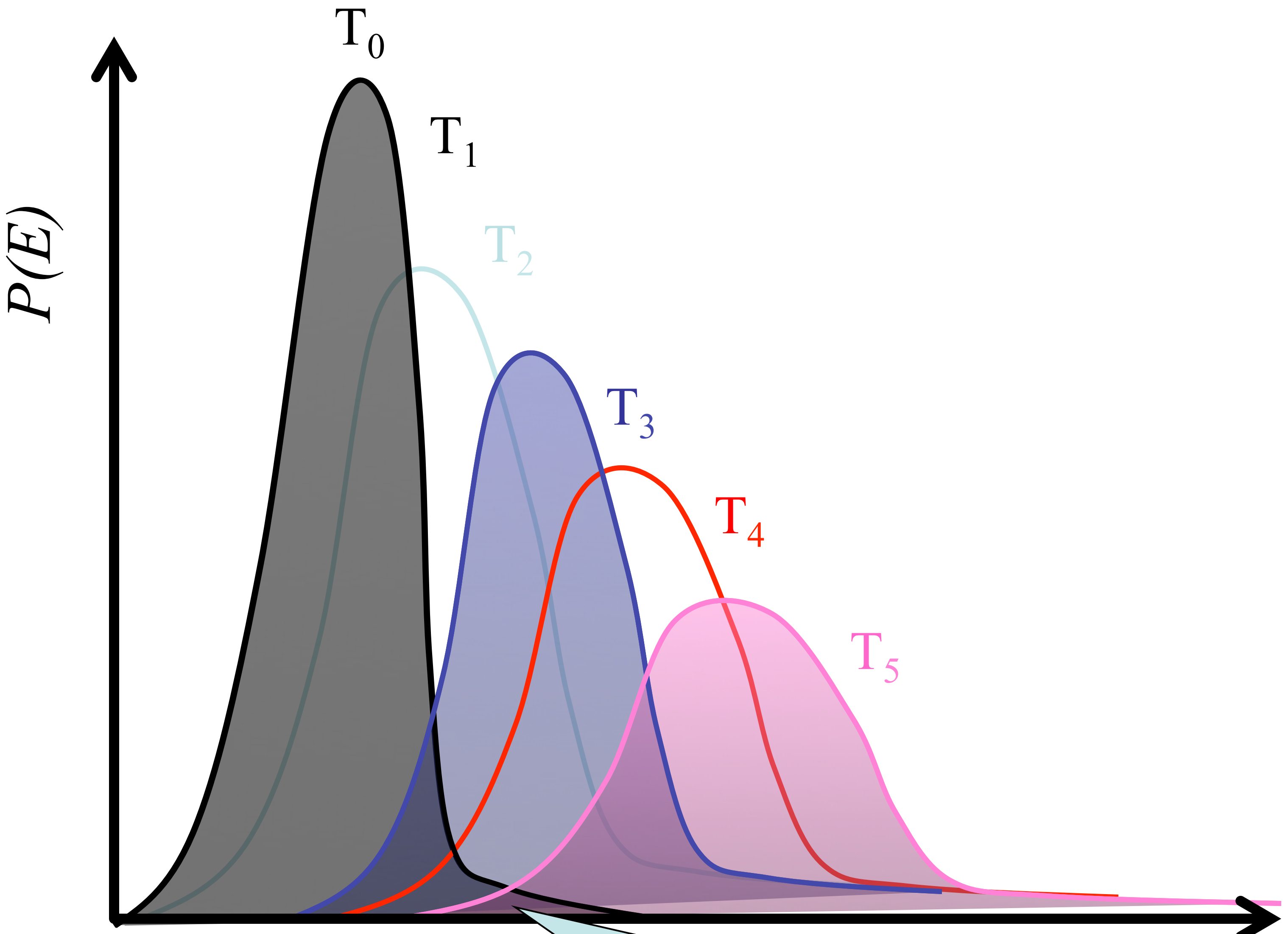
$$= \frac{\int \mathrm{dr}^N A\left(\mathrm{r}^N\right)\exp\left[-\beta_1 U\left(\mathrm{r}^N\right)\right]\exp\left[\beta_2 U\left(\mathrm{r}^N\right)-\beta_2 U\left(\mathrm{r}^N\right)\right]}{\int \mathrm{dr}^N \exp\left[-\beta_1 U\left(\mathrm{r}^N\right)\right]\exp\left[\beta_2 U\left(\mathrm{r}^N\right)-\beta_2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

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

We only need a *single* simulation!

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

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



Overlap becomes very small

Umbrella sampling

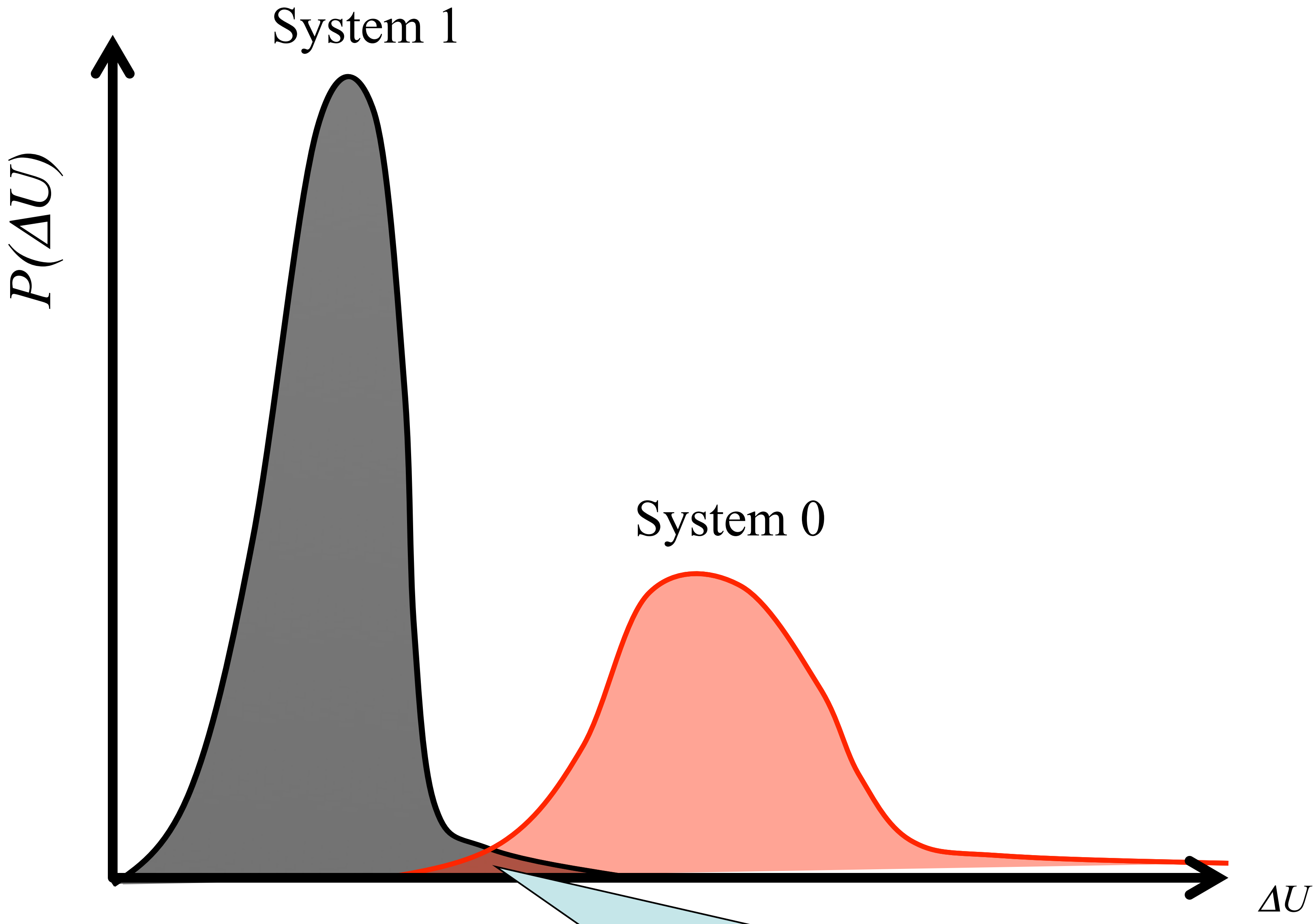
- Start with thermodynamic perturbation

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

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

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

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



Overlap becomes very small

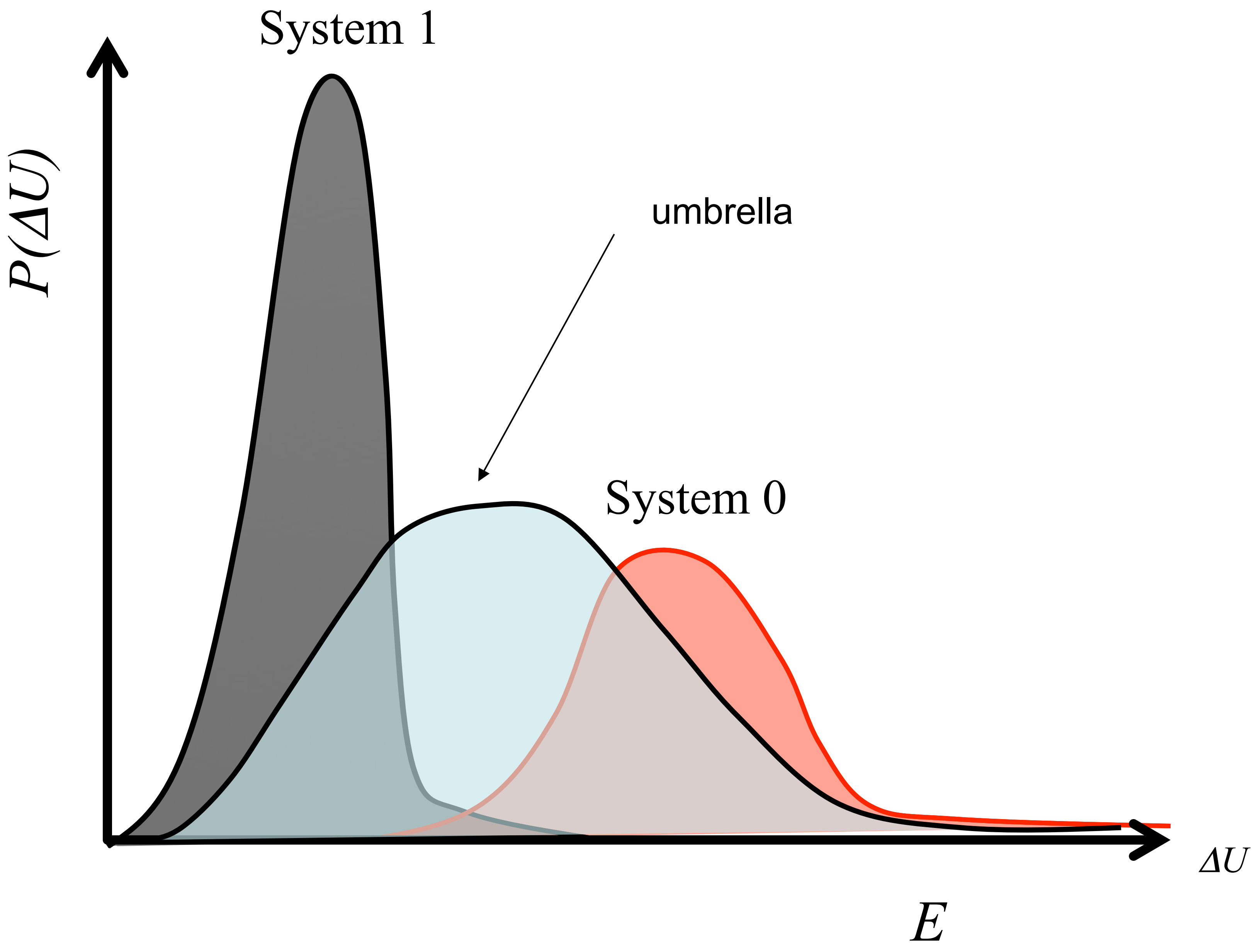
Bridging function

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

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

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

- This approach is called umbrella sampling

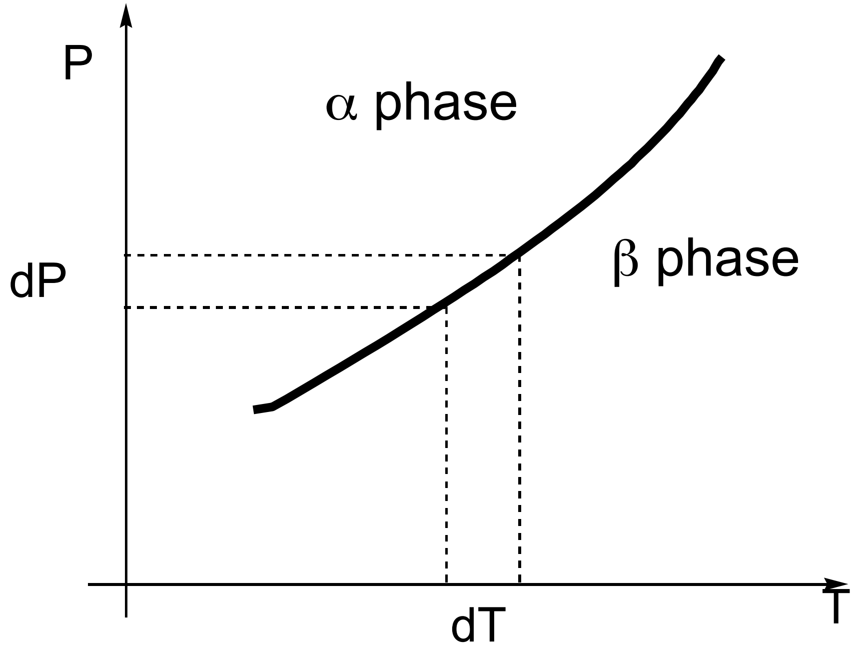

System 1
P(ΔU)
umbrella
System 0
ΔU
E

Tracing coexistence curves

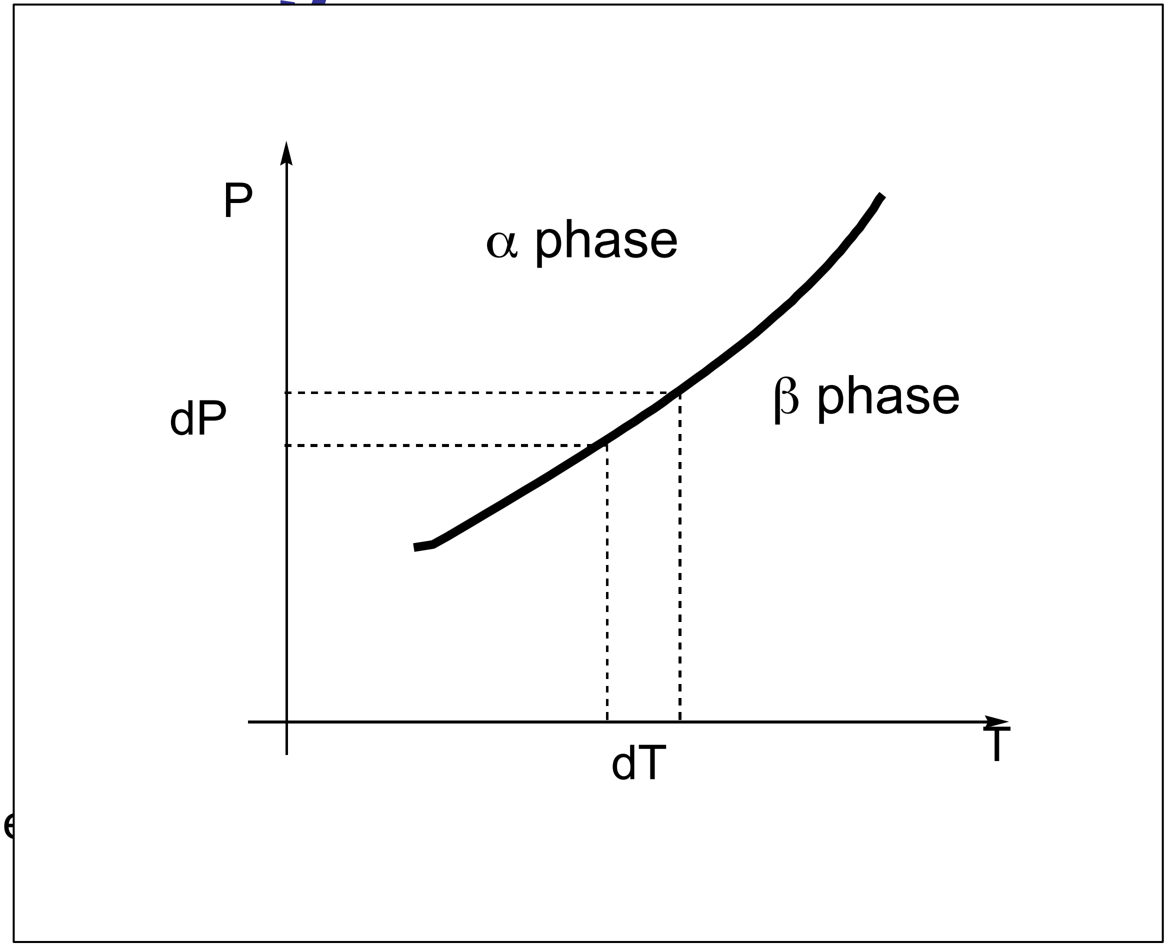
- If we have a coexistence point on the phase diagram we can integrate allong the line while maintaining coexistence.

P en T are equal along coexistence line

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



Tracing coexistence curves



Clapyeron e

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

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

Metadynamics

- Select a set of "relevant" collective variables (S_α)
- MD: Track trajectory $S_\alpha(t)$ over a time interval $[t_0, t_1]$: $\overline{S}[t_0, t_1]$
- Bias by adding repulsion at region near $\overline{S}[t_0, t_1]$
- Continue MD and iterate

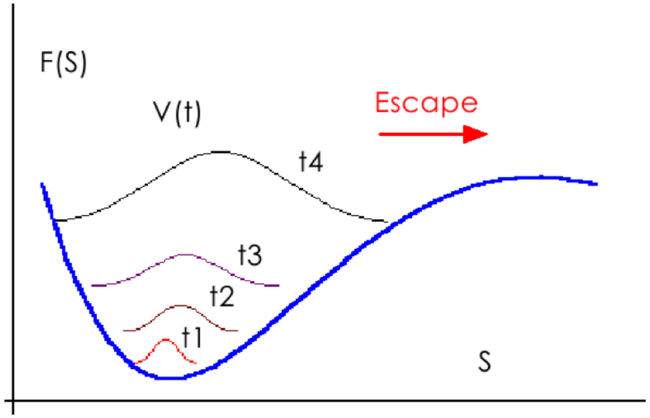
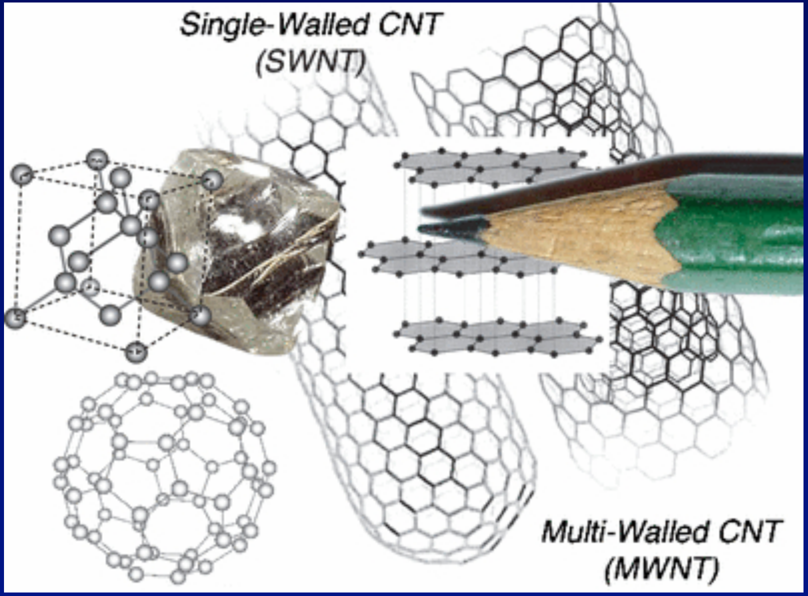
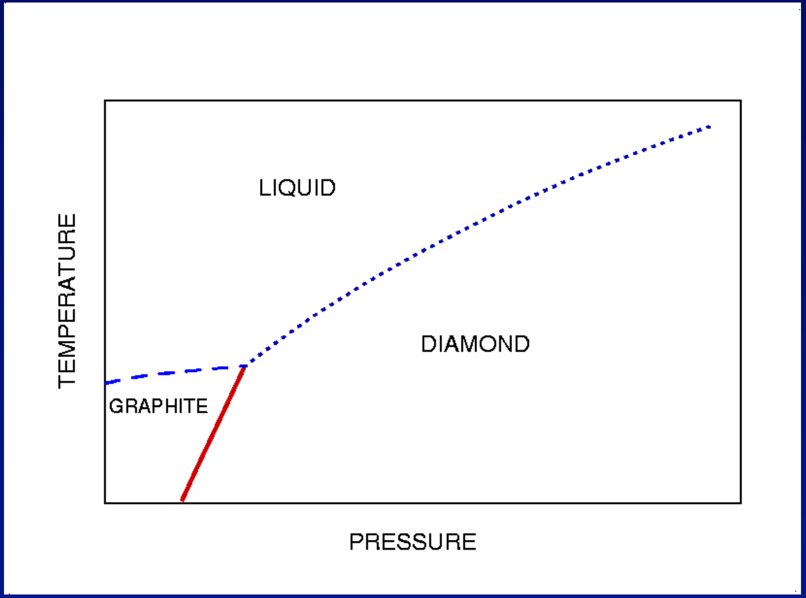


Fig by Jürg Hutter and Marcella Iannuzzi

Example:
Carbon Phase Diagram

Phase Diagram of Carbon





Why Carbon Phase Diagram?

Diamonds in the Sky!?

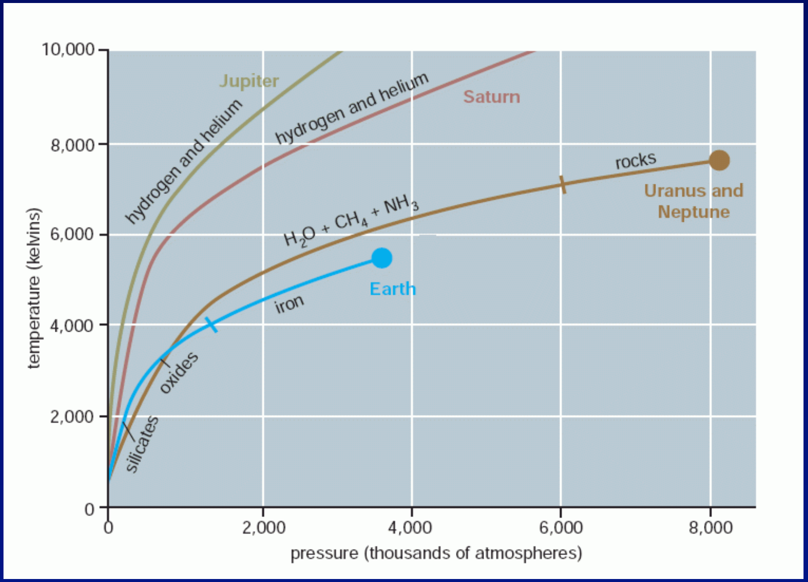
Uranus, Neptune

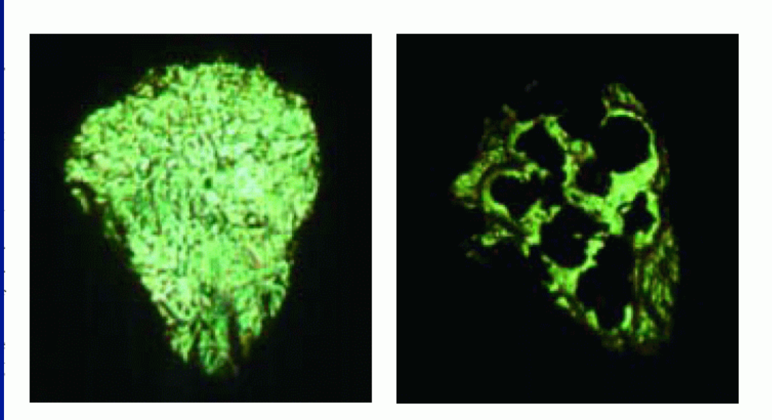
Interior rich in carbon

Temperature and Pressures extreme

5000 K , 1 GPa

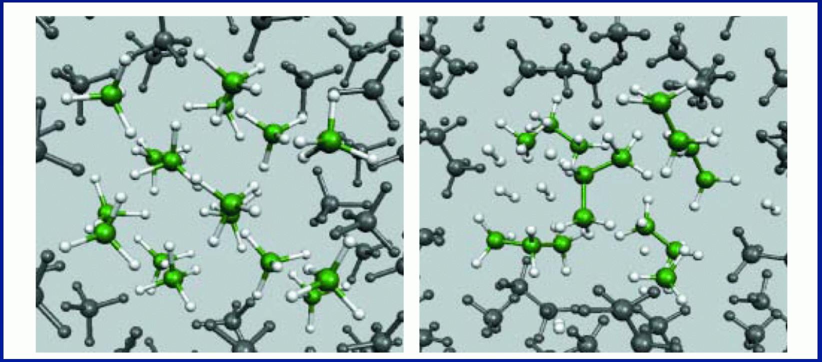
(1 GPa = 10 kbar)





CH4: Laser heating in diamond- anvil cell

(Bennedetti et al, Science 1999)



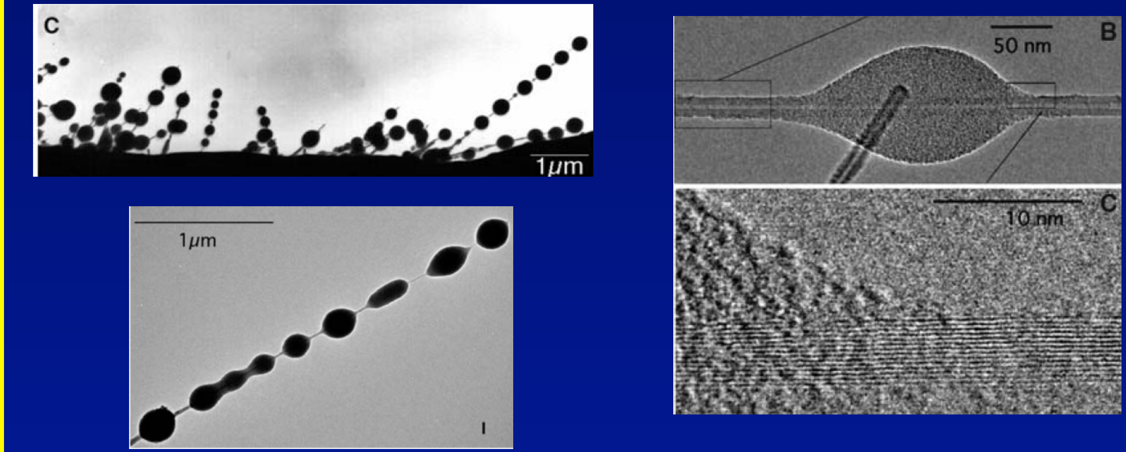
CH4: heating and pressuring in simulation (Scandolo,2003)

Why Carbon Phase Diagram?

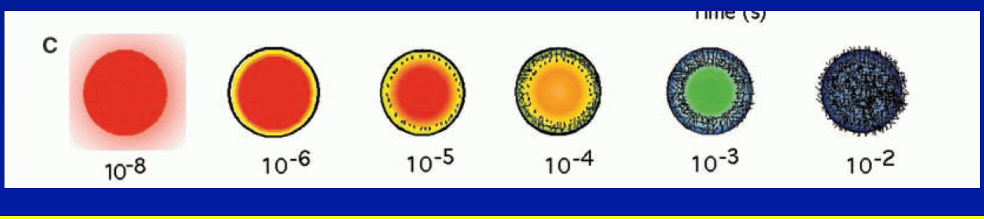
de Heer et al, Science 2005:

Multi Wall Nanotubes from liquid carbon drops

Microscopy Observations



Hypothesized Model



Model and Computational Techniques

- Atomistic Model -> Interaction Potential
- Sampling of Configuration Space by

  Monte Carlo/Molecular Dynamics Simulations

$$\langle A \rangle = \int d\mathbf{r}^N \; P(\mathbf{r}^N) A(\mathbf{r}^N) = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \; A(\mathbf{r}(t'))$$

$$\exp\left[-\beta F_N\right] \sim Q_N = \int d\mathbf{r}^N \; \exp\left[-\beta E(\mathbf{r}^N)\right]$$

- Bulk System by Periodic Boundary Conditions

Interactions: Density Functional Theory

Kohn-Sham Formulation

$$\sum_{i}^{\mathcal{N}} |\psi_i(\mathbf{r})|^2 \equiv n(\mathbf{r})$$

$$E[n] = T_s[n] + \int d\mathbf{r}\, n(\mathbf{r})\, v(\mathbf{r}) + J[n] + E_{xc}[n]$$

$$T_s[n] = \sum_{i}^{\text{occ}} \left\langle \psi_i \middle| -\frac{1}{2}\nabla^2 \middle| \psi_i \right\rangle$$

$$J[n] = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E_{xc}[n] = T[n] - T_s[n] + V_{ee}[n] - J[n]$$

Interactions: Exchange Correlation Functional

Local Density Approximation (LDA)

$$E_{xc}^{\mathsf{LDA}}[n] = \int d\mathbf{r}\, F_{xc}(n(\mathbf{r})) = \int d\mathbf{r}\, \epsilon_{xc}(n(\mathbf{r}))\, n(\mathbf{r})$$

$\epsilon_{xc}(n) =$ The exchange correlation energy per electron of the **homogeneous electron gas** at density n

+ Generalized Gradient Correction

Interconversion C-C Bonds:

~ 0.005 Ha = 5 kCal/mol

DFT-based Molecular Dynamics

Plane-wave Expansion of Kohn-Sham Orbitals

$$\phi_i(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} c_i(\vec{G})e^{i\vec{G}\cdot\vec{r}}$$

Car-Parrinello Lagrangian

$$\begin{aligned}\mathcal{L}^{CP}(\mathbf{c}, \dot{\mathbf{c}}, \mathbf{R}, \dot{\mathbf{R}}) =& \mu \sum_{i,\vec{G}} \dot{c}_i^*(\vec{G})\dot{c}_i(\vec{G}) + \frac{1}{2}\sum_I M_i \dot{\vec{R}}_i^2 - E(\mathbf{c}, \mathbf{R}) \\ &+ \sum_{ij} \Lambda_{ij} \left[\sum_{\vec{G}} c_i^*(\vec{G})c_j(\vec{G}) - \delta_{ij} \right]\end{aligned}$$

- μ : Controls seperation of ionic and “electronic” dynamics
- If “electronic” dynamics fast E(c,R) near ground state

Pseudo Potentials

$$V^{\mathrm{PS}}(\mathbf{r}, \mathbf{r}') = V_{\mathrm{loc}}^{\mathrm{PS}}(r) + \sum_{L=0}^{L_{\max}} \Delta V_L^{\mathrm{PS}}(r)|Y_L\rangle\langle Y_L|$$

Carbon

Interactions: Empirical Potential

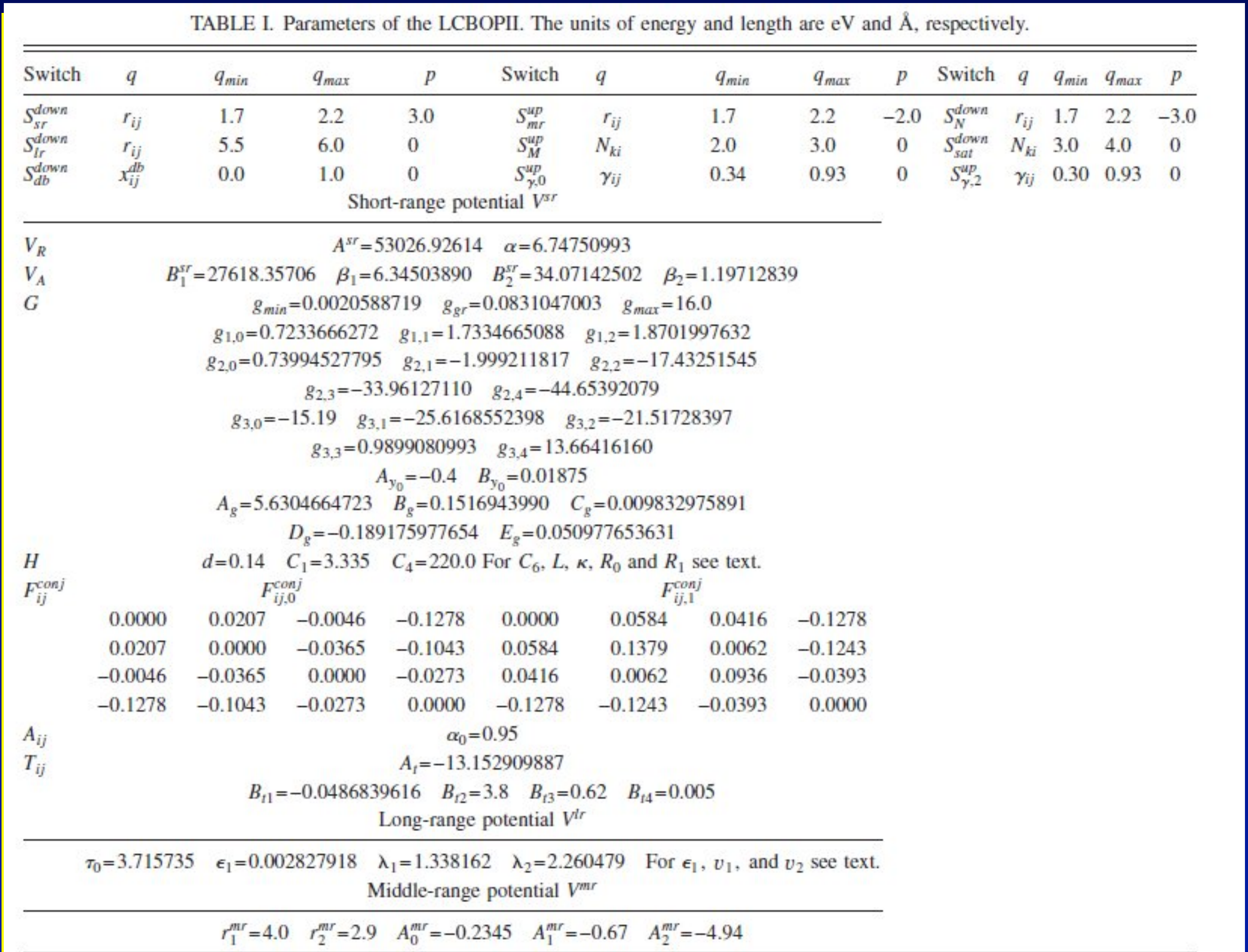


TABLE I. Parameters of the LCBOPII. The units of energy and length are eV and Å, respectively.

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

Short-range potential V^{sr}

V_R	$A^{sr}=53026.92614$ $\alpha=6.74750993$
V_A	$B_1^{sr}=27618.35706$ $\beta_1=6.34503890$ $B_2^{sr}=34.07142502$ $\beta_2=1.19712839$
G	$g_{min}=0.0020588719$ $g_{gr}=0.0831047003$ $g_{max}=16.0$ $g_{1,0}=0.7233666272$ $g_{1,1}=1.7334665088$ $g_{1,2}=1.8701997632$ $g_{2,0}=0.73994527795$ $g_{2,1}=-1.999211817$ $g_{2,2}=-17.43251545$ $g_{2,3}=-33.96127110$ $g_{2,4}=-44.65392079$ $g_{3,0}=-15.19$ $g_{3,1}=-25.6168552398$ $g_{3,2}=-21.51728397$ $g_{3,3}=0.9899080993$ $g_{3,4}=13.66416160$ $A_{y_0}=-0.4$ $B_{y_0}=0.01875$ $A_g=5.6304664723$ $B_g=0.1516943990$ $C_g=0.009832975891$ $D_g=-0.189175977654$ $E_g=0.050977653631$
H	$d=0.14$ $C_1=3.335$ $C_4=220.0$ For C_6, L, κ, R_0 and R_1 see text.

F_{ij}^{conj}

$F_{ij,0}^{conj}$				$F_{ij,1}^{conj}$			
0.0000	0.0207	−0.0046	−0.1278	0.0000	0.0584	0.0416	−0.1278
0.0207	0.0000	−0.0365	−0.1043	0.0584	0.1379	0.0062	−0.1243
−0.0046	−0.0365	0.0000	−0.0273	0.0416	0.0062	0.0936	−0.0393
−0.1278	−0.1043	−0.0273	0.0000	−0.1278	−0.1243	−0.0393	0.0000

A_{ij}	$\alpha_0=0.95$
T_{ij}	$A_t=-13.152909887$ $B_{t1}=-0.0486839616$ $B_{t2}=3.8$ $B_{t3}=0.62$ $B_{t4}=0.005$

Long-range potential V^{lr}

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

Middle-range potential V^{mr}

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

Carbon

Interactions: Empirical Potential

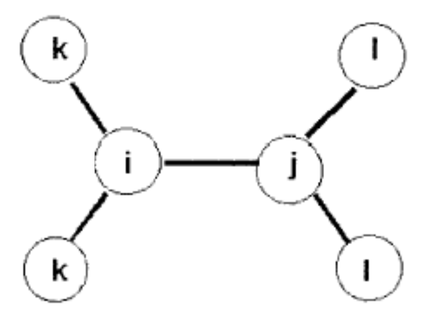
Bond-Order Potential

$$E_b = \frac{1}{2}\sum_{i,j}^{N}\left(f_{c,ij}V_{ij}^{SR} + (1 - f_{c,ij})V_{ij}^{LR} \right)$$

Short Range Part

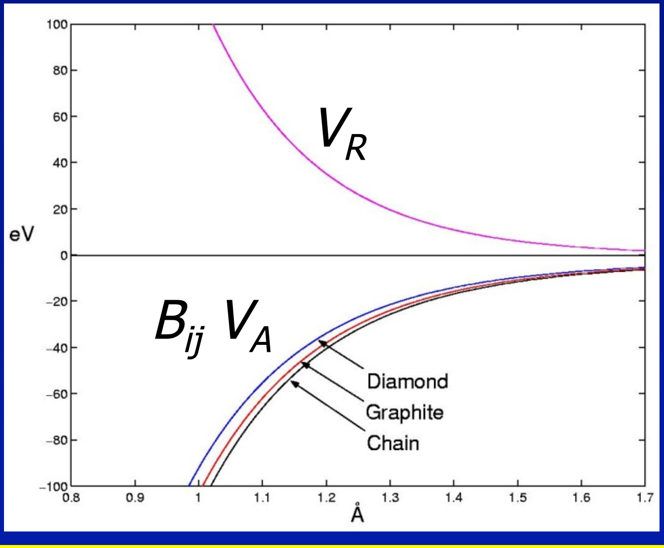
$$V_{ij}^{SR} = V_R(r_{ij}) - \underset{\underset{\text{Bond-order}}{\uparrow}}{\boxed{\bar{b}_{ij}}} V_A(r_{ij})$$

$$\begin{aligned} V_R(r) &= Ae^{-\alpha r} \\ V_A(r) &= B_1\, e^{-\beta_1 r} + B_2\, e^{-\beta_2 r} \end{aligned}$$

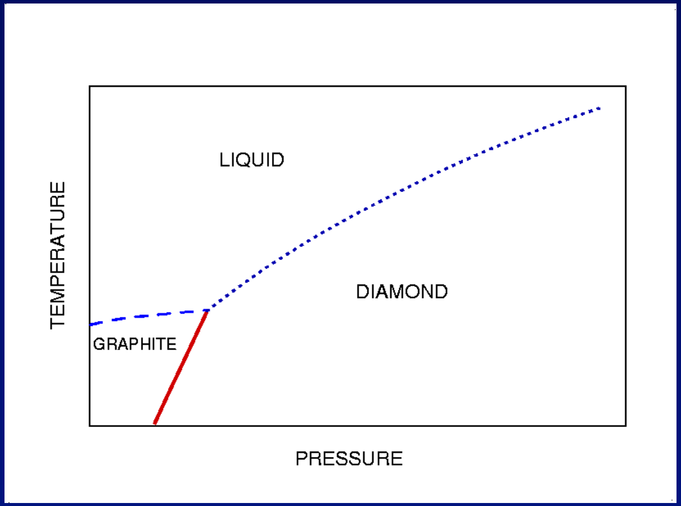


b_{ij} depends on:

- \# neighbours
- Angles (bending)
- Conjugation
- Dihedrals (torsion)



“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)

1990-2010: Improvement of empirical potentials

LCBOP

Emperical Bond-Order Potential

Los and Fasolino (PRB 2003);

Improvement by Los et al. PRB 2004: LCBOP**I**; PRB 2005: LCBOP**II**

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

Simulation Parameters

DFT Interaction

Molecular Dynamics

128 atoms

Periodic cubic box NVT

Becke-Perdew GGA DFT-Functional

LCBOP Empirical Interaction

Monte Carlo

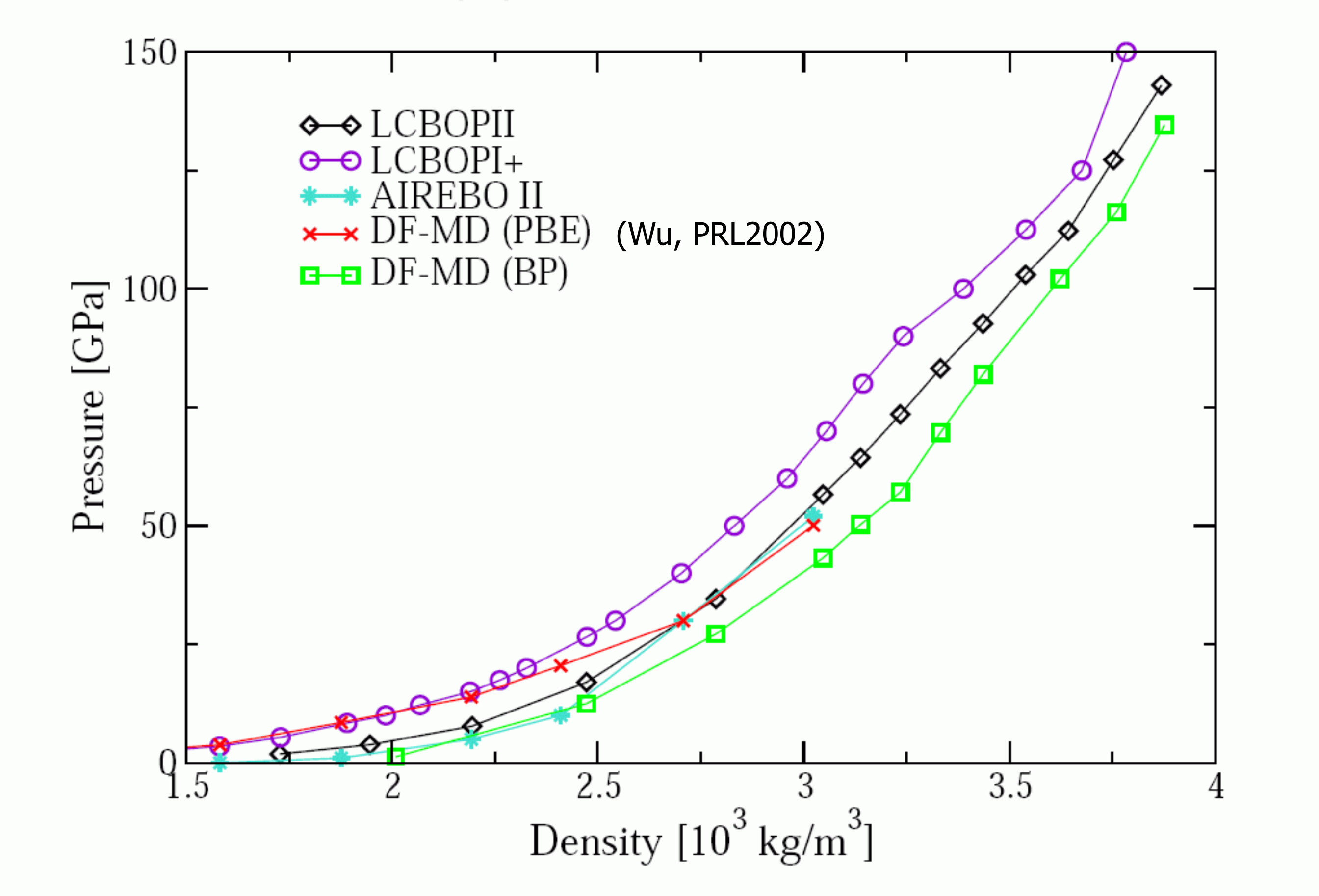
128 atoms

Periodic cubic box NPT

Liquid Properties

DFT-MD versus LCBOPI and LCBOPII at 6000K

Equation of State

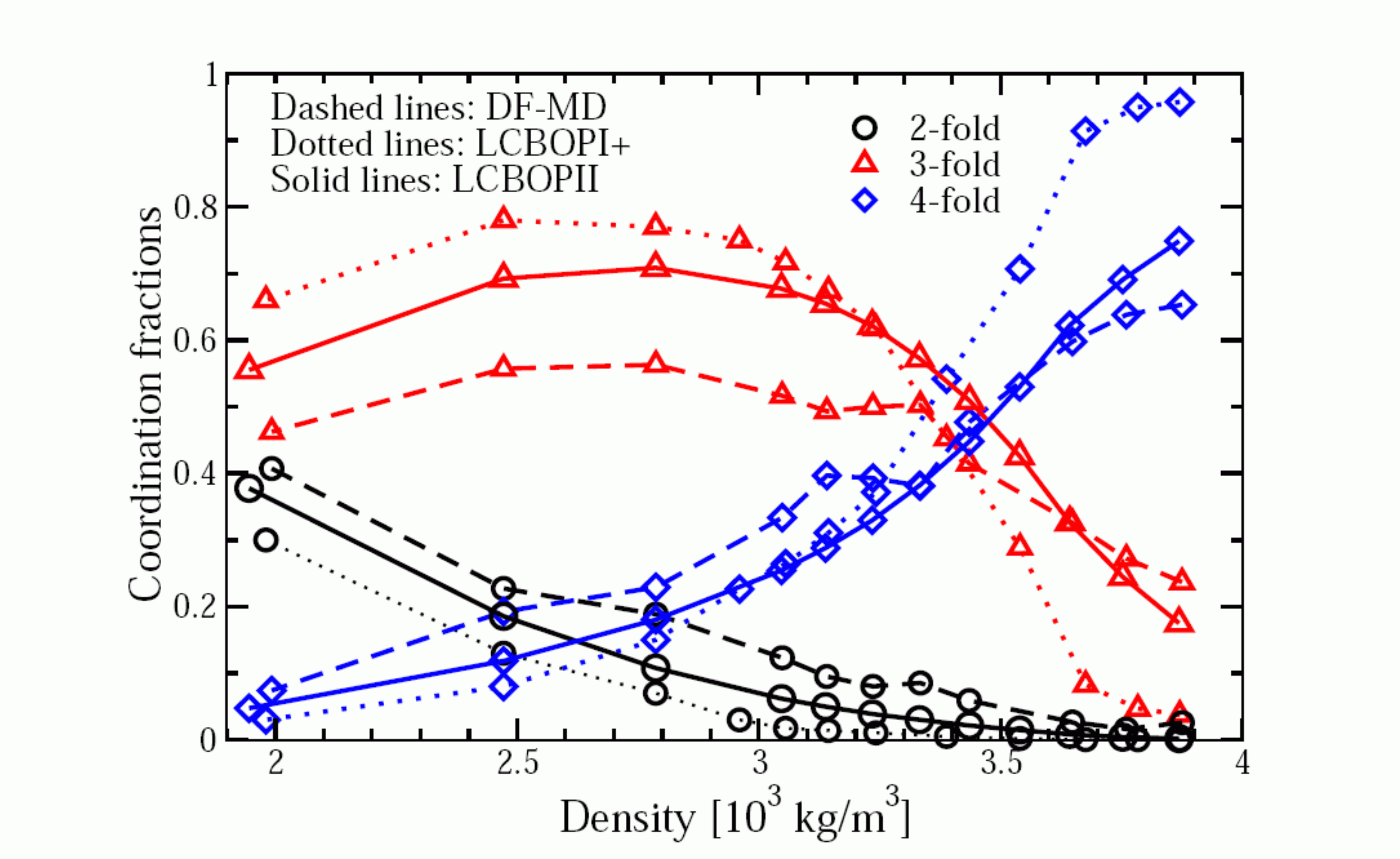


(Wu, PRL2002)

Liquid Properties

DFT-MD versus LCBOPI and LCBOPII at 6000K

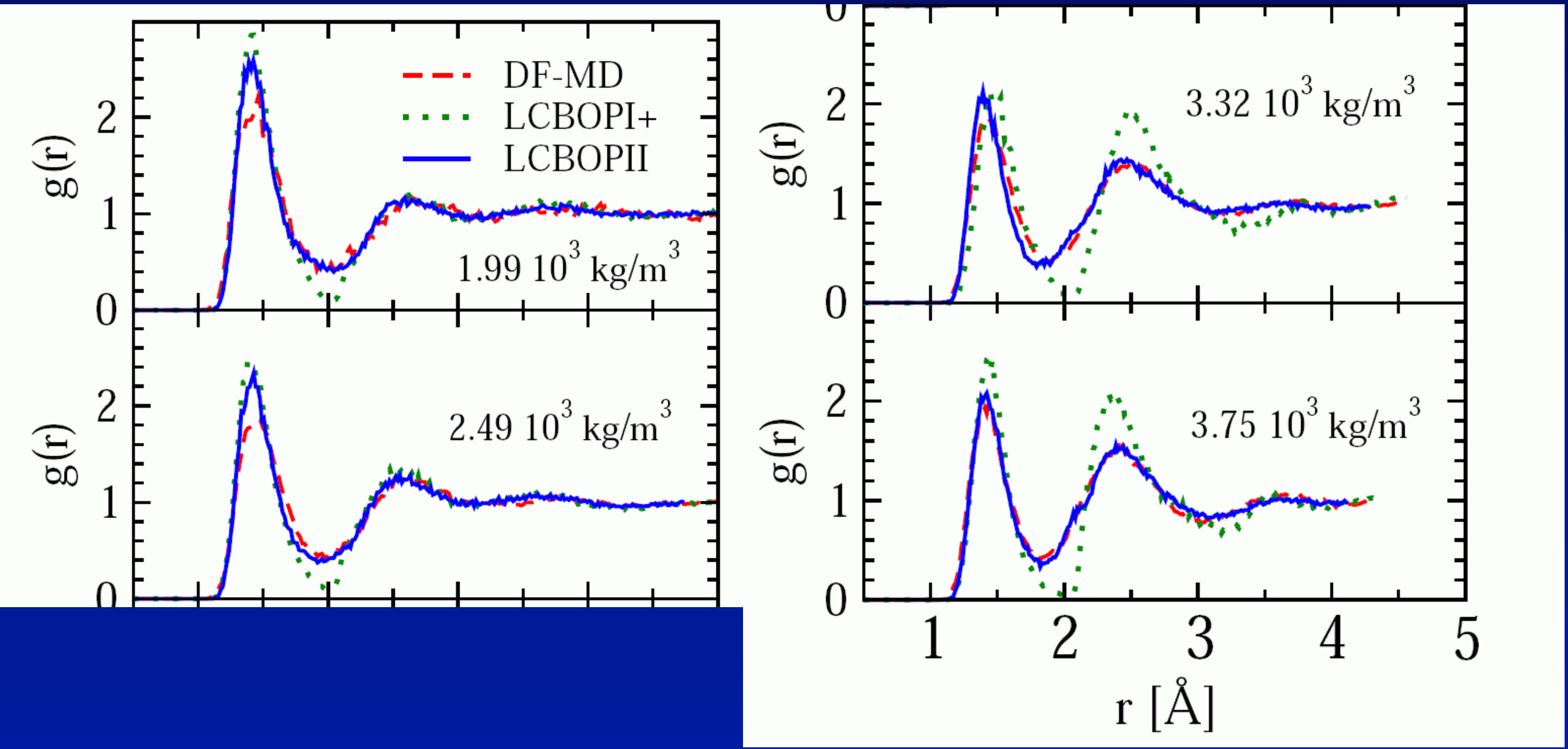
Coordination Fractions



Liquid Properties

DFT-MD versus LCBOPI and LCBOPII at 6000K

Radial Distribution Functions



Determining Coexistence Points (I)

Free-energy changes using

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

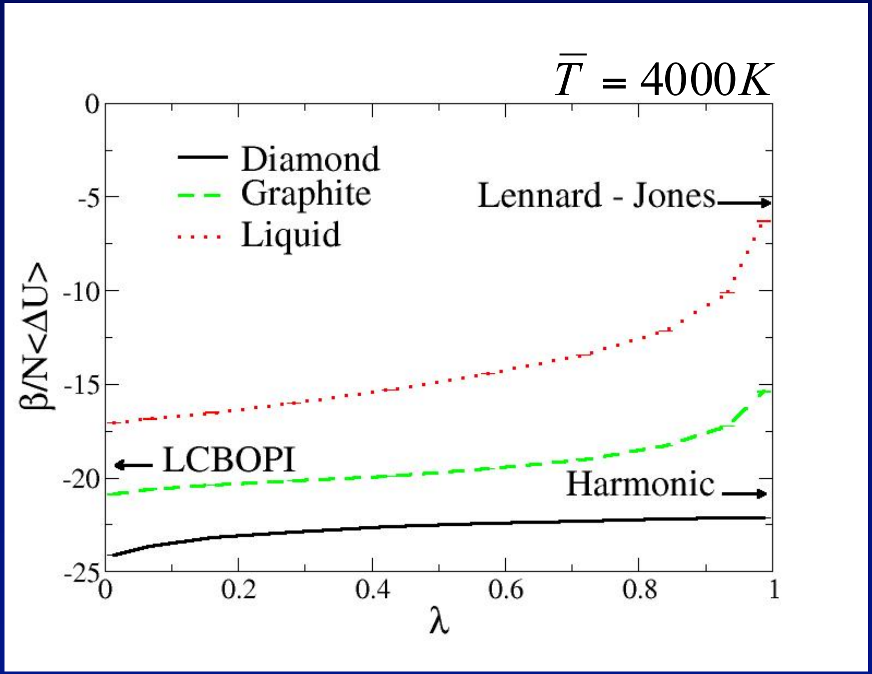
$$F^* = F^{\mathrm{ref}} + \int_0^1 \mathrm{d}\lambda \left\langle U^{\mathrm{ref}} - U^* \right\rangle_\lambda$$

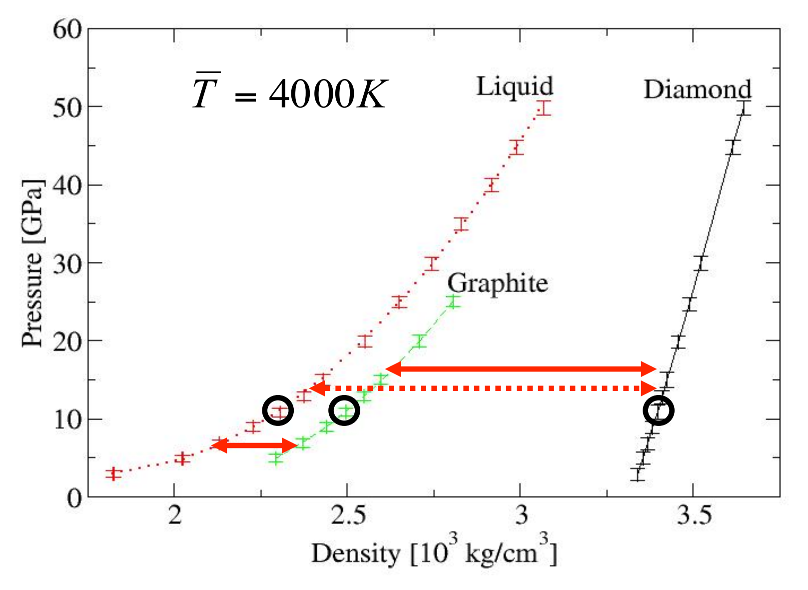
Free energy of initial state point (P=10 GPa, T=4000K)

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

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

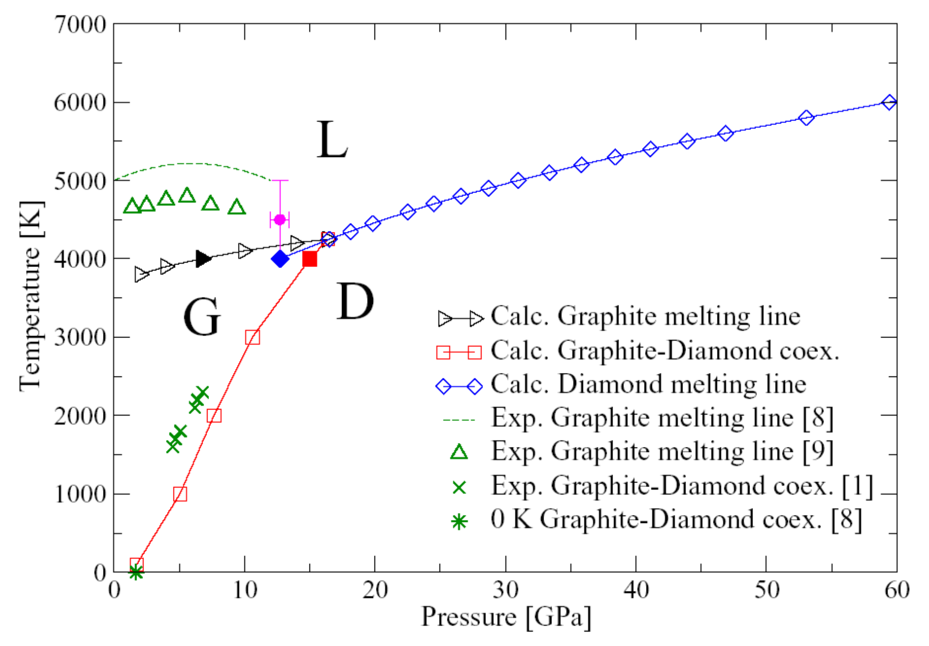
$$\mathrm{d}T/\mathrm{d}P = T\Delta v/\Delta h$$

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