

Thermostats in MD

Kinetic Energy (6.1/7.1 - Intro)
Anderson Thermostat (6.1.1/7.1.1.1)
Nosé Hoover Thermostat (6.1.2/7.1.2)

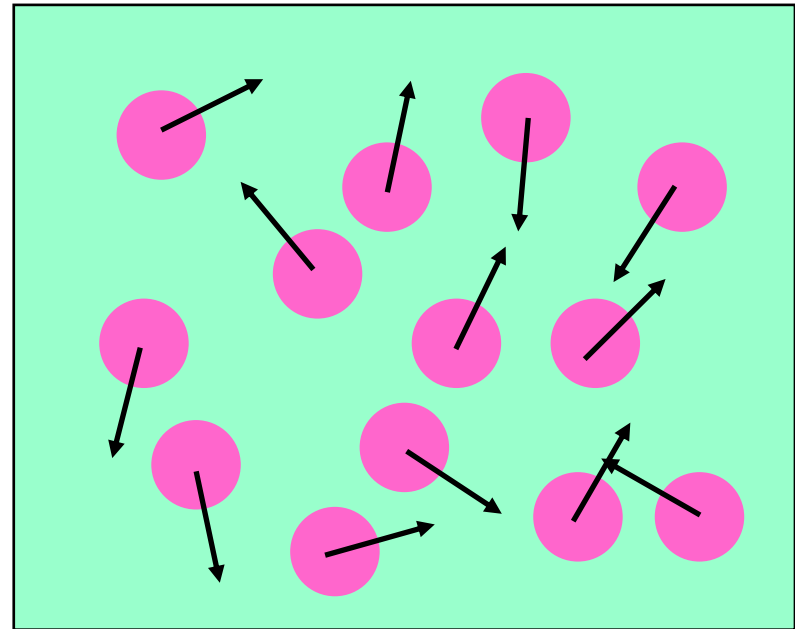
Free Energy and Phase Equilibria

Thermodynamic Integration (7.1/8.4)
Chemical Potentials (7.2/8.5)
Overlapping Distributions (7.2/8.6)
Tracing Coexistence Curves (9.2/8.3.1.3)
Application: Phase Diagram of Carbon

Andersen Thermostat

- Every particle has a fixed probability to collide with the Andersen demon
- After collision the particle is given a new velocity

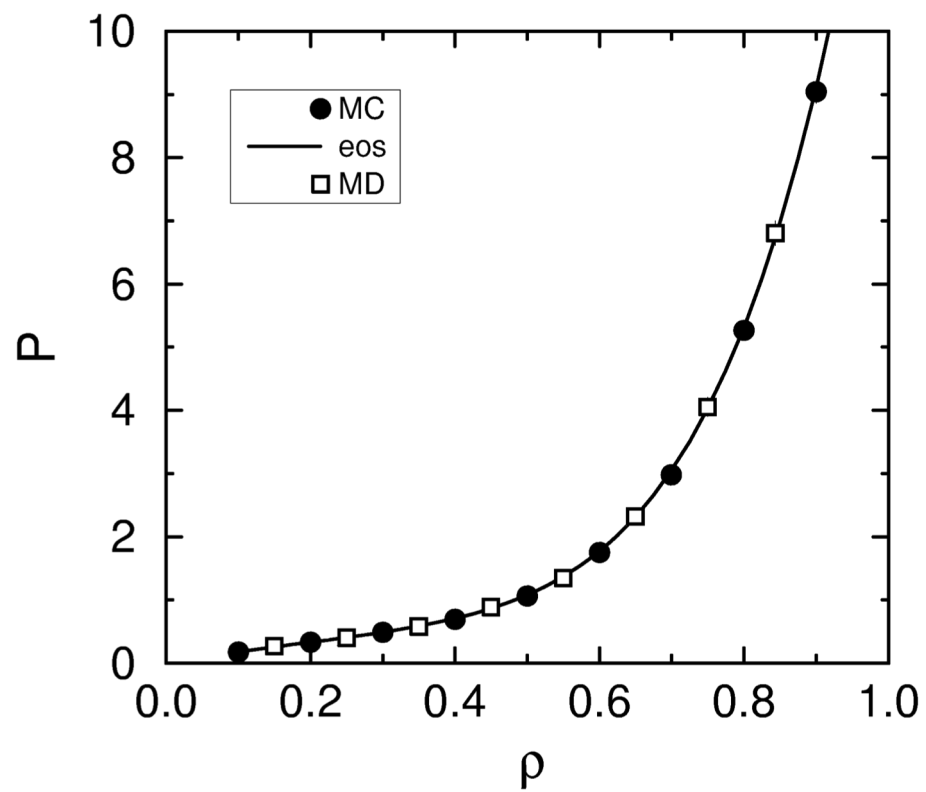
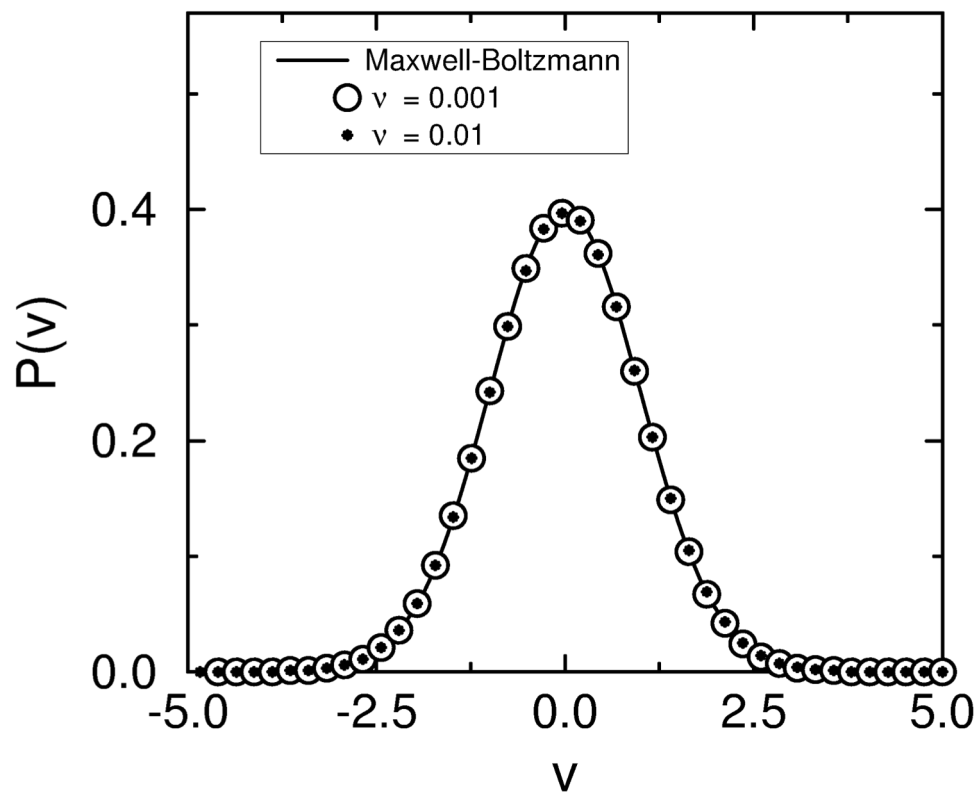
$$P(v) = \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp \left[-\beta m v^2 / 2 \right]$$



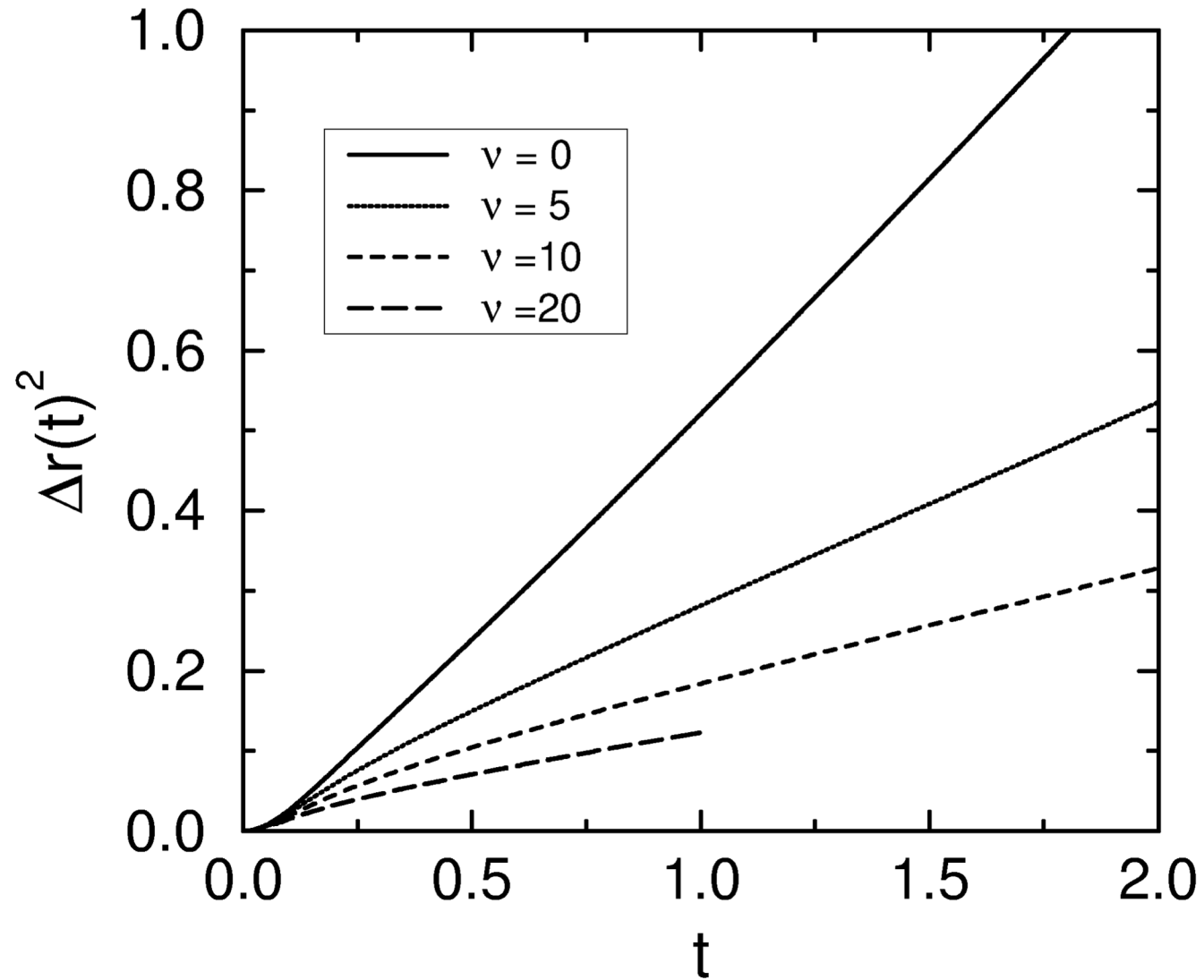
- The probabilities to collide are uncorrelated (Poisson distribution)

$$P(t; v) = v \exp[-vt]$$

Andersen thermostat: static properties



Andersen thermostat: dynamic properties



Nose Hoover thermostat

goal: compute MD trajectory sampling NVT ensemble.

Take kinetic energy out of the system and put it back in via a 'piston'.

piston can be seen as additional variable s storing kinetic energy

Approach: extended Lagrangian

extended variable

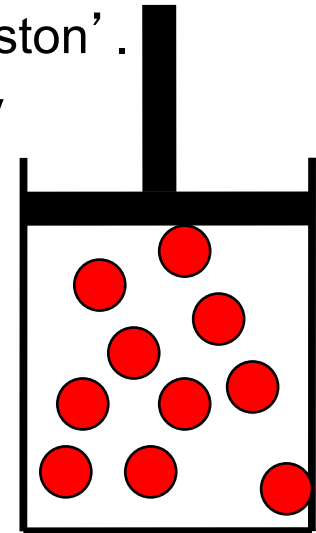
$$\mathcal{L}_{\text{Nose}} = \sum_{i=1}^N \frac{1}{2} m s^2 \dot{r}_i^2 - U(r^N) + \frac{1}{2} Q \dot{s}^2 - \frac{g}{\beta} \ln s$$

effective mass

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{r}_i} = m s^2 \dot{r}_i$$

$$p_s = \frac{\partial \mathcal{L}}{\partial \dot{s}} = Q \dot{s}$$

constant to be set



$$\mathcal{H}_{\text{Nose}} = \sum_{i=1}^N \frac{p_i^2}{2 m s^2} + \frac{p_s^2}{2 Q} + U(r^N) + \frac{g}{\beta} \ln s$$

Nose-Hoover Thermostat

$$\mathcal{H}_{\text{Nose}} = \sum_{i=1}^N \frac{p_i^2}{2ms^2} + \frac{p_s}{2Q} + U(r^N) + \frac{g}{\beta} \ln s$$

equations of motion follow from Hamilton's equations.

$$\begin{aligned} \frac{dr_i}{dt} &= \frac{\partial \mathcal{H}_{\text{Nose}}}{\partial p_i} = \frac{p_i}{ms^2} & \frac{dp_i}{dt} &= -\frac{\partial \mathcal{H}_{\text{Nose}}}{\partial r_i} = -\frac{\partial U(r^N)}{\partial r_i} \\ \frac{ds}{dt} &= \frac{\partial \mathcal{H}_{\text{Nose}}}{\partial p_s} = \frac{p_s}{Q} & \frac{dp_s}{dt} &= -\frac{\partial \mathcal{H}_{\text{Nose}}}{\partial s} = \frac{1}{s} \left(\sum \frac{p_i^2}{ms^2} - \frac{g}{\beta} \right) \end{aligned}$$

Nose Hoover implementation

NH equation of motion can be rewritten as (Hoover 1984)

$$\dot{\mathbf{r}}_i = \mathbf{p}_i / m_i$$

$$\dot{\mathbf{p}}_i = \mathbf{f}_i - \xi \mathbf{p}_i$$

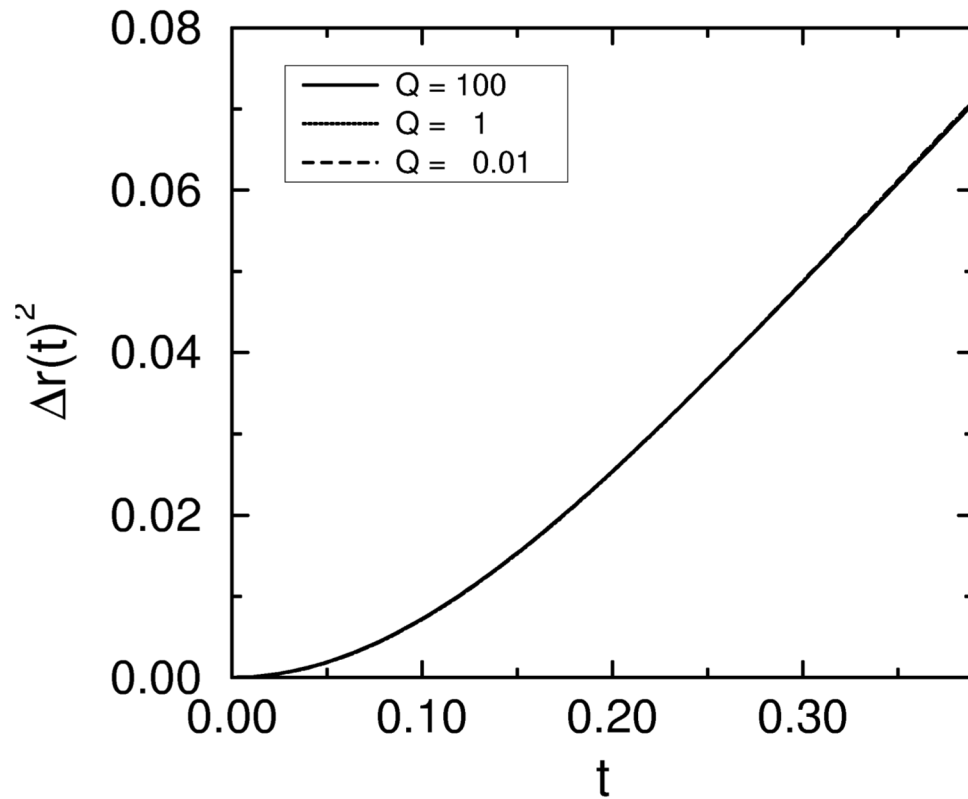
$$\dot{\xi} = \left(\sum_i p_i^2 / m_i - 3N / \beta \right) / Q$$

Where $\xi = p_s / Q$ now denotes a kind of 'friction' term

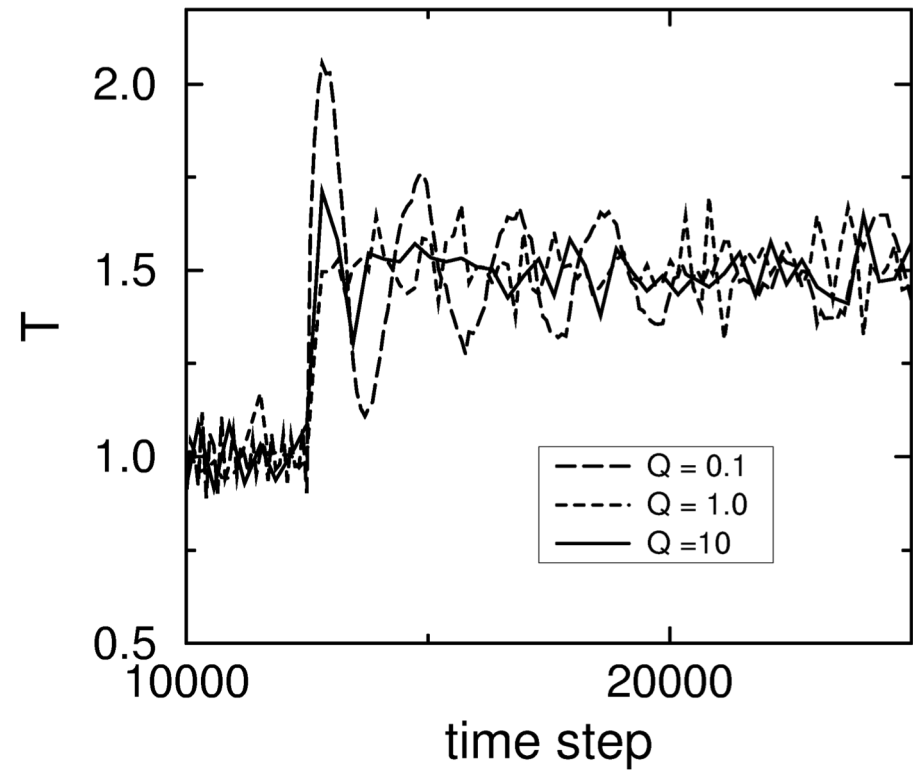
Mass Q determines the damping

Effect of mass Q

Lennard-Jones fluid



mean square displacement



temperature relaxation

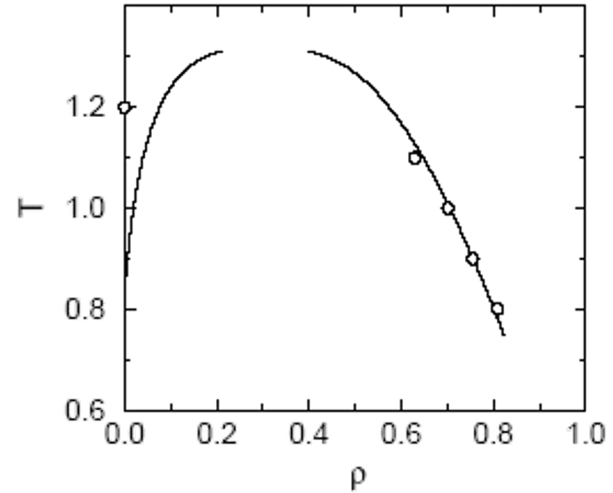
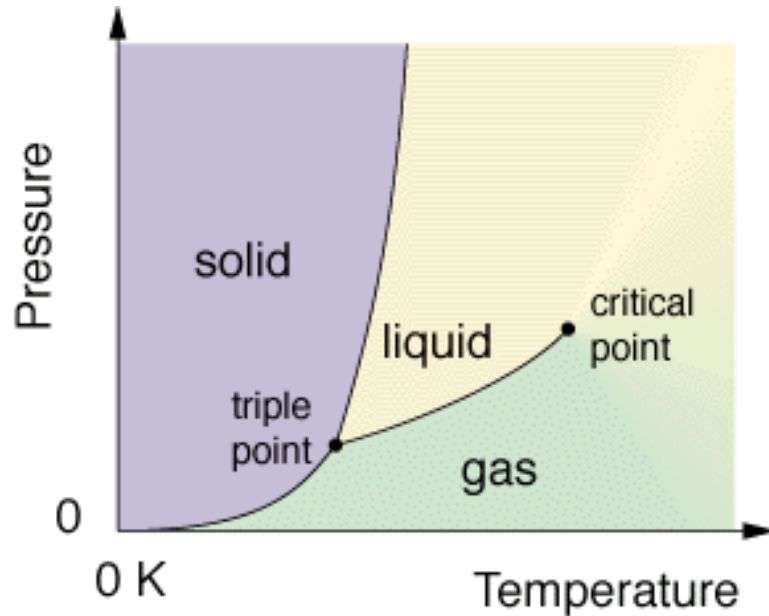
Why Free Energies?

- Reaction equilibrium constants $A \leftrightarrow B$

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

- Examples:
 - Chemical reactions: 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

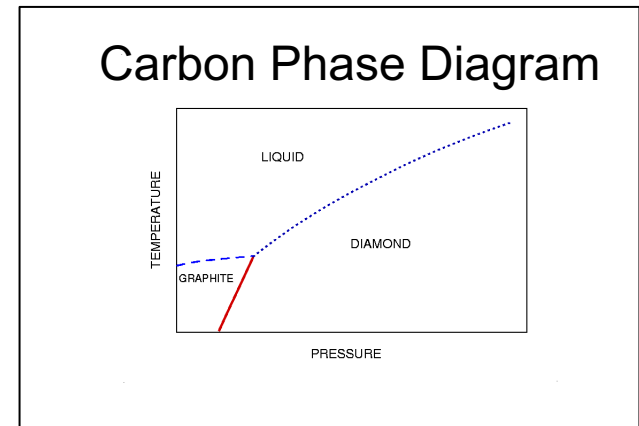


Along the liquid-gas coexistence line increasing the pressure and temperature at constant volume the liquid density becomes lower and the vapor density higher.

Critical point: no transition 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)

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

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:

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

All thermodynamic quantities can be derived from F and its derivatives

We need F (or G)

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

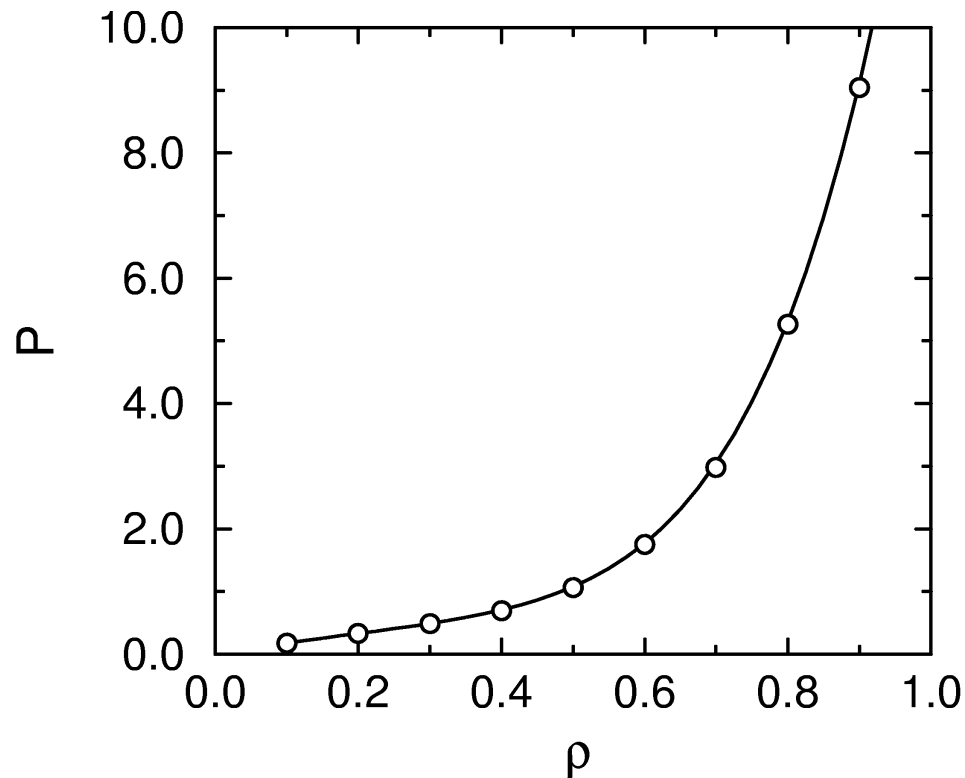
$$F(V) = F(V_0) + \int_{V_0}^V \left(\frac{\partial F}{\partial V} \right)_{N,T} dV = F(V_0) - \int P dV$$

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

- Note: for only 1 point of the equation of state F must be known
- For liquid e.o.s from ideal gas

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

Equation of state



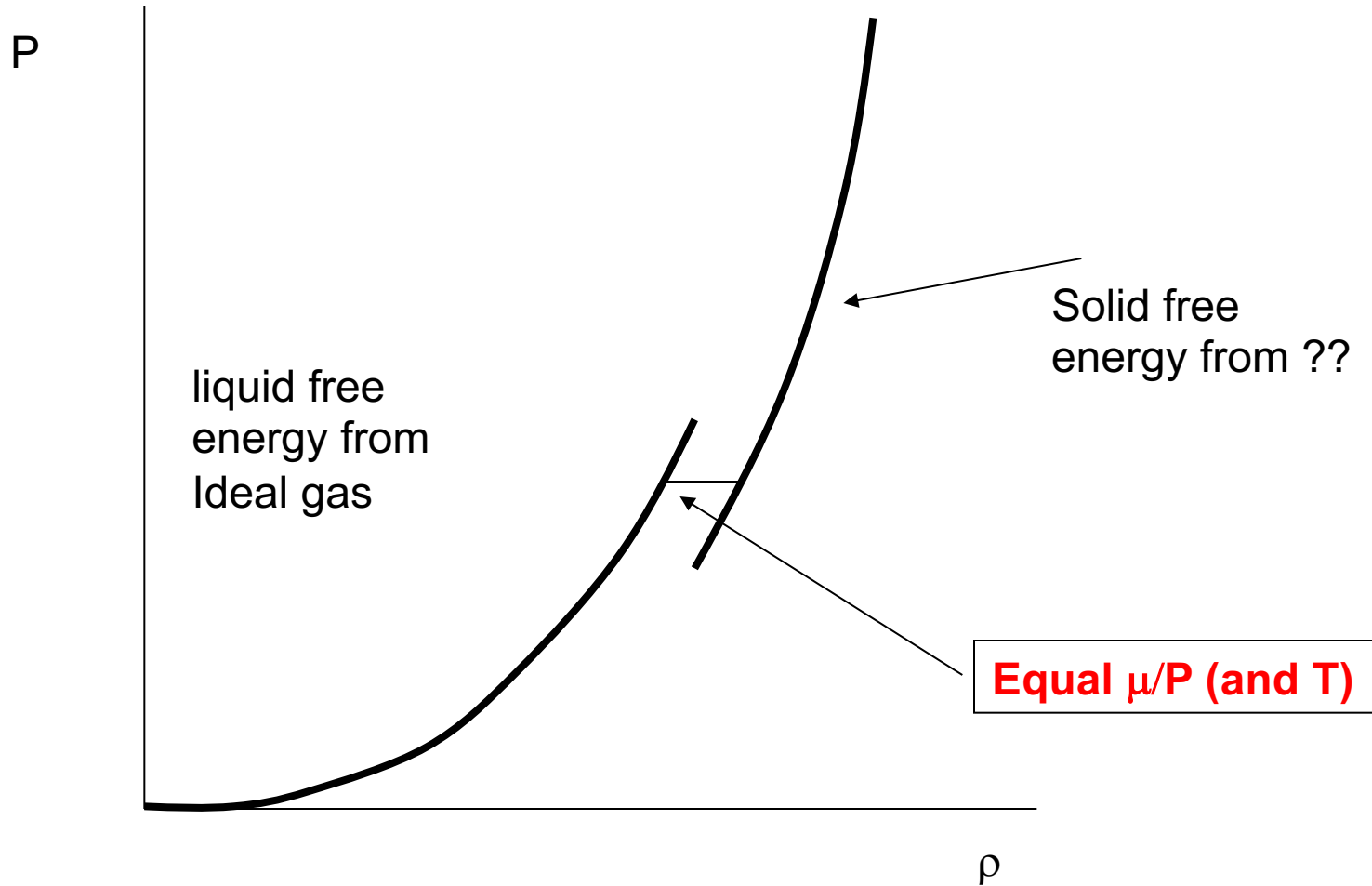
$$P = P(\rho, T)$$

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

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

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

Free Energy & Statistical Thermodynamics

Probability to find a particular configuration (NVT)

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

Partition function

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

Free energy

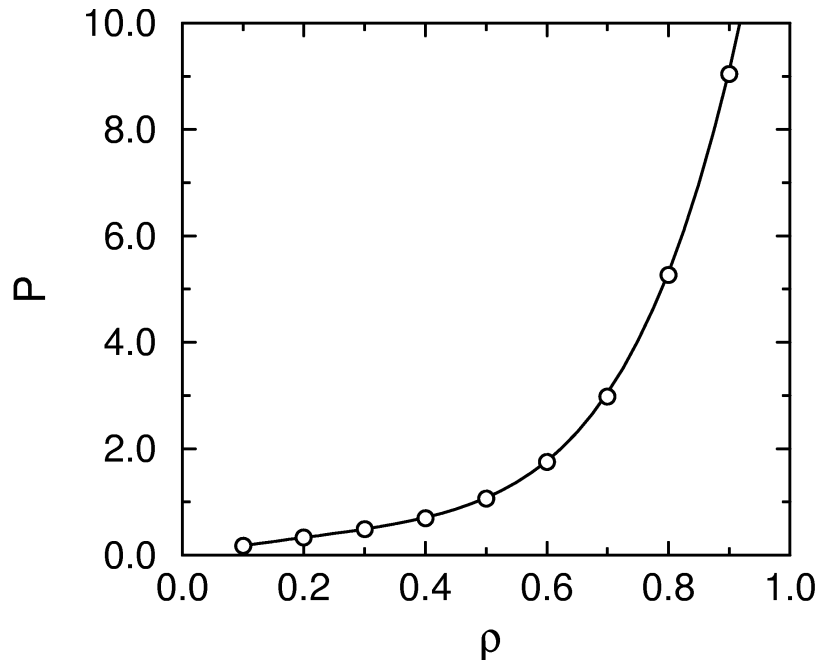
$$\beta F = -\ln(Q_{NVT})$$

F is difficult, because requires measuring the phase space volume
This is **not** a weighted average ... this is **not** sampling

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

We cannot measure “volumes” by sampling, ...

but we can measure **differences** by sampling



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

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

I - Thermodynamic integration

- Reference state - free energy known $\lambda=0$
- Target state - free energy not known $\lambda=1$

Coupling parameter

Reference System

Target System

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

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

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

Thermodynamic integration

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

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

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

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

Free-energy difference
as ensemble average!

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

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

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

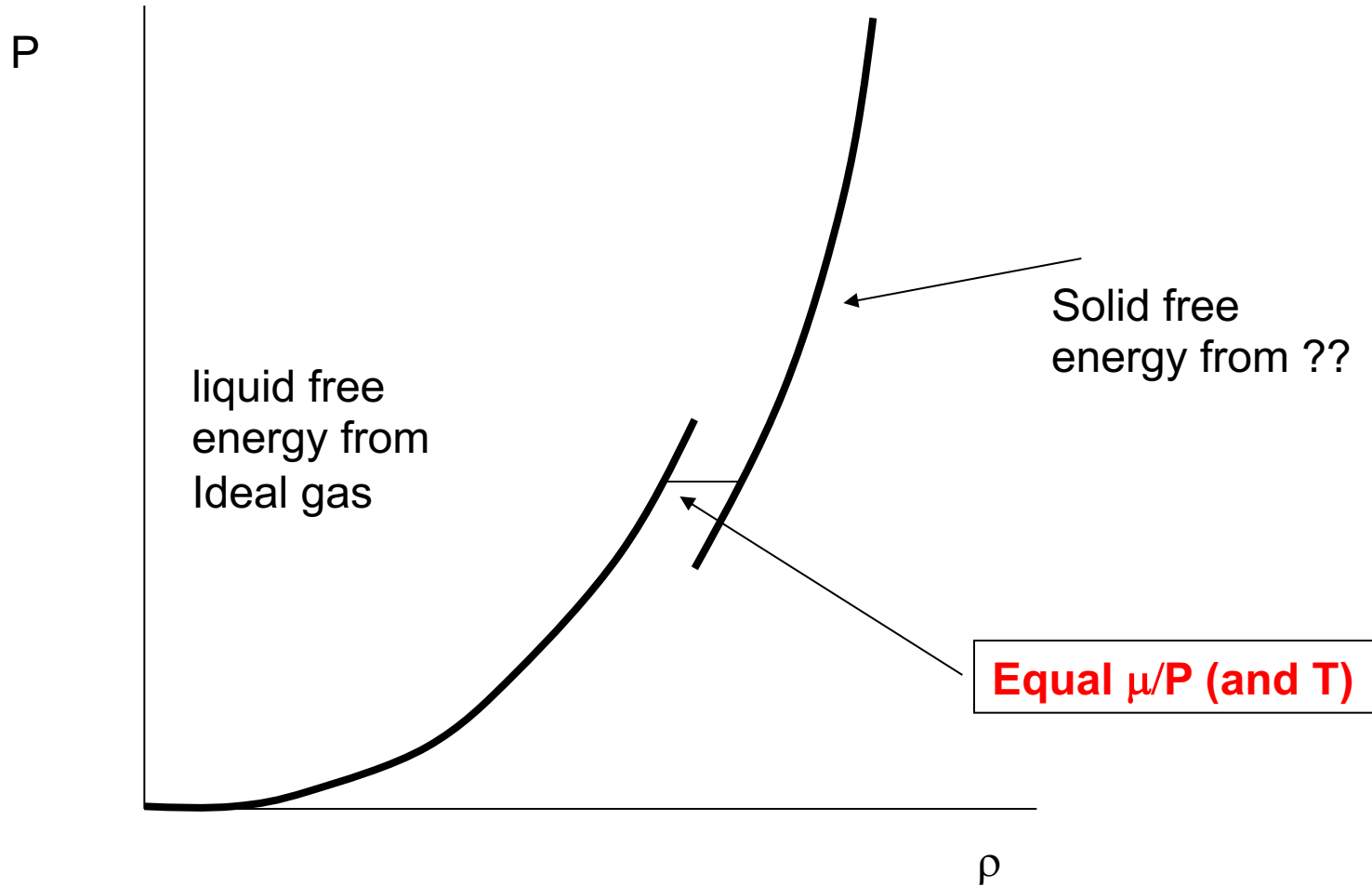
$$U(1) = U^{\text{Stockm}}}$$

Stockmayer

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

Phase Equilibrium

Free Energy Liquid and Solid



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

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

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

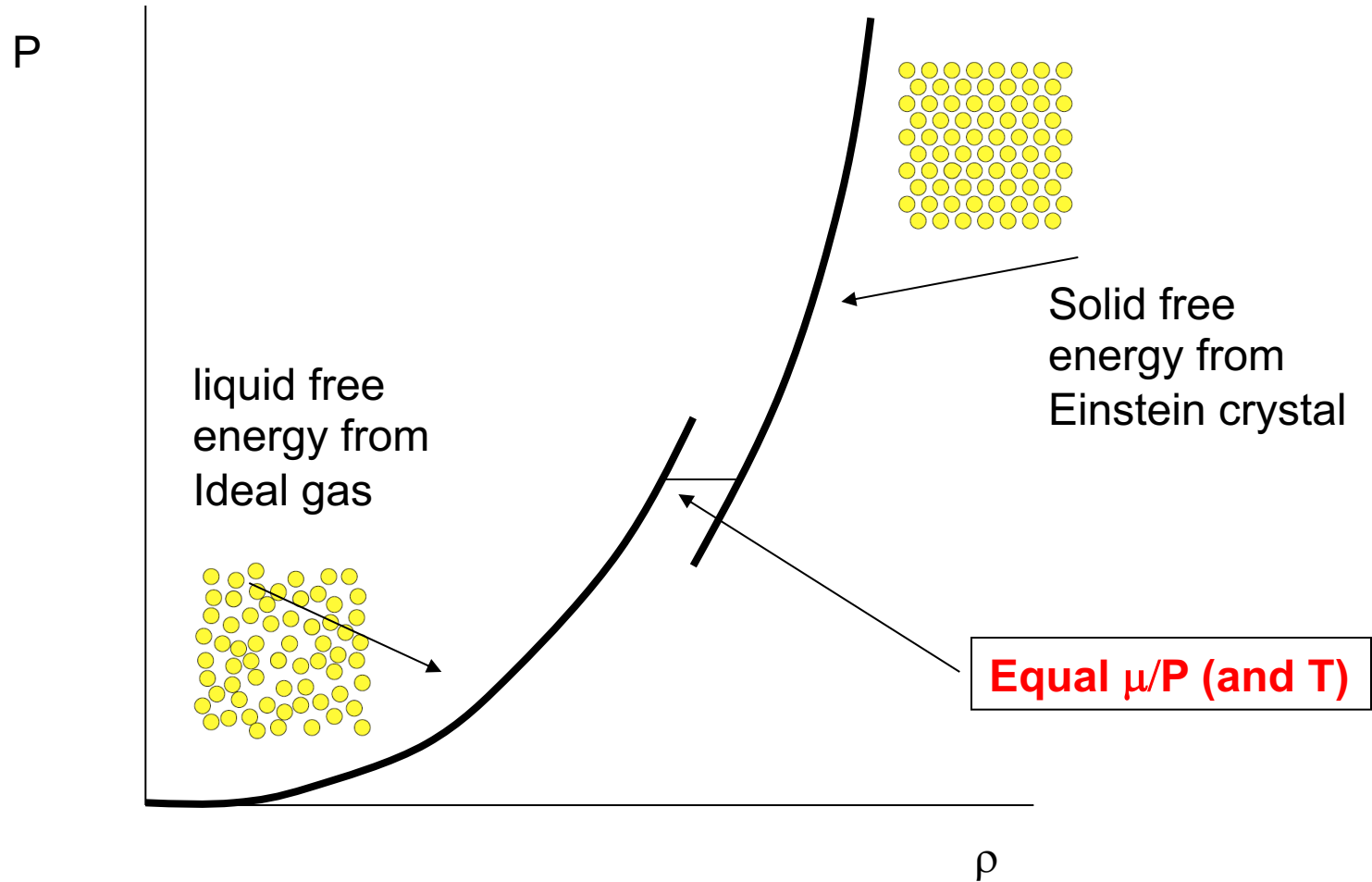
Note, here:

$\lambda = 1$ Reference System

$\lambda = 0$ Target System

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

Hard sphere freezing



Free Energies and Phase Equilibria

General Strategies

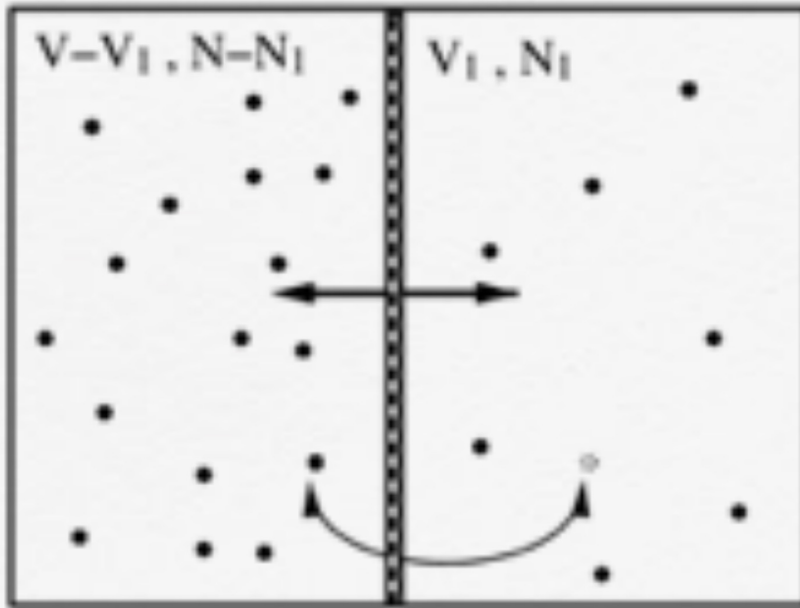
- Determine free energy of both phases separately, relative to a reference state
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Free Energies and Phase Equilibria

Gibbs Ensemble

A Sketch

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



- The system is at NVT
- we exchange particles:
 - $N = N_1 + N_2$
- we change the volume
 - $V = V_1 + V_2$

What do we have: NVT system
that is artificially split in two

Particle Insertion Method

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

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

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

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

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

Widom test particle insertion

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

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

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

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

Widom test particle insertion

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

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

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

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

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

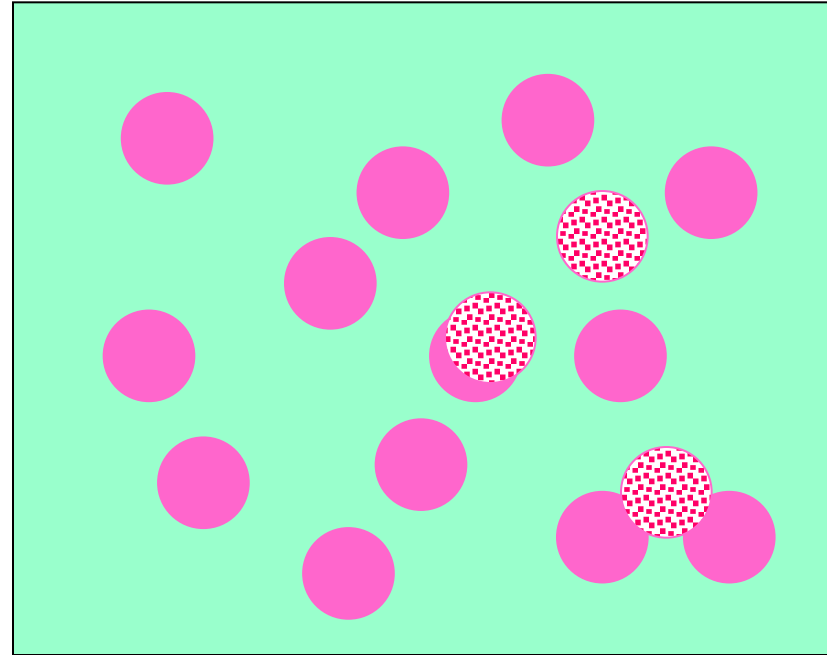
Ghost particle!

Hard spheres

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

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

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



$\left\langle \exp[-\beta\Delta U^+] \right\rangle$ 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

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

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

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

$$= -\ln \frac{\int ds^N \exp[-\beta U_1]}{\int ds^N \exp(-\beta U_0)}$$

$$= -\ln \frac{\int ds^N \exp[-\beta(U_1 - U_0)] \exp[-\beta U_0]}{\int ds^N \exp(-\beta U_0)}$$

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

Umbrella sampling

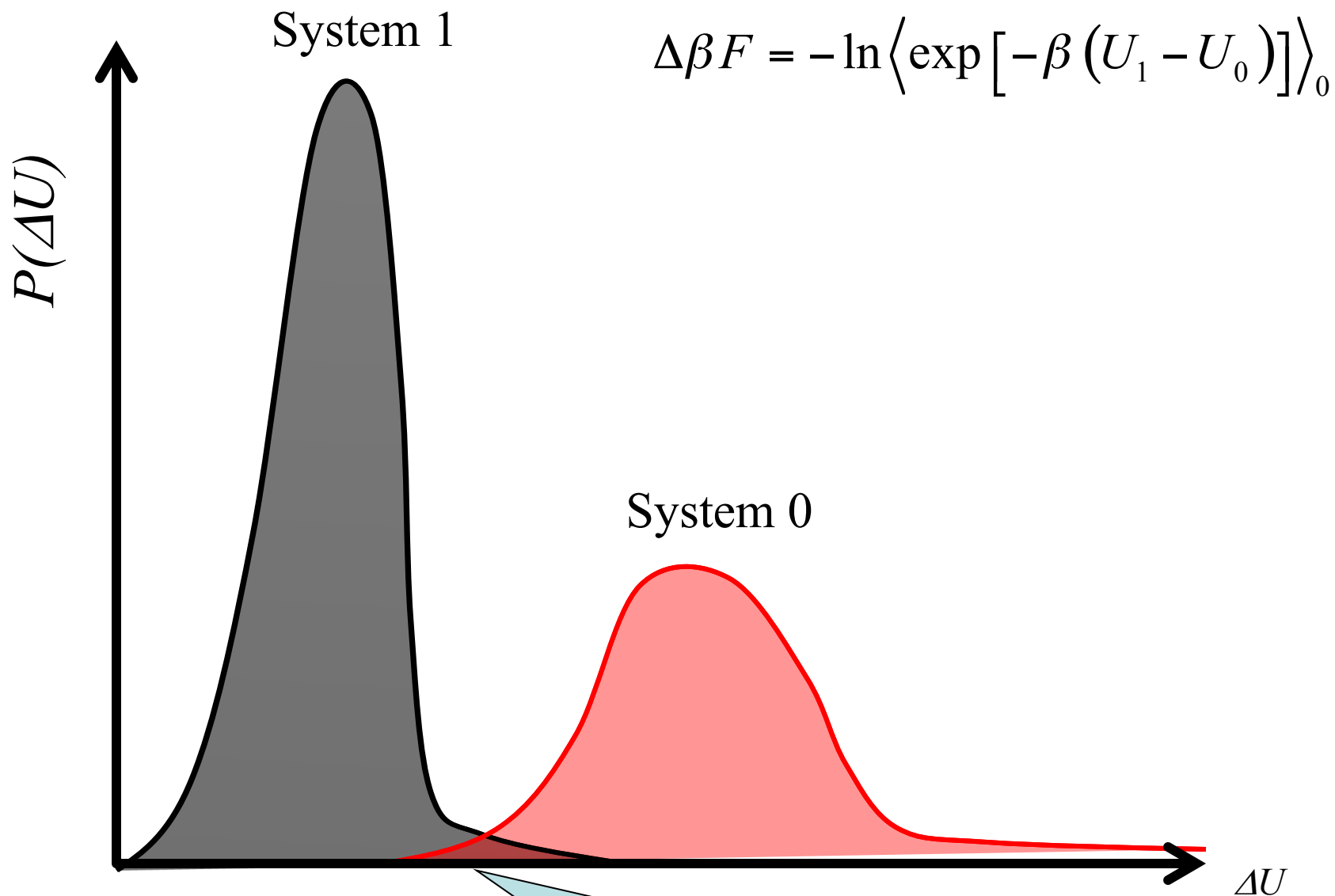
- Start with thermodynamic perturbation

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

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

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

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



Overlap becomes very small

Bridging function

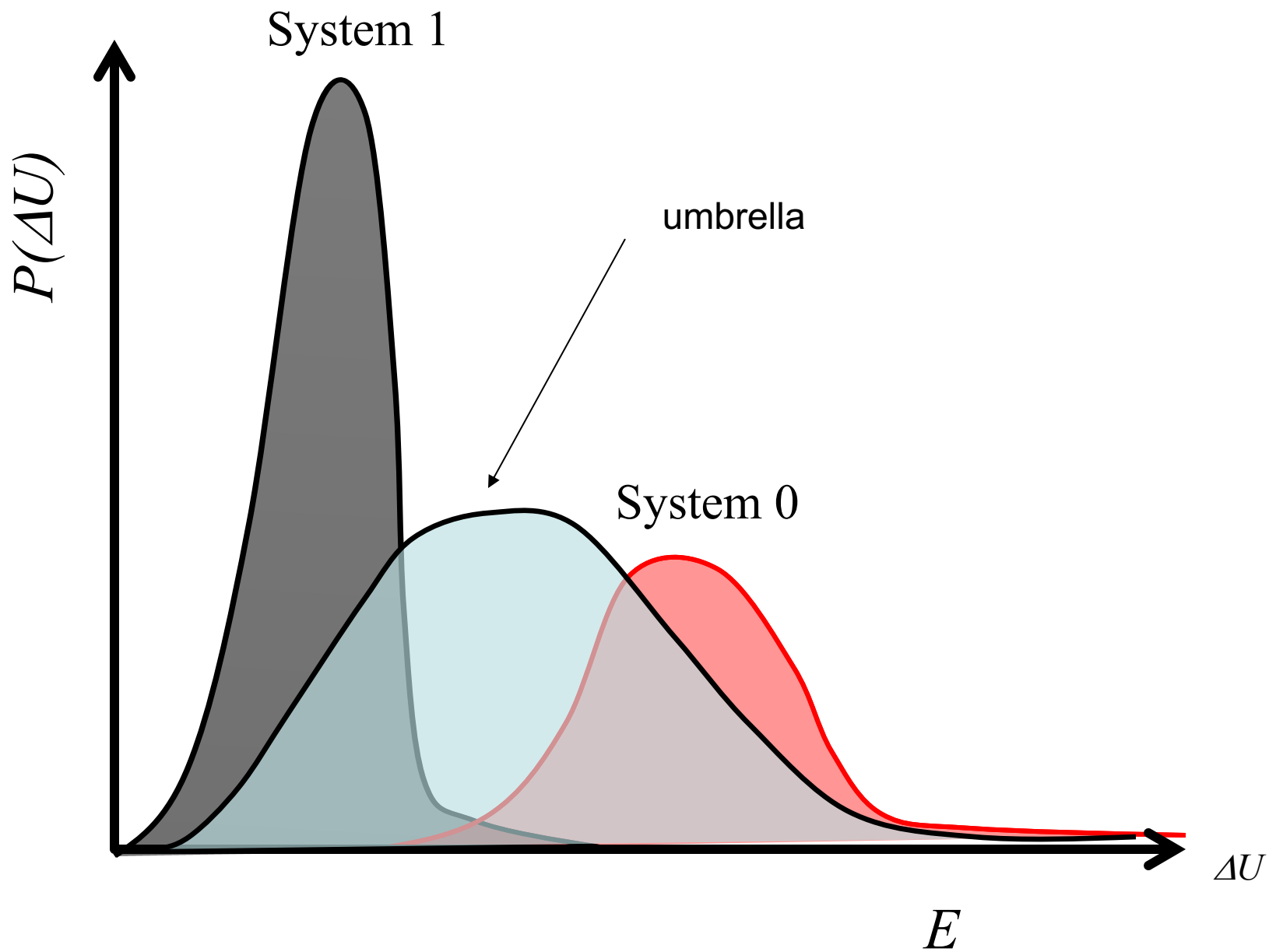
- Introduce function $\pi(\mathbf{s}^N)$ altering distribution.

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

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

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

- This approach is called umbrella sampling



II - Overlapping Distribution Method

Two systems:

System 0: N, V, T, U_0

System 1: N, V, T, U_1

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

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

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

$= \Delta U$ (δ function)

$$p_0(\Delta U) = \frac{\int ds^N \exp(-\beta U_0) \delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_0)} \quad p_1(\Delta U) = \frac{\int ds^N \exp(-\beta U_1) \delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_1)}$$

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

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

$$= \frac{Q_0}{Q_1} \exp(-\beta \Delta U) \frac{\int ds^N \exp[-\beta U_0] \delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_0)}$$

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

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

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

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

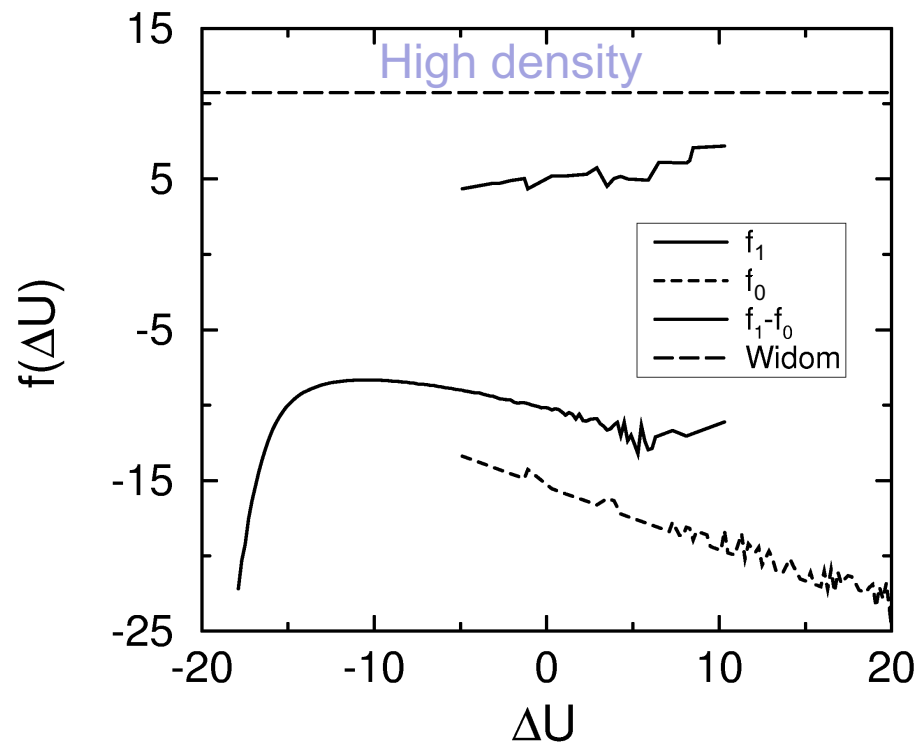
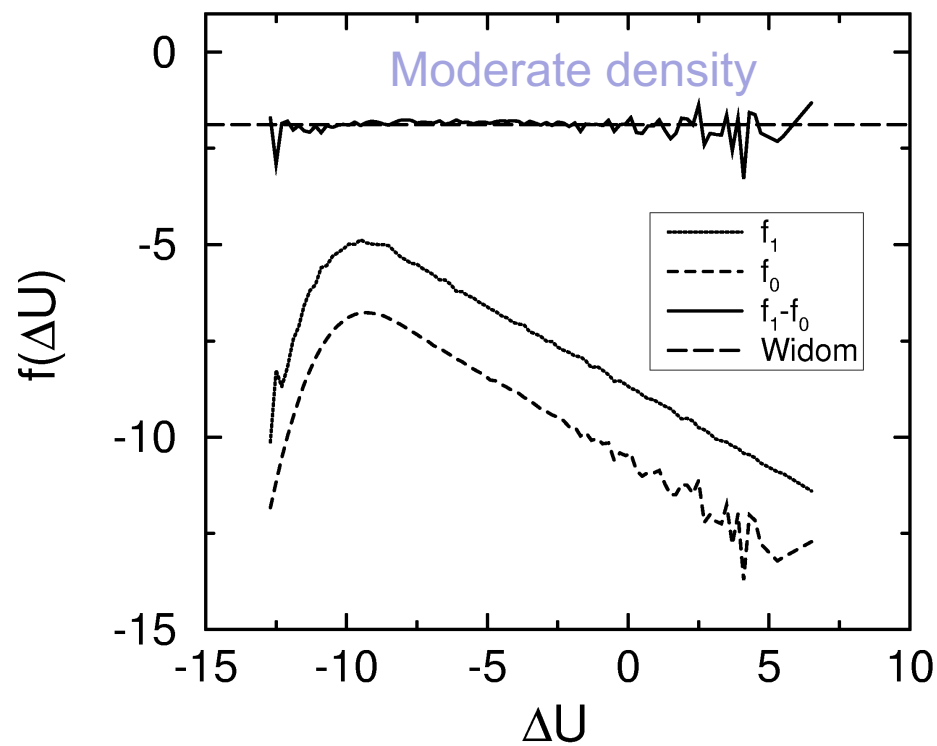
$$\Delta\beta F = \beta F_1 - \beta F_0 \equiv \beta\mu^{ex}$$

$$\Delta U = U_1 - U_0$$

System 0: test particle energy

System 1: real particle energy

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

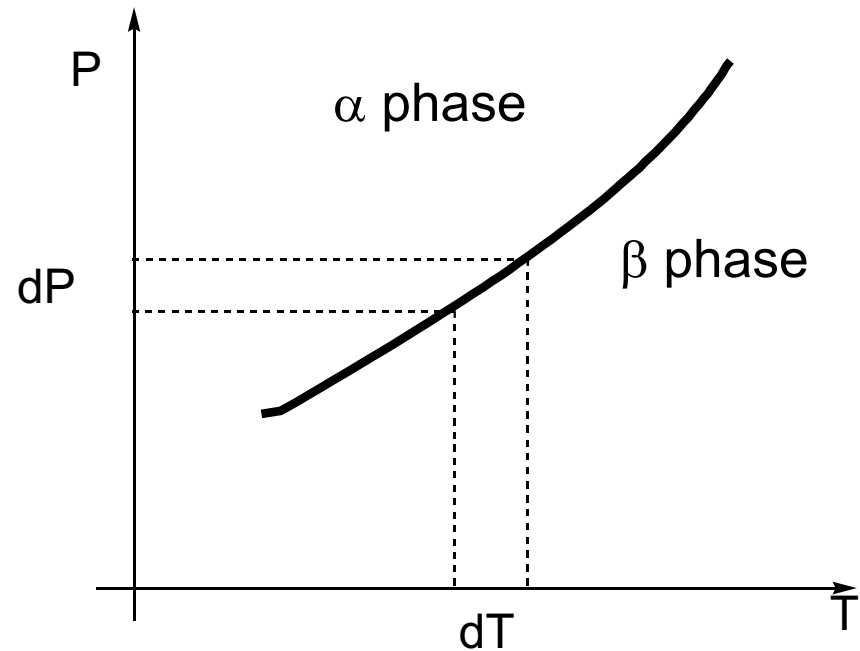


Tracing coexistence curves

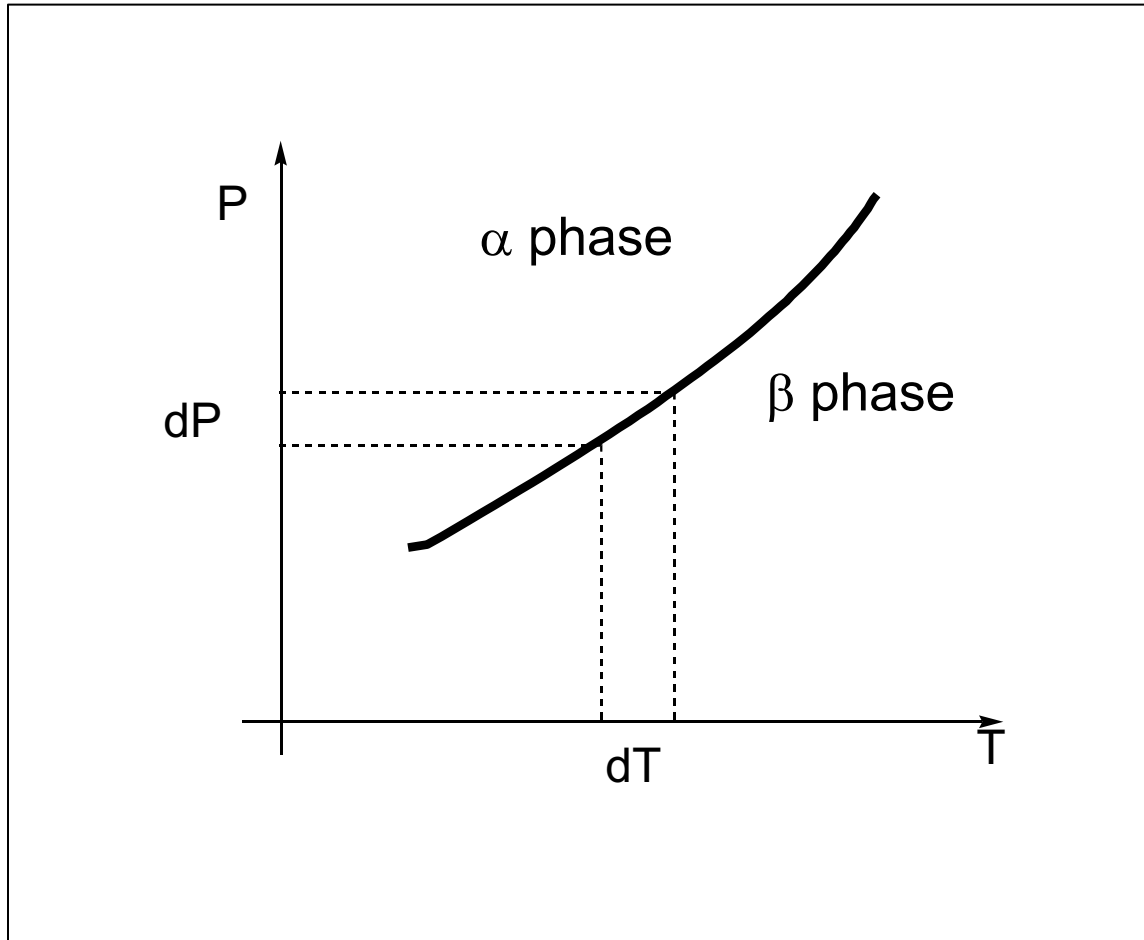
- If we have a coexistence point on the phase diagram we can integrate along the line while maintaining coexistence.

P en T are equal along coexistence line

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



Tracing coexistence curves



Clapyeron equation

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

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