

## Free Energies and Phase Equilibria

Phase equilibria / transitions / adsorption / self assembly  $\rightarrow$  best analyzed if  $G$  or  $A$  are known

Unfortunately,  $\left. \begin{array}{l} A = -kT \ln Q \quad (\text{canonical ensemble}) \\ S = k \ln \Omega \quad (\text{microcanonical ensemble}) \end{array} \right\} \begin{array}{l} \rightarrow \text{cannot obtain directly} \end{array}$

But:  $\left. \begin{array}{l} \left( \frac{\partial A}{\partial V} \right)_{N,T} = -P \\ \left( \frac{\partial(A/T)}{\partial(1/T)} \right)_{V,N} = U \end{array} \right\} \begin{array}{l} \text{derivatives of } A \\ \text{can be measured} \\ \text{directly} \end{array}$

Thermodynamic Integration: Extremely general approach

$\rightarrow$  Construct reversible path to state of known free energy (e.g. ideal gas)

$\rightarrow$  Compute free energy difference between Systems I and II.

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

$$Q(N, V, T, \lambda) = \frac{1}{N! N!} \int d\vec{r}^N \exp(-\beta U(\lambda))$$

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

$$= \frac{\frac{1}{N!} \int d\vec{r}^N \left( \frac{\partial u(\lambda)}{\partial \lambda} \right) e^{-\beta u(\lambda)}}{Q} = \left\langle \frac{\partial u(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

$$A(\lambda=1) - A(\lambda=0) = \int_{\lambda=0}^1 d\lambda \left\langle \frac{\partial u(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

A special case: Widom Test Particle Insertions:

Widom, J. Chem. Phys. 39:2802 (1963)

$$dA = -SdT - PdV + \sum_i \mu_i dN_i$$

$$\mu_i = \left. \frac{\partial A}{\partial N_i} \right|_{T, V, N_j \neq i} \quad \textcircled{1} \text{ Definition of } \mu_i$$

$$Q(N, V, T) = \frac{V^N}{N!} \int_0^1 \dots \int_0^1 d\vec{s}^N e^{-\beta u_N(\vec{s}^N; L)}$$

$\vec{s}$ : scaled coordinates =  $\vec{r}/L$

$$A = -kT \ln Q = \underbrace{-kT \ln \frac{V^N}{N!}}_{\text{ideal part}} - \underbrace{kT \ln \left( \int d\vec{s}^N e^{-\beta u_N} \right)}_{\text{excess part}} \quad \textcircled{2}$$

From  $\textcircled{1}$ , we can approximate  $\mu_i$  for large  $N_i$

$$\text{as } \mu_i = \frac{A(N+1) - A(N)}{1} = -kT \ln \frac{Q_{N+1}}{Q_N} \quad \textcircled{2}$$

$$-kT \ln \left( \frac{V}{N+1} \right) - kT \ln \left[ \frac{\int d\vec{s}^{N+1} e^{-\beta u_{N+1}}}{\int d\vec{s}^N e^{-\beta u_N}} \right] \quad \mu_{\text{ex}}$$

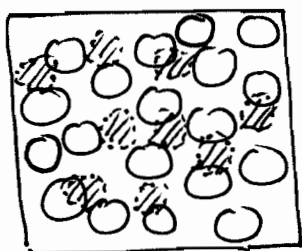
$$\therefore \left[ \mu_{\text{ex}} = -kT \ln \int d\vec{s}_{N+1} \langle e^{-\beta \Delta u} \rangle_N \right]$$

or, simply (since  $\langle e^{-\beta u} \rangle$  does not depend on position),  $\mu_{ex} = -kT \ln \langle e^{-\beta u_{test}} \rangle_N$

Physical interpretation of this expression:

The excess chemical potential is the ensemble average of a test particle energy in a system that evolves on its own (no coupling to the test particle).

→ can be implemented in MD or MC



○ : "real" particles

▨ : "test" particles —  
random positions

Example - hard spheres

$$e^{-\beta u_{test}} = \begin{cases} 0 & \text{if overlap} \\ 1 & \text{if no overlap} \end{cases}$$

$$\langle e^{-\beta u_{test}} \rangle = \text{fraction of non-overlapping random insertions} = \phi$$

$$\mu_{ex} = -kT \ln \phi$$

Reverse Widom

The exact same approach gives an equivalent expression using the energy of a "real" particle

being removed from a system:

$$\mu_i = \frac{A(N) - A(N-1)}{-1} \Rightarrow \mu_{ex} = +KT \ln \langle e^{+\beta U_{real}} \rangle$$

$U_{real}$ : energy of interaction of randomly selected particle w/ rest of system

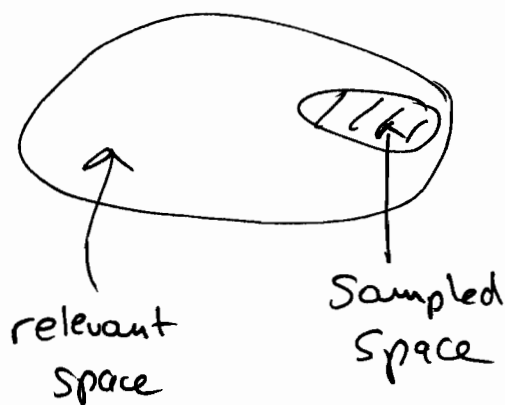
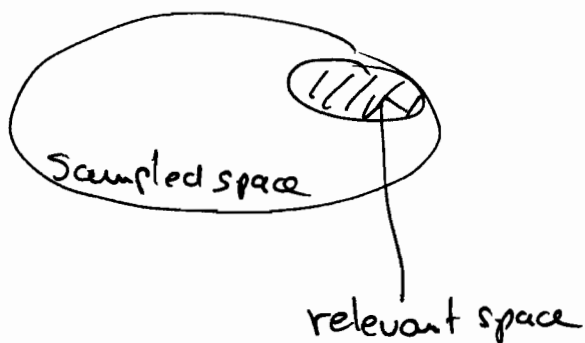
Unfortunately, even though the "real widow" expression is formally correct, it is very inaccurate in practice - e.g. fails completely for hard spheres!

$$\underbrace{-KT \ln \langle e^{-\beta U_{test}} \rangle}$$

dominated by - rare insertions w/ favorable (negative) energy

$$\underbrace{-KT \ln \langle e^{+\beta U_{real}} \rangle}$$

dominated by - extremely rare - removals of high energy particles

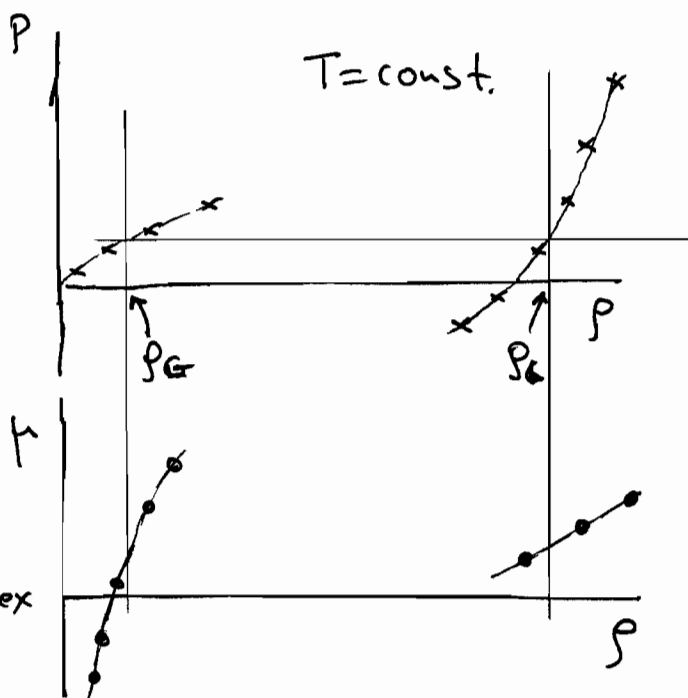


See Lutsko, J. Chem. Phys. 114: 7303 (2001) for general principles of accurate sampling in "Free Energy Perturbation" methods

## Phase Equilibria from Widom + MD or MC

Multiple runs to  
obtain Equation-of-  
state for  $P(\rho)$ ,  
 $\mu(\rho)$

Iterative solution  
of  $P(\rho_L) = P(\rho_G) = P^{vp}$   
 $\mu(\rho_L) = \mu(\rho_G) = \mu_{coex}$



For low-temperature VLE,  $P^{vp} \approx 0$

NPT + test particle methods: find  $\rho_L$  from  
 $P=0$  NPT MC (or MD) simulation

→ Widom insertions for  $\mu(\rho_L) = \mu_{coex}$

→ ideal-gas:  $\rho_G = \exp(B\mu_{coex})$

Note that Widom expression depends on ensemble.

NPT ensemble:  $\mu = -kT \ln \left\langle \frac{V e^{-\beta U_{test}}}{N+1} \right\rangle$

NVE ensemble:  $\mu_{ex} = -kT \ln \left\{ \frac{\langle T_{kin}^{3/2} e^{-\beta U_{test}} \rangle}{\langle T_{kin} \rangle^{3/2}} \right\}$

$T_{kin}$ : (fluctuating) kinetic T