PHY 341/641
Thermodynamics and Statistical Physics

Lecture 30

More about the Chemical Potential

- The Widom insertion method
- Computer simulation

26	3/30/2012	Van der Waals Equation	7.4		
27	4/02/2012	Equilibrium constants	7.4-7.5	HW 22	04/04/2012
28	4/04/2012	Equilibrium constants	7.5		
	4/06/2012	*Good Friday Holiday*			
29	4/09/2012	Review -- begin take-home exam	5-7		
	4/11/2012	No class -- work on exam	5-7		
30	4/13/2012	Simulation of chemical potential	7.2	Exam continued	
31	4/16/2012	Classical treatment of dense systmes	8.1-8.2	Exam due	
	4/18/2012				
	4/20/2012				
	4/23/2012				
	4/25/2012				
	4/27/2012				
	4/30/2012				
	5/02/2012				
	5/09/2012	9 AM Final exam			

-- student presentations 4/30, 5/2 (need to pick topics)

Chemical potential for large *N*:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \approx F(T,V,N+1) - F(T,V,N)$$
$$= -kT\left(\ln Z(T,V,N+1) - \ln Z(T,V,N)\right)$$
$$= -kT \ln\left(\frac{Z(T,V,N+1)}{Z(T,V,N)}\right)$$

For 3-dimensional ideal gas:

$$Z_{IG}(T,V,N) = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

$$\mu_{IG}(T,V,N) \approx -kT \ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right)$$

This can be derived from:

$$Z_{IG}(T,V,N) = \frac{V^N}{N!h^{3N}}\left(\int d^3p\, e^{-\frac{p^2}{2mkT}}\right)^N$$

Chemical potential for large N -- continued:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \approx F(T,V,N+1) - F(T,V,N)$$

$$= -kT\left(\ln Z(T,V,N+1) - \ln Z(T,V,N)\right)$$

$$= -kT \ln\left(\frac{Z(T,V,N+1)}{Z(T,V,N)}\right)$$

$$\frac{Z(T,V,N+1)}{Z(T,V,N)} = \frac{\sum_{s,r} e^{-\beta E_{s,r}}}{\sum_s e^{-\beta E_s}} = \frac{\sum_{s,r} e^{-\beta\left(E_{s,r}-E_s\right)} e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}$$

$$= \frac{\sum_s \left(\sum_r e^{-\beta\left(E_{s,r}-E_s\right)}\right) e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} = \left\langle \sum_r e^{-\beta\left(E_{s,r}-E_s\right)} \right\rangle$$

Chemical potential for large N -- continued:

$$\mu(T,V,N) \approx -kT \ln\left\langle \sum_r e^{-\beta\left(E_{s,r}-E_s\right)} \right\rangle$$

where the average is taken over the canonical ensemble:

$$\frac{e^{-\beta E_s}}{\sum_{s'} e^{-\beta E_{s'}}}$$

For classical system:

$$E_s = \sum_i \frac{p_i^2}{2m} + U\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \cdots \mathbf{r}_N\right)$$

$$E_{s,r} - E_s = \frac{p_r^2}{2m} + U\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \cdots \mathbf{r}_{N+1}\right) - U\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \cdots \mathbf{r}_N\right)$$

$$= \frac{p_r^2}{2m} + \Delta U$$

Chemical potential for large N -- continued:

$$\mu(T,V,N) \approx -kT \ln\left\langle \sum_r e^{-\beta\left(E_{s,r}-E_s\right)} \right\rangle$$

$$\approx \mu_{IG}(T,V,N) - kT \ln\left\langle e^{-\beta \Delta U} \right\rangle$$

where the average is taken over the canonical ensemble:

$$\frac{e^{-\beta E_s}}{\sum_{s'} e^{-\beta E_{s'}}}$$

Evaluation of $\left\langle e^{-\beta \Delta U} \right\rangle$:

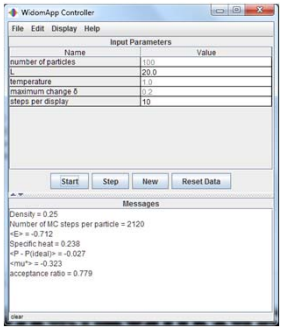
Interpret ΔU as the change in potential energy due to the addition of an imaginary test particle added to the system of N particles.

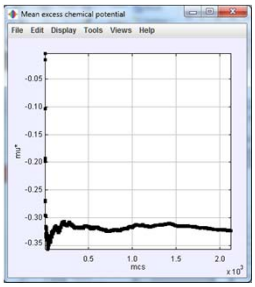
Widom insertion method for evaluating $\left\langle e^{-\beta\Delta U} \right\rangle$

Use Metropolis algorithm on a system of *N* particles modeled by interacting potential $U(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots\boldsymbol{r}_N)$ where on each "step" a particle is added at a random position to determine ΔU and to accumulate $\left\langle e^{-\beta\Delta U} \right\rangle$.

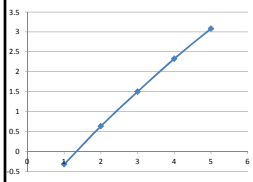
Computer simulation using Widom insertion method with Lennard-Jones fluid

stp_WidomInsertionMethod.jar



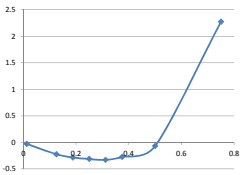


Chemical potential for density = 0.25



Temperature →

Chemical potential for temperature = 1



Density →

Some references:

B. Widom “Some topics in the theory of fluids”, J. Chem. Phys. **39**, 2808-2812 (1963)
C. H. Bennett, “Efficient estimation of free energy differences from Monte Carlo data”, C. Comp. Phys. **22**, 245-265 (1976)
K. Binder “Applications of Monte Carlo methods to statistical physics” Rep. Prog. Physics **60**, 487-559 (1997)

More recent example:
A. Arslanargin and T. L. Beck, “Free energy partitioning analysis of the driving forces that determine ion density profiles near the water liquid-vapor interface”, J. Chem. Phys. **136**, 104503 (2012)