

PHY 341/641

Lecture 30

More about the Chemical Potential

- The Widom insertion method
 - Computer simulation

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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		
	4/05/2012	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 systems	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)

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Chemical potential for large N :

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

For 3-dimensional ideal gas :

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

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

This can be derived from:

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

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Chemical potential for large N -- continued:

$$\begin{aligned}\mu &= \left(\frac{\partial F}{\partial N} \right)_{T,V} \approx F(T,V,N+1) - F(T,V,N) \\ &= -kT(\ln Z(T,V,N+1) - \ln Z(T,V,N)) \\ &= -kT \ln \left(\frac{Z(T,V,N+1)}{Z(T,V,N)} \right) \\ \frac{Z(T,V,N+1)}{Z(T,V,N)} &= \frac{\sum_{s,r} e^{-\beta E_{s,r}}}{\sum_s e^{-\beta E_s}} = \frac{\sum_{s,r} e^{-\beta(E_{s,r}-E_s)}}{\sum_s e^{-\beta E_s}} \\ &= \frac{\sum_s \left(\sum_r e^{-\beta(E_{s,r}-E_s)} \right) e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} = \left\langle \sum_r e^{-\beta(E_{s,r}-E_s)} \right\rangle\end{aligned}$$

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Chemical potential for large N -- continued:

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

where the average is taken over the canonical ensemble :

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

For classical system :

$$\begin{aligned}E_s &= \sum_i \frac{p_i^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \cdots \mathbf{r}_N) \\ E_{s,r} - E_s &= \frac{p_r^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \cdots \mathbf{r}_{N+1}) - U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \cdots \mathbf{r}_N) \\ &= \frac{p_r^2}{2m} + \Delta U\end{aligned}$$

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Chemical potential for large N -- continued:

$$\begin{aligned}\mu(T,V,N) &\approx -kT \ln \left\langle \sum_r e^{-\beta(E_{s,r}-E_s)} \right\rangle \\ &\approx \mu_{IG}(T,V,N) - kT \ln \left\langle e^{-\beta \Delta U} \right\rangle\end{aligned}$$

where the average is taken over the canonical ensemble :

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

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

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

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

Use Metropolis algorithm on a system of N particles modeled by interacting potential $U(r_1, r_2, \dots, r_N)$ where on each "step" a particle is added at a random position to determine ΔU and to accumulate $\langle e^{-\beta \Delta U} \rangle$.

Computer simulation using Widom insertion method with Lennard-Jones fluid

[stpc_WidomInsertionMethod.jar](#)

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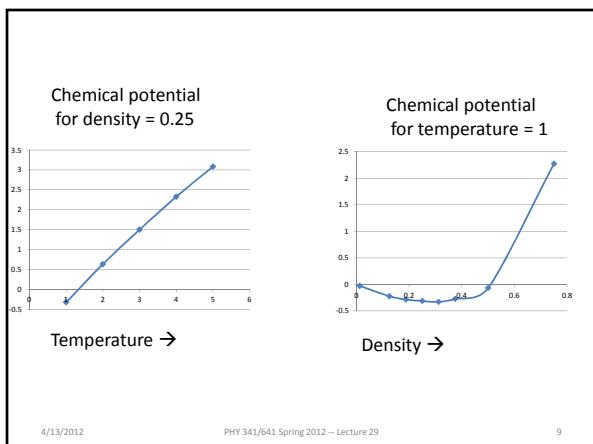
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The screenshot shows two windows of the WidomApp Controller software. The left window, titled 'WidomApp Controller', displays 'Input Parameters' with values: number of particles = 100, L = 20.0, temperature = 1.0, maximum change δ = 0.2, and steps per display = 10. It also shows a 'Messages' section with simulation statistics: Density = 0.25, Number of MC steps per particle = 2120, δ = 0.2, Specific heat = 0.238, $\langle P - P_{ideal} \rangle = -0.027$, $\langle \mu \rangle = -0.323$, acceptance ratio = 0.779. The right window, titled 'Mean excess chemical potential', is a plot of $\mu - \mu_{ideal}$ versus time in microseconds (μs) from 0 to 2.0. The y-axis ranges from -0.35 to -0.05.

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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", J. 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)
