

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	<i>Good Friday Holiday</i>			
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)

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 :

$$\begin{aligned}Z_{IG}(T, V, N) &= \frac{V^N}{N!} \left(\frac{2\pi m k T}{h^2} \right)^{3N/2} \\ \mu_{IG}(T, V, N) &\approx -kT \ln \left(\frac{V}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right)\end{aligned}$$

This can be derived from :

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

Chemical potential for large N -- continued:

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

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:

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

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

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

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

Use Metropolis algorithm on a system of N particles modeled by interacting potential $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ 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

[stp_WidomInsertionMethod.jar](#)

WidomApp Controller

File Edit Display Help

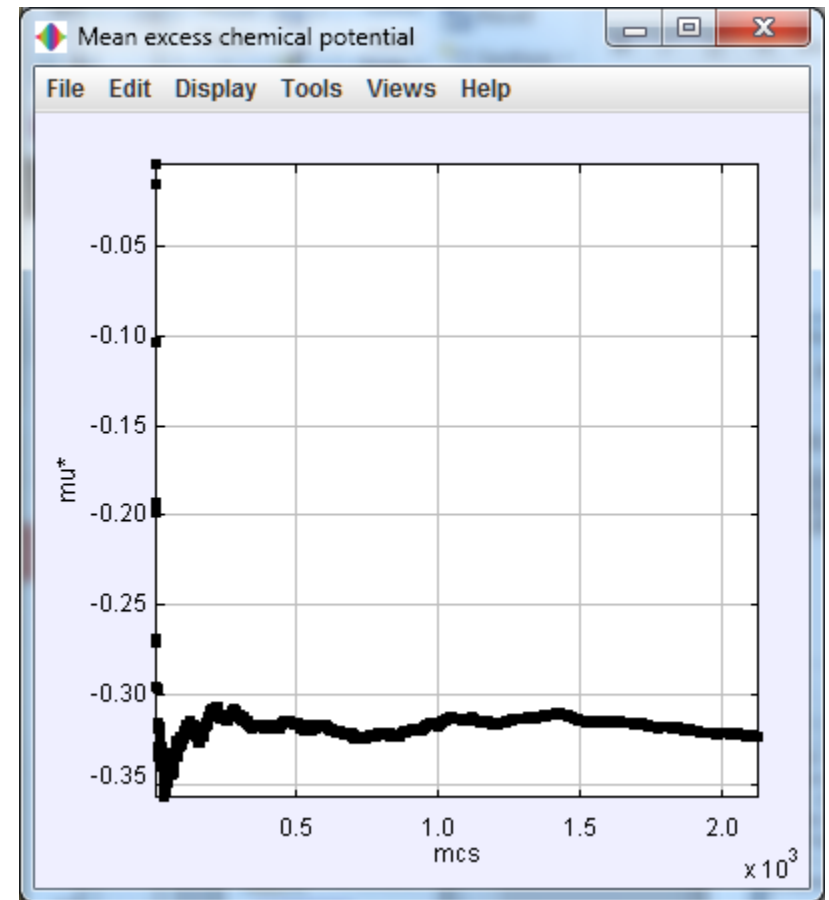
Input Parameters	
Name	Value
number of particles	100
L	20.0
temperature	1.0
maximum change δ	0.2
steps per display	10

Start Step New Reset Data

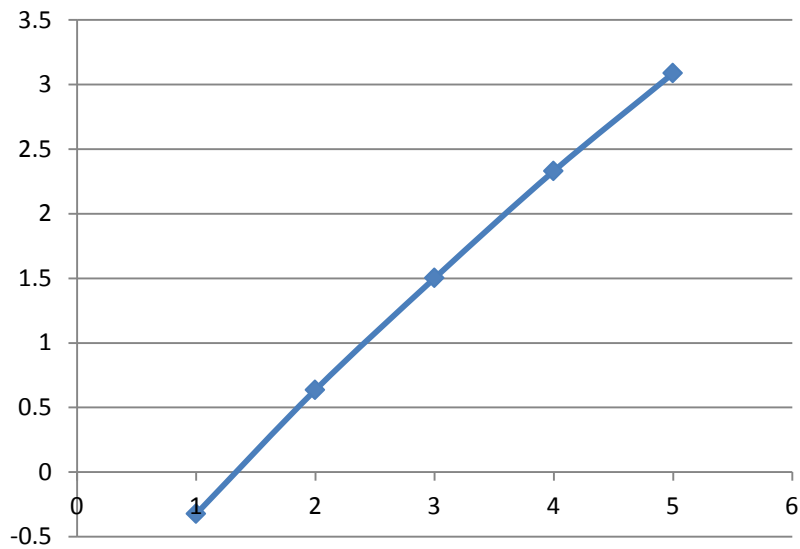
Messages

Density = 0.25
 Number of MC steps per particle = 2120
 $\langle E \rangle = -0.712$
 Specific heat = 0.238
 $\langle P - P(\text{ideal}) \rangle = -0.027$
 $\langle \mu^* \rangle = -0.323$
 acceptance ratio = 0.779

clear

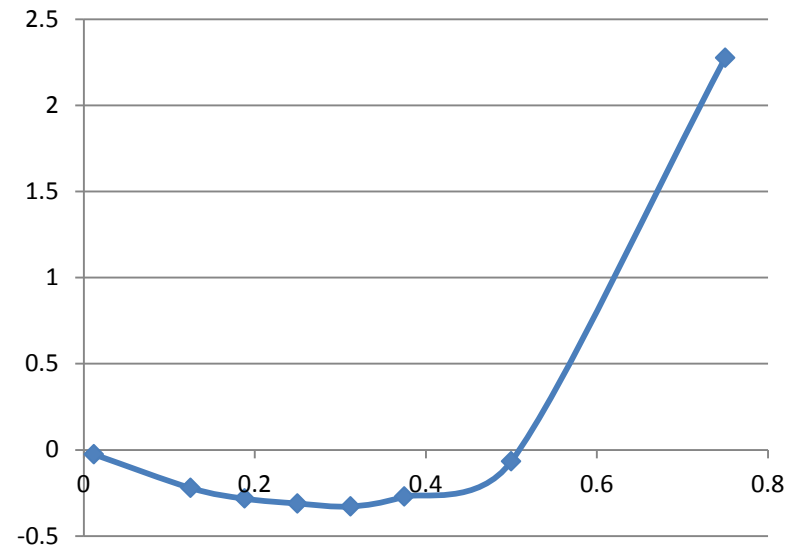


Chemical potential for density = 0.25



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)