PHY 341/641
Thermodynamics and Statistical Physics

Lecture 31

Analysis of classical gases and liquids

- Interaction potentials
- Approximations to the partition function

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 systems	8.1-8.2	Exam due	
32	4/18/2012	Virial expansion	8.3-8.4		
33	4/20/2012	Radial distribution function	8.5		
	4/23/2012				
	4/25/2012				
	4/27/2012				
	4/30/2012	Student presentations I			
	5/02/2012	Student presentations II			
	5/09/2012	9 AM Final exam			

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

Time, Einstein, and the Coolest Stuff in the Universe

A free public lecture by Nobel Laureate

Dr. William Phillips

National Institute of Standards and Technology

8:00 PM Friday, April 20

Brendle Recital Hall
Wake Forest University

Part of SPS zone 5 conference
April 20-21, 2012

www.wfu.edu/physics/sps/spszone52012conf/welcome.html

Consider a canonical ensemble of *N* particles moving in 3 dimensions within a volume *V* at temperature *T=1/kβ*

$$Z_N = \frac{1}{N!h^{3N}}\int d^3p_1 d^3p_2\cdots d^3p_N d^3r_1 d^3r_2\cdots d^3r_N e^{-\beta K-\beta U}$$

$$K \equiv \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m}$$

$$U = U(\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_N)$$

For ideal (non-interacting gas) with all particles of mass m

$$Z_{IG} = \frac{V^N}{N!h^{3N}}\int d^3p_1 d^3p_2\cdots d^3p_N e^{-\beta K}$$

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

$$Z_N = \frac{1}{N!h^{3N}}\int d^3p_1 d^3p_2\cdots d^3p_N d^3r_1 d^3r_2\cdots d^3r_N e^{-\beta K-\beta U}$$

$$= Z_{IG}\left(\frac{1}{V^N}\int d^3r_1 d^3r_2\cdots d^3r_N e^{-\beta U}\right) = Z_{IG}Z_C$$

where:

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

Free energy:

$$F(T,V,N) = -kT\ln Z_N = -kT\ln Z_{IG} - kT\ln Z_C$$

$$= F_{IG}(V,V,N) + F_C(V,V,N)$$

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

$$\frac{PV}{NkT} = 1 + \frac{V}{N}\left(\frac{\partial \ln Z_C}{\partial V}\right)_{T,N}$$

$$Z_C = \frac{1}{V^N}\int d^3r_1 d^3r_2\cdots d^3r_N e^{-\beta U}$$

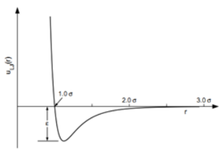
Model simulations of Z_C

Isotropic pairwise interaction potentials:

$$U(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) = \sum_{i<j} u(|\mathbf{r}_1 - \mathbf{r}_2|)$$

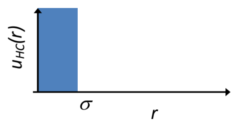
Lennard-Jones potential:

$$u_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Hard-core potential:

$$u_{HC}(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r < \sigma \end{cases}$$



For pair potential:

$$Z_C = \frac{1}{V^N}\int d^3r_1 d^3r_2 \cdots d^3r_N e^{-\beta U}$$

$$= \frac{1}{V^N}\int d^3r_1 d^3r_2 \cdots d^3r_N e^{-\beta u(r_{12}) - \beta u(r_{23}) - \beta u(r_{13}) \cdots - \beta u(r_{(N-1)N})}$$

Define:

$$f_{ij} \equiv e^{-\beta u(r_{12})} - 1$$

$$Z_C = \frac{1}{V^N}\int d^3r_1 d^3r_2 \cdots d^3r_N (1+f_{12})(1+f_{23})(1+f_{13})\cdots(1+f_{(N-1)N})$$

$$= 1 + \frac{N(N-1)}{2V^2}\int d^3r_1 d^3r_2 f_{12} + \frac{N(N-1)(N-2)}{6V^3}\int d^3r_1 d^3r_2 d^3r_3 f_{12} f_{13} f_{23} \cdots$$

"Virial" expansion of equation of state:

$$\frac{PV}{NkT} = 1 + \frac{V}{N}\left(\frac{\partial \ln Z_C}{\partial V}\right)_{T,N}$$

$$\approx 1 + \rho B_2(T) + \rho^2 B_3(T) + \cdots$$

where $\rho \equiv \frac{N}{V}$

Evaluation of $B_2(T)$:

$$\frac{N(N-1)}{2V^2}\int d^3r_1 d^3r_2 f_{12} = \frac{N(N-1)}{2V}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

$$\left(\frac{\partial}{\partial V}\left(\frac{N(N-1)}{2V}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)\right)\right)_{T,N} \approx -\frac{\rho^2}{2}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

$$\Rightarrow B_2(T) = -\frac{1}{2}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

Evaluation of $B_2(T)$ for a hard-core potential:

$$B_2(T) = -\frac{1}{2}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

Hard-core potential:

$$u_{HC}(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r > \sigma \end{cases}$$

$$\left(e^{-\beta u_{HC}(r)} - 1\right) = \begin{cases} -1 & \text{for } r < \sigma \\ 0 & \text{for } r > \sigma \end{cases}$$

$$\Rightarrow B_2(T) = \frac{2\pi\sigma^3}{3}$$

Virial expansion for hard-core potential

$$\frac{PV}{NkT} \approx 1 + \rho B_2(T)$$

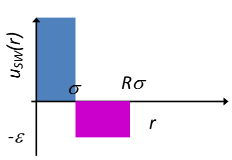
$$\approx 1 + \frac{2\pi\sigma^3}{3}\rho$$

Comparison to van der Waals equation of state:

$$P = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2}$$

$$\frac{PV}{NkT} \approx 1 + b\rho - \frac{a}{kT}\rho$$

Modified hard-core potential – square well potential



Modified hard-core potential:

$$u_{SW}(r) = \begin{cases} \infty & \text{for } 0 \le r \le \sigma \\ -\varepsilon & \text{for } \sigma \le r \le R\sigma \\ 0 & \text{for } r \ge R\sigma \end{cases}$$

Evaluation of $B_2(T)$ for a modified hard-core potential:

$$B_2(T) = -\frac{1}{2}\int d^3 r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

Modified hard-core potential:

$$u_{SW}(r) = \begin{cases} \infty & \text{for } 0 \le r \le \sigma \\ -\varepsilon & \text{for } \sigma \le r \le R\sigma \\ 0 & \text{for } r \ge R\sigma \end{cases}$$

$$\left(e^{-\beta u_{SW}(r)} - 1\right) = \begin{cases} -1 & \text{for } 0 \le r \le \sigma \\ e^{\beta\varepsilon} - 1 & \text{for } \sigma \le r \le R\sigma \\ 0 & \text{for } r \ge R\sigma \end{cases}$$

$$\Rightarrow B_2(T) = \frac{2\pi\sigma^3}{3}\left(1 - \left(e^{\beta\varepsilon} - 1\right)\left(R^3 - 1\right)\right)$$

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Virial expansion for modified hard-core potential

$$\frac{PV}{NkT} \approx 1 + \rho B_2(T)$$

$$\approx 1 + \frac{2\pi\sigma^3}{3}\left(1 - \left(e^{\beta\varepsilon} - 1\right)\left(R^3 - 1\right)\right)\rho$$

Comparison to van der Waals equation of state:

$$P = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2}$$

$$\frac{PV}{NkT} \approx 1 + b\rho - \frac{a}{kT}\rho$$

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Evaluation of $B_2(T)$ for Lennard-Jones potential:

$$B_2(T) = -\frac{1}{2}\int d^3 r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

Lennard-Jones potential:

$$u_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$B_2(T) = -2\pi\sigma^3\int_0^\infty x^2 dx\left(e^{-4\varepsilon\beta\left(\frac{1}{x^{12}} - \frac{1}{x^6}\right)} - 1\right)$$

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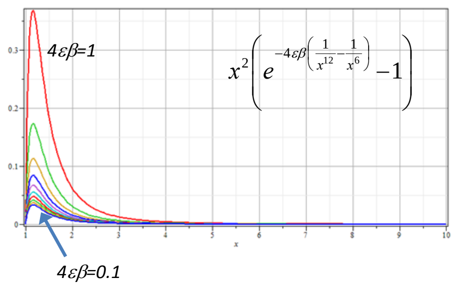
Evaluation of $B_2(T)$ for Lennard-Jones potential -- continued



Evaluation of $B_2(T)$ for Lennard-Jones potential -- continued