PHY 341/641
Thermodynamics and Statistical Physics

Lecture 33

Analysis of classical gases and liquids (STP Chapt. 8)

- Virial coefficients
- Radial distribution functions

24	3/26/2012	Bose and Fermi particles	6.5-6.11		
25	3/28/2012	Phase transformations	7.1-7.3	HW 21	03/30/2012
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 systems	8.1-8.2	Exam due	
32	4/18/2012	Review exam; Virial expansion	8.3-8.4		
33	4/20/2012	Radial distribution function	8.5		
34	4/23/2012	More topics on classical fluids	8.6-8.9		
35	4/25/2012	Review			
36	4/27/2012	Review			
	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

Received 1997 Nobel Prize with Steven Chu and Claude Cohen-Tannoudji "for development of methods to cool and trap atoms with laser light"

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

Estimate of partition function for interacting gas or fluid; virial expansion:

Free energy for interacting particles:

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

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

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

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

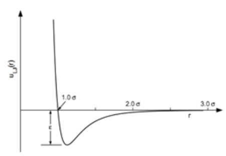
Model simulations of Z_C

Isotropic pairwise interaction potentials:

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

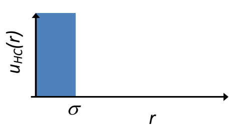
Lennard-Jones potential:

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



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:

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

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

"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 $B_2(T)$:

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

For hard sphere: $B_2(T) = \frac{2\pi\sigma^3}{3}$

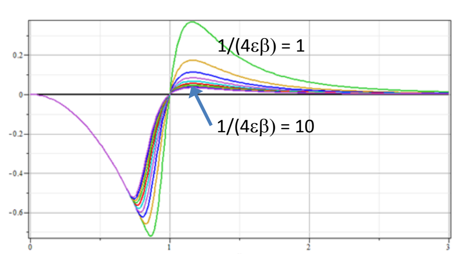
For square well: $B_2(T) = \frac{2\pi\sigma^3}{3}\left(1 - \left(e^{\beta\varepsilon} - 1\right)\left(R^3 - 1\right)\right)$

Lennard-Jones potential:

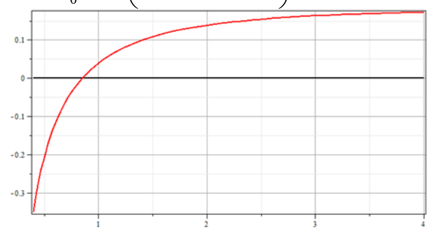
$$u_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

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

$$x^2\left(e^{-4\varepsilon\beta\left(\frac{1}{x^{12}} - \frac{1}{x^6}\right)} - 1\right)$$



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



Note: Correlates well with experimental measurements on N_2, Ne, Ar, and He (less well)

Radial distribution function *g(r)*

Previously we have defined the correlation contribution to the partition function:

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

This can be rewritten:

$$Z_C = \int d^3r_1 d^3r_2 \left(\frac{1}{V^N} \int d^3r_3 \cdots d^3r_N e^{-\beta U} \right)$$

$$Z_C = \int d^3r_1 d^3r_2 \left(\frac{1}{V^N} \int d^3r_3 \cdots d^3r_N e^{-\beta U} \right)$$

The quantity in () is related to the “pair distribution function” g($\mathbf{r}_1$,$\mathbf{r}_2$) – given a particle at $\mathbf{r}_1$ what is the probability of finding a second particle at $\mathbf{r}_2$.

$$Z_C = \int d^3r_1 d^3r_2 \left(\frac{1}{V^N} \int d^3r_3 \cdots d^3r_N e^{-\beta U} \right)$$

$$\rho^2 g(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{Z_C V^N} \int d^3r_3 \cdots d^3r_N e^{-\beta U}$$

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

Radial distribution function – continued --

$$\rho^2 g(\mathbf{r}_1,\mathbf{r}_2) = \frac{N(N-1)}{Z_C V^N}\int d^3r_3 \cdots d^3r_N e^{-\beta U}$$

If $g(\mathbf{r}_1,\mathbf{r}_2) = g(|\mathbf{r}_1-\mathbf{r}_2|)$ then

$$\rho\int 4\pi r^2 dr g(r) = N-1 \approx N$$

Measurement of g(r) by neutron scattering:

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PHYSICAL REVIEW A VOLUME 7, NUMBER 6 JUNE 1973

Structure Factor and Radial Distribution Function for Liquid Argon at 85 °K†

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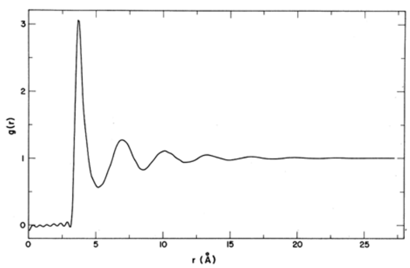

FIG. 4. Radial distribution function $g(r)$ for ^{36}Ar at 85 °K. This curve is the Fourier transform of the smoothed and extended $S(Q)$ shown as a solid line in Fig. 3.

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Experiment measures neutron scattering signal as a function of the change in neutron wave number **Q**:

$$S(Q) = 1 + \frac{4\pi\rho}{Q}\int_0^\infty (g(r)-1) r \sin(Qr) dr$$

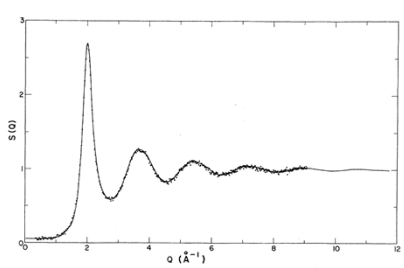

FIG. 3. Fully corrected experimental values of the liquid structure factor $S(Q)$ for ^{36}Ar at 85 °K. The solid line is a smoothed and extended $S(Q)$ obtained from the experimental data by an iterative procedure described in the text. The small dip in the experimental data near the top of the second peak ($Q = 3.75$ Å^{-1}) is apparently statistical in origin.

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Estimate of g(r) from theory:

For systems described by pair potentials in the dilute limit:

$$g(r) \approx e^{-\beta u(r)}$$