PHY 341/641
Thermodynamics and Statistical Physics

Lecture 34

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

- Virial coefficients
- Radial distribution functions
- Equation of state for classical fluid

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)

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

Free energy for interacting particles:

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

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

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

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

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

For pair potential:

$$U(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) = \sum_{i<j} u\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) \equiv \sum_{i<j} u(r_{ij})$$

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

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

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 $B_2(T)$:

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

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

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

Note: A more careful derivation of the previous result takes care to count the contributing terms in a systematic "cluster expansion". In the words of another textbook on this subject (Statistical mechanics by Normand Davidson): "The derivation given [on the previous slide] is a fraud and a hoax."

Equation of state for a classical fluid at low density $\rho \equiv \frac{N}{V}$:

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

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

More properties of 2nd virial coefficient:

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

$$= -2\pi\int dr\, r^2\left(e^{-\beta u(r)}-1\right)$$

Note that :

$$\frac{d}{dr}\left(\frac{r^3}{3}\left(e^{-\beta u(r)}-1\right)\right) = r^2\left(e^{-\beta u(r)}-1\right) - \frac{\beta r^3}{3}\frac{du(r)}{dr}e^{-\beta u(r)}$$

$$\Rightarrow B_2(T) = -\frac{2\pi\beta}{3}\int dr\, r^3\,\frac{du(r)}{dr}e^{-\beta u(r)}$$

Alternative derivation -- 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 $\mathbf{r}_2$.

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

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

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

Radial distribution function – continued --

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

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

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

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

J. L. Yarnell, M. J. Katz, and R. G. Wenzel
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

S. H. Koenig
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

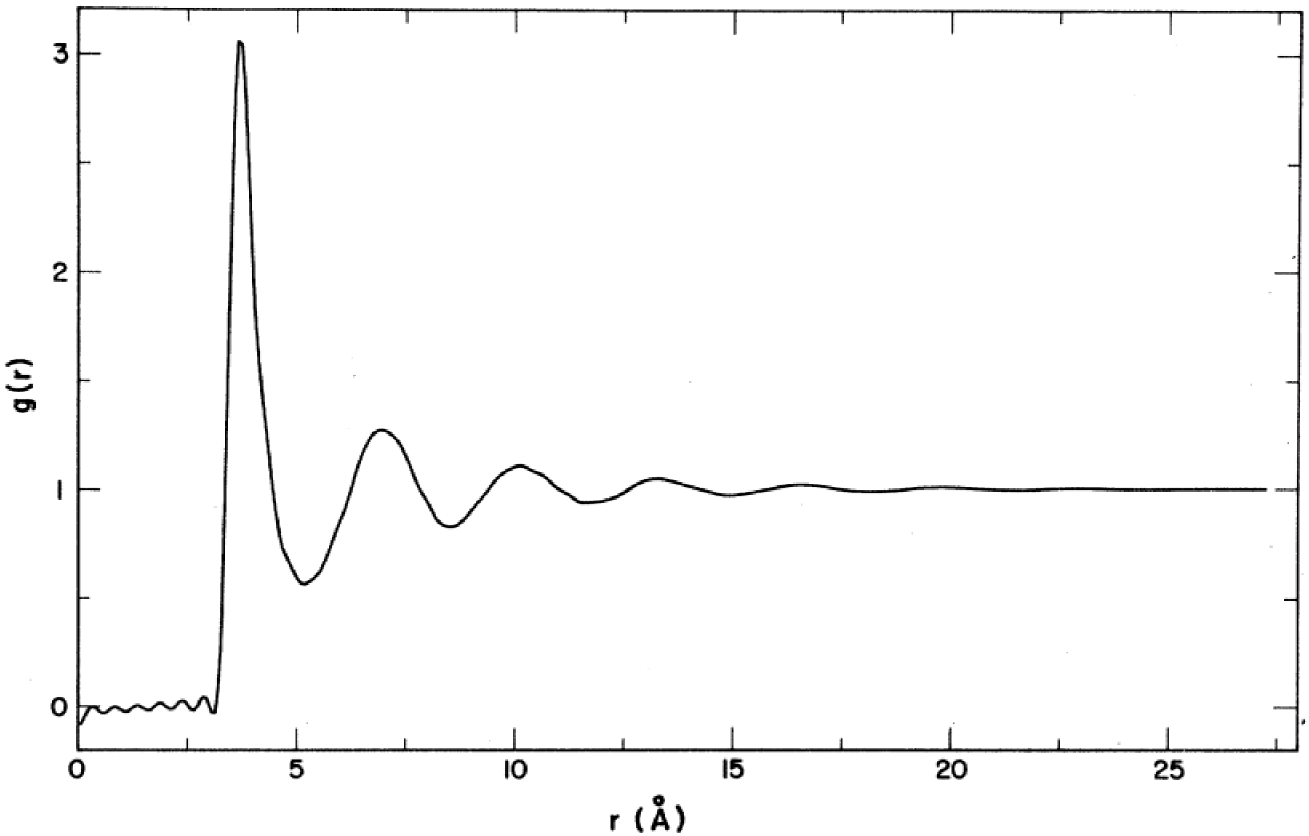

FIG. 4. Radial distribution function $g(r)$ for ^{36}Ar at 85 °K. This curve is the Fourier transform of the smoothed and extended $S(Q)$ shown as a solid line in Fig. 3.

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

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

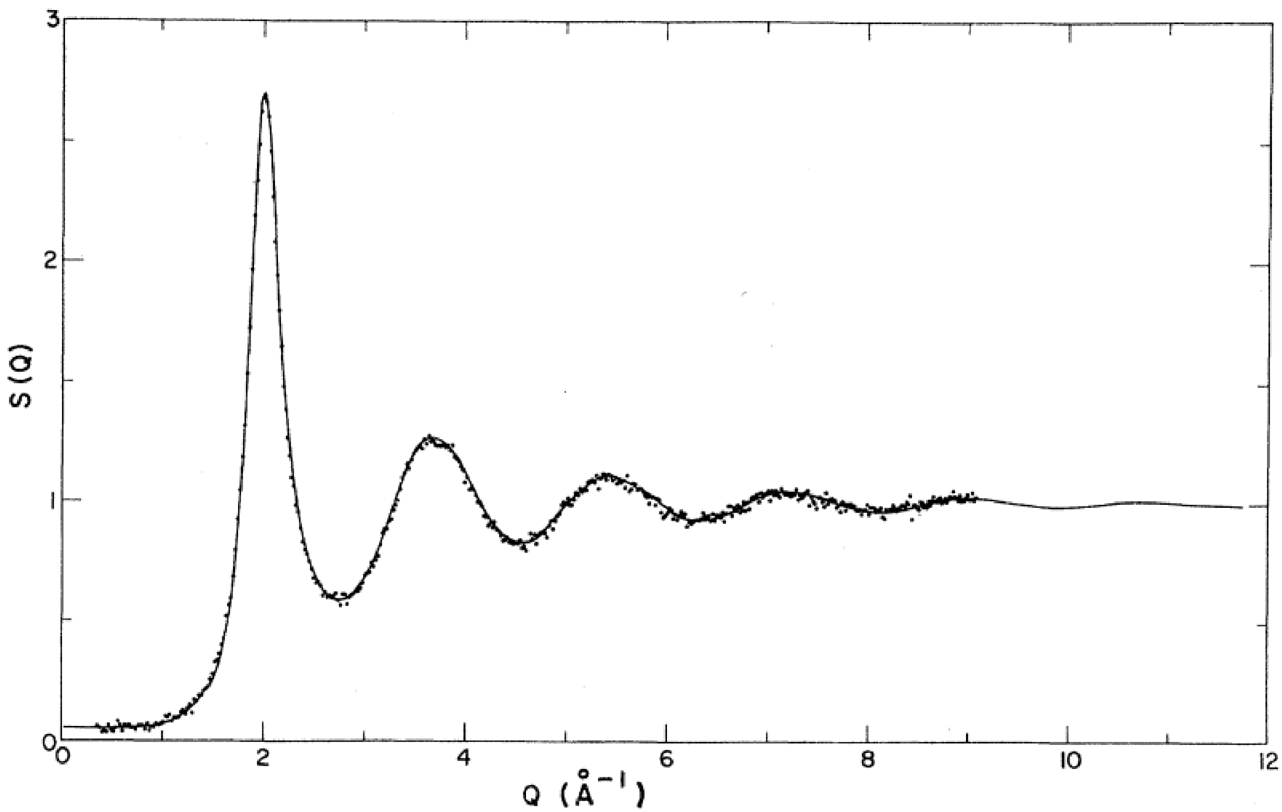

FIG. 3. Fully corrected experimental values of the liquid structure factor $S(Q)$ for ^{36}Ar at 85 °K. The solid line is a smoothed and extended $S(Q)$ obtained from the experimental data by an iterative procedure described in the text. The small dip in the experimental data near the top of the second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

Formulation of equation of state in terms of pair distribution function:

$$\langle E \rangle = -\left(\frac{\partial \ln Z_N}{\partial \beta} \right) = -\left(\frac{\partial \ln Z_{IG}}{\partial \beta} \right) - \left(\frac{\partial \ln Z_C}{\partial \beta} \right)$$

$$\langle E \rangle = \frac{3NkT}{2} + \langle U \rangle$$

$$\text{where} \quad \langle U \rangle \equiv \frac{1}{Z_C V^N} \int d^3 r_1 d^3 r_2 \cdots d^3 r_N U(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) e^{-\beta U}$$

Formulation of equation of state in terms of pair distribution function – continued:

$$\langle U \rangle \equiv \frac{1}{Z_C V^N} \int d^3r_1 d^3r_2 \cdots d^3r_N U(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) e^{-\beta U}$$

$$\text{For} \quad U(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) = \sum_{i<j} u(r_{ij})$$

$$\langle U \rangle = 2\pi\rho \int dr\, r^2 g(r)\, u(r)$$

$$\langle E \rangle = \frac{3NkT}{2} + 2\pi\rho \int dr\, r^2 g(r)\, u(r)$$

Equation of state:

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

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

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

$$\text{Evaluation for: } U(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) = \sum_{i<j} u(r_{ij})$$

Scaled coordinates:

Let $\mathbf{r}_i \equiv V^{1/3}\mathbf{x}_i$

$$\frac{du(r_{ij})}{dV} = \frac{du(r_{ij})}{dr_{ij}}\frac{dr_{ij}}{dV} = \frac{du(r_{ij})}{dr_{ij}}\frac{r_{ij}}{3V}$$

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

$$= \int d^3x_1 d^3x_2 \cdots d^3x_N e^{-\beta\sum_{i<j} u(V^{1/3}x_{ij})}$$

$$\frac{\partial Z_C}{\partial V} = -\frac{\beta}{3V}\frac{N(N-1)}{2}\int d^3x_1 d^3x_2 \frac{du(r_{12})}{dr_{12}} r_{12}\int d^3x_3 \cdots d^3x_N e^{-\beta\sum_{i<j} u(V^{1/3}x_{ij})}$$

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

$$\frac{\partial Z_C}{\partial V} = -\frac{\beta}{3V} \frac{N(N-1)}{2} \int d^3 x_1 d^3 x_2 \frac{du(r_{12})}{dr_{12}} r_{12} \int d^3 x_3 \cdots d^3 x_N e^{-\beta \sum_{i<j} u(V^{1/3} x_{ij})}$$

$$\frac{1}{Z_C} \frac{\partial Z_C}{\partial V} = -\frac{\beta}{6V} \int d^3 x_1 d^3 x_2 \frac{du(r_{12})}{dr_{12}} r_{12} \rho^2 g(r_{12})$$

$$= -\frac{\beta \rho^2}{6} 4\pi \int dr\, r^3 \frac{du(r)}{dr} g(r)$$

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

$$\frac{PV}{NkT} = 1 - \frac{2\pi N}{3kTV} \int dr\, r^3 \frac{du(r)}{dr} g(r)$$

Summary of results for classical fluid with pair potential:

Equation of state in terms of pair correlation function:

$$\frac{PV}{NkT} = 1 - \frac{2\pi N}{3kTV} \int dr\, r^3 \frac{du(r)}{dr} g(r) = 1 - \frac{2\pi\beta\rho}{3} \int dr\, r^3 \frac{du(r)}{dr} g(r)$$

Equation of state in terms of virial expansion at low density:

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

$$B_2(T) = -\frac{2\pi\beta}{3} \int dr\, r^3 \frac{du(r)}{dr} e^{-\beta u(r)}$$

$\Rightarrow$ At this limit: $\quad g(r) \approx e^{-\beta u(r)}$