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:

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

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

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

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

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

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

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 $\mathbf{r}_2$.

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

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

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

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

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

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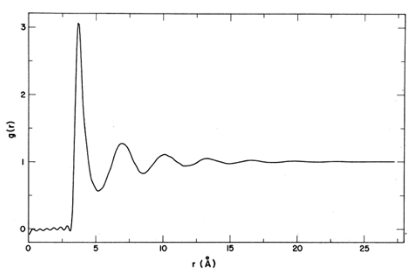

FIG. 4. Radial distribution function $g(r)$ for ^{36}Ar at 85 °K. This curve is the Fourier transform of the smoothed and extended $S(Q)$ shown as a solid line in Fig. 3.

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

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

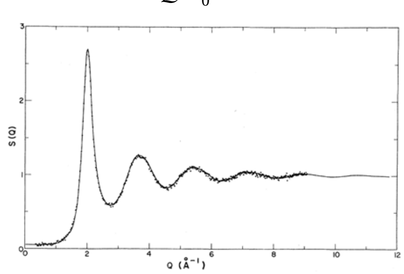

FIG. 3. Fully corrected experimental values of the liquid structure factor $S(Q)$ for ^{36}Ar at 85 °K. The solid line is a smoothed and extended $S(Q)$ obtained from the experimental data by an iterative procedure described in the text. The small dip in the experimental data near the top of the second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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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