

G25.2651: Advanced Statistical Mechanics

Problem set #2 Due: February 19, 2009

1. Suppose the interactions in an N -particle system are described by a pair potential of the form

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \sum_{j>i}^N u(|\mathbf{r}_i - \mathbf{r}_j|)$$

In the low density limit, we can assume that each particle interacts with *at most* one other particle.

- a. Show that the canonical partition function in this limit can be expressed as

$$Q(N, V, T) = \frac{(N-1)!! V^{N/2}}{N! \lambda^{3N}} \left[4\pi \int_0^\infty dr r^2 e^{-\beta u(r)} \right]^{N/2}$$

- b. Show that the radial distribution function $g(r)$ is proportional to $\exp[-\beta u(r)]$ in this limit.
c. Show that the second virial coefficient in the low density limit becomes

$$B_2(T) = -2\pi \int_0^\infty dr r^2 f(r)$$

where $f(r) = e^{-\beta u(r)} - 1$.

2. The radial distribution function $g(r)$ can be measured in neutron and X-ray scattering experiments. In such experiments, the observed intensity of scattered neutrons or X-rays at a given angle is proportional to the structure factor $S(\mathbf{k})$ given by

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \left| \sum_{j=1}^N e^{i\mathbf{k} \cdot \mathbf{r}_j} \right|^2 \right\rangle$$

where \mathbf{k} is the vector difference between the wave vectors of the incident and scattered neutrons or X-rays and N is the number of particles in the system. (Note that the term $j = k$ is *not* excluded from this sum!) Assuming a pair potential, show that $S(\mathbf{k})$ depends only on the magnitude $k = |\mathbf{k}|$ and is given in terms of $g(r)$ by

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

where ρ is the number density $\rho = N/V$

3. Often a pair potential is insufficient to describe accurately the behavior of many real liquids and gases. One then often includes *three-body* terms in the potential, which appear as follows:

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i>j} u(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i>j>k} v(|\mathbf{r}_i - \mathbf{r}_j|, |\mathbf{r}_j - \mathbf{r}_k|, |\mathbf{r}_i - \mathbf{r}_k|)$$

where the first term is the usual pair interaction term and the second contains the three-body contributions.

- a. Derive an expression for the average energy in terms of $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ and $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. What is the expression for $g^{(3)}$?

- b. Explain why $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ should only depend on $\mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{r}_3 - \mathbf{r}_2$ and $\mathbf{r}_3 - \mathbf{r}_1$. By making the following coordinate transformation:

$$\begin{aligned}\mathbf{R} &= \frac{1}{3}(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3) \\ \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \\ \mathbf{s} &= \mathbf{r}_3 - \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)\end{aligned}$$

show that $g^{(3)}$ really only depends on \mathbf{r} and \mathbf{s} . By integrating over the variable \mathbf{R} , obtain a new distribution function $\tilde{g}^{(3)}(\mathbf{r}, \mathbf{s})$.

- c. Express the average energy in terms of the radial distribution function $g(r)$ and the new function $\tilde{g}^{(3)}(\mathbf{r}, \mathbf{s})$.
- d. For isotropic systems, explain why $g^{(3)}$ should only depend on the three distances $|\mathbf{r}_1 - \mathbf{r}_2|$, $|\mathbf{r}_3 - \mathbf{r}_2|$ and $|\mathbf{r}_3 - \mathbf{r}_1|$. Show, therefore, that in terms of the variables \mathbf{r} and \mathbf{s} , the simplest distribution function can be expressed as $\bar{g}^{(3)}(r, \mu, \nu)$, i.e., as a function of the three variables r , μ , and ν , where r , μ and ν are given by

$$\begin{aligned}r &= |\mathbf{r}| \\ \mu &= \left| \mathbf{s} + \frac{1}{2}\mathbf{r} \right| + \left| \mathbf{s} - \frac{1}{2}\mathbf{r} \right| \\ \nu &= \left| \mathbf{s} + \frac{1}{2}\mathbf{r} \right| - \left| \mathbf{s} - \frac{1}{2}\mathbf{r} \right|\end{aligned}$$

(You don't need to obtain an explicit expression for $\bar{g}^{(3)}$).

4. On the course Web site, at the link

<http://www.nyu.edu/classes/tuckerman/stat.mechII/psets.html>

there is a link to a molecular dynamics trajectory of a system of 864 argon atoms in a cubic box of length $L = 34.9826 \text{ \AA}$. The trajectory contains 2000 samplings from a canonical distribution at $T = 100 \text{ K}$ in which the argon atoms interact via a Lennard-Jones potential

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

with $\sigma = 3.405 \text{ \AA}$ and $\epsilon = 119.8 \text{ K}$. The file contains the x , y , and z coordinates in \AA of each atom in the system, such that each line holds the coordinates of 1 atom. After 864 lines, the coordinates of the next configuration begin. Thus, in total, the file has 1728000 lines. The cubic box is subject to periodic boundary conditions, which means that when a particle exits one face of the cube, it re-enters through the opposite face. In a practical calculations, these boundary conditions can be imposed directly on components of the relative vector $\mathbf{r}_i - \mathbf{r}_j$ using the formula

$$dr_{ij,\alpha} = r_{i,\alpha} - r_{j,\alpha} - L * \text{NINT}[(r_{i,\alpha} - r_{j,\alpha})/L]$$

where NINT is the nearest integer function. NINT(x) returns the closest integer to x , and $\alpha = x, y, z$.

- a. Based on the information provided, calculate and plot the radial distribution function $g(r)$ for this system.
- b. From the form of the potential, at what value of r would you expect the peak to occur? How close is your actual peak to this prediction? Explain any deviations from your prediction.
- c. From your radial distribution function, $g(r)$, calculate the structure factor $S(q)$. Explain the method you employed for computing the integral.