

Interacting systems and phase transitions (5 Problems, 70 possible points)

Due on: April 27, 5:00 pm

(Email me TeX'd solutions, or scan your homework and email it to me. If you have problems finding a way to turn in your homework in these unusual times, please let me know as soon as possible!)

Note: An important part of science is communicating your understanding to other people. That is to say, a solution that may be technically correct but which I (the grader) cannot understand is not much better than an incorrect solution. So, please answer the following questions neatly, clearly, and logically – Thanks!

Problem 1 (10 points): Calculating with pictures

In Section 6.3 of the lecture notes we showed that the second virial coefficient,

$$B_2(T) = -\frac{b_2}{2}.$$

This meant we only needed to evaluate a single diagram (the integral over a single f -function). The third virial coefficient looked like it had more terms,

$$B_3(T) = b_2^2 - \frac{b_3}{3},$$

but we showed that it could be re-written in terms of a single diagram (negative one-third times “triangle” diagram, which stood for a particular integral). Expressed in terms of the cluster integrals, the 4th virial coefficient can be written as

$$B_4(T) = -\frac{b_4}{8} + \frac{3}{2}b_2b_3 - \frac{5}{2}b_2^3.$$

(That is, if I’ve done my combinatorics correctly!) That looks like a lot of graphs to evaluate (in Fig. 6.3 of the lecture notes I only drew the first handful of graphs for b_4 , for instance).

(A) Without doing any work beyond drawing pictures (or any equivalent method), given that we said B_l can be re-written in terms of sums over *one-particle irreducible clusters of size l*, tell me how many diagrams you actually need to write down in order to evaluate $B_4(T)$. Draw them for me.

Note: If you choose to answer this question “up to permutations of the labels,” make sure you tell me how many diagrams of each type you get. For instance, in the lecture notes I drew b_3 as 4 diagrams; I also could have said it was the complete triangle plus three permutations of “triangle missing one edge.”

(B) Choose any one of your diagrams from part (A), and write down the integral that this diagram corresponds to.

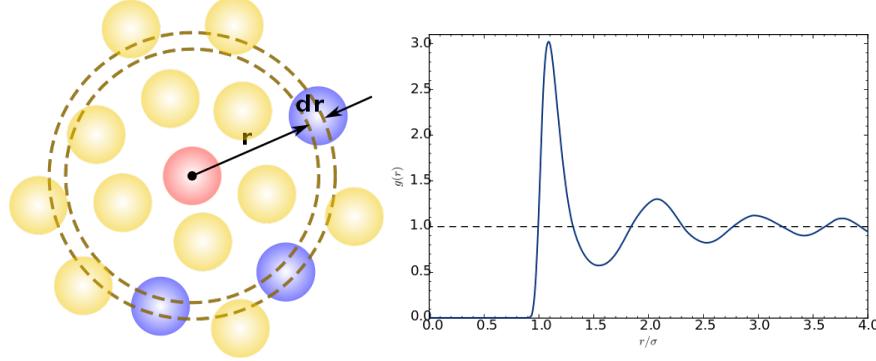


Figure 1: **Radial distribution function** (Left) Counting particles with a shell of thickness dr at a distance r away from a reference particle. In 3D, the probability of finding a particle in such a shell, given that a particle is at the origin, is $4\pi nr^2g(r)dr$. (Right) The radial distribution function for a Lennard-Jones fluid at some particular density and temperature. [Both figures from [wikipedia](#).]

Problem 2 (20 points): Radial distribution function for hard sphere fluids

The *radial distribution function*, $g(r)$, describes the probability of finding a particle in your system at some position relative to that of a given reference particle. It is defined by first considering the two-particle density (very similar to what I'm sure you remember from chapter 3!),

$$n_2(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i)(\mathbf{r}' - \mathbf{r}_j) \right\rangle.$$

Assuming the system is translationally and rotationally symmetric, $n_2(\mathbf{r}, \mathbf{r}') \rightarrow n_2(|\mathbf{r} - \mathbf{r}'|)$, and we define the radial distribution function (also called the “pair correlation function”) by normalizing this by the square of the density $n = N/V$:

$$g(|\mathbf{r} - \mathbf{r}'|) = \frac{n_2(\mathbf{r}, \mathbf{r}')}{n^2}.$$

A schematic cartoon and a plot of $g(r)$ are shown in Fig. 1. This quantity plays an important role, both as a characterization of the structure of fluids and because one can expressions for thermodynamic quantities (pressure, energy, etc) in terms of the pair correlation function: this permits an explicit link between microscopic structure and macroscopic behavior. In this problem will explore a virial expansion approach to computing $g(r)$ for hard sphere fluids in different dimensions.

- (A) We can write the pair density, with the help of the grand canonical partition function, as

$$n_2(\mathbf{r}_{12}) = \frac{1}{\mathcal{Q}(\mu, T, V)} \sum_{N=2}^{\infty} \frac{e^{\beta\mu N}}{(N-2)!} \int d^3\mathbf{r}_3 \cdots d^3\mathbf{r}_N \exp(-\beta\mathcal{U}(\{\mathbf{r}\})).$$

[Do you see where this comes from?] Using a virial-like expansion, from this equation show that you can write the radial distribution function the form

$$g(r) = \exp(-\beta\phi(\mathbf{r})) y(r),$$

where ϕ is the pair potential (i.e., $\mathcal{U} = \sum_{i < j} \phi(\mathbf{r}_{ij})$). Your function $y(r)$, called the “cavity distribution function,” should be written in terms the fugacity and integrals over various Mayer f functions. Just write out the terms of order z^2 and z^3 .

(B) The pressure of a fluid in d dimensions can be written in terms of $g(r)$ as

$$P = nk_B T \left(1 - \frac{n}{2dk_B T} \int d^3\mathbf{r} \, r g(r) \frac{d\phi}{dr} \right).$$

Now, let $\phi(\mathbf{r})$ be of a hard-sphere form in d dimension, so $\phi(r > \sigma) = 0$, and $\phi(r \leq \sigma) = \infty$. Write down expressions for the pressure in $d = 1, 2, 3$ in terms of the value of the cavity distribution function at contact, $y(\sigma)$. Note, by the way, that for hard spheres $y(\sigma) = g(\sigma)$, so in fact the pressure is completely determined by knowing how the value of the radial distribution function at contact changes with T and n . See Hansen and McDonald, *Theory of Simple Liquids* for more on this kind of liquid state theory if you’re interested.

Problem 3 (15 points): The Dieterici equations of state

The Dieterici equation is a modified version of the van der Waals equation which accounts for the fact that interactions can create gradients in pressure at the boundary of a gas. The equation of state is

$$\beta P(v - b) = \exp\left(-\beta \frac{a}{v}\right),$$

where as in the notes $v = V/N$.

- (A) Show that this equation of state has the same second virial coefficient, B_2 , as the van der Waals equation of state.
- (B) Find the location of the critical point, $\{P_c, T_c, v_c\}$, and compute the ratio $\frac{P_c v_c}{k_B T_c}$
- (C) Find the critical exponent that characterizes the pressure in terms of $v - v_c$ on the critical isotherm.
- (D) Find the critical exponent that characterizes the isothermal compressibility, κ_T as a function of $T - T_c$ on the critical isochore.

Problem 4 (15 points): Condensation of surfactants in the mean field approximation.

This question will lead you through a path very similar to the mean-field version of the van der Waals equation, and will check basic understanding of conjugate thermodynamic coordinates.

Suppose we have a fluid interface of area A with N surfactant molecules. If we ignore the coupling of the surfactants with the fluid and assume the interface is flat, the surfactants have a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i < j} \phi(\mathbf{r}_{ij}),$$

where the position and momentum vectors are in 2D.

- (A) Write down the canonical partition function $Z(T, A, N)$ from the definition (i.e., in terms of integrals over the \mathbf{r} and \mathbf{p}). Carry out the integrals over the momenta.
- (B) Assuming that the pair potential is infinite for $\mathbf{r}_{ij} < a$ and that $\int_a^\infty dr 2\pi r \phi(r) = -\varepsilon_0$, estimate the total potential energy of the system within the uniform density approximation, $n(\mathbf{r}) \approx n = N/A$.
- (C) Estimate the total amount of non-excluded volume in the system.
- (D) Using the results from part (A) - (C), write down the mean field approximation for the canonical partition function.
- (E) The work done in changing the surface area of the system is $dW = \sigma dA$. If σ_0 is the surface tension of the fluid without surfactants, and if σ_0 does not depend on temperature, what is the surface tension $\sigma(n, T)$ in the presence of the surfactants?
- (F) Show that there is a critical temperature, T_c , below which your result above must be wrong. Physically, what do you think the system looks like at high temperature, and what do you expect to happen below this temperature?

Problem 5 (10 points): Statistical physics

You have now seen the whole structure of this course on statistical physics, and it is my hope that you understand how most of these topics simultaneously (a) stand apart and can be taught independently, and (b) are deeply interconnected. Leo Kadanoff said of statistical physics that “once we get into any aspect of the subject, we can travel outward to reach the entire, rich structure. One can start from several different entry ports.”

So, imagine that you were in charge of designing a new syllabus for this course: Where would you start? What topics that we covered do you feel were essential? Inessential? What did we not cover that *should* have been part of the core course? How long would you spend on the different parts of the course? Most importantly for all of these questions: **Why?**

Please note: I have an actual rubric for grading this problem, and I am looking to see that you have thought about this course. An answer which just reads, “The way you taught it is great!” will actually get zero points!

Question: (0 points): Measurement of homework difficulty

How much time did you spend on this homework? Feel free to answer either in absolute terms (i.e., number of hours worked) or in qualitative terms relative to the average homework from last semester. Thanks!

Question: (0 points): Lecture survey

Please fill out the (tiny, extremely short, and painless) survey from the course webpage about the lectures. Much appreciated!