

**Physics 504: Statistical Mechanics and Kinetic Theory**  
**HOMEWORK SHEET 7**

Due 5pm Thur 23 April 2020 in the 504 box.

*Please attempt these questions without looking at textbooks, if you can. If you do need to refer to my notes or textbooks, the most effective way to do this is to read the relevant section, and then try the question again without looking at the book/notes.*

**Question 7–1.**

For interacting systems, it may not be possible to solve the statistical mechanics exactly or even in any well-controlled approximation scheme. Sometimes, however, it is possible to make useful progress just using dimensional analysis.

- (a) Consider a gas of classical particles of mass  $m$  in a volume  $V$  interacting via a pair potential  $U(r)$ . Sketch a typical form of  $U(r)$ . Suppose that for a particular class of substances,  $U(r)$  has the form  $U(r) = \epsilon u(r/\sigma)$ . The meaning of this is that the energy scale is set by  $\epsilon$  and the length scale by  $\sigma$ . For example, different gases might have different hard core radii  $\sigma$  and binding energies  $\epsilon$ . Working in the canonical ensemble, show that all substances in this class have the same equation of state when expressed in suitably scaled variables. i.e.  $p^* = \Pi(v^*, T^*)$ , where starred quantities are scaled pressure, volume per particle and temperature, and  $\Pi$  is a function that dimensional considerations alone cannot determine.
- (b) Show that if there is a critical point for this class of fluids, then  $p_c v_c / T_c$  is a constant independent of the particular fluid.
- (c) The above theory works very well for gases like Neon, but significant departures are observed at low temperatures for gases like He and H<sub>2</sub>. These are due to quantum effects. By dimensional analysis, show that the scaled equation of state should have the form

$$p^* = \Pi(v^*, T^*, \nu)$$

where  $\Pi$  is some function that we cannot determine by these dimensional considerations alone, and  $\nu = h/[\sigma\sqrt{m\epsilon}]$ .

- (d) Classically, the critical temperature  $k_B T_c / \epsilon$  is a constant, but quantum mechanically, it depends on  $\nu$ . By plotting an appropriate graph (you may use a computer if you wish) estimate the critical temperature of the isotope <sup>3</sup>He. You will need the following data.

	<sup>4</sup> He	H <sub>2</sub>
$k_B T_c / \epsilon$	0.529	0.896
$\sigma / \text{\AA}$	2.56	2.93
$\epsilon / k_B / \text{K}$	10.2	37

You should justify what assumptions you find it necessary to make. The mass of the proton is  $1.67 \times 10^{-27}$  Kg, and  $k_B = 1.38 \times 10^{-23}$  JK<sup>-1</sup>.

- (e) In part (c), why did we use  $\sigma$  for the length scale and not  $v^{1/3}$  ( $v \equiv V/N$ )?

**Question 7–2.**

Consider a gas of particles interacting through a simplified version of the Lennard-Jones potential:  $U(r) = \infty$  for  $r < r_0$ , and  $U(r) = -\epsilon(r_0/r)^6$  for  $r > r_0$ .

- (a) Write down the *formula* (not the numerical value) for the second virial coefficient. You will encounter an integral that can only be done by making an approximation: for reasonable estimates of  $\epsilon/k_B$  and  $r_0$  (for (e.g.) a gas such as neon) show that the integrand can be well approximated by a simple function that is easily integrated. Hence find a good approximation to the second virial coefficient.
- (b) Show that the equation of state is well approximated by Van der Waals equation,

$$\left(p + \frac{a}{v^2}\right)(v - b) = k_B T,$$

and give the expressions for  $a$  and  $b$ , and explain the interpretation of these parameters.

- (c) Find the critical point of the Van der Waals gas: i.e. calculate  $p_c$ ,  $v_c$  and  $T_c$  in terms of  $a$  and  $b$ .
- (d) Show that  $p_c v_c / k_B T_c$  is a universal constant (which you should calculate) for the Van der Waals gas.

**Question 7–3.**

In this question, you will calculate the equation of state of a plasma of ions of different species  $\alpha$ , as we considered in class. However, this time, we will use the virial equation of state to derive the pressure of the plasma. The notation in the question follows the notation in the lectures.

- (a) As we did in class when we derived the virial equation of state, write the virial  $\mathcal{V}$  as the sum of the ideal part (pressure exerted on the walls of the container) plus the contribution from the Coulomb interactions  $\mathcal{V}_c$ , and show that

$$\mathcal{V}_c = -\frac{e^2 V \sum_{\alpha} (n_{\alpha} z_{\alpha}^2)}{2\lambda}$$

where  $\lambda$  is the Debye-Hückel screening length that we calculated in lectures.

- (b) Hence show that in the Debye-Hückel theory, the equation of state for the pressure  $p$  is given by

$$p = k_B T \sum_{\alpha} n_{\alpha} (1 - 1/(18N_{\lambda}))$$

where  $N_{\lambda}$  is the total number of ions contained in a sphere of radius  $\lambda$ .