# **Review Problems**

The final exam will take place on **Tuesday December 16**, in the **Johnson Athletic Center**, from **1:30 to 4:30pm**. All topics presented in the course will be covered, with emphasis on the second half. It will be a closed book exam, but you may bring a two–sided sheet of formulas if you wish. It may also be helpful to bring along a calculator. There will be a lecture on Monday 12/8/03, and a recitation with quiz review on Wednesday 12/10/03.

The enclosed exams (and solutions) from the previous years are intended to help you review the material.

\*\*\*\*\*\*

Note that the first parts of each problem are easier than its last parts. Therefore, make sure to proceed to the next problem when you get stuck.

You may find the following information helpful:

### **Physical Constants**

Electron mass	$m_e \approx 9.1 \times 10^{-31} Kg$	Proton mass	$m_p \approx 1.7 \times 10^{-27} Kg$
Electron Charge	$e\approx 1.6\times 10^{-19}C$	Planck's constant/ $2\pi$	$\hbar\approx 1.1\times 10^{-34}Js^{-1}$
Speed of light	$c\approx 3.0\times 10^8 m s^{-1}$	Stefan's constant	$\sigma\approx 5.7\times 10^{-8}Wm^{-2}K^{-4}$
Boltzmann's constant	$k_B \approx 1.4 \times 10^{-23} J K^-$	<sup>1</sup> Avogadro's number	$N_0 \approx 6.0 \times 10^{23} mol^{-1}$

## **Conversion Factors**

 $1atm \equiv 1.0 \times 10^5 Nm^{-2}$   $1\mathring{A} \equiv 10^{-10}m$   $1eV \equiv 1.1 \times 10^4 K$ 

### Thermodynamics

dE = TdS + dW For a gas: dW = -PdV For a film:  $dW = \sigma dA$ 

### Mathematical Formulas

$\lim_{x \to \infty} \coth x = 1 + 2e^{-2x} + \mathcal{O}\left(e^{-4x}\right)$	$\lim_{x \to 0} \coth x = \frac{1}{x} + \frac{x}{3} + \mathcal{O}\left(x^2\right)$
$\int_0^\infty dx \ x^n \ e^{-\alpha x} = \frac{n!}{\alpha^{n+1}}$	$\left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$
$\int_{-\infty}^{\infty} dx \exp\left[-ikx - \frac{x^2}{2\sigma^2}\right] = \sqrt{2\pi\sigma^2} \exp\left[-\frac{\sigma^2 k^2}{2}\right]$	$\lim_{N\to\infty}\ln N! = N\ln N - N$
$\left\langle e^{-ikx} \right\rangle = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \left\langle x^n \right\rangle$	$\ln\left\langle e^{-ikx}\right\rangle = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \left\langle x^n\right\rangle_c$
$f_m^{\eta}(z) = \frac{1}{(m-1)!} \int_0^\infty dx \frac{x^{m-1}}{z^{-1}e^x - \eta} = \sum_{\alpha=1}^\infty \eta^{\alpha+1} \frac{z^{\alpha}}{\alpha^m}$	$\frac{df_m^{\eta}}{dz} = \frac{1}{z} f_{m-1}^{\eta}$
$\lim_{z \to \infty} f_m^{-}(z) = \frac{(\ln z)^m}{m!} \left[ 1 + \frac{\pi^2}{6} m(m-1)(\ln z)^{-2} + \cdots \right]$	$f_2^-(1) = \frac{\pi^2}{12}$ $f_4^-(1) = \frac{7\pi^4}{720}$
$\zeta_m \equiv f_m^+(1)$ $\zeta_{3/2} \approx 2.612$ $\zeta_2 = \frac{\pi^2}{6}$ $\zeta_{5/2} \approx$	1.341 $\zeta_3 \approx 1.202$ $\zeta_4 = \frac{\pi^4}{90}$

1. Exciton dissociation in a semiconductor: By shining an intense laser beam on a semiconductor, one can create a metastable collection of electrons (charge -e, and effective mass  $m_{\rm e}$ ) and holes (charge +e, and effective mass  $m_{\rm h}$ ) in the bulk. The oppositely charged particles may pair up (as in a hydrogen atom) to form a gas of excitons, or they may dissociate into a plasma. We shall examine a much simplified model of this process.

(a) Calculate the free energy of a gas composed of  $N_{\rm e}$  electrons and  $N_{\rm h}$  holes, at temperature T, treating them as classical non-interacting particles of masses  $m_{\rm e}$  and  $m_{\rm h}$ .

• The canonical partition function of gas of non-interacting electrons and holes is the product of contributions from the electron gas, and from the hole gas, as

$$Z_{\rm e-h} = Z_{\rm e} Z_{\rm h} = \frac{1}{N_{\rm e}!} \left(\frac{V}{\lambda_{\rm e}^3}\right)^{N_{\rm e}} \cdot \frac{1}{N_{\rm h}!} \left(\frac{V}{\lambda_{\rm h}^3}\right)^{N_{\rm h}}$$

where  $\lambda_{\alpha} = h/\sqrt{2\pi m_{\alpha}k_{\rm B}T}$  ( $\alpha = e, h$ ). Evaluating the factorials in Stirling's approximation, we obtain the free energy

$$F_{\rm e-h} = -k_{\rm B}T\ln Z_{\rm e-h} = N_{\rm e}k_{\rm B}T\ln\left(\frac{N_{\rm e}}{eV}\lambda_{\rm e}^3\right) + N_{\rm h}k_{\rm B}T\ln\left(\frac{N_{\rm h}}{eV}\lambda_{\rm h}^3\right)$$

(b) By pairing into an excition, the electron hole pair lowers its energy by  $\varepsilon$ . [The binding energy of a hydrogen-like exciton is  $\varepsilon \approx me^4/(2\hbar^2\epsilon^2)$ , where  $\epsilon$  is the dielectric constant, and  $m^{-1} = m_{\rm e}^{-1} + m_{\rm h}^{-1}$ .] Calculate the free energy of a gas of  $N_{\rm p}$  excitons, treating them as classical non-interacting particles of mass  $m = m_{\rm e} + m_{\rm h}$ .

• Similarly, the partition function of the exciton gas is calculated as

$$Z_{\rm p} = \frac{1}{N_{\rm p}!} \left(\frac{V}{\lambda_{\rm p}^3}\right)^{N_{\rm p}} e^{-\beta(-N_{\rm p}\epsilon)},$$

leading to the free energy

$$F_{\rm p} = N_{\rm p} k_{\rm B} T \ln \left(\frac{N_{\rm p}}{eV} \lambda_{\rm p}^3\right) - N_{\rm p} \epsilon,$$

where  $\lambda_{\rm p} = h/\sqrt{2\pi \left(m_{\rm e} + m_{\rm h}\right) k_{\rm B} T}$ .

(c) Calculate the chemical potentials  $\mu_{\rm e}$ ,  $\mu_{\rm h}$ , and  $\mu_{\rm p}$  of the electron, hole, and exciton states, respectively.

• The chemical potentials are derived from the free energies, through

$$\mu_{\rm e} = \left. \frac{\partial F_{\rm e-h}}{\partial N_{\rm e}} \right|_{T,V} = k_{\rm B} T \ln \left( n_{\rm e} \lambda_{\rm e}^3 \right),$$

$$\mu_{\rm h} = \left. \frac{\partial F_{\rm e-h}}{\partial N_{\rm h}} \right|_{T,V} = k_{\rm B} T \ln \left( n_{\rm h} \lambda_{\rm h}^3 \right),$$
$$\mu_{\rm p} = \left. \frac{\partial F_{\rm p}}{\partial N_{\rm p}} \right|_{T,V} = k_{\rm B} T \ln \left( n_{\rm p} \lambda_{\rm p}^3 \right) - \epsilon,$$

where  $n_{\alpha} = N_{\alpha}/V$  ( $\alpha = e, h, p$ ).

(d) Express the equilibrium condition between excitons and electron/holes in terms of their chemical potentials.

• The equilibrium condition is obtained by equating the chemical potentials of the electron and hole gas with that of the exciton gas, since the exciton results from the pairing of an electron *and* a hole,

electron + hole  $\rightleftharpoons$  exciton.

Thus, at equilibrium

$$\mu_{\rm e}(n_{\rm e}, T) + \mu_{\rm h}(n_{\rm h}, T) = \mu_{\rm p}(n_{\rm p}, T),$$

which is equivalent, after exponentiation, to

$$n_{\rm e}\lambda_{\rm e}^3 \cdot n_{\rm h}\lambda_{\rm h}^3 = n_{\rm p}\lambda_{\rm p}^3 e^{-\beta\epsilon}.$$

(e) At a high temperature T, find the density  $n_{\rm p}$  of excitons, as a function of the total density of excitations  $n \approx n_{\rm e} + n_{\rm h}$ .

• The equilibrium condition yields

$$n_{\rm p} = n_{\rm e} n_{\rm h} \frac{\lambda_{\rm e}^3 \lambda_{\rm h}^3}{\lambda_{\rm p}^3} e^{\beta \epsilon}.$$

At high temperature,  $n_{\rm p} \ll n_{\rm e} = n_{\rm h} \approx n/2$ , and

$$n_{\rm p} = n_{\rm e} n_{\rm h} \frac{\lambda_{\rm e}^3 \lambda_{\rm h}^3}{\lambda_{\rm p}^3} e^{\beta \epsilon} = \left(\frac{n}{2}\right)^2 \frac{h^3}{\left(2\pi k_{\rm B}T\right)^{3/2}} \left(\frac{m_{\rm e} + m_{\rm h}}{m_{\rm e} m_{\rm h}}\right)^{3/2} e^{\beta \epsilon}.$$

2. The Manning Transition: When ionic polymers (polyelectrolytes) such as DNA are immersed in water, the negatively charged counter-ions go into solution, leaving behind a positively charged polymer. Because of the electrostatic repulsion of the charges left behind, the polymer stretches out into a cylinder of radius a, as illustrated in the figure. While thermal fluctuations tend to make the ions wander about in the solvent, electrostatic attractions favor their return and condensation on the polymer. If the number of counterions is N, they interact with the N positive charges left behind on the rod through the potential  $U(r) = -2(Ne/L)\ln(r/L)$ , where r is the radial coordinate in a cylindrical geometry. If we ignore the Coulomb repulsion between counter-ions, they can be described by the classical Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} + 2e^2 n \ln\left(\frac{r}{L}\right) \right],$$

where n = N/L.



(a) For a cylindrical container of radius R, calculate the canonical partition function Z in terms of temperature T, density n, and radii R and a.

• The canonical partition function is

$$Z = \int \frac{\prod_{i} d^{3} p_{i} d^{3} q_{i}}{N! h^{3N}} \exp\left\{-\beta \sum_{i=1}^{N} \left[\frac{p_{i}^{2}}{2m} + 2e^{2} n \ln\left(\frac{r}{L}\right)\right]\right\}$$
$$= \left(\frac{2\pi Le}{N\lambda^{3}}\right)^{N} L^{N \cdot \beta 2e^{2}n} \left[\int_{a}^{R} r dr \cdot r^{-2e^{2}n/k_{\rm B}T}\right]^{N}$$
$$= \left(\frac{2\pi e}{n\lambda^{3}}\right)^{N} L^{2Ne^{2}n\beta} \left[\frac{R^{2\left(1-e^{2}n/k_{\rm B}T\right)} - a^{2\left(1-e^{2}n/k_{\rm B}T\right)}}{2\left(1-e^{2}n/k_{\rm B}T\right)}\right]^{N}$$

(b) Calculate the probability distribution function p(r) for the radial position of a counterion, and its first moment  $\langle r \rangle$ , the average radial position of a counter-ion. • Integrating out the unspecified N momenta and N-1 positions from the canonical distribution, one obtains the distribution function

$$p(r) = \frac{re^{-\left(2e^{2}n/k_{\rm B}T\right)\ln(r/L)}}{\int_{a}^{R} dr r e^{-\left(2e^{2}n/k_{\rm B}T\right)\ln(r/L)}} = 2\left(1 - \frac{e^{2}n}{k_{\rm B}T}\right)\frac{r^{1-2e^{2}n/k_{\rm B}T}}{R^{2\left(1 - e^{2}n/k_{\rm B}T\right)} - a^{2\left(1 - e^{2}n/k_{\rm B}T\right)}}.$$

(Note the normalization condition  $\int_{a}^{R} dr p(r) = 1$ .) The average position is then

$$\langle r \rangle = \int_{a}^{R} rp\left(r\right) dr = \left(\frac{2k_{\rm B}T - 2e^{2}n}{3k_{\rm B}T - 2e^{2}n}\right) \left(\frac{R^{3 - 2e^{2}n/k_{\rm B}T} - a^{3 - 2e^{2}n/k_{\rm B}T}}{R^{2 - 2e^{2}n/k_{\rm B}T} - a^{2 - 2e^{2}n/k_{\rm B}T}}\right)$$

(c) The behavior of the results calculated above in the limit  $R \gg a$  is very different at high and low temperatures. Identify the transition temperature, and characterize the nature of the two phases. In particular, how does  $\langle r \rangle$  depend on R and a in each case?

• Consider first low temperatures, such that  $e^2 n/k_{\rm B}T > 1$ . In the  $R \gg a$  limit, the distribution function becomes

$$p(r) = 2\left(1 - \frac{e^2n}{k_{\rm B}T}\right) \frac{r^{1-2e^2n/k_{\rm B}T}}{a^{2(1-e^2n/k_{\rm B}T)}},$$

and  $\langle r \rangle \propto a$ . To see this, either examine the above calculated average  $\langle r \rangle$  in the  $R \gg a$  limit, or notice that

$$p(r) dr = 2\left(1 - \frac{e^2 n}{k_{\rm B}T}\right) x^{1 - 2e^2 n/k_{\rm B}T} dx,$$

where x = r/a, immediately implying  $\langle r \rangle \propto a$  (as  $\int_1^\infty dx x^{1-2e^2n/k_{\rm B}T} < \infty$  if  $e^2n/k_{\rm B}T > 1$ ). On the other hand, at high temperatures  $(e^2n/k_{\rm B}T < 1)$ , the distribution function reduces to

$$p(r) = 2\left(1 - \frac{e^2n}{k_{\rm B}T}\right) \frac{r^{1-2e^2n/k_{\rm B}T}}{R^{2(1-e^2n/k_{\rm B}T)}},$$

and  $\langle r \rangle \propto R$ , from similar arguments. Thus, at temperature  $T_{\rm c} = e^2 n/k_{\rm B}$  there is a transition from a "condensed" phase, in which the counter-ions are stuck on the polymer, to a "gas" phase, in which the counter-ions fluctuate in water at typical distances from the polymer which are determined by the container size.

(d) Calculate the pressure exerted by the counter-ions on the wall of the container, at r = R, in the limit  $R \gg a$ , at all temperatures.

• The work done by the counter-ions to expand the container from a radius R to a radius R + dR is

$$dW = dF = (\text{force}) dR = -P (2\pi RL) dR,$$

leading to

$$P = -\frac{1}{2\pi RL} \frac{\partial F}{\partial R} = \frac{k_{\rm B}T}{2\pi RL} \frac{\partial \ln Z}{\partial R}.$$

At low temperatures,  $T < T_c$ , the pressure vanishes, since the partition function is independent of R in the limit  $R \gg a$ . At  $T > T_c$ , the above expression results in

$$P = \frac{k_{\rm B}T}{2\pi RL} 2N \left(1 - \frac{e^2 n}{k_{\rm B}T}\right) \frac{1}{R}$$

i.e.

$$PV = Nk_{\rm B}T\left(1 - \frac{e^2n}{k_{\rm B}T}\right).$$

(e) The character of the transition examined in part (d) is modified if the Coulomb interactions between counter-ions are taken into account. An approximate approach to the interacting problem is to allow a fraction  $N_1$  of counter-ions to condense along the polymer rod, while the remaining  $N_2 = N - N_1$  fluctuate in the solvent. The free counter-ions are again treated as non-interacting particles, governed by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} + 2e^2 n_2 \ln\left(\frac{r}{L}\right) \right],$$

where  $n_2 = N_2/L$ . Guess the equilibrium number of non-interacting ions,  $N_2^*$ , and justify your guess by discussing the response of the system to slight deviations from  $N_2^*$ . (This is a qualitative question for which no new calculations are needed.)

• Consider a deviation  $(n_2)$  from  $n_2^* \equiv N_2^*/V \equiv k_{\rm B}T/e^2$ , occuring at a temperature lower than  $T_{\rm c}$  (*i.e.*  $e^2n/k_{\rm B}T > 1$ ). If  $n_2 > n_2^*$ , the counter-ions have a tendency to condensate (since  $e^2n/k_{\rm B}T > 1$ ), thus decreasing  $n_2$ . On the other hand, if  $n_2 > n_2^*$ , the counter-ions tend to "evaporate" (since  $e^2n/k_{\rm B}T < 1$ ). In both cases, the system drives the density  $n_2$ to the (equilibrium) value of  $n_2^* = k_{\rm B}T/e^2$ . If the temperature is higher than  $T_{\rm c}$ , clearly  $n_2^* = n$  and there is no condensation.

**3.** Bose gas in d dimensions: Consider a gas of non-interacting (spinless) bosons with an energy spectrum  $\epsilon = p^2/2m$ , contained in a box of "volume"  $V = L^d$  in d dimensions. (a) Calculate the grand potential  $\mathcal{G} = -k_{\rm B}T \ln \mathcal{Q}$ , and the density n = N/V, at a chemical potential  $\mu$ . Express your answers in terms of d and  $f_m^+(z)$ , where  $z = e^{\beta\mu}$ , and

$$f_{m}^{+}(z) = \frac{1}{\Gamma(m)} \int_{0}^{\infty} \frac{x^{m-1}}{z^{-1}e^{x} - 1} dx.$$

(Hint: Use integration by parts on the expression for  $\ln Q$ .)

 $\bullet$  We have

$$\mathcal{Q} = \sum_{N=0}^{\infty} e^{N\beta\mu} \sum_{\{n_i\}}^{\sum_i n_i = N} \exp\left(-\beta \sum_i n_i \epsilon_i\right),$$
$$= \prod_i \sum_{\{n_i\}} e^{\beta(\mu - \epsilon_i)n_i} = \prod_i \frac{1}{1 - e^{\beta(\mu - \epsilon_i)}},$$

whence  $\ln \mathcal{Q} = -\sum_{i} \ln \left(1 - e^{\beta(\mu - \epsilon_{i})}\right)$ . Replacing the summation  $\sum_{i}$  with a d dimensional integration  $\int V d^{d}k / (2\pi)^{d} = \left[VS_{d} / (2\pi)^{d}\right] \int k^{d-1} dk$ , where  $S_{d} = 2\pi^{d/2} / (d/2 - 1)!$ , leads to

$$\ln \mathcal{Q} = -\frac{VS_d}{(2\pi)^d} \int k^{d-1} dk \ln \left(1 - z e^{-\beta \hbar^2 k^2/2m}\right).$$

The change of variable  $x = \beta \hbar^2 k^2 / 2m$  ( $\Rightarrow k = \sqrt{2mx/\beta}/\hbar$  and  $dk = dx\sqrt{2m/\beta x}/2\hbar$ ) results in

$$\ln \mathcal{Q} = -\frac{VS_d}{\left(2\pi\right)^d} \frac{1}{2} \left(\frac{2m}{\hbar^2 \beta}\right)^{d/2} \int x^{d/2-1} dx \ln\left(1 - ze^{-x}\right).$$

Finally, integration by parts yields

$$\ln \mathcal{Q} = \frac{VS_d}{(2\pi)^d} \frac{1}{d} \left(\frac{2m}{\hbar^2 \beta}\right)^{d/2} \int x^{d/2} dx \frac{ze^{-x}}{1 - ze^{-x}} = V \frac{S_d}{d} \left(\frac{2m}{\hbar^2 \beta}\right)^{d/2} \int dx \frac{x^{d/2}}{z^{-1}e^x - 1},$$

i.e.

$$\mathcal{G} = -k_{\rm B}T\ln\mathcal{Q} = -V\frac{S_d}{d}\left(\frac{2m}{h^2\beta}\right)^{d/2}k_{\rm B}T\Gamma\left(\frac{d}{2}+1\right)f_{\frac{d}{2}+1}^+(z)\,,$$

which can be simplified, using the property  $\Gamma(x+1) = x\Gamma(x)$ , to

$$\mathcal{G} = -\frac{V}{\lambda^d} k_{\rm B} T f_{\frac{d}{2}+1}^+(z) \,.$$

The average number of particles is calculated as

$$N = \frac{\partial}{\partial (\beta \mu)} \ln \mathcal{Q} = V \frac{S_d}{d} \left(\frac{2m}{h^2 \beta}\right)^{d/2} \int x^{d/2 - 1} dx \frac{z e^{-x}}{1 - z e^{-x}}$$
$$= V \frac{S_d}{2} \left(\frac{2m}{h^2 \beta}\right)^{d/2} \Gamma\left(\frac{d}{2}\right) f_{\frac{d}{2}}^+(z) = \frac{V}{\lambda^d} f_{\frac{d}{2}}^+(z)$$

i.e.

$$n = \frac{1}{\lambda^d} f_{\frac{d}{2}}^+(z) \,.$$

(b) Calculate the ratio PV/E, and compare it to the classical value.

• We have  $PV = -\mathcal{G}$ , while

$$E = -\frac{\partial}{\partial\beta} \ln \mathcal{Q} = +\frac{d}{2} \frac{\ln \mathcal{Q}}{\beta} = -\frac{d}{2} \mathcal{G}.$$

Thus PV/E = d/2, identical to the classical value.

(c) Find the critical temperature,  $T_{c}(n)$ , for Bose-Einstein condensation.

• The critical temperature  $T_{\rm c}\left(n\right)$  is given by

$$n = \frac{1}{\lambda^d} f_{\frac{d}{2}}^+ \left(1\right) = \frac{1}{\lambda^d} \zeta_{\frac{d}{2}}$$

for d > 2, *i.e.* 

$$T_{\rm c} = \frac{h^2}{2mk_{\rm B}} \left(\frac{n}{\zeta_{\frac{d}{2}}}\right)^{-2/d}$$

(d) Calculate the heat capacity  $C\left(T\right)$  for  $T < T_{\rm c}\left(n\right).$   $\bullet$  At  $T < T_{\rm c},\,z=1$  and

$$C(T) = \frac{\partial E}{\partial T}\Big|_{z=1} = -\frac{d}{2} \left.\frac{\partial \mathcal{G}}{\partial T}\right|_{z=1} = -\frac{d}{2} \left(\frac{d}{2}+1\right) \frac{\mathcal{G}}{T} = \frac{d}{2} \left(\frac{d}{2}+1\right) \frac{V}{\lambda^d} k_{\mathrm{B}} \zeta_{\frac{d}{2}+1}.$$

(e) Sketch the heat capacity at all temperatures.

•



(f) Find the ratio,  $C_{\max}/C (T \to \infty)$ , of the maximum heat capacity to its classical limit, and evaluate it in d = 3

• As the maximum of the heat capacity occurs at the transition,

$$C_{\max} = C\left(T_{\rm c}\right) = \frac{d}{2} \left(\frac{d}{2} + 1\right) \frac{V}{\left(\zeta_{\frac{d}{2}}/n\right)} k_{\rm B} f_{\frac{d}{2}+1}^{+}\left(1\right) = \frac{d}{2} N k_{\rm B} \left(\frac{d}{2} + 1\right) \frac{\zeta_{\frac{d}{2}+1}}{\zeta_{\frac{d}{2}}}$$

Thus

$$\frac{C_{\max}}{C\left(T \to \infty\right)} = \left(\frac{d}{2} + 1\right) \frac{\zeta_{\frac{d}{2}+1}}{\zeta_{\frac{d}{2}}},$$

which evaluates to 1.283 in d = 3.

(g) How does the above calculated ratio behave as  $d \rightarrow 2$ ? In what dimensions are your results valid? Explain.

• The maximum heat capacity, as it stands above, vanishes as  $d \to 2!$  Since  $f_m^+(x \to 1) \to \infty$  if  $m \leq 2$ , the fugacuty z is always smaller than 1. Hence, there is no macroscopic occupation of the ground state, even at the lowest temperatures, *i.e.* no Bose-Einstein condensation in  $d \leq 2$ . The above results are thus only valid for  $d \geq 2$ .

#### \*\*\*\*\*\*

**1.** Electron Magnetism: The conduction electrons in a metal can be treated as a gas of fermions of spin 1/2 (with up/down degeneracy), and density n = N/V.

(a) Ignoring the interactions between electrons, describe (in words) their ground state. Calculate the fermi wave number  $k_{\rm F}$ , and the ground-state energy density  $E_0/V$  in terms of the density n.

• In the ground state, the fermi sea is filled symmetrically by spin up and spin down particles up to  $k_{\rm F}$ , where  $k_{\rm F}$  is related to the density through

$$\frac{N}{2} = V \int_{k < k_{\rm F}} \frac{d^3k}{(2\pi)^3} = V \int_0^{k_{\rm F}} \frac{4\pi}{(2\pi)^3} k^2 dk = \frac{V k_{\rm F}^3}{6\pi^2}$$

i.e.

$$k_{\rm F} = \left(3\pi^2 n\right)^{1/3}.$$

The ground-state energy is calculated as

$$E_0 = 2V \int_{k < k_{\rm F}} \frac{\hbar^2 k^2}{2m} \frac{d^3 k}{(2\pi)^3} = 2V \frac{\hbar^2}{2m} \frac{4\pi}{5 (2\pi)^3} k_{\rm F}^5,$$

and the energy density is

$$\frac{E_0}{V} = \frac{3}{5} \left(3\pi^2\right)^{2/3} \frac{\hbar^2}{2m} n^{5/3}.$$

Electrons also interact *via* the Coulomb repulsion, which favors a wave function which is antisymmetric in position space, thus keeping them apart. Because of the full (position *and* spin) antisymmetry of fermionic wave functions, this interaction may be described as an effective spin-spin coupling which favors states with parallel spins. In a simple approximation, the effect of this interaction is represented by adding a potential

$$U = \alpha \frac{N_+ N_-}{V},$$

to the Hamiltonian, where  $N_+$  and  $N_- = N - N_+$  are the numbers of electrons with up and down spins, and V is the volume. (The parameter  $\alpha$  is related to the scattering length a by  $\alpha = 4\pi\hbar^2 a/m$ .) We would like to find out if the unmagnetized gas with  $N_+ = N_- = N/2$ still minimizes the energy, or if the gas is spontaneously magnetized.

(b) Express the modified Fermi wave numbers  $k_{\rm F+}$  and  $k_{\rm F-}$ , in terms of the densities  $n_+ = N_+/V$  and  $n_- = N_-/V$ .

• From the solution to part (a), we can read off

$$k_{F\pm} = \left(6\pi^2 n_{\pm}\right)^{1/3}$$

(c) Assuming small deviations  $n_{+} = n/2 + \delta$  and  $n_{-} = n/2 - \delta$  from the symmetric state, calculate the change in the kinetic energy of the system to second order in  $\delta$ .

• We can repeat the calculation of energy in part (a), now for two gases of spin up and spin down fermions, to get

$$\frac{E_{kin}}{V} = \frac{1}{10\pi^2} \frac{\hbar^2}{2m} \left( k_{F+}^5 + k_{F-}^5 \right) = \frac{3}{5} \left( 6\pi^2 \right)^{2/3} \frac{\hbar^2}{2m} \left( n_+^{5/3} + n_-^{5/3} \right)$$

Using  $n_{\pm} = n/2 \pm \delta$ , and expanding the above result to second order in  $\delta$ , gives

$$\frac{E_{kin}}{V} = \frac{E_0}{V} + \frac{4}{3} \left(3\pi^2\right)^{2/3} \frac{\hbar^2 n^{-1/3}}{2m} \delta^2 + \mathcal{O}\left(\delta^4\right).$$

(d) Express the spin-spin interaction density in terms of  $\delta$ . Find the critical value of  $\alpha_c$ , such that for  $\alpha > \alpha_c$  the electron gas can lower its total energy by spontaneously developing a magnetization. (This is known as the *Stoner instability*.)

• The interaction energy density is

$$\frac{U}{V} = \alpha n_{+} n_{-} = \alpha \left(\frac{n}{2} + \delta\right) \left(\frac{n}{2} - \delta\right) = \alpha \frac{n^{2}}{4} - \alpha \delta^{2}.$$

The total energy density is now given by

$$\frac{E}{V} = \frac{E_0 + \alpha n^2 / 4}{V} + \left[\frac{4}{3} \left(3\pi^2\right)^{2/3} \frac{\hbar^2 n^{-1/3}}{2m} - \alpha\right] \delta^2 + \mathcal{O}\left(\delta^4\right).$$

When the second order term in  $\delta$  is negative, the electron gas has lower energy for finite  $\delta$ , i.e. it acquires a spontaneous magnetization. This occurs for

$$\alpha > \alpha_c = \frac{4}{3} \left(3\pi^2\right)^{2/3} \frac{\hbar^2 n^{-1/3}}{2m}.$$

(e) Explain qualitatively, and sketch the behavior of the spontaneous magnetization as a function of  $\alpha$ .

• For  $\alpha > \alpha_c$ , the optimal value of  $\delta$  is obtained by expanding the energy density to fourth order in  $\delta$ . The coefficient of the fourth order term is positive, and the minimum energy is obtained for a value of  $\delta^2 \propto (\alpha - \alpha_c)$ . The magnetization is proportional to  $\delta$ , and hence grows in the vicinity of  $\alpha_c$  as  $\sqrt{\alpha - \alpha_c}$ , as sketched below



**2.** Boson magnetism: Consider a gas of non-interacting spin 1 bosons, each subject to a Hamiltonian

$$\mathcal{H}_1(\vec{p}, s_z) = \frac{\vec{p}^2}{2m} - \mu_0 s_z B \quad .$$

where  $\mu_0 = e\hbar/mc$ , and  $s_z$  takes three possible values of (-1, 0, +1). (The orbital effect,  $\vec{p} \rightarrow \vec{p} - e\vec{A}$ , has been ignored.)

(a) In a grand canonical ensemble of chemical potential  $\mu$ , what are the average occupation numbers  $\left\{ \langle n_+(\vec{k}) \rangle, \langle n_0(\vec{k}) \rangle, \langle n_-(\vec{k}) \rangle \right\}$ , of one-particle states of wavenumber  $\vec{k} = \vec{p}/\hbar$ ? • Average occupation numbers of the one-particle states in the grand canonical ensemble of chemical potential  $\mu$ , are given by the Bose-Einstein distribution

$$n_{s}(\vec{k}) = \frac{1}{e^{\beta}[\mathcal{H}(s)-\mu] - 1}, \quad \text{(for } s = -1, 0, 1)$$
$$= \frac{1}{\exp\left[\beta\left(\frac{\hbar^{2}k^{2}}{2m} - \mu_{0}sB\right) - \beta\mu\right] - 1}$$

(b) Calculate the average total numbers  $\{N_+, N_0, N_-\}$ , of bosons with the three possible values of  $s_z$  in terms of the functions  $f_m^+(z)$ .

• Total numbers of particles with spin s are given by

$$N_{s} = \sum_{\{\vec{k}\}} n_{s}(\vec{k}), \implies N_{s} = \frac{V}{(2\pi)^{3}} \int d^{3}k \frac{1}{\exp\left[\beta\left(\frac{\hbar^{2}k^{2}}{2m} - \mu_{0}sB\right) - \beta\mu\right] - 1}$$

After a change of variables,  $k \equiv x^{1/2} \sqrt{2mk_BT}/h$ , we get

$$N_s = \frac{V}{\lambda^3} f_{3/2}^+ \left( z e^{\beta \mu_0 s B} \right),$$

where

$$f_m^+(z) \equiv \frac{1}{\Gamma(m)} \int_0^\infty \frac{dx \, x^{m-1}}{z^{-1} e^x - 1}, \qquad \lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}}, \qquad z \equiv e^{\beta \mu}$$

(c) Write down the expression for the magnetization  $M(T,\mu) = \mu_0(N_+ - N_-)$ , and by expanding the result for small B find the zero field susceptibility  $\chi(T,\mu) = \partial M/\partial B|_{B=0}$ . • Magnetization is obtained from

$$M(T,\mu) = \mu_0 \left(N_+ - N_-\right)$$
  
=  $\mu_0 \frac{V}{\lambda^3} \left[ f_{3/2}^+ \left( z e^{\beta \mu_0 B} \right) - f_{3/2}^+ \left( z e^{-\beta \mu_0 s B} \right) \right].$ 

Expanding the result for small B gives

$$f_{3/2}^{+}\left(ze^{\pm\beta\mu_{0}B}\right) \approx f_{3/2}^{+}\left(z[1\pm\beta\mu_{0}B]\right) \approx f_{3/2}^{+}(z)\pm z\cdot\beta\mu_{0}B\frac{\partial}{\partial z}f_{3/2}^{+}(z).$$

Using  $zdf_m^+(z)/dz = f_{m-1}^+(z)$ , we obtain

$$M = \mu_0 \frac{V}{\lambda^3} (2\beta\mu_0 B) \cdot f_{1/2}^+(z) = \frac{2\mu_0^2}{k_B T} \frac{V}{\lambda^3} \cdot B \cdot f_{1/2}^+(z),$$

and

$$\chi \equiv \left. \frac{\partial M}{\partial B} \right|_{B=0} = \frac{2\mu_0^2}{k_B T} \frac{V}{\lambda^3} \cdot f_{1/2}^+(z).$$

To find the behavior of  $\chi(T, n)$ , where n = N/V is the total density, proceed as follows: (d) For B = 0, find the high temperature expansion for  $z(\beta, n) = e^{\beta\mu}$ , correct to second order in n. Hence obtain the first correction from quantum statistics to  $\chi(T, n)$  at high temperatures.

• In the high temperature limit, z is small. Use the Taylor expansion for  $f_m^+(z)$  to write the total density n(B=0), as

$$n(B=0) = \frac{N_{+} + N_{0} + N_{-}}{V} \bigg|_{B=0} = \frac{3}{\lambda^{3}} f_{3/2}^{+}(z)$$
$$\approx \frac{3}{\lambda^{3}} \bigg( z + \frac{z^{2}}{2^{3/2}} + \frac{z^{3}}{3^{3/2}} + \cdots \bigg).$$

Inverting the above equation gives

$$z = \left(\frac{n\lambda^3}{3}\right) - \frac{1}{2^{3/2}} \left(\frac{n\lambda^3}{3}\right)^2 + \cdots.$$

The susceptibility is then calculated as

$$\chi = \frac{2\mu_0^2}{k_B T} \frac{V}{\lambda^3} \cdot f_{1/2}^+(z),$$
  
$$\chi/N = \frac{2\mu_0^2}{k_B T} \frac{1}{n\lambda^3} \left( z + \frac{z^2}{2^{1/2}} + \cdots \right)$$
  
$$= \frac{2\mu_0^2}{3k_B T} \left[ 1 + \left( -\frac{1}{2^{3/2}} + \frac{1}{2^{1/2}} \right) \left( \frac{n\lambda^3}{3} \right) + O\left(n^2\right) \right].$$

(e) Find the temperature  $T_c(n, B = 0)$ , of Bose-Einstein condensation. What happens to  $\chi(T, n)$  on approaching  $T_c(n)$  from the high temperature side?

• Bose-Einstein condensation occurs when z = 1, at a density

$$n = \frac{3}{\lambda^3} f_{3/2}^+(1),$$

or a temperature

$$T_c(n) = \frac{h^2}{2\pi m k_B} \left(\frac{n}{3\,\zeta_{3/2}}\right)^{2/3}$$

,

where  $\zeta_{3/2} \equiv f_{3/2}^+(1) \approx 2.61$ . Since  $\lim_{z \to 1} f_{1/2}^+(z) = \infty$ , the susceptibility  $\chi(T, n)$  diverges on approaching  $T_c(n)$  from the high temperature side.

(f) What is the chemical potential  $\mu$  for  $T < T_c(n)$ , at a small but finite value of B? Which one-particle state has a macroscopic occupation number?

• Chemical potential for  $T < T_c$ : Since  $n_s(\vec{k}, B) = [z^{-1}e^{\beta \mathcal{E}_s(\vec{k}, B)} - 1]^{-1}$  is a positive number for all  $\vec{k}$  and  $s_z$ ,  $\mu$  is bounded above by the minimum possible energy, i.e.

for  $T < T_c$ , and B finite,  $ze^{\beta\mu_0 B} = 1$ ,  $\implies \mu = -\mu_0 B$ .

Hence the macroscopically occupied one particle state has  $\vec{k} = 0$ , and  $s_z = +1$ . (g) Using the result in (f), find the spontaneous magnetization,

$$\overline{M}(T,n) = \lim_{B \to 0} M(T,n,B).$$

• Spontaneous magnetization: Contribution of the excited states to the magnetization vanishes as  $B \rightarrow 0$ . Therefore the total magnetization for  $T < T_c$  is due to the macroscopic occupation of the  $(k = 0, s_z = +1)$  state, and

$$\overline{M}(T,n) = \mu_0 V n_+(k=0)$$
$$= \mu_0 V \left(n - n_{excited}\right) = \mu_0 \left(N - \frac{3V}{\lambda^3} \zeta_{3/2}\right).$$

**3.** The virial theorem is a consequence of the invariance of the phase space for a system of N (classical or quantum) particles under canonical transformations, such as a change of scale. In the following, consider N particles with coordinates  $\{\vec{q}_i\}$ , and conjugate momenta  $\{\vec{p}_i\}$  (with  $i = 1, \dots, N$ ), and subject to a Hamiltonian  $\mathcal{H}(\{\vec{p}_i\}, \{\vec{q}_i\})$ .

(a) Classical version: Write down the expression for classical partition function,  $Z \equiv Z[\mathcal{H}]$ . Show that it is invariant under the rescaling  $\vec{q_1} \rightarrow \lambda \vec{q_1}, \vec{p_1} \rightarrow \vec{p_1}/\lambda$  of a pair of conjugate variables, i.e.  $Z[\mathcal{H}_{\lambda}]$  is independent of  $\lambda$ , where  $\mathcal{H}_{\lambda}$  is the Hamiltonian obtained after the above rescaling.

• The classical partition function is obtained by appropriate integrations over phase space as

$$Z = \frac{1}{N!h^{3N}} \int \left(\prod_i d^3 p_i d^3 q_i\right) e^{-\beta \mathcal{H}}.$$

The rescaled Hamiltonian  $\mathcal{H}_{\lambda} = \mathcal{H}(\vec{p}_1/\lambda, \{\vec{p}_{i\neq 1}\}, \lambda \vec{q}_1, \{\vec{q}_{i\neq 1}\})$  leads to a rescaled partition function

$$Z\left[\mathcal{H}_{\lambda}\right] = \frac{1}{N!h^{3N}} \int \left(\prod_{i} d^{3}p_{i}d^{3}q_{i}\right) e^{-\beta\mathcal{H}_{\lambda}},$$

which reduces to

$$Z\left[\mathcal{H}_{\lambda}\right] = \frac{1}{N!h^{3N}} \int \left(\lambda^{3}d^{3}p_{1}'\right) \left(\lambda^{-3}d^{3}q_{1}'\right) \left(\prod_{i} d^{3}p_{i}d^{3}q_{i}\right) e^{-\beta\mathcal{H}} = Z,$$

under the change of variables  $\vec{q_1}' = \lambda \vec{q_1}, \vec{p_1}' = \vec{p_1}/\lambda$ .

(b) Quantum mechanical version: Write down the expression for quantum partition function. Show that it is also invariant under the rescalings  $\vec{q_1} \rightarrow \lambda \vec{q_1}$ ,  $\vec{p_1} \rightarrow \vec{p_1}/\lambda$ , where  $\vec{p_i}$ and  $\vec{q_i}$  are now quantum mechanical operators. (Hint: start with the time-independent Schrödinger equation.)

• Using the energy basis

$$Z = \operatorname{tr}\left(e^{-\beta \mathcal{H}}\right) = \sum_{n} e^{-\beta E_{n}},$$

where  $E_n$  are the energy eigenstates of the system, obtained from the Schrödinger equation

$$\mathcal{H}\left(\left\{\vec{p}_{i}\right\},\left\{\vec{q}_{i}\right\}\right)\left|\psi_{n}\right\rangle=E_{n}\left|\psi_{n}\right\rangle,$$

where  $|\psi_n\rangle$  are the eigenstates. After the rescaling transformation, the corresponding equation is

$$\mathcal{H}\left(\vec{p}_{1}/\lambda, \{\vec{p}_{i\neq1}\}, \lambda\vec{q}_{1}, \{\vec{q}_{i\neq1}\}\right) \left|\psi_{n}^{(\lambda)}\right\rangle = E_{n}^{(\lambda)} \left|\psi_{n}^{(\lambda)}\right\rangle.$$

In the coordinate representation, the momentum operator is  $\vec{p}_i = -i\hbar\partial/\partial \vec{q}_i$ , and therefore  $\psi_{\lambda}(\{\vec{q}_i\}) = \psi(\{\lambda \vec{q}_i\})$  is a solution of the rescaled equation with eigenvalue  $E_n^{(\lambda)} = E_n$ . Since the eigen-energies are invariant under the transformation, so is the partition function which is simply the sum of corresponding exponentials.

(c) Now assume a Hamiltonian of the form

$$\mathcal{H} = \sum_{i} \frac{\vec{p_i}^2}{2m} + V\left(\{\vec{q_i}\}\right).$$

Use the result that  $Z[\mathcal{H}_{\lambda}]$  is independent of  $\lambda$  to prove the *virial* relation

$$\left\langle \frac{\vec{p_1}^2}{m} \right\rangle = \left\langle \frac{\partial V}{\partial \vec{q_1}} \cdot \vec{q_1} \right\rangle,$$

where the brackets denote thermal averages. (You may formulate your answer in the classical language, as a possible quantum derivation is similar.)

• Differentiating the free energy with respect to  $\lambda$  at  $\lambda = 1$ , we obtain

$$0 = \left. \frac{\partial \ln Z_{\lambda}}{\partial \lambda} \right|_{\lambda=1} = -\beta \left\langle \left. \frac{\partial H_{\lambda}}{\partial \lambda} \right|_{\lambda=1} \right\rangle = -\beta \left\langle -\frac{\vec{p}_{1}^{2}}{m} + \frac{\partial V}{\partial \vec{q}_{1}} \cdot \vec{q}_{1} \right\rangle,$$

i.e.,

$$\left\langle \frac{\vec{p}_1^2}{m} \right\rangle = \left\langle \frac{\partial V}{\partial \vec{q}_1} \cdot \vec{q}_1 \right\rangle.$$

(d) The above relation is sometimes used to estimate the mass of distant galaxies. The stars on the outer boundary of the G-8.333 galaxy have been measured to move with velocity  $v \approx 200$  km/s. Give a numerical estimate of the ratio of the G-8.333's mass to its size.

• The virial relation applied to a gravitational system gives

$$\left\langle mv^2 \right\rangle = \left\langle \frac{GMm}{R} \right\rangle.$$

Assuming that the kinetic and potential energies of the starts in the galaxy have reached some form of equilibrium gives

$$\frac{M}{R} \approx \frac{v^2}{G} \approx 6 \times 10^{20} \text{kg/m}.$$

\*\*\*\*\*\*

1. Freezing of  $He^3$ : At low temperatures  $He^3$  can be converted from liquid to solid by application of pressure. A peculiar feature of its phase boundary is that  $(dP/dT)_{\text{melting}}$  is negative at temperatures below  $0.3 \,{}^{o}K \, [(dP/dT)_m \approx -30 \text{atm} \,{}^{o}K^{-1}$  at  $T \approx 0.1 \,{}^{o}K]$ . We will use a simple model of liquid and solid phases of  $He^3$  to account for this feature.

(a) In the solid phase, the He<sup>3</sup> atoms form a crystal lattice. Each atom has nuclear spin of 1/2. Ignoring the interaction between spins, what is the entropy per particle  $s_s$ , due to the spin degrees of freedom?

• Entropy of solid He<sup>3</sup> comes from the nuclear spin degeneracies, and is given by

$$s_s = \frac{S_s}{N} = \frac{k_B \ln(2^N)}{N} = k_B \ln 2.$$

(b) Liquid He<sup>3</sup> is modelled as an ideal Fermi gas, with a volume of  $46\mathring{A}^3$  per atom. What is its Fermi temperature  $T_F$ , in degrees Kelvin?

• The Fermi temperature for liquid <sup>3</sup>He may be obtained from its density as

$$T_F = \frac{\varepsilon_F}{k_B} = \frac{h^2}{2mk_B} \left(\frac{3N}{8\pi V}\right)^{2/3}$$
$$\approx \frac{(6.7 \times 10^{-34})^2}{2 \cdot (6.8 \times 10^{-27})(1.38 \times 10^{-23})} \left(\frac{3}{8\pi \times 46 \times 10^{-30}}\right)^{2/3} \approx 9.2^{\circ}K.$$

(c) How does the heat capacity of liquid He<sup>3</sup> behave at low temperatures? Write down an expression for  $C_V$  in terms of  $N, T, k_B, T_F$ , up to a numerical constant, that is valid for  $T \ll T_F$ .

• The heat capacity comes from the excited states at the fermi surface, and is given by

$$C_V = k_B \frac{\pi^2}{6} k_B T \ D(\varepsilon_F) = \frac{\pi^2}{6} k_B^2 T \frac{3N}{2k_B T_F} = \frac{\pi^2}{4} N k_B \frac{T}{T_F}.$$

(d) Using the result in (c), calculate the entropy per particle  $s_{\ell}$ , in the liquid at low temperatures. For  $T \ll T_F$ , which phase (solid or liquid) has the higher entropy?

• The entropy can be obtained from the heat capacity as

$$C_V = \frac{TdS}{dT}, \quad \Rightarrow \quad s_\ell = \frac{1}{N} \int_0^T \frac{C_V dT}{T} = \frac{\pi^2}{4} k_B \frac{T}{T_F}.$$

As  $T \to 0$ ,  $s_{\ell} \to 0$ , while  $s_s$  remains finite. This is an unusual situation in which the solid has more entropy than the liquid! (The finite entropy is due to treating the nuclear spins as independent. There is actually a weak coupling between spins which causes magnetic ordering at a much lower temperature, removing the finite entropy.)

(e) By equating chemical potentials, or by any other technique, prove the Clausius– Clapeyron equation  $(dP/dT)_{\text{melting}} = (s_{\ell} - s_s)/(v_{\ell} - v_s)$ , where  $v_{\ell}$  and  $v_s$  are the volumes per particle in the liquid and solid phases respectively.

• The Clausius-Clapeyron equation can be obtained by equating the chemical potentials at the phase boundary,

$$\mu_{\ell}(T, P) = \mu_s(T, P), \text{ and } \mu_{\ell}(T + \Delta T, P + \Delta P) = \mu_s(T + \Delta T, P + \Delta P).$$

Expanding the second equation, and using the thermodynamic identities

$$\left(\frac{\partial\mu}{\partial T}\right)_P = S$$
, and  $\left(\frac{\partial\mu}{\partial P}\right)_T = -V$ ,

results in

$$\left(\frac{\partial P}{\partial T}\right)_{\text{melting}} = \frac{s_{\ell} - s_s}{v_{\ell} - v_s}.$$

(f) It is found experimentally that  $v_{\ell} - v_s = 3 \mathring{A}^3$  per atom. Using this information, plus the results obtained in previous parts, estimate  $(dP/dT)_{\text{melting}}$  at  $T \ll T_F$ .

• The negative slope of the phase boundary results from the solid having more entropy than the liquid, and can be calculated from the Clausius-Clapeyron relation

$$\left(\frac{\partial P}{\partial T}\right)_{\text{melting}} = \frac{s_{\ell} - s_s}{v_{\ell} - v_s} \approx k_B \frac{\frac{\pi^2}{4} \left(\frac{T}{T_F}\right) - \ln 2}{v_{\ell} - v_s}.$$

Using the values,  $T = 0.1 \,^{o}$ K,  $T_F = 9.2 \,^{o}$ J $^{o}$ K, and  $v_{\ell} - v_s = 3 \,^{A}A^3$ , we estimate

$$\left(\frac{\partial P}{\partial T}\right)_{\text{melting}} \approx -2.7 \times 10^6 \text{Pa}^{\circ} \text{K}^{-1},$$

in reasonable agreement with the observations.

2. Non-interacting bosons: Consider a grand canonical ensemble of non-interacting bosons with chemical potential  $\mu$ . The one-particle states are labelled by a wavevector  $\vec{q}$ , and have energies  $\mathcal{E}(\vec{q})$ .

(a) What is the joint probability  $P(\{n_{\vec{q}}\})$ , of finding a set of occupation numbers  $\{n_{\vec{q}}\}$ , of the one-particle states, in terms of the fugacities  $z_{\vec{q}} \equiv \exp \left[\beta(\mu - \mathcal{E}(\vec{q}))\right]$ ?

• In the grand canonical ensemble with chemical potential  $\mu$ , the joint probability of finding a set of occupation numbers  $\{n_{\vec{q}}\}$ , for one-particle states of energies  $\mathcal{E}(\vec{q})$  is given by the normalized bose distribution

$$P(\{n_{\vec{q}}\}) = \prod_{\vec{q}} \{1 - \exp\left[\beta(\mu - \mathcal{E}(\vec{q}))\right]\} \exp\left[\beta(\mu - \mathcal{E}(\vec{q}))n_{\vec{q}}\right]$$
$$= \prod_{\vec{q}} (1 - z_{\vec{q}}) z_{\vec{q}}^{n_{\vec{q}}}, \quad \text{with} \quad n_{\vec{q}} = 0, 1, 2, \cdots, \quad \text{for each } \vec{q}$$

(b) For a particular  $\vec{q}$ , calculate the characteristic function  $\langle \exp[ikn_{\vec{q}}] \rangle$ . • Summing the geometric series with terms growing as  $(z_{\vec{q}}e^{ik})^{n_{\vec{q}}}$ , gives

$$\left\langle \exp\left[ikn_{\vec{q}}\right]\right\rangle = \frac{1 - \exp\left[\beta(\mu - \mathcal{E}(\vec{q}))\right]}{1 - \exp\left[\beta(\mu - \mathcal{E}(\vec{q})) + ik\right]} = \frac{1 - z_{\vec{q}}}{1 - z_{\vec{q}}e^{ik}}.$$

(c) Using the result of part (b), or otherwise, give expressions for the mean and variance of  $n_{\vec{q}}$ .

• Cumulates can be generated by expanding the logarithm of the characteristic function in powers of k. Using the expansion formula for  $\ln(1+x)$ , we obtain

$$\ln \langle \exp \left[ ikn_{\vec{q}} \right] \rangle = \ln \left( 1 - z_{\vec{q}} \right) - \ln \left[ 1 - z_{\vec{q}} \left( 1 + ik - k^2/2 + \cdots \right) \right]$$
$$= -\ln \left[ 1 - ik \frac{z_{\vec{q}}}{1 - z_{\vec{q}}} + \frac{k^2}{2} \frac{z_{\vec{q}}}{1 - z_{\vec{q}}} + \cdots \right]$$
$$= ik \frac{z_{\vec{q}}}{1 - z_{\vec{q}}} - \frac{k^2}{2} \left[ \frac{z_{\vec{q}}}{1 - z_{\vec{q}}} + \left( \frac{z_{\vec{q}}}{1 - z_{\vec{q}}} \right)^2 \right] + \cdots$$
$$= ik \frac{z_{\vec{q}}}{1 - z_{\vec{q}}} - \frac{k^2}{2} \frac{z_{\vec{q}}}{\left( 1 - z_{\vec{q}} \right)^2} + \cdots$$

From the coefficients in the expansion, we can read off the mean and variance

$$\langle n_{\vec{q}} \rangle = \frac{z_{\vec{q}}}{1 - z_{\vec{q}}}, \quad \text{and} \quad \langle n_{\vec{q}}^2 \rangle_c = \frac{z_{\vec{q}}}{\left(1 - z_{\vec{q}}\right)^2}.$$

(d) Express the variance in part (c) in terms of the mean occupation number  $\langle n_{\vec{q}} \rangle$ .

• Inverting the relation relating  $n_{\vec{q}}$  to  $z_{\vec{q}}$ , we obtain

$$z_{\vec{q}} = \frac{\langle n_{\vec{q}} \rangle}{1 + \langle n_{\vec{q}} \rangle}$$

Substituting this value in the expression for the variance gives

$$\left\langle n_{\vec{q}}^2 \right\rangle_c = \frac{z_{\vec{q}}}{\left(1 - z_{\vec{q}}\right)^2} = \left\langle n_{\vec{q}} \right\rangle \left(1 + \left\langle n_{\vec{q}} \right\rangle\right).$$

(e) Express your answer to part (a) in terms of the occupation numbers  $\{\langle n_{\vec{q}} \rangle\}$ .

• Using the relation between  $z_{\vec{q}}$  and  $n_{\vec{q}}$ , the joint probability can be reexpressed as

$$P(\{n_{\vec{q}}\}) = \prod_{\vec{q}} \left[ \left( \langle n_{\vec{q}} \rangle \right)^{n_{\vec{q}}} \left( 1 + \langle n_{\vec{q}} \rangle \right)^{-1 - n_{\vec{q}}} \right].$$

(f) Calculate the entropy of the probability distribution for bosons, in terms of  $\{\langle n_{\vec{q}} \rangle\}$ , and comment on its zero temperature limit.

• Quite generally, the entropy of a probability distribution P is given by  $S = -k_B \langle \ln P \rangle$ . Since the occupation numbers of different one-particle states are independent, the corresponding entropies are additive, and given by

$$S = -k_B \sum_{\vec{q}} \left[ \langle n_{\vec{q}} \rangle \ln \langle n_{\vec{q}} \rangle - (1 + \langle n_{\vec{q}} \rangle) \ln (1 + \langle n_{\vec{q}} \rangle) \right].$$

In the zero temperature limit all occupation numbers are either 0 (for excited states) or infinity (for the ground states). In either case the contribution to entropy is zero, and the system at T = 0 has zero entropy.

\*\*\*\*\*\*

**3.** Hard rods: A collection of N asymmetric molecules in two dimensions may be modeled as a gas of rods, each of length 2l and lying in a plane. A rod can move by translation of its center of mass and rotation about latter, as long as it does not encounter another rod. Without treating the hard-core interaction exactly, we can incorporate it approximately by assuming that the rotational motion of each rod is restricted (by the other rods) to an angle  $\theta$ , which in turn introduces an excluded volume  $\Omega(\theta)$  (associated with each rod). The value of  $\theta$  is then calculated self consistently by maximizing the entropy at a given density n = N/V, where V is the total accessible area.



(a) Write down the entropy of such a collection of rods in terms of N, n,  $\Omega$ , and  $A(\theta)$ , the entropy associated to the rotational freedom of a *single* rod. (You may ignore the momentum contributions throughout, and consider the large N limit.)

• Including both forms of entropy, translational and rotational, leads to

$$S = k_{\rm B} \ln\left[\frac{1}{N!} \left(V - \frac{N\Omega(\theta)}{2}\right)^N A(\theta)^N\right] \approx Nk_{\rm B} \left[\ln\left(n^{-1} - \frac{\Omega(\theta)}{2}\right) + 1 + \ln A(\theta)\right].$$

(b) Extremizing the entropy as a function of  $\theta$ , relate the density to  $\Omega$ , A, and their derivatives  $\Omega'$ , A'; express your result in the form  $n = f(\Omega, A, \Omega', A')$ .

• The extremum condition  $\partial S/\partial \theta = 0$  is equivalent to

$$\frac{\Omega'}{2n^{-1} - \Omega} = \frac{A'}{A},$$

where primes indicate derivatives with respect to  $\theta$ . Solving for the density gives

$$n = \frac{2A'}{\Omega A' + \Omega' A}.$$

(c) Express the excluded volume  $\Omega$  in terms of  $\theta$  and sketch f as a function of  $\theta \in [0, \pi]$ , assuming  $A \propto \theta$ .

• Elementary geometry yields

$$\Omega = l^2 \left(\theta + \sin \theta\right),\,$$

so that the equilibrium condition becomes

$$n = f(\theta) = \frac{2}{l^2} \left[ \theta \left( 2 + \cos \theta \right) + \sin \theta \right]^{-1},$$

with the function  $f(\theta)$  plotted below:



(d) Describe the equilibrium state at high densities. Can you identify a phase transition as the density is decreased? Draw the corresponding critical density  $n_c$  on your sketch. What is the critical angle  $\theta_c$  at the transition? You don't need to calculate  $\theta_c$  explicitly, but give an (implicit) relation defining it. What value does  $\theta$  adopt at  $n < n_c$ ? • At high densities,  $\theta \ll 1$  and the equilibrium condition reduces to

$$N \approx \frac{V}{2\theta l^2};$$

the angle  $\theta$  is as open as allowed by the close packing. The equilibrium value of  $\theta$  increases as the density is decreased, up to its "optimal" value  $\theta_{\rm c}$  at  $n_{\rm c}$ , and  $\theta (n < n_{\rm c}) = \theta_{\rm c}$ . The transition occurs at the minimum of  $f(\theta)$ , whence  $\theta_{\rm c}$  satisfies

$$\frac{d}{d\theta} \left[ \theta \left( 2 + \cos \theta \right) + \sin \theta \right] = 0,$$

i.e.

$$2(1 + \cos\theta_{\rm c}) = \theta_{\rm c}\sin\theta_{\rm c}.$$

$$********$$