

### Review Problems

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

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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	$c \approx 3.0 \times 10^8 ms^{-1}$	Stefan's constant	$\sigma \approx 5.7 \times 10^{-8} Wm^{-2}K^{-4}$
Boltzmann's constant	$k_B \approx 1.4 \times 10^{-23} JK^{-1}$	Avogadro's number	$N_0 \approx 6.0 \times 10^{23} mol^{-1}$

#### Conversion Factors

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

#### Thermodynamics

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

#### Mathematical Formulas

$$\lim_{x \rightarrow \infty} \coth x = 1 + 2e^{-2x} + \mathcal{O}(e^{-4x}) \qquad \lim_{x \rightarrow 0} \coth x = \frac{1}{x} + \frac{x}{3} + \mathcal{O}(x^2)$$

$$\int_0^\infty dx x^n e^{-\alpha x} = \frac{n!}{\alpha^{n+1}} \qquad \left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^\infty dx \exp\left[-ikx - \frac{x^2}{2\sigma^2}\right] = \sqrt{2\pi\sigma^2} \exp\left[-\frac{\sigma^2 k^2}{2}\right] \qquad \lim_{N \rightarrow \infty} \ln N! = N \ln N - N$$

$$\langle e^{-ikx} \rangle = \sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle \qquad \ln \langle e^{-ikx} \rangle = \sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle_c$$

$$f_m^\eta(z) = \frac{1}{(m-1)!} \int_0^\infty dx \frac{x^{m-1}}{z^{-1}e^x - \eta} = \sum_{\alpha=1}^\infty \eta^{\alpha+1} \frac{z^\alpha}{\alpha^m} \qquad \frac{df_m^\eta}{dz} = \frac{1}{z} f_{m-1}^\eta$$

$$\lim_{z \rightarrow \infty} f_m^-(z) = \frac{(\ln z)^m}{m!} \left[1 + \frac{\pi^2}{6} m(m-1)(\ln z)^{-2} + \dots\right] \qquad f_2^-(1) = \frac{\pi^2}{12} \qquad f_4^-(1) = \frac{7\pi^4}{720}$$

$$\zeta_m \equiv f_m^+(1) \qquad \zeta_{3/2} \approx 2.612 \qquad \zeta_2 = \frac{\pi^2}{6} \qquad \zeta_{5/2} \approx 1.341 \qquad \zeta_3 \approx 1.202 \qquad \zeta_4 = \frac{\pi^4}{90}$$

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  $m_e$ ) and holes (charge  $+e$ , and effective mass  $m_h$ ) 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  $N_e$  electrons and  $N_h$  holes, at temperature  $T$ , treating them as classical non-interacting particles of masses  $m_e$  and  $m_h$ .

• 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

$$Z_{e-h} = Z_e Z_h = \frac{1}{N_e!} \left( \frac{V}{\lambda_e^3} \right)^{N_e} \cdot \frac{1}{N_h!} \left( \frac{V}{\lambda_h^3} \right)^{N_h},$$

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

$$F_{e-h} = -k_B T \ln Z_{e-h} = N_e k_B T \ln \left( \frac{N_e}{eV} \lambda_e^3 \right) + N_h k_B T \ln \left( \frac{N_h}{eV} \lambda_h^3 \right).$$

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

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

$$Z_p = \frac{1}{N_p!} \left( \frac{V}{\lambda_p^3} \right)^{N_p} e^{-\beta(-N_p\epsilon)},$$

leading to the free energy

$$F_p = N_p k_B T \ln \left( \frac{N_p}{eV} \lambda_p^3 \right) - N_p \epsilon,$$

where  $\lambda_p = h/\sqrt{2\pi(m_e + m_h)k_B T}$ .

(c) Calculate the chemical potentials  $\mu_e$ ,  $\mu_h$ , and  $\mu_p$  of the electron, hole, and exciton states, respectively.

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

$$\mu_e = \left. \frac{\partial F_{e-h}}{\partial N_e} \right|_{T,V} = k_B T \ln(n_e \lambda_e^3),$$

$$\mu_h = \left. \frac{\partial F_{e-h}}{\partial N_h} \right|_{T,V} = k_B T \ln(n_h \lambda_h^3),$$

$$\mu_p = \left. \frac{\partial F_p}{\partial N_p} \right|_{T,V} = k_B T \ln(n_p \lambda_p^3) - \epsilon,$$

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,

$$\text{electron} + \text{hole} \rightleftharpoons \text{exciton}.$$

Thus, at equilibrium

$$\mu_e(n_e, T) + \mu_h(n_h, T) = \mu_p(n_p, T),$$

which is equivalent, after exponentiation, to

$$n_e \lambda_e^3 \cdot n_h \lambda_h^3 = n_p \lambda_p^3 e^{-\beta\epsilon}.$$

(e) At a high temperature  $T$ , find the density  $n_p$  of excitons, as a function of the total density of excitations  $n \approx n_e + n_h$ .

- The equilibrium condition yields

$$n_p = n_e n_h \frac{\lambda_e^3 \lambda_h^3}{\lambda_p^3} e^{\beta\epsilon}.$$

At high temperature,  $n_p \ll n_e = n_h \approx n/2$ , and

$$n_p = n_e n_h \frac{\lambda_e^3 \lambda_h^3}{\lambda_p^3} e^{\beta\epsilon} = \left(\frac{n}{2}\right)^2 \frac{h^3}{(2\pi k_B T)^{3/2}} \left(\frac{m_e + m_h}{m_e m_h}\right)^{3/2} e^{\beta\epsilon}.$$

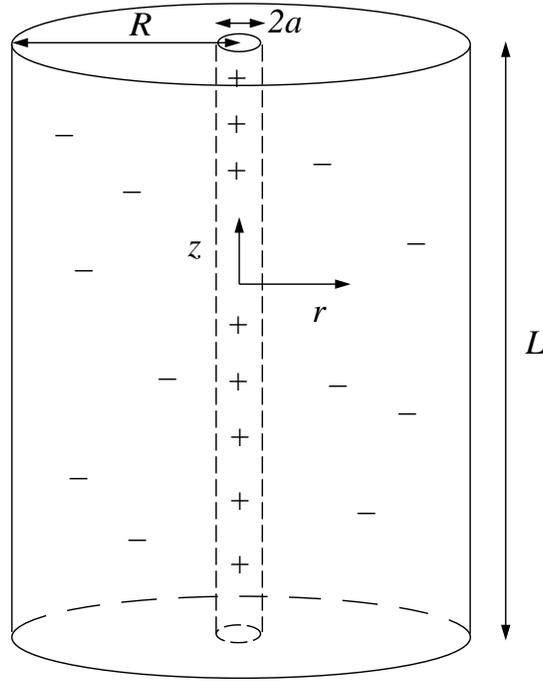
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**2. The Manning Transition:** When ionic polymers (polyelectrolytes) such as DNA are immersed in water, the negatively charged *counter-ions* go into solution, leaving behind a positively charged polymer. Because of the electrostatic repulsion of 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

$$\begin{aligned} Z &= \int \frac{\prod_i d^3 p_i d^3 q_i}{N! h^{3N}} \exp \left\{ -\beta \sum_{i=1}^N \left[ \frac{p_i^2}{2m} + 2e^2 n \ln \left( \frac{r}{L} \right) \right] \right\} \\ &= \left( \frac{2\pi L e}{N \lambda^3} \right)^N L^{N \cdot \beta 2e^2 n} \left[ \int_a^R r dr \cdot r^{-2e^2 n / k_B T} \right]^N \\ &= \left( \frac{2\pi e}{n \lambda^3} \right)^N L^{2Ne^2 n \beta} \left[ \frac{R^2(1 - e^2 n / k_B T) - a^2(1 - e^2 n / k_B T)}{2(1 - e^2 n / k_B T)} \right]^N. \end{aligned}$$

(b) Calculate the probability distribution function  $p(r)$  for the radial position of a counter-ion, 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

$$p(r) = \frac{r e^{-(2e^2 n/k_B T) \ln(r/L)}}{\int_a^R dr r e^{-(2e^2 n/k_B T) \ln(r/L)}} = 2 \left(1 - \frac{e^2 n}{k_B T}\right) \frac{r^{1-2e^2 n/k_B T}}{R^{2(1-e^2 n/k_B T)} - a^{2(1-e^2 n/k_B T)}}.$$

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

$$\langle r \rangle = \int_a^R r p(r) dr = \left(\frac{2k_B T - 2e^2 n}{3k_B T - 2e^2 n}\right) \left(\frac{R^{3-2e^2 n/k_B T} - a^{3-2e^2 n/k_B T}}{R^{2-2e^2 n/k_B T} - a^{2-2e^2 n/k_B T}}\right).$$

(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  $e^2 n/k_B T > 1$ . In the  $R \gg a$  limit, the distribution function becomes

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

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

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

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

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

and  $\langle r \rangle \propto R$ , from similar arguments. Thus, at temperature  $T_c = e^2 n/k_B$  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

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

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

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

*i.e.*

$$PV = Nk_B T \left( 1 - \frac{e^2 n}{k_B T} \right).$$

(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  $n_2^* \equiv N_2^*/V \equiv k_B T/e^2$ , occurring at a temperature lower than  $T_c$  (*i.e.*  $e^2 n/k_B T > 1$ ). If  $n_2 > n_2^*$ , the counter-ions have a tendency to condensate (since  $e^2 n/k_B T > 1$ ), thus decreasing  $n_2$ . On the other hand, if  $n_2 < n_2^*$ , the counter-ions tend to “evaporate” (since  $e^2 n/k_B T < 1$ ). In both cases, the system drives the density  $n_2$  to the (equilibrium) value of  $n_2^* = k_B T/e^2$ . If the temperature is higher than  $T_c$ , clearly  $n_2^* = n$  and there is no condensation.

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**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  $\mathcal{G} = -k_B T \ln \mathcal{Q}$ , 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  $\ln \mathcal{Q}$ .)

• We have

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

whence  $\ln \mathcal{Q} = -\sum_i \ln(1 - e^{\beta(\mu - \epsilon_i)})$ . Replacing the summation  $\sum_i$  with a  $d$  dimensional integration  $\int V d^d k / (2\pi)^d = [VS_d / (2\pi)^d] \int k^{d-1} dk$ , where  $S_d = 2\pi^{d/2} / (d/2 - 1)!$ , leads to

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

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

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

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.*

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

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

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

The average number of particles is calculated as

$$\begin{aligned}N &= \frac{\partial}{\partial(\beta\mu)} \ln \mathcal{Q} = V \frac{S_d}{d} \left(\frac{2m}{\hbar^2\beta}\right)^{d/2} \int x^{d/2-1} dx \frac{ze^{-x}}{1 - ze^{-x}}, \\ &= V \frac{S_d}{2} \left(\frac{2m}{\hbar^2\beta}\right)^{d/2} \Gamma\left(\frac{d}{2}\right) f_{\frac{d}{2}}^+(z) = \frac{V}{\lambda^d} f_{\frac{d}{2}}^+(z)\end{aligned}$$

*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

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

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

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

- The critical temperature  $T_c(n)$  is given by

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

for  $d > 2$ , *i.e.*

$$T_c = \frac{h^2}{2mk_B} \left( \frac{n}{\zeta_{\frac{d}{2}}} \right)^{2/d}.$$

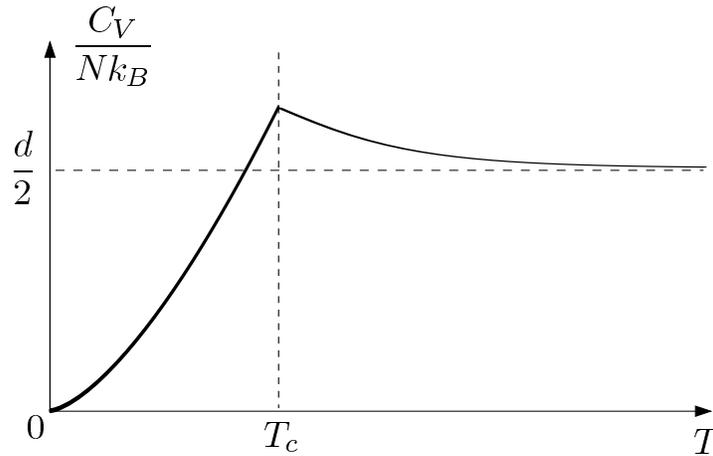
(d) Calculate the heat capacity  $C(T)$  for  $T < T_c(n)$ .

- At  $T < T_c$ ,  $z = 1$  and

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

(e) Sketch the heat capacity at all temperatures.

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(f) Find the ratio,  $C_{\max}/C(T \rightarrow \infty)$ , 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,

$$C_{\max} = C(T_c) = \frac{d}{2} \left( \frac{d}{2} + 1 \right) \frac{V}{\left( \zeta_{\frac{d}{2}}/n \right)} k_B f_{\frac{d}{2}+1}^+(1) = \frac{d}{2} N k_B \left( \frac{d}{2} + 1 \right) \frac{\zeta_{\frac{d}{2}+1}}{\zeta_{\frac{d}{2}}}.$$

Thus

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

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  $d \rightarrow 2$ ! Since  $f_m^+(x \rightarrow 1) \rightarrow \infty$  if  $m \leq 2$ , the fugacity  $z$  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  $d \geq 2$ .

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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  $k_F$ , 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  $k_F$ , where  $k_F$  is related to the density through

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

*i.e.*

$$k_F = (3\pi^2 n)^{1/3}.$$

The ground-state energy is calculated as

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

and the energy density is

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

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  $k_{F+}$  and  $k_{F-}$ , in terms of the densities  $n_+ = N_+/V$  and  $n_- = N_-/V$ .

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

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

(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

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

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

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

(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

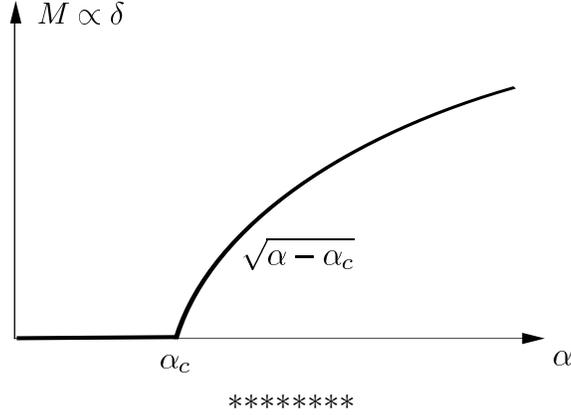
$$\frac{E}{V} = \frac{E_0 + \alpha n^2/4}{V} + \left[ \frac{4}{3} (3\pi^2)^{2/3} \frac{\hbar^2 n^{-1/3}}{2m} - \alpha \right] \delta^2 + \mathcal{O}(\delta^4).$$

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

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

(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  $\{\langle n_+(\vec{k}) \rangle, \langle n_0(\vec{k}) \rangle, \langle n_-(\vec{k}) \rangle\}$ , 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

$$\begin{aligned} n_s(\vec{k}) &= \frac{1}{e^{\beta[\mathcal{H}(s)-\mu]} - 1}, \quad (\text{for } s = -1, 0, 1) \\ &= \frac{1}{\exp\left[\beta\left(\frac{\hbar^2 k^2}{2m} - \mu_0 s B\right) - \beta\mu\right] - 1} \end{aligned}$$

(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

$$N_s = \sum_{\{\vec{k}\}} n_s(\vec{k}), \quad \implies \quad N_s = \frac{V}{(2\pi)^3} \int d^3k \frac{1}{\exp\left[\beta\left(\frac{\hbar^2 k^2}{2m} - \mu_0 s B\right) - \beta\mu\right] - 1}.$$

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

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

where

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

(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

$$\begin{aligned} M(T, \mu) &= \mu_0 (N_+ - N_-) \\ &= \mu_0 \frac{V}{\lambda^3} \left[ f_{3/2}^+(ze^{\beta\mu_0 B}) - f_{3/2}^+(ze^{-\beta\mu_0 B}) \right]. \end{aligned}$$

Expanding the result for small  $B$  gives

$$f_{3/2}^+(ze^{\pm\beta\mu_0 B}) \approx f_{3/2}^+(z[1 \pm \beta\mu_0 B]) \approx f_{3/2}^+(z) \pm z \cdot \beta\mu_0 B \frac{\partial}{\partial z} f_{3/2}^+(z).$$

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

$$\begin{aligned} n(B = 0) &= \left. \frac{N_+ + N_0 + N_-}{V} \right|_{B=0} = \frac{3}{\lambda^3} f_{3/2}^+(z) \\ &\approx \frac{3}{\lambda^3} \left( z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \dots \right). \end{aligned}$$

Inverting the above equation gives

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

The susceptibility is then calculated as

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

(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  $\lim_{z \rightarrow 1} f_{1/2}^+(z) = \infty$ , 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.

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

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,

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

- *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

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

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**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

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

which reduces to

$$Z[\mathcal{H}_\lambda] = \frac{1}{N!h^{3N}} \int (\lambda^3 d^3 p'_1) (\lambda^{-3} d^3 q'_1) \left( \prod_i d^3 p_i d^3 q_i \right) e^{-\beta \mathcal{H}} = Z,$$

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

$$Z = \text{tr} \left( e^{-\beta \mathcal{H}} \right) = \sum_n e^{-\beta E_n},$$

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

$$\mathcal{H}(\{\vec{p}_i\}, \{\vec{q}_i\}) |\psi_n\rangle = E_n |\psi_n\rangle,$$

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

$$\mathcal{H}(\vec{p}_1/\lambda, \{\vec{p}_{i \neq 1}\}, \lambda \vec{q}_1, \{\vec{q}_{i \neq 1}\}) |\psi_n^{(\lambda)}\rangle = E_n^{(\lambda)} |\psi_n^{(\lambda)}\rangle.$$

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

$$\mathcal{H} = \sum_i \frac{\vec{p}_i^2}{2m} + V(\{\vec{q}_i\}).$$

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

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

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

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

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1. *Freezing of He<sup>3</sup>*: At low temperatures He<sup>3</sup> 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 °K [ $(dP/dT)_m \approx -30 \text{ atm } ^\circ\text{K}^{-1}$  at  $T \approx 0.1 \text{ } ^\circ\text{K}$ ]. We will use a simple model of liquid and solid phases of He<sup>3</sup> 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  $46 \text{ \AA}^3$  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

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

(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  $T \rightarrow 0$ ,  $s_\ell \rightarrow 0$ , 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,

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

Expanding the second equation, and using the thermodynamic identities

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

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  $v_\ell - v_s = 3\text{\AA}^3$  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,  $T = 0.1 \text{ }^\circ\text{K}$ ,  $T_F = 9.2 \text{ J}^\circ\text{K}$ , and  $v_\ell - v_s = 3\text{\AA}^3$ , 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.

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**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  $z_{\vec{q}} \equiv \exp[\beta(\mu - \mathcal{E}(\vec{q}))]$ ?

- 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

$$\begin{aligned} P(\{n_{\vec{q}}\}) &= \prod_{\vec{q}} \{1 - \exp[\beta(\mu - \mathcal{E}(\vec{q}))]\} \exp[\beta(\mu - \mathcal{E}(\vec{q}))n_{\vec{q}}] \\ &= \prod_{\vec{q}} (1 - z_{\vec{q}}) z_{\vec{q}}^{n_{\vec{q}}}, \quad \text{with } n_{\vec{q}} = 0, 1, 2, \dots, \quad \text{for each } \vec{q}. \end{aligned}$$

- (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

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

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

- Cumulants 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

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

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

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

- (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

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

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

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

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

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

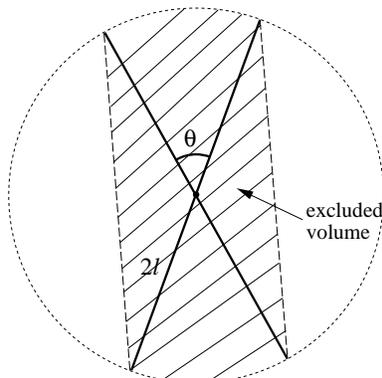
- Quite generally, the entropy of a probability distribution  $P$  is given by  $S = -k_B \langle \ln P \rangle$ . Since the occupation numbers of different one-particle states are independent, the corresponding entropies are additive, and given by

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

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.

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**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

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

(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  $A \propto \theta$ .

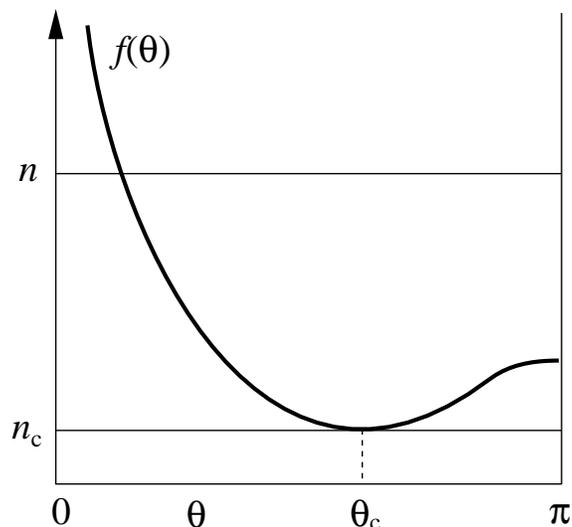
• Elementary geometry yields

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

so that the equilibrium condition becomes

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

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  $\theta_c$  at  $n_c$ , and  $\theta (n < n_c) = \theta_c$ . The transition occurs at the minimum of  $f(\theta)$ , whence  $\theta_c$  satisfies

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

*i.e.*

$$2(1 + \cos \theta_c) = \theta_c \sin \theta_c.$$

Actually, the above argument tracks the stability of a local maximum in entropy (as density is varied) which becomes unstable at  $\theta_c$ . There is another entropy maximum at  $\theta = \pi$ , corresponding to freely rotating rods, which becomes more advantageous (*i.e.* the global equilibrium state) at a density slightly below  $\theta_c$ .

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1. *Helium 4*:  ${}^4\text{He}$  at low temperatures can be converted from liquid to solid by application of pressure. An interesting feature of the phase boundary is that the melting pressure is reduced slightly from its  $T = 0\text{K}$  value, by approximately  $20\text{Nm}^{-2}$  at its minimum at  $T = 0.8\text{K}$ . We will use a simple model of liquid and solid phases of  ${}^4\text{He}$  to account for this feature.

(a) 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  $(v_\ell, s_\ell)$  and  $(v_s, s_s)$  are the volumes and entropies per atom in the liquid and solid phases respectively.

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

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

Expanding the second equation, and using the thermodynamic identities

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

results in

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

(b) The important excitations in liquid  ${}^4\text{He}$  at  $T < 1^\circ\text{K}$  are phonons of velocity  $c$ . Calculate the contribution of these modes to the heat capacity per particle  $C_V^\ell/N$ , of the liquid.

• The important excitations in liquid  ${}^4\text{He}$  at  $T < 1^\circ\text{K}$  are phonons of velocity  $c$ . The corresponding dispersion relation is  $\varepsilon(k) = \hbar ck$ . From the average number of phonons in mode  $\vec{k}$ , given by  $\langle n(\vec{k}) \rangle = [\exp(\beta\hbar ck) - 1]^{-1}$ , we obtain the net excitation energy as

$$\begin{aligned} E_{\text{phonons}} &= \sum_{\vec{k}} \frac{\hbar ck}{\exp(\beta\hbar ck) - 1} \\ &= V \times \int \frac{4\pi k^2 dk}{(2\pi)^3} \frac{\hbar ck}{\exp(\beta\hbar ck) - 1} \quad (\text{change variables to } x = \beta\hbar ck) \\ &= \frac{V}{2\pi^2} \hbar c \left(\frac{k_B T}{\hbar c}\right)^4 \frac{6}{3!} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^2}{30} V \hbar c \left(\frac{k_B T}{\hbar c}\right)^4, \end{aligned}$$

where we have used

$$\zeta_4 \equiv \frac{1}{3!} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{90}.$$

The corresponding heat capacity is now obtained as

$$C_V = \frac{dE}{dT} = \frac{2\pi^2}{15} V k_B \left( \frac{k_B T}{\hbar c} \right)^3,$$

resulting in a heat capacity per particle for the liquid of

$$\frac{C_V^\ell}{N} = \frac{2\pi^2}{15} k_B v_\ell \left( \frac{k_B T}{\hbar c} \right)^3.$$

(c) Calculate the low temperature heat capacity per particle  $C_V^s/N$ , of solid  $^4\text{He}$  in terms of longitudinal and transverse sound velocities  $c_L$ , and  $c_T$ .

- The elementary excitations of the solid are also phonons, but there are now *two* transverse sound modes of velocity  $c_T$ , and *one* longitudinal sound mode of velocity  $c_L$ . The contributions of these modes are additive, each similar in form to the liquid result calculated above, resulting in the final expression for solid heat capacity of

$$\frac{C_V^s}{N} = \frac{2\pi^2}{15} k_B v_s \left( \frac{k_B T}{\hbar} \right)^3 \times \left( \frac{2}{c_T^3} + \frac{1}{c_L^3} \right).$$

(d) Using the above results calculate the entropy difference ( $s_\ell - s_s$ ), assuming a single sound velocity  $c \approx c_L \approx c_T$ , and approximately equal volumes per particle  $v_\ell \approx v_s \approx v$ . Which phase (solid or liquid) has the higher entropy?

- The entropies can be calculated from the heat capacities as

$$s_\ell(T) = \int_0^T \frac{C_V^\ell(T') dT'}{T'} = \frac{2\pi^2}{45} k_B v_\ell \left( \frac{k_B T}{\hbar c} \right)^3,$$

$$s_s(T) = \int_0^T \frac{C_V^s(T') dT'}{T'} = \frac{2\pi^2}{45} k_B v_s \left( \frac{k_B T}{\hbar} \right)^3 \times \left( \frac{2}{c_T^3} + \frac{1}{c_L^3} \right).$$

Assuming approximately equal sound speeds  $c \approx c_L \approx c_T \approx 300 \text{ms}^{-1}$ , and specific volumes  $v_\ell \approx v_s \approx v = 46 \text{\AA}^3$ , we obtain the entropy difference

$$s_\ell - s_s \approx -\frac{4\pi^2}{45} k_B v \left( \frac{k_B T}{\hbar c} \right)^3.$$

The solid phase has more entropy than the liquid because it has two more phonon excitation bands.

(e) Assuming a small (temperature independent) volume difference  $\delta v = v_\ell - v_s$ , calculate the form of the melting curve. To explain the anomaly described at the beginning, which phase (solid or liquid) must have the higher density?

- Using the Clausius-Clapeyron equation, and the above calculation of the entropy difference, we get

$$\left(\frac{\partial P}{\partial T}\right)_{melting} = \frac{s_\ell - s_s}{v_\ell - v_s} = -\frac{4\pi^2}{45} k_B \frac{v}{\delta v} \left(\frac{k_B T}{\hbar c}\right)^3.$$

Integrating the above equation gives the melting curve

$$P_{melt}(T) = P(0) - \frac{\pi^2}{45} k_B \frac{v}{\delta v} \left(\frac{k_B T}{\hbar c}\right)^3 T.$$

To explain the reduction in pressure, we need  $\delta v = v_\ell - v_s > 0$ , i.e. the solid phase has the higher density, which is expected.

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2. *Surfactant Condensation:*  $N$  surfactant molecules are added to the surface of water over an area  $A$ . They are subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} \mathcal{V}(\vec{r}_i - \vec{r}_j),$$

where  $\vec{r}_i$  and  $\vec{p}_i$  are two dimensional vectors indicating the position and momentum of particle  $i$ .

- (a) Write down the expression for the partition function  $Z(N, T, A)$  in terms of integrals over  $\vec{r}_i$  and  $\vec{p}_i$ , and perform the integrals over the momenta.

- The partition function is obtained by integrating the Boltzmann weight over phase space, as

$$Z(N, T, A) = \int \frac{\prod_{i=1}^N d^2\vec{p}_i d^2\vec{q}_i}{N! h^{2N}} \exp \left[ -\beta \sum_{i=1}^N \frac{p_i^2}{2m} - \beta \sum_{i<j} \mathcal{V}(\vec{q}_i - \vec{q}_j) \right],$$

with  $\beta = 1/(k_B T)$ . The integrals over momenta are simple Gaussians, yielding

$$Z(N, T, A) = \frac{1}{N!} \frac{1}{\lambda^{2N}} \int \prod_{i=1}^N d^2\vec{q}_i \exp \left[ -\beta \sum_{i<j} \mathcal{V}(\vec{q}_i - \vec{q}_j) \right],$$

where as usual  $\lambda = h/\sqrt{2\pi m k_B T}$  denotes the thermal wavelength.

The inter-particle potential  $\mathcal{V}(\vec{r})$  is infinite for separations  $|\vec{r}| < a$ , and attractive for  $|\vec{r}| > a$  such that  $\int_a^\infty 2\pi r dr \mathcal{V}(r) = -u_0$ .

- (b) Estimate the total non-excluded area available in the positional phase space of the system of  $N$  particles.

- To estimate the joint phase space of particles with excluded areas, add them to the system one by one. The first one can occupy the whole area  $A$ , while the second can

explore only  $A - 2\Omega$ , where  $\Omega = \pi a^2$ . Neglecting three body effects (i.e. in the dilute limit), the area available to the third particle is  $(A - 2\Omega)$ , and similarly  $(A - n\Omega)$  for the  $n$ -th particle. Hence the joint excluded volume in this dilute limit is

$$A(A - \Omega)(A - 2\Omega) \cdots (A - (N - 1)\Omega) \approx (A - N\Omega/2)^N,$$

where the last approximation is obtained by pairing terms  $m$  and  $(N - m)$ , and ignoring order of  $\Omega^2$  contributions to their product.

(c) Estimate the total *potential* energy of the system, *assuming a constant density*  $n = N/A$ . Assuming this potential energy for all configurations allowed in the previous part, write down an approximation for  $Z$ .

• Assuming a *uniform density*  $n = N/A$ , an average attractive potential energy,  $\bar{U}$ , is estimated as

$$\begin{aligned} \bar{U} &= \frac{1}{2} \sum_{i,j} \mathcal{V}_{\text{attr.}}(\vec{q}_i - \vec{q}_j) = \frac{1}{2} \int d^2\vec{r}_1 d^2\vec{r}_2 n(\vec{r}_1) n(\vec{r}_2) \mathcal{V}_{\text{attr.}}(\vec{r}_1 - \vec{r}_2) \\ &\approx \frac{n^2}{2} A \int d^2\vec{r} \mathcal{V}_{\text{attr.}}(\vec{r}) \equiv -\frac{N^2}{2A} u_0. \end{aligned}$$

Combining the previous results gives

$$Z(N, T, A) \approx \frac{1}{N!} \frac{1}{\lambda^{2N}} (A - N\Omega/2)^N \exp \left[ \frac{\beta u_0 N^2}{2A} \right].$$

(d) The surface tension of water without surfactants is  $\sigma_0$ , approximately independent of temperature. Calculate the surface tension  $\sigma(n, T)$  in the presence of surfactants.

• Since the work done is changing the surface area is  $dW = \sigma dA$ , we have  $dF = -TdS + \sigma dA + \mu dN$ , where  $F = -k_B T \ln Z$  is the free energy. Hence, the contribution of the surfactants to the surface tension of the film is

$$\sigma_s = - \left. \frac{\partial \ln Z}{\partial A} \right|_{T,N} = -\frac{Nk_B T}{A - N\Omega/2} + \frac{u_0 N^2}{2A^2},$$

which is a two-dimensional variant of the familiar van der Waals equation. Adding the (constant) contribution in the absence of surfactants gives

$$\sigma(n, T) = \sigma_0 - \left. \frac{\partial \ln Z}{\partial A} \right|_{T,N} = -\frac{Nk_B T}{A - N\Omega/2} + \frac{u_0 N^2}{2A^2}.$$

(e) Show that below a certain temperature,  $T_c$ , the expression for  $\sigma$  is manifestly incorrect. What do you think happens at low temperatures?

- Thermodynamic stability requires  $\delta\sigma\delta A \geq 0$ , i.e.  $\sigma$  must be a monotonically increasing function of  $A$  at any temperature. This is the case at high temperatures where the first term in the equation for  $\sigma_s$  dominates, but breaks down at low temperatures when the term from the attractive interactions becomes significant. The critical temperature is obtained by the usual conditions of  $\partial\sigma_s/\partial A = \partial^2\sigma_s/\partial A^2 = 0$ , i.e. from

$$\left\{ \begin{array}{l} \frac{\partial\sigma_s}{\partial A}\Big|_T = \frac{Nk_B T}{(A - N\Omega/2)^2} - \frac{u_0 N^2}{A^3} = 0 \\ \frac{\partial^2\sigma_s}{\partial A^2}\Big|_T = -\frac{2Nk_B T}{(A - N\Omega/2)^3} + \frac{3u_0 N^2}{A^4} = 0 \end{array} \right. ,$$

The two equations are simultaneously satisfied for  $A_c = 3N\Omega/2$ , at a temperature

$$T_c = \frac{8u_0}{27k_B\Omega}.$$

As in the van der Waals gas, at temperatures below  $T_c$ , the surfactants separate into a high density (liquid) and a low density (gas) phase.

(f) Compute the heat capacities,  $C_A$  and write down an expression for  $C_\sigma$  without explicit evaluation, due to the surfactants.

- The contribution of the surfactants to the energy of the film is given by

$$E_s = -\frac{\partial \ln Z}{\partial \beta} = 2N \times \frac{k_B T}{2} - \frac{u_0 N^2}{2A}.$$

The first term is due to the kinetic energy of the surfactants, while the second arises from their (mean-field) attraction. The heat capacities are then calculated as

$$C_A = \frac{dQ}{dT}\Big|_A = \frac{\partial E}{\partial T}\Big|_A = Nk_B,$$

and

$$C_\sigma = \frac{dQ}{dT}\Big|_\sigma = \frac{\partial E}{\partial T}\Big|_\sigma - \sigma \frac{\partial A}{\partial T}\Big|_\sigma.$$

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**3. Dirac Fermions** are non-interacting particles of spin 1/2. The one-particle states come in pairs of positive and negative energies,

$$\mathcal{E}_\pm(\vec{k}) = \pm \sqrt{m^2 c^4 + \hbar^2 k^2 c^2} \quad ,$$

independent of spin.

(a) For *any* fermionic system of chemical potential  $\mu$ , show that the probability of finding an occupied state of energy  $\mu + \delta$  is the same as that of finding an unoccupied state of energy  $\mu - \delta$ . ( $\delta$  is any constant energy.)

• According to Fermi statistics, the probability of occupation of a state of energy  $\mathcal{E}$  is

$$p[n(\mathcal{E})] = \frac{e^{\beta(\mu-\mathcal{E})n}}{1 + e^{\beta(\mu-\mathcal{E})}}, \quad \text{for } n = 0, 1.$$

For a state of energy  $\mu + \delta$ ,

$$p[n(\mu + \delta)] = \frac{e^{\beta\delta n}}{1 + e^{\beta\delta}}, \quad \implies \quad p[n(\mu + \delta) = 1] = \frac{e^{\beta\delta}}{1 + e^{\beta\delta}} = \frac{1}{1 + e^{-\beta\delta}}.$$

Similarly, for a state of energy  $\mu - \delta$ ,

$$p[n(\mu - \delta)] = \frac{e^{-\beta\delta n}}{1 + e^{-\beta\delta}}, \quad \implies \quad p[n(\mu - \delta) = 0] = \frac{1}{1 + e^{-\beta\delta}} = p[n(\mu + \delta) = 1],$$

i.e. the probability of finding an occupied state of energy  $\mu + \delta$  is the same as that of finding an unoccupied state of energy  $\mu - \delta$ .

(b) At zero temperature all negative energy Dirac states are occupied and all positive energy ones are empty, i.e.  $\mu(T = 0) = 0$ . Using the result in (a) find the chemical potential at finite temperatures  $T$ .

• The above result implies that for  $\mu = 0$ ,  $\langle n(\mathcal{E}) \rangle + \langle n - \mathcal{E} \rangle$  is unchanged for any temperature; any particle leaving an occupied negative energy state goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if  $\mu$  stays at zero. Thus, the particle-hole symmetry enforces  $\mu(T) = 0$ .

(c) Show that the mean excitation energy of this system at finite temperature satisfies

$$E(T) - E(0) = 4V \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta\mathcal{E}_+(\vec{k})) + 1}.$$

• Using the label  $\pm$  for the positive (energy) states, the excitation energy is calculated as

$$\begin{aligned} E(T) - E(0) &= \sum_{k, s_z} [\langle n_+(k) \rangle \mathcal{E}_+(k) + (1 - \langle n_-(k) \rangle) \mathcal{E}_-(k)] \\ &= 2 \sum_k \langle n_+(k) \rangle \mathcal{E}_+(k) = 4V \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta\mathcal{E}_+(\vec{k})) + 1}. \end{aligned}$$

(d) Evaluate the integral in part (c) for *massless Dirac particles* (i.e. for  $m = 0$ ).

- For  $m = 0$ ,  $\mathcal{E}_+(k) = \hbar c|k|$ , and

$$\begin{aligned} E(T) - E(0) &= 4V \int_0^\infty \frac{4\pi k^2 dk}{8\pi^3} \frac{\hbar ck}{e^{\beta\hbar ck} + 1} = \quad (\text{set } \beta\hbar ck = x) \\ &= \frac{2V}{\pi^2} k_B T \left( \frac{k_B T}{\hbar c} \right)^3 \int_0^\infty dx \frac{x^3}{e^x + 1} \\ &= \frac{7\pi^2}{60} V k_B T \left( \frac{k_B T}{\hbar c} \right)^3. \end{aligned}$$

For the final expression, we have noted that the needed integral is  $3!f_4^-(1)$ , and used the given value of  $f_4^-(1) = 7\pi^4/720$ .

(e) Calculate the heat capacity,  $C_V$ , of such massless Dirac particles.

- The heat capacity can now be evaluated as

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{7\pi^2}{15} V k_B \left( \frac{k_B T}{\hbar c} \right)^3.$$

(f) Describe the qualitative dependence of the heat capacity at low temperature if the particles are massive.

- When  $m \neq 0$ , there is an energy gap between occupied and empty states, and we thus expect an exponentially activated energy, and hence heat capacity. For the low energy excitations,

$$\mathcal{E}_+(k) \approx mc^2 + \frac{\hbar^2 k^2}{2m} + \dots,$$

and thus

$$\begin{aligned} E(T) - E(0) &\approx \frac{2V}{\pi^2} mc^2 e^{-\beta mc^2} \frac{4\pi\sqrt{\pi}}{\lambda^3} \int_0^\infty dx x^2 e^{-x} \\ &= \frac{48}{\sqrt{\pi}} \frac{V}{\lambda^3} mc^2 e^{-\beta mc^2}. \end{aligned}$$

The corresponding heat capacity, to leading order thus behaves as

$$C(T) \propto k_B \frac{V}{\lambda^3} (\beta mc^2)^2 e^{-\beta mc^2}.$$

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1. *Neutron star core:* Professor Rajagopal's group has proposed that a new phase of QCD matter may exist in the core of neutron stars. This phase can be viewed as a condensate of quarks in which the low energy excitations are approximately

$$\mathcal{E}(\vec{k})_{\pm} =_{\pm} \hbar^2 \frac{(|\vec{k}| - k_F)^2}{2M} .$$

The excitations are fermionic, with a degeneracy of  $g = 2$  from spin.

(a) At zero temperature all negative energy states are occupied and all positive energy ones are empty, i.e.  $\mu(T = 0) = 0$ . By relating occupation numbers of states of energies  $\mu + \delta$  and  $\mu - \delta$ , or otherwise, find the chemical potential at finite temperatures  $T$ .

• According to Fermi statistics, the probability of occupation of a state of energy  $\mathcal{E}$  is

$$p[n(\mathcal{E})] = \frac{e^{\beta(\mu - \mathcal{E})n}}{1 + e^{\beta(\mu - \mathcal{E})}}, \quad \text{for } n = 0, 1.$$

For a state of energy  $\mu + \delta$ ,

$$p[n(\mu + \delta)] = \frac{e^{\beta\delta n}}{1 + e^{\beta\delta}}, \quad \implies \quad p[n(\mu + \delta) = 1] = \frac{e^{\beta\delta}}{1 + e^{\beta\delta}} = \frac{1}{1 + e^{-\beta\delta}}.$$

Similarly, for a state of energy  $\mu - \delta$ ,

$$p[n(\mu - \delta)] = \frac{e^{-\beta\delta n}}{1 + e^{-\beta\delta}}, \quad \implies \quad p[n(\mu - \delta) = 0] = \frac{1}{1 + e^{-\beta\delta}} = p[n(\mu + \delta) = 1],$$

i.e. the probability of finding an occupied state of energy  $\mu + \delta$  is the same as that of finding an unoccupied state of energy  $\mu - \delta$ . This implies that for  $\mu = 0$ ,  $\langle n(\mathcal{E}) \rangle + \langle n(-\mathcal{E}) \rangle$  is unchanged for an temperature; for every particle leaving an occupied negative energy state a particle goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if  $\mu$  stays at zero. Thus, the particle-hole symmetry enforces  $\mu(T) = 0$ .

(b) Assuming a constant density of states near  $k = k_F$ , i.e. setting  $d^3k \approx 4\pi k_F^2 dq$  with  $q = |\vec{k}| - k_F$ , show that the mean excitation energy of this system at finite temperature is

$$E(T) - E(0) \approx 2gV \frac{k_F^2}{\pi^2} \int_0^\infty dq \frac{\mathcal{E}_+(q)}{\exp(\beta\mathcal{E}_+(q)) + 1} .$$

- Using the label  $+(-)$  for the positive (energy) states, the excitation energy is calculated as

$$\begin{aligned}
E(T) - E(0) &= \sum_{k,s} [\langle n_+(k) \rangle \mathcal{E}_+(k) + (1 - \langle n_-(k) \rangle) \mathcal{E}_-(k)] \\
&= g \sum_k 2 \langle n_+(k) \rangle \mathcal{E}_+(k) = 2gV \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta\mathcal{E}_+(\vec{k})) + 1}.
\end{aligned}$$

The largest contribution to the integral comes for  $|\vec{k}| \approx k_F$ . and setting  $q = (|\vec{k}| - k_F)$  and using  $d^3k \approx 4\pi k_F^2 dq$ , we obtain

$$E(T) - E(0) \approx 2gV \frac{4\pi k_F^2}{8\pi^3} 2 \int_0^\infty dq \frac{\mathcal{E}_+(q)}{\exp(\beta\mathcal{E}_+(q)) + 1} = 2gV \frac{k_F^2}{\pi^2} \int_0^\infty dq \frac{\mathcal{E}_+(q)}{\exp(\beta\mathcal{E}_+(q)) + 1} .$$

(c) Give a closed form answer for the excitation energy by evaluating the above integral.

- For  $\mathcal{E}_+(q) = \hbar^2 q^2 / (2M)$ , we have

$$\begin{aligned}
E(T) - E(0) &= 2gV \frac{k_F^2}{\pi^2} \int_0^\infty dq \frac{\hbar^2 q^2 / 2M}{e^{\beta\hbar^2 q^2 / 2M} + 1} = \quad (\text{set } \beta\hbar^2 q^2 / 2M = x) \\
&= \frac{gV k_F^2}{\pi^2} k_B T \left( \frac{2M k_B T}{\hbar^2} \right)^{1/2} \int_0^\infty dx \frac{x^{1/2}}{e^x + 1} \\
&= \frac{gV k_F^2}{\pi^2} k_B T \left( \frac{2M k_B T}{\hbar^2} \right)^{1/2} \frac{\sqrt{\pi}}{2} \left( 1 - \frac{1}{\sqrt{2}} \right) \zeta_{3/2} = \left( 1 - \frac{1}{\sqrt{2}} \right) \frac{\zeta_{3/2}}{\pi} \frac{V k_F^2}{\lambda} k_B T.
\end{aligned}$$

For the final expression, we have used the value of  $f_m^-(1)$ , and introduced the thermal wavelength  $\lambda = h / \sqrt{2\pi M k_B T}$ .

(d) Calculate the heat capacity,  $C_V$ , of this system, and comment on its behavior at low temperature.

- Since  $E \propto T^{3/2}$ ,

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{3}{2} \frac{E}{T} = \frac{3\zeta_{3/2}}{2\pi} \left( 1 - \frac{1}{\sqrt{2}} \right) \frac{V k_F^2}{\lambda} k_B \propto \sqrt{T}.$$

This is similar to the behavior of a one dimensional system of bosons (since the density of states is constant in  $q$  as in  $d = 1$ ). Of course, for any fermionic system the density of states close to the Fermi surface has this character. The difference with the usual Fermi systems is the quadratic nature of the excitations above the Fermi surface.

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**2. Critical point behavior:** The pressure  $P$  of a gas is related to its density  $n = N/V$ , and temperature  $T$  by the truncated expansion

$$P = k_B T n - \frac{b}{2} n^2 + \frac{c}{6} n^3 \quad ,$$

where  $b$  and  $c$  are assumed to be *positive* temperature independent constants.

(a) Locate the critical temperature  $T_c$  below which this equation must be invalid, and the corresponding density  $n_c$  and pressure  $P_c$  of the critical point. Hence find the ratio  $k_B T_c n_c / P_c$ .

• Mechanical stability of the gas requires that any spontaneous change in volume should be opposed by a compensating change in pressure. This corresponds to  $\delta P \delta V < 0$ , and since  $\delta n = -(N/V^2)\delta V$ , any equation of state must have a pressure that is an increasing function of density. The transition point between pressure isotherms that are monotonically increasing functions of  $n$ , and those that are not (hence manifestly incorrect) is obtained by the usual conditions of  $dP/dn = 0$  and  $d^2P/dn^2 = 0$ . Starting from the cubic equation of state, we thus obtain

$$\begin{aligned}\frac{dP}{dn} &= k_B T_c - b n_c + \frac{c}{2} n_c^2 = 0 \\ \frac{d^2P}{dn^2} &= -b + c n_c = 0\end{aligned}$$

From the second equation we obtain  $n_c = b/c$ , which substituted in the first equation gives  $k_B T_c = b^2/(2c)$ . From the equation of state we then find  $P_c = b^3/(6c^2)$ , and the dimensionless ratio of

$$\frac{k_B T_c n_c}{P_c} = 3.$$

(b) Calculate the isothermal compressibility  $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$ , and sketch its behavior as a function of  $T$  for  $n = n_c$ .

• Using  $V = N/n$ , we get

$$\kappa_T(n) = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T = \frac{1}{n} \frac{\partial P}{\partial n} \Big|_T^{-1} = [n (k_B T - b n + c n^2/2)]^{-1}.$$

For  $n = n_c$ ,  $\kappa_T(n_c) \propto (T - T_c)^{-1}$ , and diverges at  $T_c$ .

(c) On the critical isotherm give an expression for  $(P - P_c)$  as a function of  $(n - n_c)$ .

• Using the coordinates of the critical point computed above, we find

$$\begin{aligned}P - P_c &= -\frac{b^3}{6c^2} + \frac{b^2}{2c} n - \frac{b}{2} n^2 + \frac{c}{6} n^3 \\ &= \frac{c}{6} \left( n^3 - 3\frac{b}{c} n^2 + 3\frac{b^2}{c^2} n - \frac{b^3}{c^3} \right) \\ &= \frac{c}{6} (n - n_c)^3.\end{aligned}$$

(d) The instability in the isotherms for  $T < T_c$  is avoided by phase separation into a liquid of density  $n_+$  and gas of density  $n_-$ . For temperatures close to  $T_c$ , these densities behave

as  $n_{\pm} \approx n_c(1 \pm \delta)$ . Using a Maxwell construction, or otherwise, find an implicit equation for  $\delta(T)$ , and indicate its behavior for  $(T_c - T) \rightarrow 0$ . (Hint: Along an isotherm, variations of chemical potential obey  $d\mu = dP/n$ .)

- According to the Gibbs–Duhem relation, the variations of the intensive variables are related by  $SdT - VdP + Nd\mu = 0$ , and thus along an isotherm ( $dT = 0$ )  $d\mu = dP/n = \partial P/\partial n|_T dn/n$ . Since the liquid and gas states are in coexistence they should have the same chemical potential. Integrating the above expression for  $d\mu$  from  $n_-$  to  $n_+$  leads to the so-called Maxwell construction, which reads

$$0 = \mu(n_+) - \mu(n_-) = \int_{n_-}^{n_+} \frac{dP}{n} = \int_{n_c(1-\delta)}^{n_c(1+\delta)} dn \left( \frac{k_B T - bn + cn^2/2}{n} \right).$$

Performing the integrals gives the equation

$$0 = k_B T \ln \left( \frac{1+\delta}{1-\delta} \right) - bn_c(2\delta) + \frac{c}{4} n_c^2 [(1+\delta)^2 - (1-\delta)^2] = k_B T \ln \left( \frac{1+\delta}{1-\delta} \right) - 2k_B T_c \delta,$$

where for the final expression, we have used  $n_c = b/c$  and  $k_B T_c = b^2/(2c)$ . The implicit equation for  $\delta$  is thus

$$\delta = \frac{T}{2T_c} \ln \left( \frac{1+\delta}{1-\delta} \right) \approx \frac{T}{T_c} (\delta - \delta^3 + \dots).$$

The leading behavior as  $(T_c - T) \rightarrow 0$  is obtained by keeping up to the cubic term, and given by

$$\delta \approx \sqrt{1 - \frac{T_c}{T}}.$$

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**3. Relativistic Bose gas in  $d$  dimensions:** Consider a gas of non-interacting (spinless) bosons with energy  $\epsilon = c|\vec{p}|$ , contained in a box of “volume”  $V = L^d$  in  $d$  dimensions.

(a) Calculate the grand potential  $\mathcal{G} = -k_B T \ln \mathcal{Q}$ , 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

$$f_m^+(z) = \frac{1}{(m-1)!} \int_0^\infty \frac{x^{m-1}}{z^{-1}e^x - 1} dx.$$

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

- We have

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

whence  $\ln \mathcal{Q} = -\sum_i \ln(1 - e^{\beta(\mu - \epsilon_i)})$ . Replacing the summation  $\sum_i$  with a  $d$  dimensional integration  $\int_0^\infty V d^d k / (2\pi)^d = [VS_d / (2\pi)^d] \int_0^\infty k^{d-1} dk$ , where  $S_d = 2\pi^{d/2} / (d/2 - 1)!$ , leads to

$$\ln \mathcal{Q} = -\frac{VS_d}{(2\pi)^d} \int_0^\infty k^{d-1} dk \ln(1 - ze^{-\beta\hbar ck}).$$

The change of variable  $x = \beta\hbar ck$  results in

$$\ln \mathcal{Q} = -\frac{VS_d}{(2\pi)^d} \left(\frac{k_B T}{\hbar c}\right)^d \int_0^\infty x^{d-1} dx \ln(1 - ze^{-x}).$$

Finally, integration by parts yields

$$\ln \mathcal{Q} = \frac{VS_d}{(2\pi)^d} \frac{1}{d} \left(\frac{k_B T}{\hbar c}\right)^d \int_0^\infty x^d dx \frac{ze^{-x}}{1 - ze^{-x}} = V \frac{S_d}{d} \left(\frac{k_B T}{\hbar c}\right)^d \int_0^\infty dx \frac{x^d}{z^{-1}e^x - 1},$$

leading to

$$\mathcal{G} = -k_B T \ln \mathcal{Q} = -V \frac{S_d}{d} \left(\frac{k_B T}{\hbar c}\right)^d k_B T d! f_{d+1}^+(z),$$

which can be somewhat simplified to

$$\mathcal{G} = -k_B T \frac{V \pi^{d/2} d!}{\lambda_c^d (d/2)!} f_{d+1}^+(z),$$

where  $\lambda_c \equiv \hbar c / (k_B T)$ . The average number of particles is calculated as

$$N = -\frac{\partial \mathcal{G}}{\partial \mu} = -\beta z \frac{\partial \mathcal{G}}{\partial z} = \frac{V \pi^{d/2} d!}{\lambda_c^d (d/2)!} f_d^+(z),$$

where we have used  $z \partial f_{d+1}(z) / \partial z = f_d(z)$ . Dividing by volume, the density is obtained as

$$n = \frac{1}{\lambda_c^d} \frac{\pi^{d/2} d!}{(d/2)!} f_d^+(z).$$

(b) Calculate the gas pressure  $P$ , its energy  $E$ , and compare the ratio  $E/(PV)$  to the classical value.

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

$$E = -\left. \frac{\partial \ln \mathcal{Q}}{\partial \beta} \right|_z = +d \frac{\ln \mathcal{Q}}{\beta} = -d\mathcal{G}.$$

Thus  $E/(PV) = d$ , identical to the classical value for a relativistic gas.

(c) Find the critical temperature,  $T_c(n)$ , for Bose-Einstein condensation, indicating the dimensions where there is a transition.

- The critical temperature  $T_c(n)$  is given by

$$n = \frac{1}{\lambda_c^d} \frac{\pi^{d/2} d!}{(d/2)!} f_d^+(z=1) = \frac{1}{\lambda_c^d} \frac{\pi^{d/2} d!}{(d/2)!} \zeta_d.$$

This leads to

$$T_c = \frac{hc}{k_B} \left( \frac{n(d/2)!}{\pi^{d/2} d! \zeta_d} \right)^{1/d}.$$

However,  $\zeta_d$  is finite only for  $d > 1$ , and thus a transition exists for all  $d > 1$ .

(d) What is the temperature dependence of the heat capacity  $C(T)$  for  $T < T_c(n)$ ?

- At  $T < T_c$ ,  $z = 1$  and  $E = -d\mathcal{G} \propto T^{d+1}$ , resulting in

$$C(T) = \left. \frac{\partial E}{\partial T} \right|_{z=1} = (d+1) \frac{E}{T} = -d(d+1) \frac{\mathcal{G}}{T} = d(d+1) \frac{V}{\lambda_c^d} k_B \frac{\pi^{d/2} d!}{(d/2)!} \zeta_{d+1} \propto T^d.$$

(e) Evaluate the dimensionless heat capacity  $C(T)/(Nk_B)$  at the critical temperature  $T = T_c$ , and compare its value to the classical (high temperature) limit.

- We can divide the above formula of  $C(T \leq T_c)$ , and the one obtained earlier for  $N(T \geq T_c)$ , and evaluate the result at  $T = T_c$  ( $z = 1$ ) to obtain

$$\frac{C(T_c)}{Nk_B} = \frac{d(d+1)\zeta_{d+1}}{\zeta_d}.$$

In the absence of quantum effects, the heat capacity of a relativistic gas is  $C/(Nk_B) = d$ ; this is the limiting value for the quantum gas at infinite temperature.

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1. *Graphene* is a single sheet of carbon atoms bonded into a *two dimensional* hexagonal lattice. It can be obtained by exfoliation (repeated peeling) of graphite. The band structure of graphene is such that the single particles excitations behave as relativistic Dirac *fermions*, with a spectrum that at low energies can be approximated by

$$\mathcal{E}_{\pm}(\vec{k}) = \pm \hbar v |\vec{k}| \quad .$$

There is spin degeneracy of  $g = 2$ , and  $v \approx 10^6 \text{ms}^{-1}$ . Recent experiments on unusual transport properties of graphene were reported in *Nature* **438**, 197 (2005). In this problem, you shall calculate the heat capacity of this material.

(a) If at zero temperature all negative energy states are occupied and all positive energy ones are empty, find the chemical potential  $\mu(T)$ .

• According to Fermi statistics, the probability of occupation of a state of energy  $\mathcal{E}$  is

$$p[n(\mathcal{E})] = \frac{e^{\beta(\mu - \mathcal{E})n}}{1 + e^{\beta(\mu - \mathcal{E})}}, \quad \text{for } n = 0, 1.$$

For a state of energy  $\mu + \delta$ ,

$$p[n(\mu + \delta)] = \frac{e^{\beta\delta n}}{1 + e^{\beta\delta}}, \quad \implies \quad p[n(\mu + \delta) = 1] = \frac{e^{\beta\delta}}{1 + e^{\beta\delta}} = \frac{1}{1 + e^{-\beta\delta}}.$$

Similarly, for a state of energy  $\mu - \delta$ ,

$$p[n(\mu - \delta)] = \frac{e^{-\beta\delta n}}{1 + e^{-\beta\delta}}, \quad \implies \quad p[n(\mu - \delta) = 0] = \frac{1}{1 + e^{-\beta\delta}} = p[n(\mu + \delta) = 1],$$

i.e. the probability of finding an occupied state of energy  $\mu + \delta$  is the same as that of finding an unoccupied state of energy  $\mu - \delta$ .

At zero temperature all negative energy Dirac states are occupied and all positive energy ones are empty, i.e.  $\mu(T = 0) = 0$ . The above result implies that for  $\mu = 0$ ,  $\langle n(\mathcal{E}) \rangle + \langle n - \mathcal{E} \rangle$  is unchanged for all temperatures; any particle leaving an occupied negative energy state goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if  $\mu$  stays at zero. Thus, the particle-hole symmetry enforces  $\mu(T) = 0$ .

(b) Show that the mean excitation energy of this system at finite temperature satisfies

$$E(T) - E(0) = 4A \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta\mathcal{E}_+(\vec{k})) + 1} \quad .$$

- Using the label +(-) for the positive (energy) states, the excitation energy is calculated as

$$\begin{aligned}
 E(T) - E(0) &= \sum_{k, s_z} [\langle n_+(k) \rangle \mathcal{E}_+(k) + (1 - \langle n_-(k) \rangle) \mathcal{E}_-(k)] \\
 &= 2 \sum_k 2 \langle n_+(k) \rangle \mathcal{E}_+(k) = 4A \int \frac{d^2 \vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta \mathcal{E}_+(\vec{k})) + 1}.
 \end{aligned}$$

(c) Give a closed form answer for the excitation energy by evaluating the above integral.

- For  $\mathcal{E}_+(k) = \hbar v |k|$ , and

$$\begin{aligned}
 E(T) - E(0) &= 4A \int_0^\infty \frac{2\pi k dk}{4\pi^2} \frac{\hbar v k}{e^{\beta \hbar v k} + 1} = \quad (\text{set } \beta \hbar v k = x) \\
 &= \frac{2A}{\pi} k_B T \left( \frac{k_B T}{\hbar v} \right)^2 \int_0^\infty dx \frac{x^2}{e^x + 1} \\
 &= \frac{3\zeta_3}{\pi} A k_B T \left( \frac{k_B T}{\hbar v} \right)^2.
 \end{aligned}$$

For the final expression, we have noted that the needed integral is  $2! f_3^-(1)$ , and used  $f_3^-(1) = 3\zeta_3/4$ .

$$E(T) - E(0) = A \int \frac{d^2 \vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta \mathcal{E}_+(\vec{k})) - 1}.$$

(d) Calculate the heat capacity,  $C_V$ , of such massless Dirac particles.

- The heat capacity can now be evaluated as

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{9\zeta_3}{\pi} A k_B \left( \frac{k_B T}{\hbar v} \right)^2.$$

(e) Explain qualitatively the contribution of phonons (lattice vibrations) to the heat capacity of graphene. The typical sound velocity in graphite is of the order of  $2 \times 10^4 \text{ms}^{-1}$ . Is the low temperature heat capacity of graphene controlled by phonon or electron contributions?

- The single particle excitations for phonons also have a linear spectrum, with  $\mathcal{E}_p = \hbar v_p |k|$  and correspond to  $\mu = 0$ . Thus qualitatively they give the same type of contribution to energy and heat capacity. The difference is only in numerical pre-factors. The precise

contribution from a single phonon branch is given by

$$\begin{aligned}
E_p(T) - E_p(0) &= A \int_0^\infty \frac{2\pi k dk}{4\pi^2} \frac{\hbar v_p k}{e^{\beta \hbar v_p k} - 1} = \quad (\text{set } \beta \hbar c k = x) \\
&= \frac{A}{2\pi} k_B T \left( \frac{k_B T}{\hbar v_p} \right)^2 \int_0^\infty dx \frac{x^2}{e^x - 1} \\
&= \frac{\zeta_3}{\pi} A k_B T \left( \frac{k_B T}{\hbar v_p} \right)^2, \quad C_{V,p} = \frac{3\zeta_3}{\pi} A k_B \left( \frac{k_B T}{\hbar v_p} \right)^2.
\end{aligned}$$

We see that the ratio of electron to phonon heat capacities is proportional to  $(v_p/v)^2$ . Since the speed of Dirac fermions is considerably larger than that of phonons, their contribution to heat capacity of graphene is negligible.

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**2. Quantum Coulomb gas:** Consider a *quantum* system of  $N$  positive, and  $N$  negative charged relativistic particles in box of volume  $V = L^3$ . The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{2N} c |\vec{p}_i| + \sum_{i<j}^{2N} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|}, \quad ,$$

where  $e_i = +e_0$  for  $i = 1, \dots, N$ , and  $e_i = -e_0$  for  $i = N + 1, \dots, 2N$ , denote the charges of the particles;  $\{\vec{r}_i\}$  and  $\{\vec{p}_i\}$  their coordinates and momenta respectively. While this is too complicated a system to solve, we can nonetheless obtain some exact results.

(a) Write down the Schrödinger equation for the eigenvalues  $\varepsilon_n(L)$ , and (in coordinate space) eigenfunctions  $\Psi_n(\{\vec{r}_i\})$ . State the constraints imposed on  $\Psi_n(\{\vec{r}_i\})$  if the particles are bosons or fermions?

• In the coordinate representation  $\vec{p}_i$  is replaced by  $-i\hbar\nabla_i$ , leading to the Schrödinger equation

$$\left[ \sum_{i=1}^{2N} c | -i\hbar\nabla_i | + \sum_{i<j}^{2N} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|} \right] \Psi_n(\{\vec{r}_i\}) = \varepsilon_n(L) \Psi_n(\{\vec{r}_i\}).$$

There are  $N$  identical particles of charge  $+e_0$ , and  $N$  identical particles of charge  $-e_0$ . We can examine the effect of permutation operators  $P_+$  and  $P_-$  on these two sets. The symmetry constraints can be written compactly as

$$P_+ P_- \Psi_n(\{\vec{r}_i\}) = \eta_+^{P_+} \cdot \eta_-^{P_-} \Psi_n(\{\vec{r}_i\}),$$

where  $\eta = +1$  for bosons,  $\eta = -1$  for fermions, and  $(-1)^P$  denotes the parity of the permutation. Note that there is no constraint associated with exchange of particles with opposite charge.

(b) By a change of scale  $\vec{r}_i' = \vec{r}_i/L$ , show that the eigenvalues satisfy a scaling relation  $\varepsilon_n(L) = \varepsilon_n(1)/L$ .

• After the change of scale  $\vec{r}_i' = \vec{r}_i/L$  (and corresponding change in the derivative  $\nabla_i' = L\nabla_i$ ), the above Schrödinger equation becomes

$$\left[ \sum_{i=1}^{2N} c \left| -i\hbar \frac{\nabla_i'}{L} \right| + \sum_{i<j}^{2N} \frac{e_i e_j}{L |\vec{r}_i' - \vec{r}_j'|} \right] \Psi_n \left( \left\{ \frac{\vec{r}_i'}{L} \right\} \right) = \varepsilon_n(L) \Psi_n \left( \left\{ \frac{\vec{r}_i'}{L} \right\} \right).$$

The coordinates in the above equation are confined to a box of unit size. We can regard it as the Schrödinger equation in such a box, with wave-functions  $\Psi_n'(\{\vec{r}_i\}) = \Psi_n(\{\vec{r}_i'/L\})$ . The corresponding eigenvalues are  $\varepsilon_n(1) = L\varepsilon_n(L)$  (obtained after multiplying both sides of the above equation by  $L$ ). We thus obtain the scaling relation

$$\varepsilon_n(L) = \frac{\varepsilon_n(1)}{L}.$$

(c) Using the formal expression for the partition function  $Z(N, V, T)$ , in terms of the eigenvalues  $\{\varepsilon_n(L)\}$ , show that  $Z$  does not depend on  $T$  and  $V$  separately, but only on a specific scaling combination of them.

• The formal expression for the partition function is

$$\begin{aligned} Z(N, V, T) &= \text{tr} \left( e^{-\beta \mathcal{H}} \right) = \sum_n \exp \left( -\frac{\varepsilon_n(L)}{k_B T} \right) \\ &= \sum_n \exp \left( -\frac{\varepsilon_n(1)}{k_B T L} \right), \end{aligned}$$

where we have used the scaling form of the energy levels. Clearly, in the above sum  $T$  and  $L$  always occur in the combination  $TL$ . Since  $V = L^3$ , the appropriate scaling variable is  $VT^3$ , and

$$Z(N, V, T) = \mathcal{Z}(N, VT^3).$$

(d) Relate the energy  $E$ , and pressure  $P$  of the gas to variations of the partition function. Prove the exact result  $E = 3PV$ .

• The average energy in the canonical ensemble is given by

$$E = -\frac{\partial \ln Z}{\partial \beta} = k_B T^2 \frac{\partial \ln Z}{\partial T} = k_B T^2 (3VT^2) \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)} = 3k_B VT^4 \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)}.$$

The free energy is  $F = -k_B T \ln Z$ , and its variations are  $dF = -SdT - PdV + \mu dN$ . Hence the gas pressure is given by

$$P = -\frac{\partial F}{\partial V} = k_B T \frac{\partial \ln Z}{\partial V} = k_B T^4 \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)}.$$

The ratio of the above expressions gives the exact identity  $E = 3PV$ .

(e) The Coulomb interaction between charges in  $d$ -dimensional space falls off with separation as  $e_i e_j / |\vec{r}_i - \vec{r}_j|^{d-2}$ . (In  $d = 2$  there is a logarithmic interaction.) In what dimension  $d$  can you construct an exact relation between  $E$  and  $P$  for *non-relativistic* particles (kinetic energy  $\sum_i \vec{p}_i^2 / 2m$ )? What is the corresponding exact relation between energy and pressure?

- The above exact result is a consequence of the simple scaling law relating the energy eigenvalues  $\varepsilon_n(L)$  to the system size. We could obtain the scaling form in part (b) since the kinetic and potential energies scaled in the same way. The kinetic energy for *non-relativistic* particles  $\sum_i \vec{p}_i^2 / 2m = -\sum_i \hbar^2 \nabla_i^2 / 2m$ , scales as  $1/L^2$  under the change of scale  $\vec{r}_i' = \vec{r}_i / L$ , while the interaction energy  $\sum_{i < j}^{2N} e_i e_j / |\vec{r}_i - \vec{r}_j|^{d-2}$  in  $d$  space dimensions scales as  $1/L^{d-2}$ . The two forms will scale the same way in  $d = 4$  dimensions, leading to

$$\varepsilon_n(L) = \frac{\varepsilon_n(1)}{L^2}.$$

The partition function now has the scaling form

$$Z(N, V = L^d, T) = \mathcal{Z}(N, (TL^2)^2) = \mathcal{Z}(N, VT^2).$$

Following steps in the previous part, we obtain the exact relationship  $E = 2PV$ .

(f) Why are the above ‘exact’ scaling laws not expected to hold in dense (liquid or solid) Coulomb mixtures?

- The scaling results were obtained based on the assumption of the existence of a single scaling length  $L$ , relevant to the statistical mechanics of the problem. This is a good approximation in a gas phase. In a dense (liquid or solid) phase, the short-range repulsion between particles is expected to be important, and the particle size  $a$  is another relevant length scale which will enter in the solution to the Schrödinger equation, and invalidate the scaling results.

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

(a) What is the joint probability  $P(\{n_{\vec{k}}\})$ , of finding a set of occupation numbers  $\{n_{\vec{k}}\}$ , of the one-particle states?

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

$$P(\{n_{\vec{k}}\}) = \prod_{\vec{k}} \frac{\exp[\beta(\mu - \mathcal{E}(\vec{k}))n_{\vec{k}}]}{1 + \exp[\beta(\mu - \mathcal{E}(\vec{k}))]}, \quad \text{where } n_{\vec{k}} = 0 \text{ or } 1, \quad \text{for each } \vec{k}.$$

- (b) Express your answer to part (a) in terms of the average occupation numbers  $\{\langle n_{\vec{k}} \rangle_{-}\}$ .
- The average occupation numbers are given by

$$\langle n_{\vec{k}} \rangle_{-} = \frac{\exp[\beta(\mu - \mathcal{E}(\vec{k}))]}{1 + \exp[\beta(\mu - \mathcal{E}(\vec{k}))]},$$

from which we obtain

$$\exp[\beta(\mu - \mathcal{E}(\vec{k}))] = \frac{\langle n_{\vec{k}} \rangle_{-}}{1 - \langle n_{\vec{k}} \rangle_{-}}.$$

This enables us to write the joint probability as

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

- (c) A random variable has a set of  $\ell$  discrete outcomes with probabilities  $p_n$ , where  $n = 1, 2, \dots, \ell$ . What is the entropy of this probability distribution? What is the maximum possible entropy?
- A random variable has a set of  $\ell$  discrete outcomes with probabilities  $p_n$ . The entropy of this probability distribution is calculated from

$$S = -k_B \sum_{n=1}^{\ell} p_n \ln p_n \quad .$$

The maximum entropy is obtained if all probabilities are equal,  $p_n = 1/\ell$ , and given by  $S_{max} = k_B \ln \ell$ .

- (d) Calculate the entropy of the probability distribution for fermion occupation numbers in part (b), and comment on its zero temperature limit.
- Since the occupation numbers of different one-particle states are independent, the corresponding entropies are additive, and given by

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

In the zero temperature limit all occupation numbers are either 0 or 1. In either case the contribution to entropy is zero, and the fermi system at  $T = 0$  has zero entropy.

- (e) Calculate the variance of the total number of particles  $\langle N^2 \rangle_c$ , and comment on its zero temperature behavior.

- The total number of particles is given by  $N = \sum_{\vec{k}} n_{\vec{k}}$ . Since the occupation numbers are independent

$$\langle N^2 \rangle_c = \sum_{\vec{k}} \langle n_{\vec{k}}^2 \rangle_c = \sum_{\vec{k}} \left( \langle n_{\vec{k}}^2 \rangle_- - \langle n_{\vec{k}} \rangle_-^2 \right) = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle_- \left( 1 - \langle n_{\vec{k}} \rangle_- \right),$$

since  $\langle n_{\vec{k}}^2 \rangle_- = \langle n_{\vec{k}} \rangle_-$ . Again, since at  $T = 0$ ,  $\langle n_{\vec{k}} \rangle_- = 0$  or  $1$ , the variance  $\langle N^2 \rangle_c$  vanishes.

(f) The number fluctuations of a gas is related to its compressibility  $\kappa_T$ , and number density  $n = N/V$ , by

$$\langle N^2 \rangle_c = Nnk_B T \kappa_T \quad .$$

Give a *numerical estimate* of the compressibility of the fermi gas in a metal at  $T = 0$  in units of  $\text{\AA}^3 eV^{-1}$ .

- To obtain the compressibility from  $\langle N^2 \rangle_c = Nnk_B T \kappa_T$ , we need to examine the behavior at small but finite temperatures. At small but finite  $T$ , a small fraction of states around the fermi energy have occupation numbers around  $1/2$ . The number of such states is roughly  $Nk_B T / \varepsilon_F$ , and hence we can estimate the variance as

$$\langle N^2 \rangle_c = Nnk_B T \kappa_T \approx \frac{1}{4} \times \frac{Nk_B T}{\varepsilon_F}.$$

The compressibility is then approximates as

$$\kappa_T \approx \frac{1}{4n\varepsilon_F},$$

where  $n = N/V$  is the density. For electrons in a typical metal  $n \approx 10^{29} m^{-3} \approx 0.1 \text{\AA}^3$ , and  $\varepsilon_F \approx 5eV \approx 5 \times 10^4 \text{ }^\circ K$ , resulting in

$$\kappa_T \approx 0.5 \text{\AA}^3 eV^{-1}.$$

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1. *Freezing of He<sup>4</sup>*: At low temperatures He<sup>4</sup> can be converted from liquid to solid by application of pressure. An interesting feature of the phase boundary is that the melting pressure is reduced slightly from its  $T = 0K$  value, by approximately  $20\text{Nm}^{-2}$  at its minimum at  $T = 0.8K$ . We will use a simple model of liquid and solid phases of <sup>4</sup>He to account for this feature.

(a) 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  $(v_\ell, s_\ell)$  and  $(v_s, s_s)$  are the volumes and entropies per atom in the liquid and solid phases respectively.

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

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

Expanding the second equation, and using the thermodynamic identities

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

results in

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

(b) The important excitations in liquid <sup>4</sup>He at  $T < 1K$  are phonons of velocity  $c$ . Calculate the contribution of these modes to the heat capacity per particle  $C_V^\ell/N$ , of the liquid.

• The dominant excitations in liquid <sup>4</sup>He at  $T < 1K$  are phonons of velocity  $c$ . The corresponding dispersion relation is  $\varepsilon(k) = \hbar ck$ . From the average number of phonons in mode  $\vec{k}$ , given by  $\langle n(\vec{k}) \rangle = [\exp(\beta\hbar ck) - 1]^{-1}$ , we obtain the net excitation energy as

$$\begin{aligned} E_{\text{phonons}} &= \sum_{\vec{k}} \frac{\hbar ck}{\exp(\beta\hbar ck) - 1} \\ &= V \times \int \frac{4\pi k^2 dk}{(2\pi)^3} \frac{\hbar ck}{\exp(\beta\hbar ck) - 1} \quad (\text{change variables to } x = \beta\hbar ck) \\ &= \frac{V}{2\pi^2} \hbar c \left(\frac{k_B T}{\hbar c}\right)^4 \frac{6}{3!} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^2}{30} V \hbar c \left(\frac{k_B T}{\hbar c}\right)^4, \end{aligned}$$

where we have used

$$\zeta_4 \equiv \frac{1}{3!} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{90}.$$

The corresponding heat capacity is now obtained as

$$C_V = \frac{dE}{dT} = \frac{2\pi^2}{15} V k_B \left( \frac{k_B T}{\hbar c} \right)^3,$$

resulting in a heat capacity per particle for the liquid of

$$\frac{C_V^\ell}{N} = \frac{2\pi^2}{15} k_B v_\ell \left( \frac{k_B T}{\hbar c} \right)^3.$$

(c) Calculate the low temperature heat capacity per particle  $C_V^s/N$ , of solid  $^4\text{He}$  in terms of longitudinal and transverse sound velocities  $c_L$ , and  $c_T$ .

- The elementary excitations of the solid are also phonons, but there are now *two* transverse sound modes of velocity  $c_T$ , and *one* longitudinal sound mode of velocity  $c_L$ . The contributions of these modes are additive, each similar in form to the liquid result calculated above, resulting in the final expression for solid heat capacity of

$$\frac{C_V^s}{N} = \frac{2\pi^2}{15} k_B v_s \left( \frac{k_B T}{\hbar} \right)^3 \times \left( \frac{2}{c_T^3} + \frac{1}{c_L^3} \right).$$

(d) Using the above results calculate the entropy difference ( $s_\ell - s_s$ ), assuming a single sound velocity  $c \approx c_L \approx c_T$ , and approximately equal volumes per particle  $v_\ell \approx v_s \approx v$ . Which phase (solid or liquid) has the higher entropy?

- The entropies can be calculated from the heat capacities as

$$s_\ell(T) = \int_0^T \frac{C_V^\ell(T') dT'}{T'} = \frac{2\pi^2}{45} k_B v_\ell \left( \frac{k_B T}{\hbar c} \right)^3,$$

$$s_s(T) = \int_0^T \frac{C_V^s(T') dT'}{T'} = \frac{2\pi^2}{45} k_B v_s \left( \frac{k_B T}{\hbar} \right)^3 \times \left( \frac{2}{c_T^3} + \frac{1}{c_L^3} \right).$$

Assuming approximately equal sound speeds  $c \approx c_L \approx c_T \approx 300 \text{ms}^{-1}$ , and specific volumes  $v_\ell \approx v_s \approx v = 46 \text{\AA}^3$ , we obtain the entropy difference

$$s_\ell - s_s \approx -\frac{4\pi^2}{45} k_B v \left( \frac{k_B T}{\hbar c} \right)^3.$$

The solid phase has more entropy than the liquid because it has two more phonon excitation bands.

(e) Assuming a small (temperature independent) volume difference  $\delta v = v_\ell - v_s$ , calculate the form of the melting curve. To explain the anomaly described at the beginning, which phase (solid or liquid) must have the higher density?

- Using the Clausius-Clapeyron equation, and the above calculation of the entropy difference, we get

$$\left(\frac{\partial P}{\partial T}\right)_{melting} = \frac{s_\ell - s_s}{v_\ell - v_s} = -\frac{4\pi^2}{45} k_B \frac{v}{\delta v} \left(\frac{k_B T}{\hbar c}\right)^3.$$

Integrating the above equation gives the melting curve

$$P_{melt}(T) = P(0) - \frac{\pi^2}{45} k_B \frac{v}{\delta v} \left(\frac{k_B T}{\hbar c}\right)^3 T.$$

To explain the reduction in pressure, we need  $\delta v = v_\ell - v_s > 0$ , i.e. the solid phase has the higher density, which is normal.

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**2. Squeezed chain:** A rubber band is modeled as a single chain of  $N$  *massless* links of fixed length  $a$ . The chain is placed inside a narrow tube that restricts each link to point parallel or anti-parallel to the tube.

(a) Ignoring any interactions amongst the links, give the number of configurations of the chain,  $\Omega(L, N)$ , where  $L$  is the end-to-end length of the chain.

- A typical configuration will have  $N_+$  steps in one direction, and  $N_-$  steps in the opposite direction, such that

$$L = (N_+ - N_-)a, \quad \text{and} \quad N = N_+ + N_-,$$

or equivalently

$$N_\pm = \frac{N \pm L/a}{2}.$$

The number of configurations is given by the binomial formula

$$\Omega(L, N) = \frac{N!}{N_+!N_-!} = \frac{N!}{[(N + L/a)/2]![(N - L/a)/2]}.$$

(b) Use Stirling's approximation to express the result for entropy as a function of  $N$  and  $x = L/(Na)$ .

- Using Stirling's approximation

$$\begin{aligned} \frac{S}{k_B} &= \ln \Omega \approx N \ln N - N_+ \ln N_+ - N_- \ln N_- \\ &= N \ln 2 - \frac{N}{2} [(1+x) \ln(1+x) + (1-x) \ln(1-x)]. \end{aligned}$$

The tube is now uniformly squeezed such that stretched configurations are energetically favored. For this problem, assume a simplified form of this energy that depends inversely on the local link density, such that the energy of a uniformly stretched state is

$$E(L, N) = -\frac{\sigma}{2}L \times \frac{L}{N} = -\frac{\sigma a^2}{2}Nx^2.$$

(Use this formula for energy for all states of given  $L$  and  $N$  in the remainder of this problem.)

(c) Calculate the free energy  $F(T, L, N)$ , and the force  $J(T, L, N)$  acting on the end points of the chain. (The work done on expanding the chain is  $dW = JdL$ .)

- The free energy is

$$F = E - TS = -\frac{\sigma}{2}\frac{L^2}{N} + \frac{k_B T}{2} [(N + L/a) \ln(N + L/a) + (N - L/a) \ln(N - L/a) - N \ln 2 - 2N \ln N].$$

The force conjugate to  $L$  is obtained as

$$J = \frac{\partial F}{\partial L} = -\sigma \frac{L}{N} + \frac{k_B T}{2a} \ln \frac{Na + L}{Na - L} = -\sigma ax + \frac{k_B T}{2a} \ln \frac{1+x}{1-x}.$$

(d) Sketch the isotherms  $J(x, T)$  at high and low temperatures, and identify the temperature  $T_c$  when the behavior changes.

- The curves  $J(x)$  start linearly at  $x = 0$  with a slope  $(k_B T/a - \sigma a)$ , and go to (plus) infinity as  $x \rightarrow 1$ . The slope changes sign at  $T_c = (\sigma a^2)/k_B$ , with the curves for  $T < T_c$  being non-monotonic in  $x$ .

(e) What is the condition for stability of the chain? What portion of the above isotherms are inherently unstable.

- The condition for stability

$$\delta J \delta L \geq 0,$$

implies that the slope of the isotherm  $J(x)$  must be positive. The portion of the isotherms below the minimum for  $T < T_c$  violate this condition, and are inherently unstable.

(f) Using the form for  $J$  obtained in part (c), find an expression for the unforced ( $J = 0$ ) chain length that is valid as  $T$  approaches  $T_c$  from below.

- As  $T \rightarrow T_c^-$ ,  $x \propto L$  goes to zero. Expanding the logarithms in the expression for  $J(x) = 0$ , we find

$$0 = \left( -\sigma a + \frac{2k_B T}{a} \right) x + \frac{2k_B T}{3a} x^3 + \mathcal{O}(x^5).$$

The solution to this equation is

$$\frac{x^2}{3} = 1 - \frac{T_c}{T}, \quad L \approx Na \sqrt{3 \left( 1 - \frac{T_c}{T} \right)}.$$

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**3. Graphene bilayer:** The layers of graphite can be peeled apart through different exfoliation processes. Many such processes generate single sheets of carbon atoms, as well as bilayers in which the two sheets are weakly coupled. The hexagonal lattice of the single layer graphene, leads to a band structure that at low energies can be approximated by  $\mathcal{E}_{\pm}^{\text{1 layer}}(\vec{k}) = \pm t_{\parallel}(ak)$ , as in relativistic Dirac *fermions*. (Here  $k = |\vec{k}|$ ,  $a$  is a lattice spacing, and  $t_{\parallel}$  is a typical in-plane hopping energy.) A weak hopping energy  $t_{\perp}$  between the two sheets of the bilayer modifies the low energy excitations drastically, to

$$\mathcal{E}_{\pm}^{\text{bilayer}}(\vec{k}) = \pm \frac{t_{\parallel}^2}{2t_{\perp}}(ka)^2 \quad ,$$

i.e. resembling massive Dirac fermions. In addition to the spin degeneracy, there are two branches of such excitations per unit cell, for an overall degeneracy of  $g = 4$ .

(a) For the undoped material with one electron per site, at zero temperature all negative energy states are occupied and all positive energy ones are empty. Find the chemical potential  $\mu(T)$ .

- According to Fermi statistics, the probability of occupation of a state of energy  $\mathcal{E}$  is

$$p[n(\mathcal{E})] = \frac{e^{\beta(\mu - \mathcal{E})n}}{1 + e^{\beta(\mu - \mathcal{E})}}, \quad \text{for } n = 0, 1.$$

For a state of energy  $\mu + \delta$ ,

$$p[n(\mu + \delta)] = \frac{e^{\beta\delta n}}{1 + e^{\beta\delta}}, \quad \implies \quad p[n(\mu + \delta) = 1] = \frac{e^{\beta\delta}}{1 + e^{\beta\delta}} = \frac{1}{1 + e^{-\beta\delta}}.$$

Similarly, for a state of energy  $\mu - \delta$ ,

$$p[n(\mu - \delta)] = \frac{e^{-\beta\delta n}}{1 + e^{-\beta\delta}}, \quad \implies \quad p[n(\mu - \delta) = 0] = \frac{1}{1 + e^{-\beta\delta}} = p[n(\mu + \delta) = 1],$$

i.e. the probability of finding an occupied state of energy  $\mu + \delta$  is the same as that of finding an unoccupied state of energy  $\mu - \delta$ .

At zero temperature all negative energy Dirac states are occupied and all positive energy ones are empty, i.e.  $\mu(T = 0) = 0$ . The above result implies that for  $\mu = 0$ ,  $\langle n(\mathcal{E}) \rangle + \langle n - \mathcal{E} \rangle$  is unchanged for all temperatures; any particle leaving an occupied negative energy state goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if  $\mu$  stays at zero. Thus, the particle-hole symmetry enforces  $\mu(T) = 0$ .

(b) Show that the mean excitation energy of this system at finite temperature satisfies

$$E(T) - E(0) = 2gA \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta\mathcal{E}_+(\vec{k})) + 1}.$$

• Using the label +(-) for the positive (energy) states, the excitation energy is calculated as

$$\begin{aligned} E(T) - E(0) &= \sum_{k,s_z,\alpha} [\langle n_+(k) \rangle \mathcal{E}_+(k) + (1 - \langle n_-(k) \rangle) \mathcal{E}_-(k)] \\ &= g \sum_k 2 \langle n_+(k) \rangle \mathcal{E}_+(k) = 2gA \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta\mathcal{E}_+(\vec{k})) + 1}. \end{aligned}$$

(c) Give a closed form answer for the excitation energy *of the bilayer* by evaluating the above integral.

• Let  $\mathcal{E}_+(k) = \alpha k^2$ , with  $\alpha = (t_{\parallel}a)^2/(2t_{\perp})$ , to get

$$\begin{aligned} E(T) - E(0) &= 2gA \int_0^{\infty} \frac{2\pi k dk}{4\pi^2} \frac{\alpha k^2}{e^{\beta\alpha k^2} + 1} = \quad (\text{set } \beta\alpha k^2 = x) \\ &= \frac{gA}{2\pi} k_B T \left( \frac{k_B T}{\alpha} \right) \int_0^{\infty} dx \frac{x}{e^x + 1} \\ &= \frac{g\pi}{24} A k_B T \left( \frac{k_B T}{\alpha} \right) = \frac{\pi}{3} \frac{A}{a^2} \left( \frac{k_B T}{t_{\parallel}} \right)^2 t_{\perp}. \end{aligned}$$

For the final expression, we have noted that the needed integral is  $f_2^-(1)$ , and used  $f_2^-(1) = \zeta_2/2 = \pi^2/12$ .

(d) Calculate the heat capacity,  $C_A$ , of such massive Dirac particles.

• The heat capacity can now be evaluated as

$$C_A = \left. \frac{\partial E}{\partial T} \right|_A = \frac{2\pi}{3} \frac{A}{a^2} k_B \left( \frac{k_B T t_{\perp}}{t_{\parallel}^2} \right).$$

(e) A sample contains an equal proportion of single and bilayers. Estimate (in terms of the hopping energies) the temperature below which the electronic heat capacity is dominated by the bilayers.

• As stated earlier, the monolayer excitations for phonons have a linear spectrum, with  $\mathcal{E}^{\text{1 layer}} = \pm t_{\parallel}(ka)$ . Their contribution to energy and heat capacity can be calculated as

before. Including the various prefactors (which are not required for the solution), we have

$$\begin{aligned}
 E^{\text{1 layer}}(T) &= 2gA \int_0^\infty \frac{2\pi k dk}{4\pi^2} \frac{t_{\parallel} a k}{e^{\beta t_{\parallel} a k} + 1} = \quad (\text{set } \beta t_{\parallel} a k = x) \\
 &= \frac{gA}{\pi} k_B T \left( \frac{k_B T}{t_{\parallel} a} \right)^2 \int_0^\infty dx \frac{x^2}{e^x + 1} \\
 &\propto \frac{A}{a^2} k_B T \left( \frac{k_B T}{t_{\parallel}} \right)^2, \quad C_A^{\text{1 layer}} \propto \frac{A}{a^2} k_B \left( \frac{k_B T}{t_{\parallel}} \right)^2.
 \end{aligned}$$

The bilayer heat capacity, which is proportional to  $T$  is more important at lower temperatures. By comparing the two expressions, it is apparent that the electronic heat capacity per particle is larger in the bilayer for temperatures smaller than  $T^* \approx t_{\perp}/k_B$ .

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