

### Review Problems and Solutions

The final exam will take place on **Wednesday 12/15/2021**, from **9:00am to 12:00noon** in **room 32-141**. All topics presented in the course will be covered, with emphasis on the second half.

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

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Note that the some parts of each problem may be easier than other 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

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

#### Thermodynamics

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

#### Mathematical Formulas

$$\begin{aligned} \lim_{x \rightarrow \infty} \coth x &= 1 + 2e^{-2x} + \mathcal{O}(e^{-4x}) & \lim_{x \rightarrow 0} \coth x &= \frac{1}{x} + \frac{x}{3} + \mathcal{O}(x^2) \\ \int_0^\infty dx \, x^n e^{-\alpha x} &= \frac{n!}{\alpha^{n+1}} & (\frac{1}{2})! &= \frac{\sqrt{\pi}}{2} \\ \int_{-\infty}^\infty dx \exp \left[ -ikx - \frac{x^2}{2\sigma^2} \right] &= \sqrt{2\pi\sigma^2} \exp \left[ -\frac{\sigma^2 k^2}{2} \right] & \lim_{N \rightarrow \infty} \ln N! &= N \ln N - N \\ \langle e^{-ikx} \rangle &= \sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle & \ln \langle e^{-ikx} \rangle &= \sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle_c \\ f_m^\eta(z) &= \frac{1}{(m-1)!} \int_0^\infty dx \frac{x^{m-1}}{z^{-1}e^x - \eta} = \sum_{\alpha=1}^\infty \eta^{\alpha+1} \frac{z^\alpha}{\alpha^m} & \frac{df_m^\eta}{dz} &= \frac{1}{z} f_{m-1}^\eta \quad f_1^\eta(z) = -\eta \ln(1 - \eta z) \\ \lim_{z \rightarrow \infty} f_m^-(z) &= \frac{(\ln z)^m}{m!} \left[ 1 + \frac{\pi^2}{6} m(m-1)(\ln z)^{-2} + \dots \right] & f_m^-(1) &= (1 - 2^{1-m}) \zeta_m \\ \zeta_m &\equiv f_m^+(1) & \zeta_{3/2} &\approx 2.612 \quad \zeta_2 = \frac{\pi^2}{6} \quad \zeta_{5/2} \approx 1.341 \quad \zeta_3 \approx 1.202 \quad \zeta_4 = \frac{\pi^4}{90} \end{aligned}$$

1. *Density of states:* Consider a system of *non-interacting identical* degrees of freedom, with a set of single-particle energies  $\{\varepsilon_n\}$ , and ground state  $\varepsilon_0 = 0$ . In a grand canonical ensemble at temperature  $T = (k_B\beta)^{-1}$ , the number of particles  $N$  is related to the chemical potential  $\mu$  by

$$N = \sum_n \frac{1}{e^{\beta(\varepsilon_n - \mu)} - \eta} = \int_0^\infty d\varepsilon \rho(\varepsilon) \frac{1}{e^{\beta(\varepsilon - \mu)} - \eta} \quad ,$$

where  $\rho(\varepsilon)$  is the density of single-particle states of energy  $\varepsilon$ , and  $\eta = +1(-1)$  for bosons (fermions).

(a) Write a corresponding expression (in terms of  $\rho(\varepsilon)$ ,  $\beta$ , and  $\mu$ ) for the total energy  $E$  of the system.

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$$E = \sum_n \frac{\varepsilon_n}{e^{\beta(\varepsilon_n - \mu)} - \eta} = \int_0^\infty d\varepsilon \rho(\varepsilon) \frac{\varepsilon}{e^{\beta(\varepsilon - \mu)} - \eta} \quad .$$

(b) For bosons write an implicit (integral) equation whose solution gives the critical temperature for Bose condensation.

• At the onset of Bose condensation  $\mu = \varepsilon_0 = 0$  (the lowest energy state), and since the occupation of this state is still not macroscopic, we have

$$N = \int_0^\infty d\varepsilon \rho(\varepsilon) \frac{1}{e^{\beta_c \varepsilon} - 1} \quad .$$

Solving this implicit integral equation leads to  $\beta_c$  and hence the condensation temperature  $T_c$ .

For any function  $g(x)$ , the Sommerfeld expansion indicates that as  $\beta \rightarrow \infty$ ,

$$\int_0^\infty dx \frac{g(x)}{e^{\beta(x - \mu)} + 1} \simeq \int_0^\mu dx g(x) + \frac{\pi^2}{6\beta^2} g'(\mu) + \dots \quad .$$

(c) Use the above expansion to express the low temperature behavior of  $\mu - E_F$ , where  $E_F$  is the Fermi energy, in terms of  $\beta$ ,  $\rho(E_F)$  and  $\rho'(E_F)$ .

• Performing the Sommerfeld expansion on the expression for  $N$  gives

$$N = \int_0^\mu dE \rho(E) + \frac{\pi^2}{6\beta^2} \rho'(\mu) + \dots$$

Since  $\mu = E_F$  when  $T = 0$  ( $\beta \rightarrow \infty$ ), expanding  $\mu$  around  $E_F$  to the lowest order yields

$$N = \int_0^{E_F} dE \rho(E) + (\mu - E_F) \rho(E_F) + \frac{\pi^2}{6\beta^2} \rho'(E_F) + \dots$$

The initial integral is simply  $N$ , since this is how  $E_F$  is determined at zero temperatures. Setting the rest of the series to zero gives

$$\mu - E_F = -\frac{\pi^2}{6\beta^2} \frac{\rho'(E_F)}{\rho(E_F)} + \dots$$

(d) As in the last part, find an expression for the increase in energy,  $E(T) - E(T=0)$ , at low temperatures.

- Applying the Sommerfeld expansion to the expression for  $E$  gives

$$E(T) = \int_0^\mu dE E \rho(E) + \frac{\pi^2}{6\beta^2} (\rho(\mu) + \mu \rho'(\mu)) + \dots$$

Expanding  $\mu$  around  $E_F$  to the lowest order yields

$$E(T) = \int_0^{E_F} dE \rho(E) E + (\mu - E_F) \rho(E_F) E_F + \frac{\pi^2}{6\beta^2} (\rho(E_F) + E_F \rho'(E_F)) + \dots$$

The first integral defines  $E(T=0)$ , and using the expression for  $\mu - E_F$  from the previous part leads to

$$\begin{aligned} E(T) - E(T=0) &= -\frac{\pi^2}{6\beta^2} \frac{\rho'(E_F)}{\rho(E_F)} \times \rho(E_F) E_F + \frac{\pi^2}{6\beta^2} (\rho(E_F) + E_F \rho'(E_F)) + \dots \\ &= \frac{\pi^2}{6\beta^2} \rho(E_F). \end{aligned}$$

(e) Find the low temperature heat capacity of this system of fermions.

- The low temperature heat capacity is given by

$$C(T) = \frac{dE}{dT} = \frac{\pi^2}{3} k_B \rho(E_F) k_B T + \dots,$$

i.e. it vanishes linearly with a coefficient proportional to the density of states at the Fermi energy.

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**2. Ring diagrams mimicking bosons:** Motivated by the statistical attraction between bosons, consider a *classical* system of identical particles, interacting with a pairwise potential  $V(|\vec{q} - \vec{q}'|)$ , such that

$$f(\vec{r}) = e^{-\beta V(r)} - 1 = \exp\left(-\frac{\pi r^2}{\lambda^2}\right), \text{ and } \tilde{f}(\vec{\omega}) = \lambda^3 \exp\left(-\frac{\lambda^2 \omega^2}{4\pi}\right),$$

where  $\tilde{f}(\vec{\omega})$  is the Fourier transform of  $f(\vec{r})$ .

(a) In a perturbative cluster expansion of the partition function, we shall retain only the diagrams forming a ring, which (after a summation over all powers of  $V$  between any pair of points) are proportional to

$$R_\ell = \int \frac{d^3 \vec{q}_1}{V} \cdots \frac{d^3 \vec{q}_\ell}{V} f(\vec{q}_1 - \vec{q}_2) f(\vec{q}_2 - \vec{q}_3) \cdots f(\vec{q}_\ell - \vec{q}_1).$$

Use properties of Fourier transforms to show that

$$R_\ell = \frac{1}{V^{\ell-1}} \int \frac{d^3 \vec{\omega}}{(2\pi)^3} \tilde{f}(\vec{\omega})^\ell = \frac{\lambda^{3\ell}}{\ell^{3/2} \lambda^3 V^{\ell-1}}.$$

- The contribution of the ring diagrams to the partition function is

$$\begin{aligned} R_\ell &= \int \frac{d^3 \vec{q}_1}{V} \frac{d^3 \vec{q}_2}{V} \cdots \frac{d^3 \vec{q}_\ell}{V} f(\vec{q}_1 - \vec{q}_2) f(\vec{q}_2 - \vec{q}_3) \cdots f(\vec{q}_\ell - \vec{q}_1) \\ &= \frac{1}{V^\ell} \int \cdots \int d^3 \vec{x}_1 d^3 \vec{x}_2 \cdots d^3 \vec{x}_{\ell-1} d^3 \vec{q}_\ell f(\vec{x}_1) f(\vec{x}_2) \cdots f(\vec{x}_{\ell-1}) f\left(-\sum_{i=1}^{\ell-1} \vec{x}_i\right), \end{aligned}$$

where we introduced the new set of variables  $\{\vec{x}_i \equiv \vec{q}_i - \vec{q}_{i+1}\}$ , for  $i = 1, 2, \dots, \ell - 1$ . Note that since the integrand is independent of  $\vec{q}_\ell$ ,

$$R_\ell = \frac{1}{V^{\ell-1}} \int \cdots \int d^3 \vec{x}_1 d^3 \vec{x}_2 \cdots d^3 \vec{x}_{\ell-1} f(\vec{x}_1) f(\vec{x}_2) \cdots f\left(-\sum_{i=1}^{\ell-1} \vec{x}_i\right).$$

Using the inverse Fourier transform

$$f(\vec{q}) = \frac{1}{(2\pi)^3} \int d^3 \vec{\omega} \tilde{f}(\vec{\omega}) e^{-i\vec{q} \cdot \vec{\omega}},$$

the integral becomes

$$\begin{aligned} R_\ell &= \frac{1}{(2\pi)^{3\ell} V^{\ell-1}} \int \cdots \int d^3 \vec{x}_1 \cdots d^3 \vec{x}_{\ell-1} \tilde{f}(\vec{\omega}_1) e^{-i\vec{\omega}_1 \cdot \vec{x}_1} \tilde{f}(\vec{\omega}_2) e^{-i\vec{\omega}_2 \cdot \vec{x}_2} \\ &\quad \cdots \tilde{f}(\vec{\omega}_\ell) \exp\left(-i \sum_{k=1}^{\ell-1} \vec{\omega}_\ell \cdot \vec{x}_k\right) d^3 \vec{\omega}_1 \cdots d^3 \vec{\omega}_\ell. \end{aligned}$$

Since

$$\int \frac{d^3 \vec{q}}{(2\pi)^3} e^{-i\vec{\omega} \cdot \vec{q}} = \delta^3(\vec{\omega}),$$

we have

$$R_\ell = \frac{1}{(2\pi)^3 V^{\ell-1}} \int \cdots \int \left( \prod_{k=1}^{\ell-1} \delta(\vec{\omega}_k - \vec{\omega}_\ell) \tilde{f}(\vec{\omega}_k) d^3 \vec{\omega}_k \right) d^3 \vec{\omega}_\ell,$$

resulting finally in

$$R_\ell = \frac{1}{V^{\ell-1}} \int \frac{d^3 \vec{\omega}}{(2\pi)^3} \tilde{f}(\vec{\omega})^\ell = \frac{1}{V^{\ell-1}} \int \frac{d^3 \vec{\omega}}{(2\pi)^3} \lambda^{3\ell} \exp\left(-\frac{\ell \lambda^2 \omega^2}{4\pi}\right) = \frac{\lambda^{3\ell}}{\ell^{3/2} \lambda^3 V^{\ell-1}}.$$

Including the multiplicity of ring diagrams, the expansion for the partition function can be written as

$$\ln Z_{\text{rings}} = \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{N^\ell}{2\ell} R_\ell.$$

(You do not have to prove this expression.)

(b) Show that in the ring approximation, the partition function is given by

$$\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{2\lambda^3} f_{5/2}^+(n\lambda^3) - \frac{N}{2},$$

where  $Z_0$  is the partition function of the non-interacting gas, and  $n = N/V$  is the number density.

- Inserting the result for  $R_\ell$  in the expansion for the partition function yields

$$\begin{aligned} \ln Z_{\text{rings}} &= \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{N^\ell}{2\ell} \frac{\lambda^{3\ell}}{\ell^{3/2} \lambda^3 V^{\ell-1}} \\ &= \ln Z_0 + \frac{V}{2\lambda^3} \sum_{\ell=2}^{\infty} \frac{(n\lambda^3)^\ell}{\ell^{5/2}} \\ &= \ln Z_0 + \frac{V}{2\lambda^3} \left[ f_{5/2}^+(n\lambda^3) - n\lambda^3 \right] \\ &= \ln Z_0 + \frac{V}{2\lambda^3} f_{5/2}^+(n\lambda^3) - \frac{N}{2}. \end{aligned}$$

The missing  $\ell = 1$  term is added to make the series correspond to that of the function  $f_{5/2}^+$ ; the additional term corresponds merely to  $N/2$ .

(c) Compute the pressure  $P$  of the gas within the ring approximation.

- Since  $\beta P = \partial \ln Z / \partial V$ , and using the standard result for the ideal gas, we obtain

$$\beta P = \frac{\partial \ln Z}{\partial V} = n + \frac{1}{2\lambda^3} f_{5/2}^+(n\lambda^3) + \frac{V}{2\lambda^3} \left( \frac{-N\lambda^3}{V^2} \right) \frac{f_{3/2}^+(n\lambda^3)}{n\lambda^3},$$

where we have taken advantage of  $df_m^+(x)/dx = f_{m-1}^+(x)/x$ , and thus

$$\beta P = n \left[ 1 + \frac{1}{2n\lambda^3} \left( f_{5/2}^+(n\lambda^3) - f_{3/2}^+(n\lambda^3) \right) \right].$$

(d) By examining the compressibility, or equivalently  $\partial P/\partial n|_T$ , show that this classical system of interacting particles must undergo a condensation transition.

- Taking a derivative of the expression for  $P$  at constant  $T$  (and hence constant  $\beta$  and  $\lambda$ ), we find

$$\beta \frac{\partial P}{\partial n} \Big|_T = 1 + \frac{1}{2n\lambda^3} \left[ f_{3/2}^+(n\lambda^3) - f_{1/2}^+(n\lambda^3) \right].$$

As density increases towards the point  $n\lambda^3 = 1$ , the term proportional to  $f_{1/2}^+(n\lambda^3)$  becomes highly negative (and divergent). The compressibility  $\partial V/\partial P = -\frac{N}{n^2} \partial n/\partial P$  thus becomes positive indicating a mechanical instability. The gas must thus undergo a phase transition at a point  $n\lambda^3 < 1$  to avoid this instability.

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**3. Stoner ferromagnetism:** The conduction electrons in a metal can be treated as a gas of fermions of spin 1/2 (with up/down degeneracy), and density  $n = N/V$ . The Coulomb repulsion favors wave functions which are antisymmetric in position coordinates, thus keeping the electrons apart. Because of the full (position *and* spin) antisymmetry of fermionic wave functions, this interaction may be approximated by an effective spin-spin coupling which favors states with parallel spins. In this simple approximation, the net effect is described by an interaction energy

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

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  $\alpha = 4\pi\hbar^2 a/m$ .)

(a) The ground state consists of two Fermi spheres filled by the spin up and spin down electrons. Express the corresponding Fermi wavevectors  $k_{F\pm}$  in terms of the densities  $n_{\pm} = N_{\pm}/V$ .

- In the ground state, all available wavevectors are filled up in a sphere. Using the appropriate density of states, the corresponding radii of  $k_{F\pm}$  are calculated as

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

leading to

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

(b) Calculate the kinetic energy density of the ground state as a function of the densities  $n_{\pm}$ , and fundamental constants.

- For each Fermi sea, the kinetic energy is given by

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

where  $m$  is the mass of the electron. The total kinetic energy density is thus equal to

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

(c) Assuming small deviations  $n_{\pm} = n/2 \pm \delta$  from the symmetric state, expand the kinetic energy to *fourth order* in  $\delta$ .

- Using the expansion

$$(x + \delta)^{5/3} = x^{5/3} + \frac{5}{3} x^{2/3} \delta + \frac{10}{9} x^{-1/3} \frac{\delta^2}{2} - \frac{10}{27} x^{-4/3} \frac{\delta^3}{6} + \frac{40}{81} x^{-7/3} \frac{\delta^4}{24} + \mathcal{O}(\delta^5),$$

the kinetic energy calculated in the previous part can be written as

$$\frac{E_{\text{kin}}}{V} = \frac{\hbar^2}{2m} \frac{6}{5} (6\pi^2)^{2/3} \left[ \left(\frac{n}{2}\right)^{5/3} + \frac{5}{9} \left(\frac{n}{2}\right)^{-1/3} \delta^2 + \frac{5}{243} \left(\frac{n}{2}\right)^{-7/3} \delta^4 + \mathcal{O}(\delta^6) \right].$$

(d) Express the spin-spin interaction density  $U/V$  in terms of  $n$  and  $\delta$ . 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 has the form

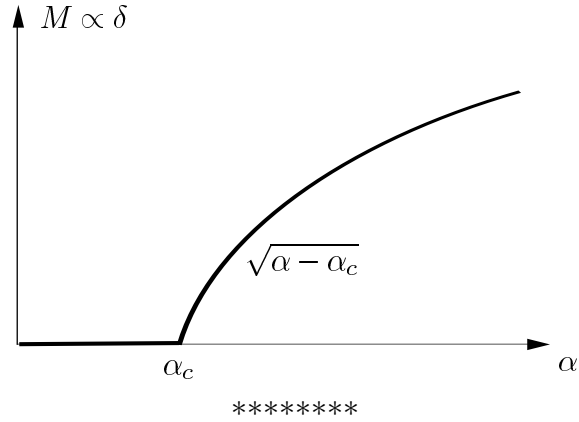
$$\frac{E}{V} = \frac{E_0 + \alpha n^2/4}{V} + \left[ \frac{4}{3} (3\pi^2)^{2/3} \frac{\hbar^2}{2m} n^{-1/3} - \alpha \right] \delta^2 + \mathcal{O}(\delta^4).$$

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

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

(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 minimizing the energy density. Since the coefficient of the fourth order term is positive, and the optimal  $\delta$  goes to zero continuously as  $\alpha \rightarrow \alpha_c$ ; 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.





1. *Quantum point particle condensation:* Consider a *quantum gas* of  $N$  spin-less point particles of mass  $m$  at temperature  $T$ , and volume  $V$ . An unspecified weak pairwise attraction between particles reduces the energy of any state by an amount  $-uN^2/(2V)$  with  $u > 0$ , such that the partition function is

$$Z(T, N, V) = Z_0(T, N, V) \times \exp\left(\frac{\beta u N^2}{2V}\right),$$

where  $Z_0(T, N, V)$  is the partition function of the ideal quantum gas, and  $\beta = (k_B T)^{-1}$ .

(a) Using the above relation between partition functions relate the pressure  $P(n, T)$ , as a function of the density  $n = N/V$ , to the corresponding pressure  $P_0(n, T)$  of an ideal quantum gas.

- The pressure is related to the partition function by

$$\beta P = \frac{\partial \ln Z}{\partial V} = \frac{\partial \ln Z_0}{\partial V} - \frac{\beta u N^2}{2V^2}, \quad \Rightarrow \quad P(n, T) = P_0(n, T) - \frac{un^2}{2}.$$

(b) Use standard results for the non-relativistic gas to show that

$$\left. \frac{\partial P}{\partial n} \right|_T = -un + k_B T \frac{f_{3/2}^\eta(z)}{f_{1/2}^\eta(z)}, \quad \text{with} \quad f_{3/2}^\eta(z) = n\lambda^3 \quad \text{and} \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

- For a non-relativistic quantum gas, the pressure and density are related to the fugacity  $z$  by

$$P_0 = \frac{1}{\lambda^3} f_{5/2}^\eta(z) \quad \text{and} \quad n = \frac{1}{\lambda^3} f_{3/2}^\eta(z).$$

Taking derivatives of both expressions with respect to  $n$  at constant  $T$  yields

$$\left. \frac{\partial P_0}{\partial n} \right|_T = \frac{1}{\lambda^3 z} f_{3/2}^\eta(z) \left. \frac{\partial z}{\partial n} \right|_T \quad \text{and} \quad 1 = \frac{1}{\lambda^3 z} f_{1/2}^\eta(z) \left. \frac{\partial z}{\partial n} \right|_T.$$

Eliminating  $\partial z / \partial n|_T$  between the above two expressions yields

$$\left. \frac{\partial P}{\partial n} \right|_T = -un + \left. \frac{\partial P_0}{\partial n} \right|_T = -un + k_B T \frac{f_{3/2}^\eta(z)}{f_{1/2}^\eta(z)}.$$

(c) Find the critical value of the coupling  $u_c(n, T)$  at which the gas becomes unstable, in the low density (non-degenerate) limit  $n\lambda^3 \ll 1$ , including the *first* correction that distinguishes between fermi and bose statistics.

- Stability of the gas requires  $\partial P/\partial n|_T > 0$ , and thus instability sets in at the critical coupling

$$u_c = \frac{k_B T}{n} \frac{f_{3/2}^\eta(z)}{f_{1/2}^\eta(z)}.$$

To express the result in terms of density, we must solve for  $z(n)$ . Using the standard expansions of the functions  $f_m^\eta(z)$ , we find

$$n\lambda^3 = f_{3/2}^\eta(z) = z + \eta \frac{z^2}{2^{3/2}} + \dots, \implies z = n\lambda^3 - \eta \frac{(n\lambda^3)^2}{2^{3/2}} + \dots.$$

Expanding the result for  $u_c$ ,

$$u_c = \frac{k_B T}{n} \frac{z + \eta z^2/2^{3/2} + \dots}{z + \eta z^2/2^{1/2} + \dots} = \frac{k_B T}{n} \left[ 1 - \eta \frac{z}{2^{3/2}} + \dots \right],$$

we observe that the first order correction in  $z$  already distinguishes between fermions and bosons, and thus to this order

$$u_c = \frac{k_B T}{n} \left[ 1 - \eta \frac{n\lambda^3}{2^{3/2}} + \dots \right].$$

The critical coupling is diminished for bosons and increased for fermions.

(d) For fermions, relate the limiting behavior of  $u_c(n, T)$  in the low temperature (degenerate limit  $n\lambda^3 \gg 1$ ) to the fermi energy  $\epsilon_F$ . (This is somewhat similar to the Chandrasekhar instability of neutron stars.)

- In the degenerate limit for fermions  $z \gg 1$ , and expansions of  $f_m^-(z)$  in this limit yield

$$u_c = \frac{k_B T}{n} \frac{(\ln z)^{3/2}/(3/2)!}{(\ln z)^{1/2}/(1/2)!} = \frac{k_B T}{n} \frac{\ln z}{3/2} = \frac{2}{3} \frac{\epsilon_F}{n},$$

since in this limit  $\ln z = \beta \epsilon_F$ .

(e) What happens to  $u_c$  for bosons as temperature is decreased towards to quantum degenerate regime?

- On approaching the condensation point of the ideal bose gas, the fugacity  $z \rightarrow 1$ ,  $f^{+3/2}(z) \rightarrow \zeta_{3/2}$ ,  $f^{+1/2}(z) \rightarrow \infty$ , and thus  $u_c \rightarrow 0$ .

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**2. Zero point energy:** The classical Hamiltonian for a harmonic oscillator of frequency  $\omega$  is

$$\mathcal{H}_{\text{cl}} = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}.$$

We will assume that in quantum mechanics the energy levels are quantized as

$$\mathcal{H}_{\text{qm}} = x + yn, \quad \text{for } n = 0, 1, 2, \dots,$$

and aim to find the parameters  $x$  and  $y$  by matching to classical counterparts.

(a) Compute the classical partition function  $Z_{\text{cl}}(\beta)$ , and energy  $E_{\text{cl}}(\beta)$  at temperature  $T = (k_B\beta)^{-1}$ , using  $(dp dq)/h$  as dimensionless measure of phase space.

- The classical partition function is

$$Z_{\text{cl}}(\beta) = \int \frac{dq dp}{h} e^{-\frac{\beta p^2}{2m} - \frac{\beta m \omega^2 q^2}{2}} = \frac{2\pi}{h\beta\omega},$$

and the energy is

$$E_{\text{cl}}(\beta) = -\frac{\partial \ln Z_{\text{cl}}}{\partial \beta} = \frac{1}{\beta} = k_B T.$$

(b) Compute the quantum partition function  $Z_{\text{qm}}(\beta)$ , and obtain  $y$  by matching to  $Z_{\text{cl}}(\beta)$  at high temperatures.

- The partition function with the postulated quantized energies is

$$Z_{\text{qm}}(\beta) = \sum_{n=0}^{\infty} e^{-\beta(x+yn)} = \frac{e^{-\beta x}}{1 - e^{-\beta y}}, \quad \implies \quad \lim_{\beta \rightarrow 0} Z_{\text{qm}}(\beta) = \frac{1}{\beta y}.$$

Matching the latter to the classical result yields

$$y = \frac{h\omega}{2\pi} = \hbar\omega.$$

(c) Compute the energy  $E_{\text{qm}}(\beta)$ , and expand the result for  $\beta \rightarrow 0$ , including the leading two terms. By matching to  $E_{\text{cl}}(\beta)$  find the parameter  $x$ .

- The energy of the quantized oscillator is given by

$$E_{\text{qm}}(\beta) = -\frac{\partial \ln Z_{\text{qm}}}{\partial \beta} = x + \frac{y}{e^{\beta y} - 1}.$$

Expanding the above result in  $\beta$  gives

$$\lim_{\beta \rightarrow 0} E_{\text{qm}}(\beta) = x + \frac{y}{\beta y(1 + \beta y/2 + \dots)} = \frac{1}{\beta} + \left(x - \frac{y}{2}\right) + \mathcal{O}(\beta).$$

Demanding agreement with the classical energy at this order, then yields

$$x = \frac{y}{2} = \frac{1}{2}\hbar\omega \quad !$$

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**3. Rotating gas:** Consider a gas of  $N$  identical atoms confined to a spherical harmonic trap in three dimensions, i.e. the particles are subject to the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N \left[ \frac{p_i^2}{2m} + \frac{K}{2} r_i^2 \right].$$

Since angular momentum  $\vec{L} = \sum_{i=1}^N \vec{r}_i \times \vec{p}_i$  is a conserved quantity, i.e.  $\{\vec{L}, \mathcal{H}\} = 0$ , a generalized canonical distribution can be defined with probability

$$p[\mu \equiv \{\vec{p}_i, \vec{r}_i\}] = \frac{1}{Z(\beta, \vec{\Omega})} \exp \left( -\beta \mathcal{H}(\mu) - \beta \vec{\Omega} \cdot \vec{L}(\mu) \right).$$

(a) Compute the classical partition function for this gas of identical particles, assuming  $\vec{\Omega} = \Omega \hat{z}$ , with  $\Omega < \sqrt{K/m}$ . (Hint:  $L_z = xp_y - yp_x$ .)

- Since the Hamiltonian describes  $N$  identical non-interacting particles,

$$Z(N, \beta, \vec{\Omega}) = \frac{1}{N!} Z_1^N.$$

For  $\vec{\Omega} = \Omega \hat{z}$ , the terms acting on a single particle are

$$\mathcal{H}_1 + \vec{\Omega} \cdot \vec{L}_1 = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \frac{K(x^2 + y^2 + z^2)}{2} + \Omega(xp_y - yp_x).$$

The single particle partition function is thus given by

$$Z_1 = \int \frac{dz dp_z}{h} e^{-\frac{\beta p_z^2}{2m} - \frac{\beta K z^2}{2}} \int \frac{dx dp_y}{h} e^{-\frac{\beta p_y^2}{2m} - \frac{\beta K x^2}{2} - \beta \Omega x p_y} \int \frac{dy dp_x}{h} e^{-\frac{\beta p_x^2}{2m} - \frac{\beta K y^2}{2} + \beta \Omega y p_x}.$$

Performing the Gaussian integrals over the momenta yields

$$Z_1 = \frac{1}{\lambda^3} \int dz e^{-\frac{\beta p_z^2}{2m}} \int dx e^{-\frac{\beta(K - m\Omega^2)x^2}{2}} \int dy e^{-\frac{\beta(K - m\Omega^2)y^2}{2}} = \sqrt{\frac{2\pi}{\beta K}} \left( \frac{2\pi}{\beta(K - m\Omega^2)} \right),$$

where  $\lambda_T = h/\sqrt{2\pi m k_B T}$  is the thermal wavelength. (Note that the condition  $K > m\Omega^2$  is required to keep the particles confined.) Thus the overall partition function is given by

$$Z(N, \beta, \vec{\omega}) = \frac{1}{N! \lambda_T^{3N}} \left[ \sqrt{\frac{2\pi}{\beta K}} \left( \frac{2\pi}{\beta(K - m\Omega^2)} \right) \right]^N.$$

(b) Find the expectation value of angular momentum  $\langle L_z \rangle$ .

- From the form of the probability, it is easy to observe that

$$\langle L_z \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \Omega} = N k_B T \frac{2m\Omega}{K - m\Omega^2}.$$

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4. *Capillary waves* on the surface of a thick liquid have frequency  $\omega(\vec{k})$  related to the two-dimensional wavevector  $\vec{k}$  by  $\omega^2 = (\sigma/\rho)k^3$ , where  $\sigma$  is the surface tension, and  $\rho$  is the liquid density.

(a) Calculate the contribution of such capillary modes to the heat capacity per unit area of the film in the low temperature limit  $k_B T \ll \hbar \omega_{\max}$ . (Hint: Change variables from  $k$  to  $x = \beta \hbar \omega(k)$ .)

- Each mode can be regarded as a harmonic oscillator, and thus

$$\begin{aligned} E &= \sum_{\vec{k}} \hbar \omega(\vec{k}) \left( \langle n_{\vec{k}} \rangle + \frac{1}{2} \right) \\ &= E_0 + A \int \frac{d^2 k}{(2\pi)^2} \frac{\hbar \omega(\vec{k})}{e^{\beta \hbar \omega(\vec{k})} - 1}. \end{aligned}$$

Change variables from  $k$  to  $x = \beta \hbar \omega(k) = \beta \hbar \sqrt{\sigma/\rho} k^{3/2}$ , such that

$$\frac{d^2 k}{(2\pi)^2} = \frac{2\pi k dk}{4\pi^2} = \frac{1}{2\pi} \times \left( \frac{\rho}{\sigma} \right)^{1/3} \left( \frac{x}{\beta \hbar} \right)^{2/3} \times \frac{2}{3} \left( \frac{\rho}{\sigma} \right)^{1/3} \left( \frac{x}{\beta \hbar} \right)^{2/3} \frac{dx}{x},$$

and

$$E = E_0 + \frac{A}{3\pi} \left( \frac{\rho}{\sigma} \right)^{2/3} \left( \frac{k_B T}{\hbar} \right)^{4/3} (k_B T) \int_0^\infty dx \frac{x^{4/3}}{e^x - 1}.$$

Using the definition of the zeta function, the final integral evaluates to  $(4/3)! \zeta_{7/3}$ , and thus

$$E = E_0 + \frac{A}{3\pi} \left( \frac{4}{3} \right)! \zeta_{7/3} \hbar \left( \frac{\rho}{\sigma} \right)^{2/3} \left( \frac{k_B T}{\hbar} \right)^{7/3}.$$

The contribution of these modes to heat capacity is thus

$$\frac{C(T)}{k_B} = \frac{A}{3\pi} \left( \frac{7}{3} \right)! \zeta_{7/3} \left( \frac{\rho}{\sigma} \right)^{2/3} \left( \frac{k_B T}{\hbar} \right)^{4/3}.$$

(b) For films of finite thickness  $H$ , the capillary spectrum is modified such that  $\omega^2 = (\sigma/\rho)k^3 \tanh(kH)$ . How does the heat capacity of thin films scale with  $T$  at very low

temperatures. (A qualitative argument is sufficient to obtain the scaling without need for explicit calculations.)

- At low temperatures the heat capacity is dominated by modes of small frequency, and hence small wave vector  $k$ . As  $k \rightarrow 0$  for this films,  $\omega^2 \rightarrow (\sigma/\rho)k^4H$ . Excited modes have frequency  $\hbar\omega \leq k_B T$ , corresponding to  $k \leq (\rho/\sigma H)^{1/4}(k_B T/\hbar)^{1/2}$ . The heat capacity (in units of  $k_B$ ) is roughly the number of excited modes, around  $Ak_{\max}^2$  in two dimensions, and thus

$$\frac{C}{k_B} \propto A \sqrt{\frac{\rho}{\sigma H}} \times \frac{k_B T}{\hbar}.$$

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1. *Harmonic confinement of Fermions:* A classical gas of fermions of mass  $m$  is confined in a  $d$ -dimensional anisotropic harmonic potential

$$U(\vec{r}) = \frac{m}{2} \sum_{\alpha} \omega_{\alpha}^2 x_{\alpha}^2,$$

with different restoring frequencies  $\{\omega_{\alpha}\}$  along the different directions. We are interested in the limit of wide traps such that  $\hbar\omega_{\alpha} \ll k_B T$ , and the discreteness of the allowed energies can be ignored.

(a) Show that in this limit, the number of states  $N(E)$  with energy less than or equal to  $E$ , and the density of states  $\rho(E)$ , are respectively given by

$$N(E) = \frac{1}{d!} \prod_{\alpha=1}^d \left( \frac{E}{\hbar\omega_{\alpha}} \right), \quad \text{and} \quad \rho(E) = \frac{1}{(d-1)!} \frac{E^{d-1}}{\prod_{\alpha} \hbar\omega_{\alpha}}.$$

- The energy of the quantized harmonic oscillator is given by

$$E = \sum_{\alpha} \hbar\omega_{\alpha} \left( n_{\alpha} + \frac{1}{2} \right).$$

Ignoring the effects of discreteness (and ground state energies), states with energy less than or equal to  $E$  are confined within a hyper-pyramid with sides of length  $\mathcal{N}_{\alpha} = E/(\hbar\omega_{\alpha})$ . The number of states is simply the volume of this pyramid, which in  $d$  dimensions is given by

$$N(E) \approx \frac{1}{d!} \prod_{\alpha=1}^d \mathcal{N}_{\alpha} = \frac{1}{d!} \prod_{\alpha=1}^d \left( \frac{E}{\hbar\omega_{\alpha}} \right).$$

The density of states is the derivative of this expression, and hence

$$\rho(E) = \frac{dN(E)}{dE} = \frac{1}{(d-1)!} \frac{E^{d-1}}{\prod_{\alpha} \hbar\omega_{\alpha}}.$$

(b) Show that in a grand canonical ensemble, the number of particles in the trap is

$$\langle N \rangle = f_d^-(z) \prod_{\alpha} \left( \frac{k_B T}{\hbar\omega_{\alpha}} \right).$$

- Ignoring discreteness effects, the number of particles is given by

$$\langle N \rangle = \sum_{\{n_\alpha\}} \frac{1}{z^{-1}e^{\beta E} + 1} \approx \int_0^\infty \frac{\rho(E)dE}{z^{-1}e^{\beta E} + 1} = \frac{1}{\prod_\alpha \hbar\omega_\alpha} \frac{1}{(d-1)!} \int_0^\infty \frac{dE E^{d-1}}{z^{-1}e^{\beta E} + 1}.$$

After the change of variables to  $x = \beta E$ , we are left with a standard integral, and

$$\langle N \rangle = \prod_\alpha \left( \frac{k_B T}{\hbar\omega_\alpha} \right) f_d^-(z).$$

(c) Compute the energy of  $E$  in the grand canonical ensemble. (Ignore the zero point energy of the oscillators.)

- Ignoring the ground state contribution, the amount of energy in the trap is given by

$$E = \langle \mathcal{H} \rangle = \sum_{\{n_\alpha\}} \frac{E}{z^{-1}e^{\beta E} + 1} \approx \int_0^\infty \frac{\rho(E)EdE}{z^{-1}e^{\beta E} + 1} = \frac{1}{\prod_\alpha \hbar\omega_\alpha} \frac{1}{(d-1)!} \int_0^\infty \frac{dE E^d}{z^{-1}e^{\beta E} + 1}.$$

After the change of variables to  $x = \beta E$ , we are left with a standard integral, and

$$E = \prod_\alpha \left( \frac{k_B T}{\hbar\omega_\alpha} \right) dk_B T f_{d+1}^-(z).$$

(d) From the limiting forms of the expressions for energy and number, compute the leading term for energy per particle in the high temperature limit.

- In the high temperature limit,  $f_d^-(z) \approx z$ , and hence

$$N = \prod_\alpha \left( \frac{k_B T}{\hbar\omega_\alpha} \right) z, \quad \text{while} \quad E = \prod_\alpha \left( \frac{k_B T}{\hbar\omega_\alpha} \right) dk_B T z.$$

Dividing the two expressions, we find the usual results of  $E/N = dk_B T$ .

(e) Compute the limiting value of the chemical potential at zero temperature.

- Using the Sommerfeld expansion, the number of particles can be written as

$$N = \frac{1}{(\beta\epsilon)^d} \frac{(\ln z)^d}{d!} \left[ 1 + \frac{\pi^2}{6} \frac{d(d-1)}{(\ln z)^2} + \dots \right],$$

where we have introduced the energy scale  $\epsilon = (\prod_\alpha \hbar\omega_\alpha)^{1/d}$ . Inverting this expression, we find

$$\beta\epsilon_F \equiv \ln z = \beta\epsilon (d!N)^{1/d} \left[ 1 - \frac{\pi^2}{6} \frac{(d-1)}{(\ln z)^2} + \dots \right] = \beta\epsilon_F \left[ 1 - \frac{\pi^2}{6} \frac{(d-1)}{(\beta\epsilon_F)^2} + \dots \right],$$



where we have defined a Fermi energy

$$\epsilon_F = \lim_{T \rightarrow 0} k_B T \ln z = \left( d! N \prod_{\alpha} \hbar \omega_{\alpha} \right)^{1/d}.$$

(f) Give the expression for the heat capacity of the gas at low temperatures, correct up to numerical factors that you need not compute.

- Since the confined gas has a finite Fermi energy, its specific heat must scale as usual, as

$$\frac{C}{Nk_B} = a \frac{k_B T}{\epsilon_F},$$

where  $\epsilon_F$  computed above. The numerical coefficient  $a$  is obtained from an analysis that incorporates the subleading correction in the Sommerfeld expansion, as

$$\beta E = \frac{d}{(\beta \epsilon)^d} \frac{(\ln z)^{d+1}}{(d+1)!} \left[ 1 + \frac{\pi^2}{6} \frac{(d+1)d}{(\ln z)^2} + \dots \right].$$

Dividing by the similar expansion for  $N$ , we obtain

$$\frac{\beta E}{N} = \frac{d \ln z}{(d+1)} \left[ 1 + \frac{\pi^2}{6} \frac{2d}{(\ln z)^2} + \dots \right].$$

Substituting the value of  $\ln z$  from the earlier part gives

$$\frac{\beta E}{N} = \frac{d \beta \epsilon_F}{(d+1)} \left[ 1 + \frac{\pi^2}{6} \frac{d+1}{(\beta \epsilon_F)^2} + \dots \right].$$

The heat capacity is then obtained as

$$\frac{C}{N} = \frac{1}{N} \frac{dE}{dT} = \frac{d \epsilon_F}{(d+1)} \frac{\pi^2}{6} (d+1) \frac{2k_B^2 T}{\epsilon_F^2} + \dots = k_B \left[ d \frac{\pi^2}{3} \frac{k_B T}{\epsilon_F} + \dots \right].$$

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**2. Surface adsorption of an ideal Bose gas:** Consider adsorption of particles of an ideal (spin-less) Bose gas onto a two dimensional surface.

(a) Treating the ambient gas as a *non-degenerate* ideal gas of temperature  $T$  and pressure  $P$ , find its chemical potential  $\mu(T, P)$ .

- In the grand canonical ensemble for a gas

$$\beta P = \frac{\ln Q}{V} = \frac{1}{\lambda^3} f_{5/2}^{\eta}(z) \approx \frac{z}{\lambda^3}, \quad \implies \quad \mu = k_B T \ln z = k_B T \ln \left( \frac{P \lambda^3}{k_B T} \right).$$

(b) The gas is in contact with a attractive surface, such that a particle gains an energy  $u$  upon adsorption to the surface. Treating the particles on the surface as a two dimensional ideal gas (in equilibrium with the ambient gas), find the areal density  $n_2$  as a function of  $P$ ,  $u$ , and temperature ( $T$ ,  $\beta$ , and/or  $\lambda$ ).

- The average number of particles on the surface is

$$N_2 = \sum_{\vec{k}} \frac{1}{z^{-1} e^{\beta \epsilon(\vec{k})} - 1}, \quad \text{where} \quad \epsilon(\vec{k}) = -u + \frac{\hbar^2 k^2}{2m}.$$

Converting the sum to an integral, the surface density is obtained as

$$n_2 = \frac{N_2}{A} = \int \frac{d^2 \vec{k}}{(2\pi)^2} \frac{1}{z^{-1} e^{-\beta u + \beta \frac{\hbar^2 k^2}{2m}} - 1}.$$

Changing variables to  $x = \beta \hbar^2 k^2 / 2m$ , and noting  $k dk = dx(2\pi/\lambda^2)$ , we find

$$n_2 = \frac{1}{\lambda^2} \int_0^\infty dx \frac{1}{z^{-1} e^{-\beta u + x} - 1} = \frac{1}{\lambda^2} f_1^+(ze^{\beta u}) = \frac{1}{\lambda^2} f_1^+\left(\frac{\beta P}{\lambda^3} e^{\beta u}\right).$$

(c) Find the maximum pressure  $P^*$  before complete condensation to the surface.

- The function  $f_1^+$  diverges when its argument approaches unity, indicating adsorption of all particles to the surface. Thus the maximum possible pressure is

$$P^* = \frac{k_B T}{\lambda^3} e^{\frac{u}{k_B T}}.$$

(d) Find the singular behavior of  $n_2$  for  $\delta P = P^* - P \rightarrow 0$ .

- For  $P$  close to  $P^*$ , the argument of  $f_1^+$  is

$$\frac{\beta P}{\lambda^3} e^{\beta u} = \frac{\beta P^*}{\lambda^3} e^{\beta u} - \frac{\delta P \beta}{\lambda^3} e^{\beta u} = 1 - \frac{\delta P}{P^*}.$$

Since  $f_1^+(z) = -\ln(1-z)$ , we conclude that the density diverges as  $P \rightarrow P^*$  as

$$n_2 = \frac{1}{\lambda^2} \ln\left(\frac{P^*}{\delta P}\right).$$

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**3. Rotational heat capacity at high temperatures:**

(a) It can be shown that  $\sum_{\ell=0}^{\infty} (2\ell+1)e^{-u\ell(\ell+1)} = \frac{1}{u} + \frac{1}{3} + \frac{u}{15} + \mathcal{O}(u^2)$ . Use this result to calculate the energy of a quantum rotor with moment of inertia  $I$  at high temperatures.

- Allowed energies of a Harmonic oscillator are  $\hbar^2\ell(\ell+1)/2I$  for integer  $\ell$ , with degeneracy  $(2\ell+1)$ . Using the above result, the corresponding partition function is

$$Z_{\text{rot.}} = \sum_{\ell=0}^{\infty} (2\ell+1)e^{-u\ell(\ell+1)} = \frac{1}{u} + \frac{1}{3} + \frac{u}{15} + \mathcal{O}(u^2), \quad \text{for } u = \frac{\beta\hbar^2}{2I},$$

and

$$\ln Z_{\text{rot.}} = -\ln u + \ln \left( 1 + \frac{u}{3} + \frac{u^2}{15} + \dots \right) = -\ln u + \frac{u}{3} + \frac{u^2}{15} - \frac{u^3}{18} + \dots$$

The energy is then obtained from

$$\begin{aligned} E_{\text{rot.}} &= -\frac{\partial \ln Z_{\text{rot.}}}{\partial \beta} = -\frac{\hbar^2}{2I} \frac{\partial \ln Z_{\text{rot.}}}{\partial u} \\ &= \frac{\hbar^2}{2I} \left( \frac{1}{u} - \frac{1}{3} - \frac{u}{45} + \dots \right) = k_B T - \frac{\hbar^2}{6I} - \frac{\hbar^4}{180I^2 k_B T} + \dots \end{aligned}$$

(b) Find the first quantum correction to rotational heat capacity at high temperatures.

- The heat capacity is obtained from the temperature derivative of the energy as

$$C_{\text{rot.}} = \frac{dE_{\text{rot.}}}{dT} = k_B \left[ 1 + \frac{1}{180} \left( \frac{\hbar^2}{2Ik_B T} \right)^2 + \dots \right].$$

Unlike the case of vibrations, quantum corrections increase the rotational heat capacity at high temperatures.

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**4. Inertia of superfluid helium:** Changes in frequency of a torsional oscillator immersed in liquid helium can be used to track the “normal fraction” of the liquid as a function of temperature. This problem aims at computing the contribution of phonons (dominant at low temperatures) to the fraction of superfluid that moves with the oscillator plates. Consider a superfluid confined between two parallel plates moving with velocity  $\vec{v}$ .

(a) The isolated stationary superfluid has a branch of low energy excitations characterized by energy  $\epsilon(p)$ , where  $p = |\vec{p}|$  is the magnitude of the momentum  $\vec{p}$ . Show that for excitations produced by walls (of large mass  $M$ ) moving with velocity  $\vec{v}$ , this spectrum is modified (due to consideration of momentum and energy of the walls) to  $\epsilon_{\vec{v}}(\vec{p}) = \epsilon(p) - \vec{p} \cdot \vec{v}$ .

- Due to momentum conservation, upon creation of an excitation of momentum  $\vec{p}$  within the superfluid, the velocity of the walls is reduced to  $\vec{v}' = \vec{v} - \vec{p}/M$ . This corresponds to

a reduction in the kinetic energy of the walls, such that the net energy required to create the excitation is

$$\epsilon_{\vec{v}}(\vec{p}) = \epsilon(p) + \frac{M}{2}v'^2 - \frac{M}{2}v^2 = \epsilon(p) + \frac{M}{2} \left[ \left( \vec{v} - \frac{\vec{p}}{M} \right)^2 - v^2 \right] = \epsilon(p) - \vec{p} \cdot \vec{v} + \mathcal{O} \left( \frac{1}{M} \right).$$

(b) Using the standard Bose occupation number for particles of energy  $\epsilon_{\vec{v}}(\vec{p})$ , obtain an integral expression for the net momentum  $\vec{P}$  carried by the excitations in the superfluid. (**Hint:**  $\sum_{\vec{p}} = V \int d^3\vec{p}/h^3$ , where  $V$  is the volume.)

• Since the occupation number of a Boson is  $\langle n(\vec{p}) \rangle = [e^{\beta\epsilon_{\vec{v}}(\vec{p})} - 1]^{-1}$ , the net momentum carried by these excitations is

$$\vec{P} = \sum_{\vec{p}} \frac{\vec{p}}{e^{\beta\epsilon_{\vec{v}}(\vec{p})} - 1} = \frac{V}{h^3} \int d^3\vec{p} \frac{\vec{p}}{e^{\beta\epsilon_{\vec{v}}(\vec{p})} - 1}.$$

(c) Expanding the result for small velocities, show that  $P_\alpha = V\rho_n v_\alpha$ , and give an integral expression for  $\rho_n$ . (**Hint:** The angular average of  $p_\alpha p_\gamma$  is  $p^2\delta_{\alpha\gamma}/3$ .)

• Using  $\epsilon_{\vec{v}}(\vec{p}) = \epsilon(p) - \vec{p} \cdot \vec{v}$ , and expanding the denominator for small  $\vec{v}$ , we obtain

$$P_\alpha = \frac{V}{h^3} \int d^3\vec{p} \left[ \frac{p_\alpha}{e^{\beta\epsilon(p)} - 1} + \frac{p_\alpha \beta e^{\beta\epsilon(p)} \vec{p} \cdot \vec{v}}{(e^{\beta\epsilon(p)} - 1)^2} + \dots \right].$$

Since  $\epsilon(p)$  is spherically symmetric, the first integral is zero. To evaluate the second integral, note that the angular average of  $p_\alpha p_\beta = p^2\delta_{\alpha\beta}/3$  to get

$$P_\alpha = \frac{V}{h^3} \int_0^\infty 4\pi p^2 dp \frac{\beta e^{\beta\epsilon(p)} v_\alpha p^2/3}{(e^{\beta\epsilon(p)} - 1)^2} + \dots = v_\alpha V\rho_n + \dots,$$

where

$$\rho_n = \frac{4\pi}{3} \frac{\beta}{h^3} \int_0^\infty \frac{p^4 e^{\beta\epsilon(p)} dp}{(e^{\beta\epsilon(p)} - 1)^2}.$$

(d) Compute the contribution of phonons, with  $\epsilon(p) = cp$ , to  $\rho_n$ . (An answer that is correct up to a numerical coefficient is sufficient.)

• Using  $\epsilon(p) = cp$ , and changing variables to  $x = \beta cp$ , leads to

$$\rho_n = \frac{4\pi}{3} \frac{\beta}{h^3} \frac{1}{(\beta c)^5} \int_0^\infty \frac{x^4 e^x dx}{(e^x - 1)^2}.$$

The final integral can be evaluated through integration by parts, yielding

$$\rho_n = \frac{4\pi}{3} \frac{(k_B T)^4}{h^3 c^5} \int_0^\infty \frac{4x^3 dx}{e^x - 1} = \frac{16\pi}{3} \frac{(k_B T)^4}{h^3 c^5} 4! \zeta_4 = 128\pi \frac{(k_B T)^4}{h^3 c^5} \frac{\pi^4}{90} = \frac{8\pi^2}{45} \frac{(k_B T)^4}{h^3 c^5}.$$

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**1. 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 quantities  $z_{\vec{q}} \equiv ze^{-\beta\mathcal{E}(\vec{q})} = \exp[\beta(\mu - \mathcal{E}(\vec{q}))]$ ?

• 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  $n_{\vec{q}}$  in terms of  $z_{\vec{q}}$ .

• Cumulnats 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

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

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

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

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

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

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

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

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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**2. Surface adsorption of an ideal Fermi gas:** Consider adsorption of particles of an ideal (spin-1/2) Fermi gas onto a two dimensional surface.

(a) Treating the ambient gas as a *non-degenerate* ideal gas of temperature  $T$  and pressure  $P$ , find its chemical potential  $\mu(T, P)$ .

- In the grand canonical ensemble for a gas

$$\beta P = \frac{\ln Q}{V} = \frac{g}{\lambda^3} f_{5/2}^\eta(z) \approx \frac{g}{\lambda^3} z, \quad \implies \quad \mu = k_B T \ln z = k_B T \ln \left( \frac{P \lambda^3}{g k_B T} \right),$$

with  $g = 2$  for spin-1/2 fermions.

(b) The gas is in contact with a attractive surface, such that a particle gains an energy  $u$  upon adsorption to the surface. Treating the particles on the surface as a two dimensional quantum ideal gas (in equilibrium with the ambient three dimensional gas), find the areal density  $n_2$  as a function of  $P$ ,  $u$ , and temperature ( $T$ ,  $\beta$ , and/or  $\lambda$ ).

- The average number of particles on the surface is

$$N_2 = g \sum_{\vec{k}} \frac{1}{z^{-1} e^{\beta \epsilon(\vec{k})} + 1}, \quad \text{where} \quad \epsilon(\vec{k}) = -u + \frac{\hbar^2 k^2}{2m}.$$

Converting the sum to an integral, the surface density is obtained as

$$n_2 = \frac{N_2}{A} = g \int \frac{d^2 \vec{k}}{(2\pi)^2} \frac{1}{z^{-1} e^{-\beta u + \beta \frac{\hbar^2 k^2}{2m}} + 1}.$$

Changing variables to  $x = \beta \hbar^2 k^2 / 2m$ , and noting  $k dk = dx(2\pi/\lambda^2)$ , we find

$$n_2 = \frac{g}{\lambda^2} \int_0^\infty dx \frac{1}{z^{-1} e^{-\beta u + x} + 1} = \frac{g}{\lambda^2} f_1^- (ze^{\beta u}) = \frac{g}{\lambda^2} f_1^- \left( \frac{\beta P \lambda^3 e^{\beta u}}{g} \right).$$

(c) State the conditions on  $P$  such that the three dimensional gas is non-degenerate, while the two dimensional absorbed gas is degenerate.

- The 3-d gas is non-degenerate if  $\beta P \lambda^3 / g \ll 1$ , while the 2d gas is degenerate if  $\beta P \lambda^3 e^{\beta u} / g \gg 1$ . The two conditions imply

$$\frac{g}{\beta \lambda^3} e^{-\beta u} \ll P \ll \frac{g}{\beta \lambda^3},$$

which is certainly achievable if  $\beta u$  is large enough.

(d) Find the limiting value of  $n_2$  at low temperatures *assuming* that the 3d gas remains *non-degenerate*.

- It is easy to check from the power series expansion, the Sommerfeld expansion, or otherwise that  $f_1^-(z) = \ln(1+z)$ , and hence

$$n_2 = \frac{g}{\lambda^2} \ln \left( 1 + \frac{\beta P \lambda^3 e^{\beta u}}{g} \right) \approx \frac{2\pi m k_B T g}{h^2} (\beta u + \ln(\beta P \lambda^3 / g)) \approx \frac{2\pi m g u}{h^2}.$$

(e) What is the limiting behavior of the density  $n_2$  at high pressure, now treating the ambient gas as *degenerate*.

- Treating the ambient gas as degenerate, its pressure is related to  $z$  by

$$\beta P = \frac{g}{\lambda^3} f_{5/2}^-(z) \approx \frac{g}{\lambda^3} \frac{(\ln z)^{5/2}}{(5/2)!}, \quad \Rightarrow \quad \ln z = \left[ \frac{15\sqrt{\pi}}{8g} \beta P \lambda^3 \right]^{2/5}.$$

Note that the limiting value of  $\ln z$  is proportional to  $\beta$ , and we can indeed define  $\ln z \simeq \beta \epsilon_F(P)$ , with a Fermi energy that is proportional to  $P^{2/5}$ . Substituting in the expression for  $n_2$ , we then find

$$n_2 \approx \frac{g}{\lambda^2} \left[ \beta u + \left( \frac{15\sqrt{\pi}}{8g} \beta P \lambda^3 \right)^{2/5} \right] \approx \frac{2\pi m g}{h^2} (u + \epsilon_F(P)).$$

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**3. Partitions of Integers:** In mathematics, the partition  $P(E)$  of an integer  $E$  refers to the number of ways the integer can be written as sums of smaller integers. For example,  $P(5) = 7$  since  $5 = [5, 4+1, 3+2, 3+1+1, 2+2+1, 2+1+1+1, 1+1+1+1+1]$ . A celebrated result due to Hardy and Ramanujan is that the asymptotically at large  $E$ ,

$$P(E) \sim \frac{1}{4E\sqrt{3}} \exp \left( \pi \sqrt{\frac{2E}{3}} \right).$$

The leading asymptotic dependence can in fact be obtained by considering the statistical mechanics of a gas of ‘photons’ in one dimension. Working in a system of units such that  $k_B = \hbar = c = 1$ , the single particle energies of such a gas are integers, i.e.  $\epsilon_k = k$  for  $k = 1, 2, 3, \dots$ , and

$$E = \sum_{k=1}^{\infty} k n_k \quad .$$

(a) Compute a ‘partition function’  $Z(\beta)$  in the limit  $\beta \rightarrow 0$ , after replacing sums over  $k$  with integrals. (Note that the number of ‘photons’ is arbitrary.)

- Since there is no constraint on the number of photons, the partition function is

$$Z(\beta) = \sum_{\{n_k\}} e^{-\beta \sum_k k n_k} = \prod_{k=1}^{\infty} \sum_{n_k=0}^{\infty} e^{-\beta k n_k} = \prod_{k=1}^{\infty} [1 - e^{-\beta k}]^{-1}.$$

Using the approximation,

$$\sum_{k=1}^{\infty} f(\beta k) = \sum_{k=0}^{\infty} f(\beta(k+1)) \simeq \int_0^{\infty} dk f(\beta + \beta k) + \frac{1}{2} f(\beta) + \dots,$$



$\ln Z$  can be expanded as

$$\ln Z(\beta) = - \sum_{k=1}^{\infty} \ln(1 - e^{-\beta k}) = - \int_0^{\infty} dk \ln[1 - e^{-\beta(k+1)}] + \frac{1}{2} \ln[1 - e^{-\beta}] + \dots$$

The first integral can be evaluated through integration by parts, and

$$\begin{aligned} \ln Z(\beta) &= + \int_0^{\infty} dk k \frac{\beta e^{-\beta(k+1)}}{1 - e^{-\beta(k+1)}} + \frac{1}{2} \ln[1 - e^{-\beta}] + \dots \\ &= \int_0^{\infty} dk k \frac{\beta}{e^{\beta} e^{\beta k} - 1} + \frac{1}{2} \ln[1 - e^{-\beta}] + \dots \\ &= \frac{1}{\beta} \int_0^{\infty} \frac{x dx}{e^{\beta} e^x - 1} + \frac{1}{2} \ln[1 - e^{-\beta}] + \dots \\ &= \frac{1}{\beta} f_2^+(e^{-\beta}) + \frac{1}{2} \ln[1 - e^{-\beta}] + \dots \\ &= \frac{1}{\beta} \zeta_2 + \frac{1}{2} \ln \beta + \dots, \end{aligned}$$

with the last line obtain by taking the limit of  $\beta \rightarrow 0$  in the arguments of the two functions.

(b) Compute the average energy, and use the result to find  $T \equiv 1/\beta$  as a function of  $E$ , to leading order for  $E \gg 1$ .

- The average energy is obtained as

$$E = - \frac{d \ln Z}{d\beta} = \frac{\zeta_2}{\beta^2} - \frac{1}{2\beta} + \dots$$

Note that for  $E \gg 1$ ,  $\beta \ll 1$ , and to leading order

$$T = \frac{1}{\beta} = \sqrt{\frac{E}{\zeta_2}}.$$

(c) Compute the entropy  $S(E)$  for  $E \gg 1$ . Is your result consistent with the Hardy–Ramanujan formula for partitions of integers?

- Since in the thermodynamic limit  $\ln Z = -\beta(E - TS)$ , we have

$$S(E) = \ln Z + \beta E = \frac{\zeta_2}{\beta} + \frac{1}{2} \ln \beta + \frac{\zeta_2}{\beta} + \dots = \frac{2\zeta_2}{\beta} + \frac{1}{2} \ln \beta + \dots = 2\sqrt{\zeta_2 E} + \frac{1}{2} \ln \sqrt{\frac{\zeta_2}{E}} + \dots$$

Since  $\zeta_2 = \pi^2/6$ , we find

$$S(E) = \pi \sqrt{\frac{2E}{3}} - \frac{1}{4} \ln E + \mathcal{O}(E^0).$$

While the leading order result for  $S(E)$  agrees with the Hardy–Ramanujan formula, the subleading correction computed here,  $-\ln E/4$  is distinct from the correct result of  $-\ln E$ . To obtain the latter exactly, one has to evaluate  $\Omega(E)$  from the inverse Laplace transform of  $Z(\beta)$  including the range of integration in  $\beta$  in addition to the saddle-point value of the integrand.

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**4. Particle in the micro-canonical ensemble:** Consider an ensemble comprising one particle in a box of volume  $V$ , and energy  $E < \frac{p^2}{2m} < E + \delta E$ , with  $\delta E \ll E$ .

(a) What is the (properly normalized) density matrix in the momentum basis  $\vec{p}$ ? (Dimensions of the box are much larger than characteristic quantum wavelength of the particle.)

- The density is diagonal in this basis and given by

$$\rho(\vec{p}) = \frac{1}{\Omega(E)} \begin{cases} 1 & \text{if } E < \frac{p^2}{2m} < E + \delta E \\ 0 & \text{otherwise} \end{cases}.$$

The normalization  $\Omega(E)$  is obtained by summing over all states in phase space. For large boxes discretization of allowed momenta is not relevant, and the result is the same as integrating over available classical phase space, leading to

$$\Omega(E) = \frac{V}{h^3} 4\pi p^2 \delta p,$$

where  $p = \sqrt{2mE}$  and  $\delta p = \sqrt{m/2E} \delta E$ , leading to

$$\Omega(E) = \frac{4\pi V}{h^3} \sqrt{2mE} m \delta E.$$

(b) What is the corresponding density matrix in the position basis  $\vec{x}$ ?

- Plane waves  $\langle \vec{p} | \vec{x} \rangle = \exp\left(\frac{i\vec{p} \cdot \vec{x}}{\hbar}\right) / \sqrt{V}$  can be used to change from position to coordinate basis, resulting in

$$\langle \vec{x} | \rho | \vec{x}' \rangle = \sum_{\vec{p}} \langle \vec{x} | \vec{p} \rangle \rho(\vec{p}) \langle \vec{p} | \vec{x}' \rangle = \frac{V}{h^3} \int d^3 \vec{p} \rho(\vec{p}) \frac{\exp\left[\frac{i\vec{p} \cdot (\vec{x}' - \vec{x})}{\hbar}\right]}{V}.$$

Substituting  $\rho(\vec{p})$  from previous part, and switching to spherical coordinates for the integration, we find

$$\langle \vec{x} | \rho | \vec{x}' \rangle = \frac{1}{h^3 \Omega} 2\pi p^2 \delta p \int d\theta \sin \theta \exp\left[\frac{ip|\vec{x}' - \vec{x}| \cos \theta}{\hbar}\right] = \frac{1}{V} \frac{\sin(p|\vec{x}' - \vec{x}|)}{p|\vec{x}' - \vec{x}|}.$$

Note that the diagonal terms for  $\vec{x} = \vec{x}'$  indicate a uniform probability of  $1/V$  in the box.

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1. *Critical point behavior:* Consider a system of  $N$  classical point particles of mass  $m$  at temperature  $T$ , and volume  $V$ . An unspecified form of interaction between the particles modifies the energy of any configuration by an amount  $-bN^2/(2V) + cN^3/(6V^2)$  with  $b, c > 0$ , such that the partition function is

$$Z(T, N, V) = Z_{\text{ideal gas}}(T, N, V) \times \exp\left(\frac{\beta b N^2}{2V} - \frac{\beta c N^3}{6V^2}\right),$$

where  $Z_{\text{ideal gas}}(T, N, V)$  is the partition function of a classical gas, and  $\beta = (k_B T)^{-1}$ .

(a) Using the partition function, or otherwise, compute the pressure  $P(n, T)$ , as a function of the density  $n = N/V$ .

- Since the ideal gas partition function is proportional to  $V^N$ , we have

$$\ln Z = N \ln V + \frac{\beta b N^2}{2V} - \frac{\beta c N^3}{6V^2} + (V - \text{independent terms}).$$

The pressure is obtained from

$$\beta P = \frac{\partial \ln Z}{\partial V} = \frac{N}{V} - \frac{\beta b N^2}{2V^2} + \frac{\beta c N^3}{3V^2}, \quad \Rightarrow \quad P = nk_B T - \frac{bn^2}{2} + \frac{cn^3}{3}.$$

(b) Locate the critical temperature  $T_c$  below which this equation must be invalid, and the corresponding density  $n_c$ .

- 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

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

From the second equation we obtain  $n_c = b/(2c)$ , which substituted in the first equation gives  $k_B T_c = b^2/(4c)$ .

- (c) Find the pressure  $P_c$  at the critical point, and hence obtain the ratio  $k_B T_c n_c / P_c$ .

- From the equation of state we then find  $P_c = b^3/(24c^2)$ , and the dimensionless ratio of

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

- (d) 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

$$\begin{aligned} P - P_c &= -\frac{b^3}{24c^2} + \frac{b^2}{4c}n - \frac{b}{2}n^2 + \frac{c}{3}n^3 \\ &= \frac{c}{3} \left( n^3 - 3\frac{b}{2c}n^2 + 3\frac{b^2}{4c^2}n - \frac{b^3}{8c^3} \right) \\ &= \frac{c}{6} (n - n_c)^3 . \end{aligned}$$

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- 2. Quantum-Classical correspondence:** The Hamiltonian for a single particle is given by

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

- (a) Use the Baker-Campbell-Hausdorff expansion

$$\exp(\beta A) \exp(\beta B) = \exp \left[ \beta(A + B) + \beta^2[A, B]/2 + \mathcal{O}(\beta^3) \right] ,$$

to show that the quantum partition function reduces to its classical form in the high temperature limit.

- The partition function is

$$Z = \text{tr} \left[ e^{-\beta \mathcal{H}} \right] = \text{tr} \left[ \exp \left( -\beta \frac{p^2}{2m} - \beta U(\vec{q}) \right) \right] \approx \text{tr} \left[ \exp \left( -\beta \frac{p^2}{2m} \right) \exp(-\beta U(\vec{q})) \right] ,$$

where the last approximation follows from the BCH formula, and is valid to order of  $\beta^2$ . We can evaluate the trace using a complete set of either coordinate ( $|\vec{q}\rangle$ ) or momentum ( $|\vec{p}\rangle$ ) basis, e.g. as

$$Z \approx \sum_{\vec{q}} \left[ \langle \vec{q} | \exp \left( -\beta \frac{p^2}{2m} \right) \exp(-\beta U(\vec{q})) | \vec{q} \rangle \right] .$$

To simultaneously evaluate both operators, we can insert additional momentum/coordinate sums, such as

$$Z \approx \sum_{\vec{q}, \vec{q}', \vec{p}, \vec{p}'} \left[ \langle \vec{q} | \vec{p} \rangle \langle \vec{p} | \exp \left( -\beta \frac{p^2}{2m} \right) \vec{p}' \rangle \langle \vec{p}' | \vec{q}' \rangle \langle \vec{q}' | \exp(-\beta U(\vec{q})) | \vec{q} \rangle \right] .$$

The needed matrix elements are now diagonal, leading to

$$Z \approx \sum_{\vec{q}, \vec{p}} \left[ \langle \vec{q} | \vec{p} \rangle \langle \vec{p} | \exp \left( -\beta \frac{p^2}{2m} \right) \vec{p} \rangle \langle \vec{p} | \vec{q} \rangle \langle \vec{q} | \exp(-\beta U(\vec{q})) | \vec{q} \rangle \right].$$

For the relevant normalizations, note that in one dimensions

$$\langle x' | x \rangle = \delta(x' - x) = \int \frac{dk}{2\pi} e^{ik(x' - x)} = \int \frac{dp}{2\pi\hbar} e^{ip(x - x')/\hbar} = \sum_p \langle x' | p \rangle \langle p | x \rangle,$$

with appropriate generalization to higher dimensions. Thus with the choice of  $\langle \vec{q} | \vec{p} \rangle = \exp(-i\vec{p} \cdot \vec{q}/\hbar)$ , we get  $\sum_{\vec{p}} \rightarrow \int d^3\vec{p}/h^3$ , and

$$Z \approx \int \frac{d^3\vec{q} d^3\vec{p}}{h^3} \exp \left( -\beta \frac{p^2}{2m} - \beta U(\vec{q}) \right),$$

which is the classical partition function, made dimensionless by division with  $h^3$ .

(b) For a particle in a box (with  $U(\vec{q}) = 0$  inside the box, and infinite otherwise), the single particle states have energies  $\epsilon(\vec{k}) = \hbar^2 k^2 / 2m$ , with (quantized) allowed values of  $\vec{k}$  determined by the shape of the box. Use the above result to show that in the limit of a large box of volume  $V$

$$\sum_{\vec{k}} \rightarrow V \int \frac{d^3\vec{k}}{(2\pi)^3}.$$

- In this special case of a general potential, the integration over coordinate  $\vec{q}$  simply yields the volume of the box. Evaluating the classical partition function starting from the classical perspective yields:

$$Z = \int \frac{d^3\vec{q} d^3\vec{p}}{h^3} \exp \left( -\beta \frac{p^2}{2m} - \beta U(\vec{q}) \right) = V \int \frac{d^3\vec{p}}{h^3} \exp \left( -\beta \frac{p^2}{2m} \right) = V \int \frac{d^3\vec{k}}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m}}.$$

The quantum formula gives

$$Z = \text{tr} e^{-\beta \mathcal{H}} = \sum_{\vec{k}} e^{-\beta \hbar^2 k^2 / 2m}.$$

Matching the two formulae yields the required result.

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

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

independent of spin. This particle-hole symmetry ensures that, for equal numbers of positive and negative excitations, the chemical potential is zero at all temperatures.

(a) Using  $\mu(T) = 0$ , show that the mean excitation energy of this system at finite temperature satisfies

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

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

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

(b) Evaluate the integral in the previous part 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  $f_4^-(1) = 7\pi^4/720$ .

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

• The heat capacity can now be evaluated as

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

(d) 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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**4. Fermi gas in two dimensions:** Consider a non-relativistic gas of non-interacting spin 1/2 fermions of mass  $m$  in two dimensions.

(a) Find an explicit relation between the fugacity  $z$  and the areal density  $n = N/A$ . (If needed, note that  $f_1^-(z) = \ln(1+z)$ .)

• Using the Fermi occupation number, the total number of particles in the grand-canonical ensemble is

$$N = 2 \sum_{\vec{k}} \langle n(\vec{k}) \rangle_- = 2A \int \frac{d^2p}{h^2} \frac{1}{z^{-1} e^{\frac{\beta p^2}{2m}} + 1} = 2A \int_0^\infty \frac{2\pi}{h^2} \frac{p dp (\beta/m)}{z^{-1} e^{\frac{\beta p^2}{2m}} + 1} m k_B T.$$

After a change of variable to  $x = \beta p^2/2m$ , the integral is easily evaluated to yield

$$n = \frac{N}{A} = \frac{4\pi m k_B T}{h^2} \int_0^\infty dx \frac{z e^{-x}}{1 + z e^{-x}} = \frac{2}{\lambda^2} \ln(1+z).$$

(b) Give an explicit expression for the chemical potential  $\mu(n, T)$ , and provide its limiting forms at zero and high temperatures.

• From the previous result we find

$$z = e^{\beta\mu} = e^{n\lambda^2/2} - 1 \quad \implies \quad \mu = k_B T \ln[e^{n\lambda^2/2} - 1].$$

In the high temperature limit,  $n\lambda^2 \rightarrow 0$ , and  $\mu \approx k_B T \ln(n\lambda^2/2)$ . In the low temperature limit  $n\lambda^2 \rightarrow \infty$ , and  $\mu \approx k_B T n\lambda^2/2 = \frac{nh^2}{4\pi m}$ .

(c) Find the temperature at which  $\mu = 0$ .

• Setting  $\mu = 0$  and  $z = 1$  yields

$$n = \frac{4\pi m k_B T_0}{h^2} \ln 2 \quad \implies \quad k_B T_0 = \frac{nh^2}{4\pi \ln 2 m}.$$

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**5. 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

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



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

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

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) 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  $d > 1$ .

(c) 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

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

(d) 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. *Fermions pairing into Bosons:* As a primitive model of superconductivity, consider a gas of non-interacting non-relativistic electrons (spin-1/2 and mass  $m$ ). Assume that electrons of opposite spin can bind into a composite boson (spin 0, mass  $2m$ ) of rest energy  $-\epsilon$  with  $\epsilon > 0$ .

(a) In a grand canonical ensemble with chemical potential  $\mu$  for each electron, write down the expressions for the densities  $n_e$  and  $n_b$  of free electrons, and bound electron pairs. (You do not need to derive the relevant expressions. Express your answer in terms of the fugacity  $z = e^{\beta\mu}$ ,  $y = e^{\beta\epsilon}$ , and the electron thermal wavelength  $\lambda = h/\sqrt{2\pi m k_B T}$ .)

• Using standard formulae for the grand canonical ensemble, and the definitions provided in the problem, the electron density is given by

$$n_e = \frac{2}{\lambda^3} f_{3/2}^-(z).$$

To create a bound pair, two electrons are needed (hence  $2\mu$ ), resulting in a composite object with single particle energies  $\varepsilon(\vec{k}) = -\epsilon + (\hbar k)^2/(4m)$  (since mass is  $2m$ ). Due to doubling of mass, the thermal wavelength for the composite boson is  $\lambda_b = \lambda/\sqrt{2}$ . Including the binding energy, the effective fugacity of the bosons is  $z_b = z^2 y$ , resulting in

$$n_b = \frac{2^{3/2}}{\lambda^3} f_{3/2}^+(z^2 y).$$

(b) What is the value of  $z = z_c$  at the onset of Bose condensation? Write the expression for the total (bound plus unbound) electron density  $n_c$  at the onset of Bose condensation.

• Bose condensation occurs when the argument of  $f_{3/2}^+$  is unity, which occurs for

$$z_c = y^{-1/2} = e^{-\beta\epsilon/2}.$$

Summing the expressions for  $n_e$  and  $n_b$  from the previous part (including the factor of two for bound pairs), gives

$$n_c = n_e(z_c) + 2n_b(z_c) = \frac{2}{\lambda^3} \left[ f_{3/2}^-(y^{-1/2}) + 2^{3/2} \zeta_{3/2} \right].$$

(c) Give the expression for pressure  $P$  in the condensed phase ( $n > n_c$ ).

• Throughout the condensate phase,  $z = z_c$ . As the condensed fraction exerts no pressure, the net pressure is the sum of contributions from free electrons  $\beta P_e = 2f_{5/2}^-(z_c)/\lambda^3$ , and bound (non-condensate) electrons  $\beta P_b = 2^{3/2} f_{5/2}^+(1)/\lambda^3$ , leading to

$$P = \frac{1}{\beta \lambda^3} \left[ 2f_{5/2}^-(y^{-1/2}) + 2^{3/2} \zeta_{5/2} \right].$$

(d) Find the dimensionless ratio  $(\beta P_c/n_c)$  at the *onset of condensation*. Evaluate its limiting values for  $\beta\epsilon \rightarrow \infty$  and  $\beta\epsilon \rightarrow 0$ .

• Dividing expressions obtained in the previous parts gives

$$\frac{\beta P_c}{n_c} = \frac{2f_{5/2}^-(y^{-1/2}) + 2^{3/2}\zeta_{5/2}}{2f_{3/2}^-(y^{-1/2}) + 2^{5/2}\zeta_{3/2}} = \frac{f_{5/2}^-(y^{-1/2}) + 2^{1/2}\zeta_{5/2}}{f_{3/2}^-(y^{-1/2}) + 2^{3/2}\zeta_{3/2}}.$$

In the limit of  $\beta\epsilon \rightarrow \infty$ ,  $y^{-1/2} \rightarrow 0$ , and since  $f_m^-(0) = 0$ , we find

$$\frac{\beta P_c}{n_c} = \frac{\zeta_{5/2}}{\zeta_{3/2}}.$$

In the limit of  $\beta\epsilon \rightarrow 0$ ,  $y^{-1/2} \rightarrow 1$ , and since  $f_m^-(1) = (1 - 2^{1-m})\zeta_m$ , we find

$$\frac{\beta P_c}{n_c} = \frac{\zeta_{5/2}}{\zeta_{3/2}} \cdot \frac{1 - 2^{-3/2} + 2^{1/2}}{1 - 2^{-1/2} + 2^{3/2}} = \frac{\zeta_{5/2}}{\zeta_{3/2}} \cdot \frac{3 + 2\sqrt{2}}{6 + 2\sqrt{2}}.$$

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**2. Bose condensation in  $d$ -dimensions:** Consider a gas of non-interacting (spinless) bosons with single particle energies  $\epsilon = p^2/2m$ , 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  $\int V d^d k / (2\pi)^d = [V S_d / (2\pi)^d] \int k^{d-1} dk$ , where  $S_d = 2\pi^{d/2} / (d/2 - 1)!$ , leads to

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

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

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

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.*

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

(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, noting the behavior for  $T > T_c(n)$ .

- The heat capacity at high temperatures takes the form

$$C_V = \frac{d}{2} k_B \frac{V}{\lambda^d} \left[ \left( \frac{d}{2} + 1 \right) f_{\frac{d}{2}+1}^+(z) + \frac{T}{z} \left. \frac{dz}{dT} \right|_V f_{\frac{d}{2}}^+(z) \right].$$

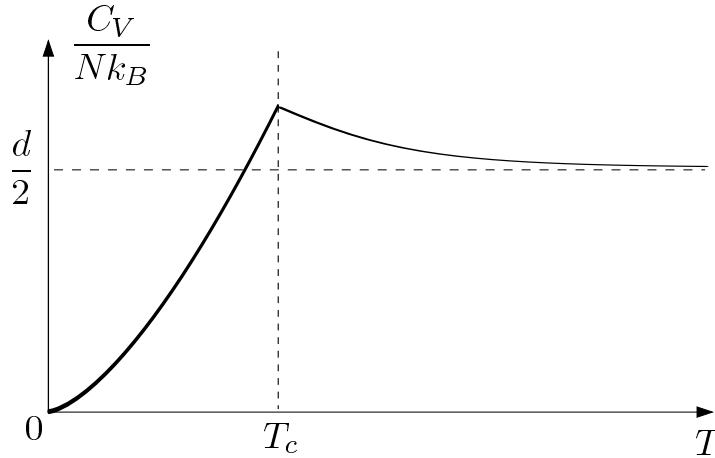
At constant volume (and hence density), taking the derivative of the expression for  $n$  gives

$$0 = \left. \frac{dn}{dT} \right|_V = \frac{1}{\lambda^d} \left[ \frac{d}{2T} f_{\frac{d}{2}}^+(z) + \frac{1}{z} \left. \frac{dz}{dT} \right|_V f_{\frac{d}{2}-1}^+(z) \right].$$

Inserting the result for  $dz/dT$  in the expression for  $C_V$  yields

$$C_V = \frac{d}{2} k_B \frac{V}{\lambda^d} \left[ \left( \frac{d}{2} + 1 \right) f_{\frac{d}{2}+1}^+(z) - \frac{d f_{\frac{d}{2}}^+(z)^2}{2 f_{\frac{d}{2}-1}^+(z)} \right].$$

In dimensions  $d \leq 4$ , the second term on the right hand side vanishes as  $z \rightarrow 1$ . The result then matches the heat capacity for  $T < T_c(n)$ , and there is no discontinuity as in the figure below.



For  $d > 4$ , there will be a discontinuity in the heat capacity curve.

(f) Find the ratio,  $C_{\max}/C(T \rightarrow \infty)$ , of the maximum heat capacity to its classical limit for  $d \leq 4$ , 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  $d = 3$ .

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**3. Neutron star core:** The core of neutron stars is proposed to consist of a new phase of QCD matter, composed of 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) 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

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

- (b) 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  $\lambda = h / \sqrt{2\pi M k_B T}$ .

(c) 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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**4. Attractive shell potential:** Consider a gas of particles in three dimensions interacting through a pair-wise central potential,  $\mathcal{V}(r)$ , where

$$\mathcal{V}(r) = \begin{cases} +\infty & \text{for } 0 < r < a, \\ -\varepsilon & \text{for } a < r < b, \\ 0 & \text{for } b < r < \infty. \end{cases}$$

(a) Calculate the second virial coefficient  $B_2(T)$ .

- The second virial coefficient is obtained from

$$B_2 \equiv -\frac{1}{2} \int d^3 r_{12} \{ \exp[-\beta \mathcal{V}(r_{12})] - 1 \},$$

where  $r_{12} \equiv |\vec{r}_1 - \vec{r}_2|$ , as

$$\begin{aligned}
B_2 &= -\frac{1}{2} \left[ \int_0^a d^3 r_{12} (-1) + \int_a^b d^3 r_{12} (e^{\beta \varepsilon} - 1) \right] \\
&= -\frac{1}{2} \{ V_3(a)(-1) + [V_3(b) - V_3(a)] \cdot [\exp(\beta \varepsilon) - 1] \},
\end{aligned}$$

where

$$V_3(r) = \frac{4\pi}{3} r^3 ,$$

is the volume of a 3-dimensional sphere of radius  $r$ . Thus,

$$B_2(T) = \frac{1}{2} V_3(b) - \frac{1}{2} \exp(\beta\varepsilon) [V_3(b) - V_3(a)] = \frac{2\pi}{3} [b^3 - (b^3 - a^3)e^{\beta\varepsilon}] .$$

(b) Find the limiting behavior of  $B_2(T)$  at high temperature (including the first correction to order of  $\beta$ ), and comment on the low temperature behavior of  $B_2(T)$ .

- For high temperatures  $\exp(\beta\varepsilon) \approx 1 + \beta\varepsilon$ , and

$$B_2(T) \approx \frac{1}{2} V_3(a) - \frac{\beta\varepsilon}{2} [V_3(b) - V_3(a)] = \frac{2\pi}{3} [a^3 - \beta\varepsilon(b^3 - a^3)] .$$

At the highest temperatures,  $\beta\varepsilon \ll 1$ , the hard-core part of the potential is dominant, and

$$B_2(T) \approx \frac{1}{2} V_3(a) = \frac{2\pi}{3} a^3 .$$

For low temperatures  $\beta \gg 1$ , the attractive component takes over, and

$$\begin{aligned} B_2 &= -\frac{1}{2} \{V_3(a)(-1) + [V_3(b) - V_3(a)] \cdot [\exp(\beta\varepsilon) - 1]\} \\ &\approx -\frac{1}{2} [V_3(b) - V_3(a)] \exp(\beta\varepsilon) = -\frac{2\pi}{3} (b^3 - a^3) e^{\beta\varepsilon} , \end{aligned}$$

resulting in  $B_2 < 0$ .

(c) Calculate the first correction to isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{T,N} .$$

- The isothermal compressibility is defined by

$$\kappa_T \equiv -\frac{1}{V} \frac{\partial V}{\partial P} T, N .$$

From the expansion

$$\frac{P}{k_B T} = \frac{N}{V} + \frac{N^2}{V^2} B_2 ,$$

for constant temperature and particle number, we get

$$\frac{1}{k_B T} dP = -\frac{N}{V^2} dV - 2B_2 \frac{N^2}{V^3} dV .$$



Thus

$$\frac{\partial V}{\partial P} T, N = -\frac{1}{k_B T} \frac{1}{N/V^2 + 2B_2 N^2/V^3} = -\frac{V^2}{Nk_B T} \left( \frac{1}{1 + 2B_2 N/V} \right),$$

and

$$\kappa_T = \frac{V}{Nk_B T} \left( \frac{1}{1 + 2B_2 N/V} \right) \approx \frac{V}{Nk_B T} \left( 1 - 2B_2 \frac{N}{V} \right).$$

(d) In the high temperature limit, reorganize the equation of state into the van der Waals form, and identify the van der Waals parameters.

• Including the correction introduced by the second virial coefficient, the equation of state becomes

$$\frac{PV}{Nk_B T} = 1 + \frac{N}{V} B_2(T).$$

Using the expression for  $B_2$  in the high temperature limit,

$$\frac{PV}{Nk_B T} = 1 + \frac{N}{2V} \{V_3(a) - \beta \varepsilon [V_3(b) - V_3(a)]\},$$

and

$$P + \frac{N^2}{2V^2} \varepsilon [V_3(b) - V_3(a)] = k_B T \frac{N}{V} \left( 1 + \frac{N}{2V} V_3(a) \right).$$

Using the variable  $n = N/V$ , and noting that for low concentrations

$$1 + \frac{n}{2} V_3(a) \approx \left( 1 - \frac{n}{2} V_3(a) \right)^{-1} = V \left( V - \frac{N}{2} V_3(a) \right)^{-1},$$

the equation of state becomes

$$\left( P + \frac{n^2 \varepsilon}{2} [V_3(b) - V_3(a)] \right) \cdot \left( V - \frac{N}{2} V_3(a) \right) = Nk_B T.$$

This can be recast in the usual van der Waals form

$$(P + an^2) \cdot (V - Nb) = Nk_B T,$$

with

$$a = \frac{\varepsilon}{2} [V_3(b) - V_3(a)] = \frac{2\pi}{3} (b^3 - a^3) \varepsilon,$$

and

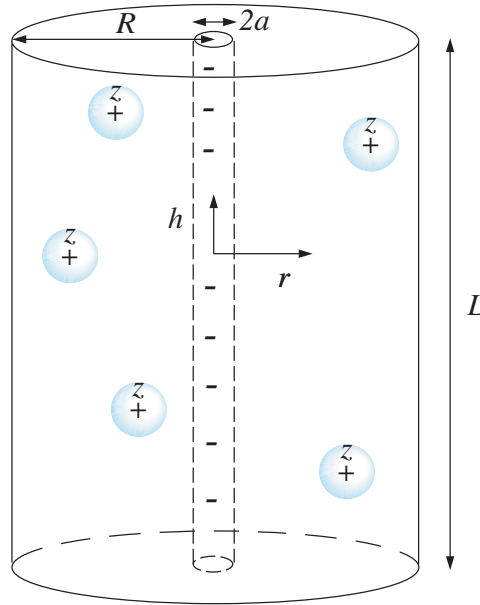
$$b = \frac{1}{2} V_3(a) = \frac{2\pi}{3} a^3.$$

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1. *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 in the figure below. While thermal fluctuations favor ions wandering in the solvent, electrostatic attractions prefer their return and condensation on the polymer. If the number of counter-ions is  $N$ , they interact with the  $N$  positive charges left behind on the rod through the potential  $\phi(r) = -2(Ne/L) \ln(r/a)$ , 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

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

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.*

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

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## 2. Bardeen–Schrieffer–Cooper (BCS) superconductor:

(a) Electrons in a good conductor can be approximated as spin 1/2 fermions with momentum  $\vec{p} = \hbar \vec{k}$  and energy  $\varepsilon(\vec{k}) = \hbar^2 k^2 / (2m)$ , with  $k = |\vec{k}|$ . Find the fermi momentum and energy,  $k_F$  and  $\varepsilon_F$  respectively, as a function of density  $n = N/V$ .

- All states of the Fermi sea with  $|\vec{k}| \leq k_F$ , forming a sphere are occupied. Equating the number of these states to  $N$  gives

$$N = g \sum_{\vec{k}} 1 = 2 \left( \frac{4\pi}{3} k_F^3 \right) \frac{V}{(2\pi)^3} = \frac{V}{3\pi^2} K_F^3, \Rightarrow k_F = (3\pi^2 n)^{1/3} \quad \text{and} \quad \varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}.$$

(b) In a superconductor, induced effective interactions bind electrons of opposite spins and momentum into “Cooper pairs.” Elementary excitations of the superconducting ground state are again fermions with degeneracy  $g = 2$ , whose energy can be approximated by

$$\varepsilon_x(\vec{k}) = \sqrt{\Delta^2 + \left( \frac{\hbar^2 k^2}{2m} - \varepsilon_F \right)^2},$$

where  $\Delta$  is the ‘superconducting energy gap.’ Expand  $\varepsilon_x(\vec{k})$  to lowest order in  $(k - k_F)$ , and use this expansion in the rest of the problem.

- Since  $\Delta$  is the largest term within the square root, we find

$$\varepsilon_x(\vec{k}) = \Delta \sqrt{1 + \frac{1}{\Delta^2} \left( \frac{\hbar^2 k^2}{2m} - \varepsilon_F \right)^2} \approx \Delta + \frac{1}{2\Delta} \left( \frac{\hbar^2 k^2}{2m} - \varepsilon_F \right)^2.$$

Using  $\varepsilon_F = \hbar^2 k_F^2 / (2m)$  and  $(k^2 - k_F^2) = (k + k_F)(k - k_F) \approx 2k_F(k - k_F)$  to lowest order, we find

$$\varepsilon_x(\vec{k}) \approx \Delta + \frac{\hbar^2}{m} \frac{\varepsilon_F}{\Delta} (k - k_F)^2.$$

(c) As long as the total number of excitations,  $N_x$ , is less than the total number of electrons,  $N$ , the constraint on the total number of excitations can be ignored, treating them as a gas of particles with  $\mu = 0$ . Check this condition’s self-consistently by writing the expression for  $N_x(T)$ , assuming  $\mu = 0$  and  $k_B T \ll \Delta$ , and evaluating the expression using the saddle-point approximation. Express your result in the form

$$N_x(T) = N \left( \frac{k_B T}{\varepsilon_F} \right)^\alpha \left( \frac{\Delta}{\varepsilon_F} \right)^\beta f \left( \frac{k_B T}{\Delta} \right),$$

in terms of a function  $f(x)$  and exponents  $\alpha$  and  $\beta$  that you compute.

- Using fermionic occupation numbers with  $\mu = 0$ , we have

$$N_x(T) = g \sum_{\vec{k}} \frac{1}{e^{\beta \varepsilon_x(\vec{k})} + 1} \approx 2V \int \frac{d^3 k}{(2\pi)^3} e^{-\beta \varepsilon_x(\vec{k})},$$

where the last approximation relies on the small occupation numbers resulting from  $\beta \varepsilon_x(\vec{k}) \geq \beta \Delta \gg 1$ . Since the integrand depends only on  $|\vec{k}|$ , we can further use  $d^3 k = 4\pi k^2 dk$  to get

$$N_x(T) \approx \frac{V}{\pi^2} \int_0^\infty k^2 dk e^{-\beta \left[ \Delta + \frac{\hbar^2}{m} \frac{\varepsilon_F}{\Delta} (k - k_F)^2 \right]}.$$

The maximum of the integrand occurs for  $k = k_F$ , and the Gaussian factor in the integrand admits a range of values of  $k$  in the vicinity of  $k_F$ , with variance  $(\delta k)^2 = k_B T \frac{m \Delta}{4 \hbar^2 \varepsilon_F} \ll k_F^2$ . A saddle point evaluation of the integral thus yields

$$N_x(T) \approx \frac{V}{\pi^2} k_F^2 e^{-\frac{\Delta}{k_B T}} \sqrt{2\pi k_B T \frac{m \Delta}{4 \hbar^2 \varepsilon_F}}.$$

Setting  $V = N/n$  and using  $n = k_F^3/(3\pi^2)$ , we find

$$N_x(T) = \frac{3N}{k_F} \sqrt{\frac{2mk_BT}{\hbar^2}} \frac{\sqrt{\pi}}{2} \sqrt{\frac{\Delta}{\varepsilon_F}} e^{-\frac{\Delta}{k_BT}}.$$

Taking  $k_F$  inside the square root, the result can be rearranged as

$$N_x(T) = N \left( \frac{k_BT}{\varepsilon_F} \right)^{1/2} \left( \frac{\Delta}{\varepsilon_F} \right)^{1/2} \left[ \frac{3\sqrt{\pi}}{2} e^{-\frac{\Delta}{k_BT}} \right].$$

(d) Within the above approximation write an expression for the total excitation energy  $E_x(T)$  of the superconductor at temperature  $T$ , and evaluate this expression for  $\varepsilon_F \gg \Delta \gg k_BT$  using the saddle point approximation.

- Using fermionic occupation numbers with  $\mu = 0$ , we have

$$E_x(T) = g \sum_{\vec{k}} \frac{\varepsilon_x(\vec{k})}{e^{\beta\varepsilon_x(\vec{k})} + 1} \approx 2V \int \frac{d^3k}{(2\pi)^3} \varepsilon_x(\vec{k}) e^{-\beta\varepsilon_x(\vec{k})},$$

where the last approximation relies on the small occupation numbers resulting from  $\beta\varepsilon_x(\vec{k}) \gg 1$ . Since the integrand depends only on  $|\vec{k}|$ , we can further use  $d^3k = 4\pi k^2 dk$  to get

$$E_x(T) \approx \frac{V}{\pi^2} \int_0^\infty k^2 dk \left[ \Delta + \frac{\hbar^2}{m} \frac{\varepsilon_F}{\Delta} (k - k_F)^2 \right] e^{-\beta \left[ \Delta + \frac{\hbar^2}{m} \frac{\varepsilon_F}{\Delta} (k - k_F)^2 \right]}.$$

The maximum of the integrand occurs for  $k = k_F$ , and the Gaussian factor in the integrand admits a range of values of  $k$  in the vicinity of  $k_F$ , with  $(\delta k)^2 = k_BT \frac{m\Delta}{4\hbar^2\varepsilon_F} \ll k_F^2$ . A saddle point evaluation of the integral thus yields

$$E_x(T) \approx \frac{V}{\pi^2} k_F^2 \Delta e^{-\frac{\Delta}{k_BT}} \sqrt{2\pi k_BT \frac{m\Delta}{4\hbar^2\varepsilon_F}}.$$

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**3. Density matrices:** Consider non-interacting quantum particles with single particle energies  $\varepsilon(\vec{k}) = \hbar^2 k^2/(2m)$  in a box of volume  $V$  and temperature  $T$ , with  $V \gg \lambda^3$ .

(a) For *one particle* compute the canonical density matrix  $\langle \vec{x} | \rho_1 | \vec{x}' \rangle$  in position coordinates.

- Transforming to the  $\vec{k}$ -basis where energy is diagonal, we find

$$\langle \vec{x} | \rho_1 | \vec{x}' \rangle = \sum_{\vec{k}} \langle \vec{x} | \vec{k} \rangle \frac{e^{-\beta \frac{\hbar^2 k^2}{2m}}}{Z_1} \langle \vec{k} | \vec{x}' \rangle = \frac{V}{V Z_1} \int \frac{d^3k}{(2\pi)^3} \exp \left[ i \vec{k} \cdot (\vec{x} - \vec{x}') - \beta \frac{\hbar^2 k^2}{2m} \right].$$

Performing the Gaussian integration yields

$$\langle \vec{x} | \rho_1 | \vec{x}' \rangle = \frac{1}{Z_1 \lambda^3} \exp \left[ -\frac{\pi}{\lambda^2} (\vec{x} - \vec{x}')^2 \right], \quad \text{with} \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

Finally, the requirement  $\text{tr} \rho_1 = \int d^3 x \langle \vec{x} | \rho_1 | \vec{x} \rangle = 1$ , sets  $Z_1 = V/\lambda^3$ , and hence

$$\langle \vec{x} | \rho_1 | \vec{x}' \rangle = \frac{1}{V} \exp \left[ -\frac{\pi}{\lambda^2} (\vec{x} - \vec{x}')^2 \right].$$

(b) For two *distinguishable particles* with the same single particle energies as above, what is the corresponding two particle density matrix  $\langle \vec{x}_1, \vec{x}_2 | \rho_2^D | \vec{x}_1', \vec{x}_2' \rangle$ .

- Quantum states of distinguishable particles are simple products of one-particles states, and computations similar to above can be carried out independently for each particle. This leads to a two particle density that is the product of one-particle densities, i.e.

$$\langle \vec{x}_1, \vec{x}_2 | \rho_2^D | \vec{x}_1', \vec{x}_2' \rangle = \langle \vec{x}_1 | \rho_1 | \vec{x}_1' \rangle \langle \vec{x}_2 | \rho_1 | \vec{x}_2' \rangle = \frac{1}{V^2} \exp \left[ -\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_1')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_2')^2 \right].$$

(c) For two *bosons* with the same single particle energies as above, what is the corresponding two particle density matrix  $\langle \vec{x}_1, \vec{x}_2 | \rho_2^B | \vec{x}_1', \vec{x}_2' \rangle$ .

- The two particle states for bosons can be constructed by symmetrization as  $|\vec{k}_1, \vec{k}_2\rangle_+ = (|\vec{k}_1\rangle |\vec{k}_2\rangle + |\vec{k}_2\rangle |\vec{k}_1\rangle) / \sqrt{2}$  (with appropriate change of normalization if  $\vec{k}_1 = \vec{k}_2$ ). In terms of these states, the density matrix takes the form

$$\langle \vec{x}_1, \vec{x}_2 | \rho_2^B | \vec{x}_1', \vec{x}_2' \rangle = \sum_{\vec{k}_1, \vec{k}_2} \langle \vec{x}_1, \vec{x}_2 | \vec{k}_1, \vec{k}_2 \rangle_+ \frac{e^{-\beta \frac{\hbar^2 (\vec{k}_1^2 + \vec{k}_2^2)}{2m}}}{Z_2} \langle \vec{k}_1, \vec{k}_2 | \vec{x}_1', \vec{x}_2' \rangle_+,$$

where the sum is restricted to one pair of distinct  $\vec{k}_1 \neq \vec{k}_2$ , with appropriate modification if  $\vec{k}_1 = \vec{k}_2$ . The restriction can be removed in the continuum limit of large volume by setting  $\sum'_{\vec{k}_1, \vec{k}_2} = \frac{V^2}{2} \int \frac{d^3 k_1 d^3 k_2}{(2\pi)^6}$ . While it appears that the contribution from  $\vec{k}_1 = \vec{k}_2$  is not properly accounted for, in fact the resulting error is of the order of  $(\lambda^3/V)$ , and can be ignored in the large volume limit. The product of symmetrized states yields 4 terms which simplify to

$$\begin{aligned} \langle \vec{x}_1, \vec{x}_2 | \rho_2^B | \vec{x}_1', \vec{x}_2' \rangle &= \frac{1}{2Z_2} \int \frac{d^3 k_1 d^3 k_2}{(2\pi)^6} e^{-\beta \frac{\hbar^2 (\vec{k}_1^2 + \vec{k}_2^2)}{2m}} \times \\ &\quad \left[ e^{i\vec{k}_1 \cdot (\vec{x}_1 - \vec{x}_1') + i\vec{k}_2 \cdot (\vec{x}_2 - \vec{x}_2')} + e^{i\vec{k}_1 \cdot (\vec{x}_1 - \vec{x}_2') + i\vec{k}_2 \cdot (\vec{x}_2 - \vec{x}_1')} \right] \\ &= \frac{1}{2Z_2 \lambda^6} \left[ e^{-\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_1')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_2')^2} + e^{-\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_2')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_1')^2} \right] \\ &= \frac{1}{V^2} \left[ e^{-\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_1')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_2')^2} + e^{-\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_2')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_1')^2} \right]. \end{aligned}$$

(The final expression is obtained by noting that  $Z_2 = (V/\lambda^3)^2/2 + \mathcal{O}(V/\lambda^3)$ .)

(d) What is the probability density function,  $p(\vec{x}_1 - \vec{x}_2)$  for the relative position of two bosons.

- The diagonal elements of the density matrix provide the probability density as

$$p(\vec{x}_1, \vec{x}_2) = \langle \vec{x}_1, \vec{x}_2 | \rho_2^B | \vec{x}_1, \vec{x}_2 \rangle = \frac{1}{V^2} \left[ 1 + \exp \left( -\frac{2\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_2)^2 \right) \right].$$

Integrating over the center of mass, yields the probability density function for the relative position of two bosons as

$$p(\vec{x}_1 - \vec{x}_2) = \frac{1}{V} \left[ 1 + \exp \left( -\frac{2\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_2)^2 \right) \right].$$

The normalization factor is actually larger than  $V$  by order of  $\lambda^3$  which is negligible.

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**4. Ortho/para-hydrogen:** Hydrogen molecules can exist in ortho and para states.

(a) The two nuclei (protons) of  $H_2$  in para-hydrogen form a singlet (antisymmetric) state. The orbital angular momentum can thus only take even values; i.e.

$$\mathcal{H}_p = \frac{\hbar^2}{2I} \ell(\ell + 1),$$

where  $\ell = 0, 2, 4, \dots$ . Calculate the rotational partition function of para-hydrogen, and evaluate its low and high temperature limits.

- Since there are  $2\ell + 1$  states for each  $\ell$ ,

$$Z_p = \sum_{\ell : \text{even}} (2\ell + 1) e^{-\beta \hbar^2 \ell(\ell+1)/2I} = \sum_{n=0}^{\infty} (4n + 1) e^{-\beta \hbar^2 n(2n+1)/I}.$$

In the low temperature limit, only the first few terms matter, and to leading order

$$Z_p \approx 1 + 5e^{-3\beta \hbar^2/I}.$$

In the high temperature limit,

$$\begin{aligned} Z_p &= \sum_{n=0}^{\infty} (4n + 1) e^{-\beta \hbar^2 n(2n+1)/I} \approx \frac{I}{\beta \hbar^2} \sum_{n=0}^{\infty} e^{-2 \left( \sqrt{\frac{\beta}{I}} \hbar n \right)^2} 4 \left( \sqrt{\frac{\beta}{I}} \hbar n \right) \left( \sqrt{\frac{\beta}{I}} \hbar \right) \\ &= \frac{I}{\beta \hbar^2} \int_0^{\infty} 4x e^{-2x^2} dx = \frac{I}{\beta \hbar^2}. \end{aligned}$$



(b) In ortho-hydrogen the protons are in a triply degenerate symmetric state, hence

$$\mathcal{H}_o = \frac{\hbar^2}{2I} \ell(\ell+1),$$

with  $\ell = 1, 3, 5, \dots$ . Calculate the rotational partition function of ortho-hydrogen, and evaluate its low and high temperature limits.

- Since there are  $2\ell + 1$  states for each  $\ell$ , and a 3-fold degeneracy in the spin state,

$$Z_o = 3 \sum_{\ell : \text{odd}} (2\ell + 1) e^{-\beta \hbar^2 \ell(\ell+1)/2I} = 3 \sum_{n=0}^{\infty} (4n + 3) e^{-\beta \hbar^2 (n+1)(2n+1)/I}.$$

In the low temperature limit, only the first few terms matter, and to leading order

$$Z_o \approx 9e^{-\beta \hbar^2/I}.$$

In the high temperature limit,

$$\begin{aligned} Z_o &= \sum_{n=0}^{\infty} (4n + 3) e^{-\beta \hbar^2 (n+1)(2n+1)/I} \approx \frac{3I}{\beta \hbar^2} \sum_{n=0}^{\infty} e^{-2 \left( \sqrt{\frac{\beta}{I}} \hbar n \right)^2} 4 \left( \sqrt{\frac{\beta}{I}} \hbar n \right) \left( \sqrt{\frac{\beta}{I}} \hbar \right) \\ &= \frac{3I}{\beta \hbar^2} \int_0^{\infty} 4x e^{-2x^2} dx = \frac{3I}{\beta \hbar^2}. \end{aligned}$$

(c) For an equilibrium gas of  $N$  hydrogen molecules calculate the partition function.

(Hint: Sum over contributions from mixtures of  $N_p$  para- and  $N_o = N - N_p$  ortho-hydrogen particles. Ignore vibrational degrees of freedom.)

•

$$Z = \sum_{N_p} \frac{1}{(N - N_p)! N_p!} Z_p^{N_p} Z_o^{N - N_p} = \frac{1}{N!} (Z_o + Z_p)^N,$$

which is what we should expect.

(d) Write down the expression for the rotational contribution to the internal energy  $\langle E_{\text{rot.}} \rangle$ , and comment on its low and high temperature limits.

•

$$\langle E_{\text{rot}} \rangle = -\frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial \ln(Z_o + Z_p)}{\partial \beta}.$$

In the low energy limit,

$$Z_o + Z_p \approx 1 + 9e^{-\beta \hbar^2/I},$$

giving up to leading order,

$$\langle E_{\text{rot}} \rangle \approx \frac{9N\hbar^2}{I} e^{-\beta \hbar^2/I}.$$

In the high energy limit,

$$Z_0 + Z_p \approx \frac{4I}{\beta \hbar^2},$$

giving,

$$\langle E_{rot} \rangle \approx Nk_B T,$$

which is what we expect since we have 2 rotational degrees of freedom.

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1. *Atomic/molecular hydrogen:* A container of volume  $V$  at temperature  $T$  contains  $N$  atoms of hydrogen, some forming hydrogen molecules. The gas is sufficiently dilute that interactions and quantum degeneracies can be ignored.

(a) The Hamiltonian for  $N_1$  hydrogen atoms is

$$H_a = \sum_{i=1}^{N_1} \frac{p_i^2}{2m}.$$

Calculate the partition function  $Z_a(N_1, T, V)$ .

- Using standard results for classical particles,

$$Z_a(N_1, T, V) = \frac{1}{N_1!} \left( \frac{V}{\lambda_a^3} \right)^{N_1}, \quad \text{with} \quad \lambda_a = \frac{h}{\sqrt{2\pi m k_B T}}.$$

(b) The Hamiltonian for  $N_2 = (N - N_1)/2$  hydrogen molecules is

$$H_m = \sum_{i=1}^{N_2} \left[ \frac{p_i^2}{4m} + \frac{L_i^2}{2I} - \epsilon \right],$$

where  $\epsilon$  is the energy gained on forming a molecule, the mass of the molecule is twice the atomic mass, and  $I$  is its moment of inertia. It is assumed that the temperature is such that the vibrational levels of the molecule are frozen, while the rotational levels are fully excited and can be treated classically. Calculate the partition function  $Z_m(N_2, T, V)$ .

- There is now an additional contribution to the single particle partition function due to the rotational degrees of freedom, given by

$$Z_{\text{rot.}} = \int \frac{d^2\Omega d^2L}{h^2} e^{-\beta L^2/2I} = \frac{4\pi}{h^2} \left( \sqrt{2\pi I k_B T} \right)^2.$$

Including the binding energy per molecule, the partition function of the  $N_2$  molecules is given by

$$Z_m(N_2, T, V) = \frac{1}{N_2!} \left[ \left( \frac{V}{\lambda_m^3} \right) \left( \frac{8\pi^2 I k_B T}{h^2} \right) e^{\beta\epsilon} \right]^{N_2}, \quad \text{with} \quad \lambda_m = \frac{h}{\sqrt{4\pi m k_B T}}.$$

(c) Find the ratio  $n_m/n_a^2$ , where  $n_a = N_a/V$  and  $n_m = N_m/V$  are the densities of atomic and molecular hydrogen in equilibrium.

- The partition function for the mixture of atomic and molecular gases is obtained as

$$Z(N, T, V) = \sum_{N_2=1}^{N/2} Z_a(N - 2N_2, T, V) Z_m(N_2, T, V).$$

The largest term in the sum is obtained from the condition

$$\frac{\partial \ln Z_m}{\partial N_2} = 2 \frac{\partial \ln Z_a}{\partial N_1}.$$

With the standard simplifications for large  $N$ , the above equality yields

$$\ln \left[ \left( \frac{V}{N_2 \lambda_m^3} \right) \left( \frac{8\pi^2 I k_B T}{h^2} \right) e^{\beta \epsilon} \right] = 2 \ln \left[ \left( \frac{V}{N_1 \lambda_a^3} \right) \right].$$

Rearranging the above expression yields

$$\frac{n_m}{n_a^2} = \left( \frac{N_2}{V} \right) \left( \frac{V}{N_1} \right)^2 = \left( \frac{\lambda_m^3}{\lambda_a^6} \right) \left( \frac{h^2}{8\pi^2 I k_B T} \right) e^{-\beta \epsilon}.$$

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**2. Graphene** is a single sheet of carbon atoms bonded into a *two dimensional* hexagonal lattice. 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

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

There is spin degeneracy of  $g = 2$ , and  $v \approx 10^6 \text{ms}^{-1}$ .

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

- 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  $f_3^-(1) = 3\zeta_3/4$ .

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

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

• The heat capacity can now be evaluated as

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

(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

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

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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**3. Fermionic density matrices:** Consider non-interacting *spin-1/2 fermions* with single particle Hamiltonians

$$H_1 = \frac{p^2}{2m} \mathbb{1} - \mu_B B \sigma_z,$$

describing 1-particle energies  $\varepsilon(\vec{k}, s) = \hbar^2 k^2 / (2m) - \mu_B B s$ , with spin index  $s = \pm 1$ . The particles are in a box of volume  $V$  and temperature  $T$ , with  $V \gg \lambda^3$ .

(a) For *one particle* compute the canonical density matrix  $\langle (\vec{x}, s) | \rho_1 | (\vec{x}', s') \rangle$  in position basis, with  $s, s' = \pm 1$  indicating the particle spin.

- Since the Hamiltonian is diagonal in the spin degrees of freedom, so is the density matrix. Transforming from coordinates to the  $\vec{k}$ -basis where energy is diagonal, we find

$$\begin{aligned} \langle (\vec{x}, s) | \rho_1 | (\vec{x}', s') \rangle &= \delta_{ss'} \sum_{\vec{k}} \langle \vec{x} | \vec{k} \rangle \frac{e^{-\beta \frac{\hbar^2 k^2}{2m} + \beta \mu_B B s}}{Z_1} \langle \vec{k} | \vec{x}' \rangle \\ &= \frac{V \delta_{ss'}}{V Z_1} \int \frac{d^3 k}{(2\pi)^3} \exp \left[ i \vec{k} \cdot (\vec{x} - \vec{x}') - \beta \frac{\hbar^2 k^2}{2m} + \beta \mu_B B s \right]. \end{aligned}$$

Performing the Gaussian integration yields

$$\langle (\vec{x}, s) | \rho_1 | (\vec{x}', s') \rangle = \frac{\delta_{s,s'}}{Z_1 \lambda^3} \exp \left[ -\frac{\pi}{\lambda^2} (\vec{x} - \vec{x}')^2 + \beta \mu_B B s \right], \quad \text{with} \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

Finally, the requirement  $\text{tr } \rho_1 = \sum_s \int d^3x \langle (\vec{x}, s) | \rho_1 | (\vec{x}, s) \rangle = 1$ , sets

$$Z_1 = \frac{V}{\lambda^3} (e^{+\beta\mu_B B} + e^{-\beta\mu_B B}),$$

and hence

$$\langle (\vec{x}, s) | \rho_1 | (\vec{x}', s') \rangle = \frac{\delta_{s,s'} e^{\beta\mu_B B s}}{V (e^{+\beta\mu_B B} + e^{-\beta\mu_B B})} \exp \left[ -\frac{\pi}{\lambda^2} (\vec{x} - \vec{x}')^2 \right].$$

(b) Now consider the limit of strong magnetic field, so that only the  $s = +1$  spin state is allowed. For two such fermions find the two particle density matrix  $\langle \vec{x}_1, \vec{x}_2 | \rho_2 | \vec{x}_1', \vec{x}_2' \rangle$ .

- Single both particles have the same spin (a symmetric product), the appropriate two particle states for fermions can be constructed by anti-symmetrizing the momentum component of the state as  $|\vec{k}_1, \vec{k}_2\rangle_- = (|\vec{k}_1\rangle |\vec{k}_2\rangle - |\vec{k}_2\rangle |\vec{k}_1\rangle) / \sqrt{2}$  (with  $\vec{k}_1 \neq \vec{k}_2$ ). In terms of these states, the density matrix takes the form

$$\langle \vec{x}_1, \vec{x}_2 | \rho_2 | \vec{x}_1', \vec{x}_2' \rangle = \sum'_{\vec{k}_1, \vec{k}_2} \langle \vec{x}_1, \vec{x}_2 | \vec{k}_1, \vec{k}_2 \rangle_- \frac{e^{-\beta \frac{\hbar^2(k_1^2 + k_2^2)}{2m} + 2\beta\mu_B B}}{Z_2} \langle \vec{k}_1, \vec{k}_2 | \vec{x}_1', \vec{x}_2' \rangle_- ,$$

where the sum is restricted to one pair of distinct  $\vec{k}_1 \neq \vec{k}_2$ . The restriction can be removed in the continuum limit of large volume by setting  $\sum'_{\vec{k}_1, \vec{k}_2} = \frac{V^2}{2} \int \frac{d^3k_1 d^3k_2}{(2\pi)^6}$ . While it appears that a contribution from  $\vec{k}_1 = \vec{k}_2$  is incorrectly added, in fact the resulting error is of the order of  $(\lambda^3/V)$ , and can be ignored in the large volume limit. The product of symmetrized states yields 4 terms which simplify to

$$\begin{aligned} \langle \vec{x}_1, \vec{x}_2 | \rho_2 | \vec{x}_1', \vec{x}_2' \rangle &= \frac{1}{2Z_2} \int \frac{d^3k_1 d^3k_2}{(2\pi)^6} e^{-\beta \frac{\hbar^2(k_1^2 + k_2^2)}{2m} + 2\beta\mu_B B} \times \\ &\quad \left[ e^{i\vec{k}_1 \cdot (\vec{x}_1 - \vec{x}_1') + i\vec{k}_2 \cdot (\vec{x}_2 - \vec{x}_2')} - e^{i\vec{k}_1 \cdot (\vec{x}_1 - \vec{x}_2') + i\vec{k}_2 \cdot (\vec{x}_2 - \vec{x}_1')} \right] \\ &= \frac{e^{+2\beta\mu_B B}}{2Z_2 \lambda^6} \left[ e^{-\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_1')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_2')^2} - e^{-\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_2')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_1')^2} \right] \\ &= \frac{1}{V^2} \left[ e^{-\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_1')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_2')^2} - e^{-\frac{\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_2')^2 - \frac{\pi}{\lambda^2} (\vec{x}_2 - \vec{x}_1')^2} \right]. \end{aligned}$$

(The final expression is obtained by noting that  $Z_2 = e^{+2\beta\mu_B B} (V/\lambda^3)^2 / 2 + \mathcal{O}(V/\lambda^3)$ .)

(c) What is the probability density function,  $p(\vec{x}_1 - \vec{x}_2)$  for the relative position of two fermions at high magnetic fields.

- The diagonal elements of the density matrix provide the probability density as

$$p(\vec{x}_1, \vec{x}_2) = \langle \vec{x}_1, \vec{x}_2 | \rho_2 | \vec{x}_1, \vec{x}_2 \rangle = \frac{1}{V^2} \left[ 1 - \exp \left( -\frac{2\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_2)^2 \right) \right].$$

Integrating over the center of mass, yields the probability density function for the relative position of two bosons as

$$p(\vec{x}_1 - \vec{x}_2) = \frac{1}{V} \left[ 1 - \exp \left( -\frac{2\pi}{\lambda^2} (\vec{x}_1 - \vec{x}_2)^2 \right) \right] .$$

The normalization factor is actually larger than  $V$  by order of  $\lambda^3$  which is negligible.

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**4. Anharmonic trap:** A collection of *non-interacting identical* particles is placed in an *anharmonic* trap, with one-particle Hamiltonian

$$H_1 = \frac{p^2}{2m} + Kr^n ,$$

where  $r$  is the radial distance (in 3 dimensions) from the center of the trap.

(a) Show that the one particle density of state can be written as  $\rho(\varepsilon) = \frac{C}{(p-1)!} \varepsilon^{p-1}$ , where  $p = 3/2 + 3/n$  and  $C$  is an amplitude *that you do not need to evaluate*.

- The surface of constant one particle energy  $\varepsilon$  is a convex shape in the six-dimensional phase space that extends to  $p_{max} = (2m\varepsilon)^{1/2}$  in the momentum direction, and  $r_{max} = (\varepsilon/K)^{1/n}$  in the radial coordinate. The volume of this shape in 6 dimensions is  $\Omega(\varepsilon) = g(p_{max}r_{max})^3$ , where  $g$  is a dimensionless constant. Thus  $\Omega(\varepsilon) \propto \varepsilon^p$  with  $p = 3(1/2 + 1/n)$ . The density of space is then obtained from  $\rho(\varepsilon) = d\Omega/d\varepsilon$ , and can be written as  $\rho(\varepsilon) = \frac{C}{(p-1)!} \varepsilon^{p-1}$  with  $C = gp!(2m)^{3/2}K^{-3/n}$ .

(b) At high densities, quantization of one particle energy levels,  $\{\varepsilon_j\}$ , can be ignored, such that in a grand canonical ensemble at temperature  $T = (k_B\beta)^{-1}$  and chemical potential  $\mu$ , the number of particles is given by

$$N = \sum_j \frac{1}{e^{\beta(\varepsilon_j - \mu)} - \eta} = \int_0^\infty d\varepsilon \rho(\varepsilon) \frac{1}{e^{\beta(\varepsilon - \mu)} - \eta} ,$$

with  $\eta = +1(-1)$  for bosons (fermions). Give the expression for  $N$  in terms of the functions  $f_m^\eta(z)$  with  $z = e^{\beta\mu}$ .

- 

$$N = \int_0^\infty d\varepsilon \frac{C\varepsilon^{p-1}}{(p-1)!} \frac{1}{e^{\beta(\varepsilon - \mu)} - \eta} .$$

Changing variables to  $x = \beta\varepsilon$  (i.e. setting  $\varepsilon = k_B T x$ ) gives

$$N = C(k_B T)^p \int_0^\infty \frac{dx}{(p-1)!} \frac{x^{p-1}}{z^{-1}e^x - \eta} = C(k_B T)^p f_p^\eta(z) .$$



(c) Obtain the corresponding expression for the total energy  $E$  of the system.

•

$$E = \sum_n \frac{\varepsilon_n}{e^{\beta(\varepsilon_n - \mu)} - \eta} = \int_0^\infty d\varepsilon \rho(\varepsilon) \frac{\varepsilon}{e^{\beta(\varepsilon - \mu)} - \eta} = \int_0^\infty d\varepsilon \frac{C \varepsilon^{p-1}}{(p-1)!} \frac{\varepsilon}{e^{\beta(\varepsilon - \mu)} - \eta}.$$

Setting  $\varepsilon = k_B T x$  now results in

$$E = C(k_B T)^{p+1} \int_0^\infty \frac{dx}{(p-1)!} \frac{x^p}{z^{-1} e^x - \eta} = p C(k_B T)^{p+1} f_{p+1}^\eta(z).$$

(d) For bosons find the expression for the heat capacity  $C$  close to zero temperature.

• Since  $p > 1$ , the Bose gas will undergo Bose-Einstein condensation at some temperature  $T_c$ , such that  $z = 1$  close to zero temperature. The expression for energy thus simplifies to  $E = p C(k_B T)^{p+1} \zeta_{p+1}$ , where  $\zeta_{p+1}$  is the zeta-function at  $(p+1)$ . The heat capacity is then obtained as

$$C = \frac{dE}{dT} = k_B p(p+1) C(k_B T)^p \zeta_{p+1}.$$

(e) For a gas of  $N$  fermions, find the Fermi energy  $E_F = \lim_{T \rightarrow 0} \mu$ .

• Using the Sommerfeld expansion, we find

$$N = C(k_B T)^p \frac{(\ln z)^p}{p!} \left[ 1 + \frac{\pi^2}{6} \frac{p(p+1)}{\ln^2 z} + \dots \right].$$

The leading asymptotic term leads to

$$E_F = \lim_{T \rightarrow 0} (k_B T \ln z) = \left( \frac{p! N}{C} \right)^{1/p}.$$

(f) *Without explicit calculation* state the behavior of heat capacity for this Fermi gas at temperatures  $T \ll E_F/k_B$ .

• For  $T \ll E_F/k_B$  only particles within a distance  $k_B T$  of the Fermi energy are excited. As the excited fraction is  $k_B T/E_F$ , (up to a proportionality constant) the heat capacity behaves as

$$C \propto k_B N \frac{k_B T}{E_F}.$$

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1. *Molecular oxygen* has a net magnetic spin,  $\vec{S}$ , of unity, i.e.  $S^z$  is quantized to -1, 0, or +1. The Hamiltonian for an ideal gas of  $N$  such molecules in a magnetic field  $\vec{B} \parallel \hat{z}$  is

$$\mathcal{H} = \sum_{i=1}^N \left[ \frac{\vec{p}_i^2}{2m} - \mu B S_i^z \right],$$

where  $\{\vec{p}_i\}$  are the center of mass momenta of the molecules. The corresponding coordinates  $\{\vec{q}_i\}$  are confined to a volume  $V$ . (Ignore all other degrees of freedom.)

(a) Treating  $\{\vec{p}_i, \vec{q}_i\}$  classically, but the spin degrees of freedom as quantized, calculate the Gibbs partition function,  $\mathcal{Z}(T, N, V, B)$ .

•

$$\mathcal{Z} = \sum_{\mu_s} e^{-\beta \mathcal{H}(\mu_s)} = \sum_{\mu_s} e^{-\beta \sum (\vec{p}_i^2/2m - \mu B S_i^z)} = \frac{1}{N!} \left( \frac{V}{\lambda^3} (e^{\beta \mu B} + 1 + e^{-\beta \mu B}) \right)^N,$$

where,

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

(b) What are the probabilities for  $S_i^z$  of a specific molecule to take on values of -1, 0, +1 at a temperature  $T$ ?

• The probabilities for  $S_i^z$  of a given molecule to take values -1, 0, +1, are,

$$\frac{e^{-\beta \mu B}}{2 \cosh \beta \mu B + 1}, \quad \frac{1}{2 \cosh \beta \mu B + 1}, \quad \frac{e^{\beta \mu B}}{2 \cosh \beta \mu B + 1},$$

respectively.

(c) Find the average magnetic dipole moment,  $\langle M \rangle / V$ , where  $M = \mu \sum_{i=1}^N S_i^z$ .

•

$$\begin{aligned} \langle M \rangle &= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial B} = \frac{1}{\beta} \frac{\partial N \ln(2 \cosh \beta \mu B + 1)}{\partial B} \\ &= N \mu \left( \frac{2 \sinh \beta \mu B}{2 \cosh \beta \mu B + 1} \right). \end{aligned}$$

(d) Calculate the zero field susceptibility  $\chi = \partial \langle M \rangle / \partial B|_{B=0}$ .

•

$$\chi = N \beta \mu^2 \left. \frac{2 \cosh \beta \mu B (2 \cosh \beta \mu B + 1) - 4 \sinh \beta \mu B \sinh \beta \mu B}{(2 \cosh \beta \mu B + 1)^2} \right|_{B=0} = \frac{2}{3} N \beta \mu^2.$$

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**2. 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* at low temperatures 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) 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 (monolayer) 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

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

As  $T \rightarrow 0$ , the heat capacity will be dominated by electrons, as ultimately their linear contribution is greater than the quadratic one coming from phonons.

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**3. 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

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

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  $E = 3PV$ .

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**4. Continuum with trap:** Consider an ideal spin-less ( $g = 1$ ) Bose gas of  $N$  particles in a box of volume  $V$  in three dimensions. In addition to the continuum of one particle states of energy  $\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$ , there is a single one particle (trap) state of negative energy  $E_t = -\Delta < 0$ .

(a) In a grand canonical ensemble of temperature  $T = 1/(k_B\beta)$  and chemical potential  $\mu$ , what are the occupation numbers  $\langle N_t \rangle$  of the trap state, and the total occupation number  $\langle N_{\times} \rangle$  of *all* excited (continuum) states? (You don't need to derive the results if you know the answers.)

- Using the standard results for Bose occupation numbers, we have

$$\langle N_t \rangle = \frac{1}{e^{-\beta(\mu+\Delta)} - 1},$$

and (since  $g = 1$ )

$$\langle N_{\times} \rangle = \frac{V}{\lambda^3} f_{3/2}^+(z),$$

with  $z = e^{\beta\mu}$  and  $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ .

(b) What is the limiting value of  $\mu$  at low temperatures.

- For Bosons, the chemical potential cannot exceed the lowest energy level, and hence  $\mu \leq -\Delta$ .

(c) Find the critical density  $n_c(T)$  for Bose-Einstein condensation, and give its asymptotic form close to zero temperature.

- Bose-Einstein condensation occurs when net occupation of the continuum states is less than the total number of particles. At this point, the trap state with  $\mu = -\Delta$  accommodates a macroscopic fraction of particles. The limiting density thus corresponds to

$$n_c(T) = \frac{N}{V} = \frac{1}{\lambda^3} f_{3/2}^+(e^{-\beta\Delta}).$$

As  $T \rightarrow 0$ , the argument of  $f_{3/2}^+$  vanishes, and using  $f_{3/2}^+(z) \approx z$ , we obtain

$$\lim_{T \rightarrow 0} n_c(T) = \frac{(2\pi m k_B T)^{3/2}}{h^3} \exp\left(-\frac{\Delta}{k_B T}\right).$$

(d) Give the expression for pressure  $P(T)$  in the Bose condensed phase, and provide its asymptotic form close to zero temperature.

- The pressure comes entirely from the continuum states, and we can thus use the usual results for pressure of an ideal Bose gas, but setting the chemical potential to its limiting value. Hence,

$$P(T) = \frac{k_B T}{\lambda^3} f_{5/2}^+(e^{-\beta\Delta}).$$

As  $T \rightarrow 0$ , the argument of  $f_{5/2}^+$  vanishes, and using  $f_{5/2}^+(z) \approx z$ , we obtain

$$\lim_{T \rightarrow 0} P(T) = k_B T \frac{(2\pi m k_B T)^{3/2}}{h^3} \exp\left(-\frac{\Delta}{k_B T}\right).$$

(e) Give the expression for Energy  $E(T)$  in the Bose condensed phase.

- The energy has two contributions: One from the continuum states for which we can use the standard result for an ideal Bose gas after setting the chemical potential to its limiting value, as

$$E_{\times}(T) = \frac{3}{2}PV = \frac{3Vk_B T}{2\lambda^3} f_{5/2}^+(e^{-\beta\Delta}).$$

The second contribution is from particles in the trap state, as  $E_t = -\Delta N_t$ . The number of particles in the trap state is simply the number not in the continuum states, i.e.  $N_t(T) = N - \langle N_{\times} \rangle$ , leading to

$$E_t(T) = -\Delta N_t = -\Delta(N - \langle N_{\times} \rangle) = -\Delta \left[ N - \frac{V}{\lambda^3} f_{3/2}^+(e^{-\beta\Delta}) \right].$$

The total energy is thus

$$E(T) = E_t(T) + E_{\times}(T) = -\Delta N + \frac{V}{\lambda^3} \left[ \frac{3k_B T}{2} f_{5/2}^+(e^{-\beta\Delta}) + \Delta f_{3/2}^+(e^{-\beta\Delta}) \right].$$

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1. *Quantum rotor:* A rotor in two dimensions is described by conjugate coordinates  $(\theta, L)$ , with Hamiltonian  $\mathcal{H} = L^2/2I$  ( $I$  is the moment of inertia). The quantized values of energy, and corresponding eigenstates (noting  $\psi(\theta) = \psi(\theta + 2\pi)$ ) are given by

$$\langle \theta | n \rangle = \frac{1}{\sqrt{2\pi}} \exp(in\theta), \quad E_n = \frac{\hbar^2 n^2}{2I}, \quad \text{with } n = 0, \pm 1, \pm 2, \dots$$

(a) Calculate the classical (1-particle) partition function,  $Z_1^c$  at temperature  $T = (k_B\beta)^{-1}$ .

•

$$Z_1^c = \frac{1}{h} \int_0^{2\pi} d\theta \int_{-\infty}^{\infty} dL e^{-\beta L^2/2I} = \frac{\sqrt{2\pi I k_B T}}{h}.$$

(b) Write the expression for the corresponding quantum partition function,  $Z_1^q$ , and evaluate its high temperature limit, as well as its low temperature limit to the lowest non-trivial order.

•

$$Z_1^q = \sum_{n=-\infty}^{\infty} e^{-\beta \hbar^2 n^2 / 2I}.$$

The high temperature limit is obtained by replacing the sum with an integral and leads to

$$\lim_{\beta \rightarrow 0} Z_1^q \approx \int_{-\infty}^{\infty} dn e^{-\beta \hbar^2 n^2 / 2I} = \frac{\sqrt{2\pi I k_B T}}{h},$$

coinciding with the classical result. The low temperature limit, to the leading non-trivial order, is given by

$$\lim_{\beta \rightarrow \infty} Z_1^q = 1 + 2e^{-\beta \hbar^2 / 2I} + \dots$$

(c) Write the expression for the density matrix  $\langle \theta' | \rho_1 | \theta \rangle$  at temperature  $T$ , and evaluate its high temperature limit, and its low temperature limit to the lowest non-trivial order.

• The density matrix in the canonical ensemble is given by

$$\rho_1 = \frac{1}{Z_1^q} \sum_n |n\rangle e^{-\beta \hbar^2 n^2 / 2I} \langle n|,$$

which in angular basis becomes

$$\langle \theta' | \rho | \theta \rangle = \frac{1}{2\pi} \frac{\sum_n e^{in(\theta - \theta')} e^{-\beta \hbar^2 n^2 / 2I}}{\sum_n e^{-\beta \hbar^2 n^2 / 2I}}.$$

In the high temperature limit ( $\hbar^2\beta/2I \ll 1$ ), by taking  $x = n\sqrt{\hbar^2\beta/2I}$  we may write,

$$\begin{aligned}\sum_n e^{-\beta\hbar^2 n^2/2I} &\rightarrow \sqrt{\frac{2I}{\hbar^2\beta}} \int dx e^{-x^2}, \\ \sum_n e^{in(\theta-\theta')} e^{-\beta\hbar^2 n^2/2I} &\rightarrow \sqrt{\frac{2I}{\hbar^2\beta}} \int dx e^{-x^2} e^{i\sqrt{\frac{2I}{\hbar^2\beta}}(\theta-\theta')x} \\ &= \sqrt{\frac{2I}{\hbar^2\beta}} e^{-I(\theta-\theta')^2/2\beta\hbar^2} \int dx e^{-x^2},\end{aligned}$$

and thus,

$$\langle\theta'|\rho_1|\theta\rangle \approx \frac{1}{2\pi} e^{-\frac{I(\theta-\theta')^2}{2\beta\hbar^2}}.$$

Note that this expression is valid as long as  $(\theta - \theta') \sim \sqrt{\hbar^2\beta/2I} \ll 1$ , since this is our scale of coarse graining. That's why the  $\rho$  matrix element for  $\theta - \theta' = 2\pi$  is different from that for  $\theta - \theta' = 0$  in this approximation; it simply doesn't apply for  $\Delta\theta \sim 1$ .

At low temperatures ( $\hbar^2\beta/2I \gg 1$ ) the ground state dominates, since  $e^{-\beta\hbar^2/2I} \ll 1$ . The leading non-trivial order contributions come from states with  $n = \pm 1$ , resulting in

$$\langle\theta'|\rho_1|\theta\rangle \approx \frac{1}{2\pi} \frac{[1 + 2e^{-2\hbar^2/2I} \cos(\theta - \theta') + \dots]}{[1 + 2e^{-2\hbar^2/2I} + \dots]} \approx \frac{1}{2\pi} \left[ 1 - 4e^{-2\hbar^2/2I} \sin^2 \frac{\theta - \theta'}{2} + \dots \right].$$

(d) Now consider  $n$  non-interacting identical (boson or fermion) rotor particles. Without doing detailed calculation, indicate the condition on  $n$  and  $T$  for relevance of quantum degeneracy.

- The high temperature limit of the density matrix indicates a characteristic angular scale  $\phi = \hbar/\sqrt{Ik_B T}$  over which off-diagonal (quantum) correlations are present. The typical angular scale for  $n$  particles is  $2\pi/n$ . It is thus expected that quantum degeneracy becomes relevant for

$$n \frac{\hbar}{\sqrt{Ik_B T}} \geq 2\pi.$$

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

(a) In the solid phase, the  $\text{He}^3$  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  $\text{He}^3$  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) How does the heat capacity of liquid  $\text{He}^3$  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

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

(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

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

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.)

(d) 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

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

(e) It is known experimentally that solid helium is denser than the liquid. Use this information to *qualitatively* account for the observed sign of  $(dP/dT)_{\text{melting}}$  at low temperatures (less than the Fermi temperature).

- 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

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

Using the values,  $T = 0.1 \text{ K}$ ,  $T_F = 9.2 \text{ J K}$ , 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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**3. Quantum entropy:** Consider a grand canonical ensemble of non-interacting identical particles (bosons or fermions) with chemical potential  $\mu$ . The one-particle states are labelled by index  $k$ , and have energies  $\mathcal{E}_k$ .

(a) Give the expression for  $\ln \mathcal{Q}_\eta$ , where  $\mathcal{Q}_\eta$  is the grand partition function, with  $\eta = -$  for fermions and  $\eta = +$  for bosons.

- 

$$\ln \mathcal{Q}_\eta = -\eta \sum_k \ln \left(1 - \eta z e^{-\beta \mathcal{E}_k}\right), \quad \text{with } z = e^{\beta \mu}.$$

(b) What is the joint probability  $P_\eta(\{n_k\})$ , of finding a set of occupation numbers  $\{n_k\}$ , of the one-particle states?

- In the grand canonical ensemble with chemical potential  $\mu$ , the joint probability of finding a set of occupation numbers  $\{n_k\}$ , for one-particle states of energies  $\mathcal{E}_k$  is given by

$$P_\eta(\{n_k\}) = \frac{1}{\mathcal{Q}_\eta} \prod_k \exp[\beta(\mu - \mathcal{E}_k)n_k],$$

with  $n_k = 0$  or  $1$  for fermions, and any integer for bosons.

(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  $P_{\eta}(\{n_k\})$  for occupation numbers in terms of the total particle number  $N$  and energy  $E$ , as well as  $\ln \mathcal{Q}_{\eta}$ .

- Using the general formula for the entropy of a probability distribution, we obtain

$$\frac{S}{k_B} = -\langle \ln [P_{\eta}(\{n_k\})] \rangle = \ln \mathcal{Q}_{\eta} - \sum_k \beta(\mu - \mathcal{E}_k) \langle n_k \rangle .$$

Noting  $N = \sum_k \langle n_k \rangle$ , and  $E = \sum_k \mathcal{E}_k \langle n_k \rangle$ , we arrive at

$$\frac{S}{k_B} = \ln \mathcal{Q}_{\eta} - \beta \mu N + \beta E ,$$

which is equivalent to

$$\ln \mathcal{Q}_{\eta} = -\beta(E - TS - \mu N) = -\beta \mathcal{G} .$$

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**4. Degenerate absorbed gas:** A dilute gas of density  $n_3$  and temperature  $T$  is in contact with an absorbing surface. Each particle gains an energy  $\epsilon$  upon absorption, but can then freely move on the surface. While the three dimensional gas is sufficiently dilute to be non-degenerate, the two dimensional gas of density  $n_2$  may be quantum-degenerate.

(a) Given that the particles have mass  $m$  and spin degeneracy of  $g$ , find the chemical potential  $\mu_3(T, n_3)$  of the dilute (non-degenerate) gas.

- For a non-degenerate gas

$$\frac{n_3 \lambda^3}{g} = f_{3/2}^{\eta}(z_3) \approx z_3 = e^{\beta \mu_3}, \quad \text{where} \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}} .$$

The gas chemical potential is thus given by

$$\mu_3 = k_B T \ln \left( \frac{n_3 \lambda^3}{g} \right) .$$

(b) Treating the absorbed particles as a *two dimensional* ideal quantum gas, find an expression for the chemical potential  $\mu_2^\eta(T, n_2)$ , for bosons ( $\eta = +$ ) or fermions ( $\eta = -$ ). Note that  $f_1^\eta(z) = -\eta \ln(1 - \eta z)$ .

- For the two-dimensional gas

$$\frac{n_2 \lambda^2}{g} = f_1^\eta(z_2) = -\eta \ln(1 - \eta z_2).$$

Solving for  $z_2$ , we find

$$z_2 = \eta \left[ 1 - \exp \left( -\eta \frac{n_2 \lambda^2}{g} \right) \right],$$

and hence

$$\mu_2 = k_B T \ln \left\{ \eta \left[ 1 - \exp \left( -\eta \frac{n_2 \lambda^2}{g} \right) \right] \right\}.$$

(c) For weak absorption,  $\beta\epsilon \sim \mathcal{O}(1)$ , find  $n_2$  as a function of  $n_3$  and other relevant parameters.

- The chemical potentials are related by

$$z_3 e^{\beta\epsilon} = z_2.$$

In the weak absorption limit both  $z_2$  and  $z_3$  are small, and

$$\frac{n_3 \lambda^3}{g} e^{\beta\epsilon} = \frac{n_2 \lambda^2}{g},$$

and hence

$$n_2 = n_3 \lambda e^{\beta\epsilon}.$$

(d) If the particles are *fermions*, and  $\beta\epsilon \gg 1$ , find the expression for  $n_2$ .

- For the fermi gas, the relation between chemical potentials gives

$$\frac{n_3 \lambda^3}{g} e^{\beta\epsilon} = z_2 = -1 + \exp \left( +\frac{n_2 \lambda^2}{g} \right).$$

The strong absorption leads to a degenerate fermi gas on the surface, and thus

$$\frac{n_2 \lambda^2}{g} \approx \beta\epsilon + \ln \left( \frac{n_3 \lambda^3}{g} \right).$$

(e) If the particles are *bosons*, find the density  $n_3^*$  above which we can no longer treat the absorbed film as an ideal gas of non-interacting particles.

- The chemical potential  $z_2$  can not be greater than unity. Thus the relationship  $z_3 e^{\beta\epsilon} = z_2$  will be invalid for densities

$$n_3 > n_3^*(T) = \frac{g}{\lambda^3} e^{-\beta\epsilon}.$$

If the density is increased beyond this value the additional particles will condense onto the film resulting in unrealistically high densities for the absorbed film.

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