

**Problem 1. Non-equilibrium entropies of Fermi, Bose, and Boltzmann distributions** Consider a gas out of equilibrium with a slightly non-uniform density in  $n(x)$  and mean density  $\bar{n} = V^{-1} \int n(x) d^3x$ . We know that if the gas obeys Boltzmann statistics, its entropy is  $S = - \int n \log n dV$ .

**1.1** Argue that this formula is valid only if the gradients are small:  $|\nabla_x n| \ll \bar{n}^{4/3}$  (“coarse-graining condition”) and that  $|n(x) - \bar{n}| \ll \bar{n}$ .

**1.2** Remove the second condition in 1.1 and obtain the general formula for the entropy for both Fermi and Bose gases.

**Problem 2. Quantum correction to the Boltzmann thermodynamics** Find the quantum correction to the free energy of the Boltzmann gas (the leading  $\hbar$ -dependent term in the expansion of the free energy at small  $\hbar$ ) for Bose and Fermi gases. From there, find the correction to the pressure. Does the quantum correction increase or decrease the pressure (and why is the answer predictable)?

**Problem 3. Degenerate Fermi gas** Consider a Fermi gas in 1, 2, and 3 spatial dimensions with density  $\bar{n} = N/V$ .

**3.1** First, set the temperature to zero ( $T = 0$ ) and find the Fermi momentum, Fermi energy, and the total energy in all three cases as a function of density.

**Solution.** The particles in a completely degenerate Fermi gas ( $T = 0$ ) are distributed among the lowest energy states, which correspond to the lowest momentum states. These states have momentum less than or equal to the Fermi momentum  $p_0$ .

The number of quantum states in the interval  $(p, p + dp)$  is, in each case [?, p. 152],

$$\frac{gL}{2\pi\hbar} dp \quad (d=1), \quad \frac{2\pi gA}{(2\pi\hbar)^2} p dp \quad (d=2), \quad \frac{4\pi gV}{(2\pi\hbar)^3} p^2 dp \quad (d=3), \quad (1)$$

where  $g = 2s + 1$  with  $s$  being the spin of the particle, and  $L$ ,  $A$ , and  $V$  indicate the volume in 1, 2, and 3 spatial dimensions.

Let  $N$  be the number of particles occupying these states, which is found by integrating these quantities from  $p = 0$  to  $p = p_0$ . For each case,

$$\begin{aligned} (d=1) \quad N &= \frac{gL}{2\pi\hbar} \int_0^{p_0} dp = \frac{gL}{2\pi\hbar} \left[ p \right]_0^{p_0} = \frac{gLp_0}{2\pi\hbar}, \\ (d=2) \quad N &= \frac{2\pi gA}{(2\pi\hbar)^2} \int_0^{p_0} p dp = \frac{2\pi gA}{(2\pi\hbar)^2} \left[ \frac{p^2}{2} \right]_0^{p_0} = \frac{gAp_0^2}{4\pi\hbar^2}, \\ (d=3) \quad N &= \frac{4\pi gV}{(2\pi\hbar)^3} \int_0^{p_0} p^2 dp = \frac{4\pi gV}{(2\pi\hbar)^3} \left[ \frac{p^3}{3} \right]_0^{p_0} = \frac{gVp_0^3}{6\pi^2\hbar^3}. \end{aligned}$$

Solving each case for  $p_0$ , we find

$$\begin{aligned} (d=1) \quad p_0 &= \frac{2\pi\hbar N}{gL} = \frac{2\pi\hbar\bar{n}}{g}, \\ (d=2) \quad p_0 &= \sqrt{\frac{4\pi\hbar^2 N}{gA}} = 2\hbar\sqrt{\frac{\pi\bar{n}}{g}}, \\ (d=3) \quad p_0 &= \left( \frac{6\pi^2\hbar^3 N}{gV} \right)^{1/3} = \hbar \left( \frac{6\pi^2\bar{n}}{g} \right)^{1/3}. \end{aligned} \quad (2)$$

The Fermi energy is found by  $\epsilon_0 = p_0^2/2m$  in all cases [?, p. 152]. Thus, we have

$$\begin{aligned} (d=1) \quad \epsilon_0 &= \frac{1}{2m} \left( \frac{2\pi\hbar\bar{n}}{g} \right)^2 = \frac{2\pi^2\hbar^2\bar{n}^2}{mg^2}, \\ (d=2) \quad \epsilon_0 &= \frac{1}{2m} \left( 2\hbar\sqrt{\frac{\pi\bar{n}}{g}} \right)^2 = \frac{2\pi\hbar^2\bar{n}}{mg}, \\ (d=3) \quad \epsilon_0 &= \frac{1}{2m} \left[ \hbar \left( \frac{6\pi^2\bar{n}}{g} \right)^{1/3} \right]^2 = \frac{\hbar^2}{2m} \left( \frac{6\pi^2\bar{n}}{g} \right)^{2/3}. \end{aligned} \quad (3)$$

The total energy of the gas is found by multiplying Eq. (1) by  $\epsilon = p^2/m$  and integrating from  $p = 0$  to  $p = p_0$  [? , p. 153]. This gives us

$$(d = 1) \quad E = \frac{g}{2m} \frac{L}{2\pi\hbar} \int_0^{p_0} p^2 dp = \frac{g}{2m} \frac{L}{2\pi\hbar} \left[ \frac{p^3}{3} \right]_0^{p_0} = \frac{g}{6m} \frac{L}{2\pi\hbar} \left( \frac{2\pi\hbar\bar{n}}{g} \right)^3 = \frac{(2\pi\hbar)^2 L}{6mg^2} \bar{n}^3 = \frac{2\pi^2 \hbar^2 N \bar{n}^2}{3mg^2},$$

$$(d = 2) \quad E = \frac{g}{2m} \frac{2\pi A}{(2\pi\hbar)^2} \int_0^{p_0} p^3 dp = \frac{g}{2m} \frac{2\pi A}{(2\pi\hbar)^2} \left[ \frac{p^4}{4} \right]_0^{p_0} = \frac{g}{8m} \frac{2\pi A}{(2\pi\hbar)^2} \left( 2\pi\hbar \sqrt{\frac{\bar{n}}{\pi g}} \right)^4 = \frac{(2\pi\hbar)^2 A}{4\pi mg} \bar{n}^2 \\ = \frac{\pi \hbar^2 N \bar{n}}{mg},$$

$$(d = 3) \quad E = \frac{g}{2m} \frac{4\pi V}{(2\pi\hbar)^3} \int_0^{p_0} p^4 dp = \frac{g}{2m} \frac{4\pi V}{(2\pi\hbar)^3} \left[ \frac{p^5}{5} \right]_0^{p_0} = \frac{g}{10m} \frac{4\pi V}{(2\pi\hbar)^3} \left[ 2\pi\hbar \left( \frac{3\bar{n}}{4\pi g} \right)^{1/3} \right]^5 \\ = \frac{4\pi (2\pi\hbar)^2 g V}{10m} \left( \frac{3\bar{n}}{4\pi g} \right)^{5/3} = \frac{3\hbar^2}{10m} \left( \frac{6\pi^2 \bar{n}}{g} \right)^{2/3},$$

where we have used Eq. (2).

**3.2** Then compute the leading terms of the small temperature corrections to the basic thermodynamic quantities: thermodynamic potential, free energy, energy, pressure, entropy, and specific heat.

**Solution.** The thermodynamic potential for a Fermi gas is [? , p. 145]

$$\Omega = -T \sum_k \ln \left( 1 + e^{(\mu - \epsilon_k)/T} \right),$$

where  $\mu$  is the chemical potential of the gas. We may replace the sum by an integral from  $p = 0$  to  $\infty$  using Eq. (1), transform variables to  $\epsilon$ , and integrate by parts [? , pp. 148–149]. Note that

$$\epsilon = \frac{p^2}{2m} \quad \implies \quad 2m d\epsilon = 2p dp \quad \implies \quad dp = \frac{m}{p} d\epsilon = \frac{m}{\sqrt{2m\epsilon}} d\epsilon = \sqrt{\frac{m}{2\epsilon}} d\epsilon.$$

Then in each case, we find

$$\begin{aligned}
 (d=1) \quad \Omega &= -gT \frac{L}{2\pi\hbar} \int_0^\infty \ln(1 + e^{(\mu-\epsilon)/T}) d\epsilon = -gT \sqrt{\frac{m}{2}} \frac{L}{2\pi\hbar} \int_0^\infty \frac{1}{\sqrt{\epsilon}} \ln(1 + e^{(\mu-\epsilon)/T}) d\epsilon \\
 &= -gT \sqrt{\frac{m}{2}} \frac{L}{2\pi\hbar} \left( \left[ 2\sqrt{\epsilon} \ln(1 + e^{(\mu-\epsilon)/T}) \right]_0^\infty + \frac{2}{T} \int_0^\infty \frac{\sqrt{\epsilon}}{1 + e^{(\epsilon-\mu)/T}} d\epsilon \right) \\
 &= -g\sqrt{2m} \frac{L}{2\pi\hbar} \int_0^\infty \frac{\sqrt{\epsilon}}{1 + e^{(\epsilon-\mu)/T}} d\epsilon,
 \end{aligned}$$

$$\begin{aligned}
 (d=2) \quad \Omega &= -gT \frac{2\pi A}{(2\pi\hbar)^2} \int_0^\infty p \ln(1 + e^{(\mu-\epsilon)/T}) d\epsilon = -gTm \frac{2\pi A}{(2\pi\hbar)^2} \int_0^\infty \ln(1 + e^{(\mu-\epsilon)/T}) d\epsilon \\
 &= -gTm \frac{2\pi A}{(2\pi\hbar)^2} \left( \left[ \epsilon \ln(1 + e^{(\mu-\epsilon)/T}) \right]_0^\infty + \frac{1}{T} \int_0^\infty \frac{\epsilon}{1 + e^{(\epsilon-\mu)/T}} d\epsilon \right) \\
 &= -gm \frac{2\pi A}{(2\pi\hbar)^2} \int_0^\infty \frac{\epsilon}{1 + e^{(\epsilon-\mu)/T}} d\epsilon,
 \end{aligned}$$

$$\begin{aligned}
 (d=3) \quad \Omega &= -gT \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty p^2 \ln(1 + e^{(\mu-\epsilon)/T}) d\epsilon = -gT\sqrt{2m^3} \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty \sqrt{\epsilon} \ln(1 + e^{(\mu-\epsilon)/T}) d\epsilon \\
 &= -gT\sqrt{2m^3} \frac{4\pi V}{(2\pi\hbar)^3} \left( \left[ \frac{2}{3} \epsilon^{3/2} \ln(1 + e^{(\mu-\epsilon)/T}) \right]_0^\infty + \frac{2}{3T} \int_0^\infty \frac{\epsilon^{3/2}}{1 + e^{(\epsilon-\mu)/T}} d\epsilon \right) \\
 &= -g\sqrt{2m^3} \frac{8\pi V}{3(2\pi\hbar)^3} \int_0^\infty \frac{\epsilon^{3/2}}{1 + e^{(\epsilon-\mu)/T}} d\epsilon,
 \end{aligned}$$

where we have used

$$\frac{d}{d\epsilon} \left( \ln(1 + e^{(\mu-\epsilon)/T}) \right) = -\frac{1}{T} \frac{e^{(\mu-\epsilon)/T}}{1 + e^{(\mu-\epsilon)/T}} = -\frac{1}{T} \frac{1}{1 + e^{(\epsilon-\mu)/T}}.$$

All three expressions have integrals of the form

$$I = \int_0^\infty \frac{f(\epsilon)}{1 + e^{(\epsilon-\mu)/T}} d\epsilon = T \int_{-\mu/T}^\infty \frac{f(\mu + Tz)}{1 + e^z} dz,$$

where we have made the substitution  $\epsilon - \mu = Tz$ . The first two terms of the Taylor series for this integral are given by [?, p. 155]

$$I \approx \int_0^\mu f(\epsilon) d\epsilon + \frac{\pi^2 T^2}{6} f'(\mu).$$

Thus, the leading term of the correction is given by the second term.

Let  $\Omega_0$  be the thermodynamic potential at  $T = 0$ . Then the leading corrections are given by

$$(d=1) \quad \Omega = \Omega_0 - g\sqrt{2m} \frac{L}{2\pi\hbar} \frac{\pi^2 T^2}{6} \frac{\partial}{\partial \mu} (\sqrt{\mu}) = \Omega_0 - \frac{\pi^2}{12} \sqrt{\frac{2m}{\mu}} \frac{gNT^2}{(2\pi\hbar)\bar{n}} = \Omega_0 - \frac{\pi gNT^2}{6\hbar\bar{n}} \sqrt{\frac{2m}{\mu}},$$

$$(d=2) \quad \Omega = \Omega_0 - gm \frac{2\pi A}{(2\pi\hbar)^2} \frac{\pi^2 T^2}{6} \frac{\partial \mu}{\partial \mu} = \Omega_0 - \frac{\pi^3}{3} \frac{mgNT^2}{(2\pi\hbar)^2 \bar{n}} = \Omega_0 - \frac{\pi mgNT^2}{12\hbar^2 \bar{n}},$$

$$(d=3) \quad \Omega = \Omega_0 - g\sqrt{2m^3} \frac{8\pi V}{3(2\pi\hbar)^3} \frac{\pi^2 T^2}{6} \frac{\partial}{\partial \mu} (\mu^{3/2}) = \Omega_0 - g\sqrt{2m^3} \mu \frac{2\pi^3 NT^2}{3(2\pi\hbar)^3 \bar{n}} = \Omega_0 - \frac{gNT^2}{12\hbar^3 \bar{n}} \sqrt{2m^3 \mu}.$$

For the free energy, we will use the relation  $(\delta F)_{T,V,N} = (\delta \Omega)_{T,V,\mu}$  [?, pp. 69, 156]. In order to express the correction to  $\Omega$  in terms of  $T$ ,  $V$ , and  $N$  only, we will make the approximation  $\mu = \epsilon_0$ , which is exact at  $T = 0$  [?

, p. 153]. Applying Eq. (3) and letting  $F_0$  denote the free energy at  $T = 0$ , we have

$$(d = 1) \quad F = F_0 - \frac{\pi g N T^2}{6 \hbar \bar{n}} \sqrt{2 m^3 \frac{m g^2}{2 \pi^2 \hbar^2 \bar{n}^2}} = F_0 - \frac{\pi g N T^2}{6 \hbar \bar{n}} \frac{m^2 g}{\pi \hbar \bar{n}} = F_0 - \frac{m^2 g^2 N T^2}{6 \pi \hbar^2 \bar{n}^2},$$

$$(d = 2) \quad F = F_0 - \frac{\pi m g N T^2}{12 \hbar^2 \bar{n}},$$

$$(d = 3) \quad F = F_0 - \frac{g N T^2}{12 \hbar^3 \bar{n}} \sqrt{2 m^3 \frac{\hbar^2}{2 m} \left( \frac{6 \pi^2 \bar{n}}{g} \right)^{2/3}} = F_0 - \frac{g N T^2}{12 \hbar^3 \bar{n}} m \hbar \left( \frac{6 \pi^2 \bar{n}}{g} \right)^{1/3} = F_0 - \frac{m N T^2}{2 \hbar^2} \left( \frac{\pi g}{6 \bar{n}} \right)^{2/3}.$$

Energy may be calculated from free energy by  $E = -T^2(\partial(F/T)/\partial T)_V$  [?, p. 47]. This gives us

$$(d = 1) \quad E = E_0 + T^2 \frac{\partial}{\partial T} \left( \frac{m^2 g^2 N T}{6 \pi \hbar^2 \bar{n}^2} \right) = E_0 + \frac{m^2 g^2 N T^2}{6 \pi \hbar^2 \bar{n}^2},$$

$$(d = 2) \quad E = E_0 + T^2 \frac{\partial}{\partial T} \left( \frac{\pi m g N T}{12 \hbar^2 \bar{n}} \right) = E_0 + \frac{\pi m g N T^2}{12 \hbar^2 \bar{n}},$$

$$(d = 3) \quad E = E_0 + T^2 \frac{\partial}{\partial T} \left( \frac{m N T}{2 \hbar^2} \left( \frac{\pi g}{6 \bar{n}} \right)^{2/3} \right) = E_0 + \frac{m N T^2}{2 \hbar^2} \left( \frac{\pi g}{6 \bar{n}} \right)^{2/3},$$

where  $E_0$  is the energy at  $T = 0$ .

The pressure may be found by the definition of the thermodynamic potential,  $\Omega = -PV$  [?, p. 69]. Again using  $\mu = \epsilon_0$  and letting  $P_0$  be the pressure at  $T = 0$ , we have

$$(d = 1) \quad P = P_0 + \frac{1}{V} \frac{\pi g N T^2}{6 \hbar \bar{n}} \sqrt{2 m^3 \frac{m g^2}{2 \pi^2 \hbar^2 \bar{n}^2}} = P_0 + \frac{\pi g N T^2}{6 \hbar \bar{n}} \sqrt{2 m^3 \frac{m g^2}{2 \pi^2 \hbar^2 \bar{n}^2}},$$

$$(d = 2) \quad \Omega = P_0 + \frac{1}{V} \frac{\pi m g N T^2}{12 \hbar^2 \bar{n}} = P_0 + \frac{\pi m g T^2}{12 \hbar^2},$$

$$(d = 3) \quad \Omega = P_0 + \frac{1}{V} \frac{m N T^2}{2 \hbar^2} \left( \frac{\pi g}{6 \bar{n}} \right)^{2/3} = P_0 + \frac{m T^2}{2 \hbar^2} \bar{n}^{1/3} \left( \frac{\pi g}{6} \right)^{2/3}.$$

Entropy may be calculated from free energy by  $S = -(\partial F/\partial T)_V$  [?, p. 46]. The entropy is zero at  $T = 0$  for any system due to Nernst's theorem [?, p. 66]. Then the leading-order corrections to the entropy are

$$(d = 1) \quad S = \frac{\partial}{\partial T} \left( \frac{m^2 g^2 N T^2}{6 \pi \hbar^2 \bar{n}^2} \right) = \frac{m^2 g^2 N T}{3 \pi \hbar^2 \bar{n}^2},$$

$$(d = 2) \quad S = \frac{\partial}{\partial T} \left( \frac{\pi m g N T^2}{12 \hbar^2 \bar{n}} \right) = \frac{\pi m g N T}{6 \hbar^2 \bar{n}},$$

$$(d = 3) \quad S = \frac{\partial}{\partial T} \left( \frac{m N T^2}{2 \hbar^2} \left( \frac{\pi g}{6 \bar{n}} \right)^{2/3} \right) = \frac{m N T}{\hbar^2} \left( \frac{\pi g}{6 \bar{n}} \right)^{2/3}.$$

Another consequence of Nernst's theorem is that  $C_p = C_v$  for  $T \rightarrow 0$ , so we can find the specific heat  $C$  by

$C_v = T(\partial S/\partial T)_V$  [?, pp. 45, 66]. So we have

$$\begin{aligned} (d=1) \quad C &= T \frac{\partial}{\partial T} \left( \frac{m^2 g^2 N T}{3\pi \hbar^2 \bar{n}^2} \right) = \frac{m^2 g^2 N T}{3\pi \hbar^2 \bar{n}^2}, \\ (d=2) \quad C &= T \frac{\partial}{\partial T} \left( \frac{\pi m g N T}{6 \hbar^2 \bar{n}} \right) = \frac{\pi m g N T}{6 \hbar^2 \bar{n}}, \\ (d=3) \quad C &= T \frac{\partial}{\partial T} \left( \frac{m N T}{\hbar^2} \left( \frac{\pi g}{6 \bar{n}} \right)^{2/3} \right) = \frac{m N T}{\hbar^2} \left( \frac{\pi g}{6 \bar{n}} \right)^{2/3}. \end{aligned}$$

#### Problem 4. Degenerate Bose gas

**4.1** The chemical potential of the degenerate Bose gas vanishes below  $T^*$  (the critical temperature of the BEC). Find its temperature dependence at temperatures slightly above  $T^*$ .

**Solution.** In three dimensions, the energy distribution of a Bose gas is [?, p. 149]

$$dN_\epsilon = \frac{gV}{\pi^2 \hbar^3} \sqrt{\frac{m^3}{2}} \frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/T} - 1} d\epsilon.$$

Integrating over all energies, we find the total number of molecules [?, p. 149]. This gives an expression relating the chemical potential  $\mu$  and the density  $\bar{n}$  [?, p. 159]:

$$\bar{n} = \frac{g}{\pi^2 \hbar^3} \sqrt{\frac{m^3}{2}} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/T} - 1} d\epsilon. \quad (4)$$

The critical temperature  $T^*$  satisfies this relation for  $\mu = 0$ , and can be found by making the substitution  $z = \epsilon T^*$ :

$$\bar{n} = \frac{g}{\pi^2 \hbar^3} \sqrt{\frac{m^3}{2}} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\epsilon/T^*} - 1} d\epsilon = \frac{g}{\pi^2 \hbar^3} \sqrt{\frac{m^3 T^{*3}}{2}} \int_0^\infty \frac{\sqrt{z}}{e^z - 1} dz.$$

The integral may be evaluated using the formula [?, p. 156]

$$\int_0^\infty \frac{z^{x-1}}{e^z - 1} dz = \Gamma(x) \zeta(x), \quad (5)$$

with  $x > 1$ . The relevant values are  $\Gamma(3/2) = \sqrt{\pi}/2$ , and  $\zeta(3/2) = 2.612$  [?, p. 156]. Thus,

$$\bar{n} = \frac{g}{\pi^2 \hbar^3} \sqrt{\frac{m^3 T^{*3}}{2}} (2.612) \frac{\sqrt{\pi}}{2} = \frac{g}{\pi^2 \hbar^3} \sqrt{\frac{m^3 T^{*3}}{2}} (2.612) \frac{\sqrt{\pi}}{2} = \frac{0.9235 g}{\hbar^3} \left( \frac{m T^*}{\pi} \right)^{3/2}.$$

Define the function

$$\bar{n}^*(T) = \frac{g}{\pi^2 \hbar^3} \sqrt{\frac{m^3}{2}} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\epsilon/T} - 1} d\epsilon = \frac{0.9235 g}{\hbar^3} \left( \frac{m T}{\pi} \right)^{3/2},$$

and note that  $\bar{n}^*(T^*) = \bar{n}$ . Then we can rewrite Eq. (4) as

$$\bar{n} = \bar{n}^*(T) + \frac{g}{\pi^2 \hbar^3} \sqrt{\frac{m^3}{2}} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/T} - 1} d\epsilon - \bar{n}^*(T) = \bar{n}^*(T) + \frac{g}{\pi^2 \hbar^3} \sqrt{\frac{m^3}{2}} \int_0^\infty \left( \frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/T} - 1} - \frac{\sqrt{\epsilon}}{e^{\epsilon/T} - 1} \right) d\epsilon.$$

Expanding the integrand for small exponential powers using  $e^x \approx 1 + x$ , we find

$$\frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/T} - 1} - \frac{\sqrt{\epsilon}}{e^{\epsilon/T} - 1} \approx \frac{\sqrt{\epsilon}}{1 + (\epsilon - \mu)/T - 1} - \frac{\sqrt{\epsilon}}{1 + \epsilon/T - 1} = \frac{T\sqrt{\epsilon}}{\epsilon - \mu} - \frac{T}{\sqrt{\epsilon}} = \frac{T\epsilon - T(\epsilon - \mu)}{\sqrt{\epsilon}(\epsilon - \mu)} = \frac{T\mu}{\sqrt{\epsilon}(\epsilon - \mu)}.$$

Then the integral is

$$T\mu \int_0^\infty \frac{d\epsilon}{\sqrt{\epsilon}(\epsilon - \mu)} = T\mu \frac{\pi}{\sqrt{-\mu}} = \pi T \sqrt{-\mu},$$

so long as  $\mu < 0$ , which is true for the Bose distribution [?, p. 145]. Making this substitution and solving for  $\mu$ , we find

$$\bar{n} = \bar{n}^*(T) - \frac{gT}{\pi\hbar^3} \sqrt{-\mu m^3} \quad \Rightarrow \quad \mu = -\frac{2}{m^3} \left( \frac{\pi\hbar^3[\bar{n}^*(T) - \bar{n}]}{gT} \right)^2 = -\frac{2\pi^2\hbar^6[\bar{n}^*(T) - \bar{n}]^2}{m^3 g^2 T^2}.$$

Note that

$$\bar{n}^*(T) - \bar{n} = \bar{n} \left( \frac{\bar{n}^*(T)}{\bar{n}} - 1 \right) = \bar{n} \left( \frac{\bar{n}^*(T)}{\bar{n}^*(T^*)} - 1 \right) = \bar{n} \left( \frac{T^{3/2}}{T^{*3/2}} - 1 \right),$$

since  $\bar{n}^*(T^*) = \bar{n}$ . Then the relationship between chemical potential and temperature is

$$\mu = -\frac{2\pi^2\hbar^6\bar{n}^2}{m^3 g^2 T^2} \left( \frac{T^{3/2}}{T^{*3/2}} - 1 \right)^2 = -\frac{2\pi^2\hbar^6\bar{n}^2}{m^3 g^2} \left( \frac{T^{1/2}}{T^{*3/2}} - \frac{1}{T} \right)^2.$$

Since  $T/T^* \approx 1$ , the leading behavior is  $\mu \propto -1/T^2$ .

**4.2** Find the discontinuities in the derivatives of thermodynamic quantities at the BEC transition. Which order is this phase transition?

**4.3 (\*)** Can the ideal Bose gas condense in spatial dimensions 1 and 2? Discuss what happens in these cases.

**Problem 5. Thermodynamics of radiation** Compute the following thermodynamic quantities of a radiation field in a 1D and a 2D cavity and compare it with the textbook example of a 3D cavity.

**5.1** Planck formula and the Rayleigh-Jeans and Wien limits of the distribution over frequencies.

**Solution.** Planck's formula gives the spectral energy distribution of blackbody radiation. We start with Planck's distribution, which gives the mean number of photons in quantum state  $k$ :

$$\bar{n}_k = \frac{1}{e^{\hbar\omega_k/T} - 1},$$

where  $\omega_k$  is the eigenfrequency for state  $k$  in the cavity of volume  $V$  [?, p. 163].

The number of states in the interval  $(f, f + df)$ , where  $f = \omega/c$  is the wave number, is in each case [?, p. 163]

$$\frac{L}{2\pi} df = \frac{L}{2\pi c} d\omega \quad (d=1), \quad \frac{2\pi A}{(2\pi)^2} f df = \frac{A}{2\pi c^2} \omega d\omega \quad (d=2). \quad (6)$$

(In both 1D and 2D, there is only one polarization direction for photons, so we do not need to multiply these expressions by a constant.)

In each case, the number of photons in each interval is [?, p. 163]

$$dN_\omega = \frac{L}{2\pi c} \frac{d\omega}{e^{\hbar\omega/T} - 1} \quad (d=1), \quad dN_\omega = \frac{A}{2\pi c^2} \frac{\omega}{e^{\hbar\omega/T} - 1} d\omega \quad (d=2). \quad (7)$$

Transforming to total energy  $\epsilon = \hbar\omega$ , Planck's distribution is

$$dE_\omega = \frac{\hbar L}{2\pi c} \frac{\omega}{e^{\hbar\omega/T} - 1} d\omega \quad (d=1), \quad dE_\omega = \frac{\hbar A}{2\pi c^2} \frac{\omega^2}{e^{\hbar\omega/T} - 1} d\omega \quad (d=2).$$

The 3D equivalent is [?, p. 163]

$$dE_\omega = \frac{\hbar V}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/T} - 1} d\omega \quad (d=3).$$

Comparing the formulae, it appears that

$$dE_\omega \propto \frac{\hbar L^d}{c^d} \frac{\omega^d}{e^{\hbar\omega/T} - 1} d\omega,$$

where  $d$  is the number of spatial dimensions and  $A \equiv L^2$ ,  $V \equiv L^3$ .

The Rayleigh-Jeans limit is  $\hbar\omega \ll T$ . Letting  $u = \hbar\omega/T$  and expanding about  $u = 0$ , we obtain

$$\begin{aligned} (d=1) \quad dE_\omega &= \frac{LT}{2\pi c} \frac{u}{e^u - 1} d\omega \approx \frac{LT}{2\pi c} \left\{ \lim_{u \rightarrow 0} \left( \frac{u}{e^u - 1} \right) + u \left[ \frac{\partial}{\partial u} \left( \frac{u}{e^u - 1} \right) \right]_{u \rightarrow 0} \right\} d\omega \\ &= \frac{LT}{2\pi c} \left\{ 1 + u \left[ \frac{1}{e^u - 1} - \frac{e^u u}{(e^u - 1)^2} \right]_{u \rightarrow 0} \right\} d\omega = \frac{LT}{2\pi c} \left( 1 - \frac{u}{2} \right) d\omega = \frac{L}{2\pi c} \left( T - \frac{\hbar\omega}{2} \right) d\omega, \\ (d=2) \quad dE_\omega &= \frac{AT^2}{2\pi \hbar c^2} \frac{u^2}{e^u - 1} d\omega \approx \frac{AT^2}{2\pi \hbar c^2} \left\{ \lim_{u \rightarrow 0} \left( \frac{u^2}{e^u - 1} \right) + u \left[ \frac{\partial}{\partial u} \left( \frac{u^2}{e^u - 1} \right) \right]_{u \rightarrow 0} \right\} d\omega \\ &= \frac{AT^2}{2\pi \hbar c^2} \left\{ u \left[ \frac{2u}{e^u - 1} - \frac{e^u u^2}{(e^u - 1)^2} \right]_{u \rightarrow 0} \right\} d\omega = \frac{AT^2}{2\pi \hbar c^2} u = \frac{AT}{2\pi c^2} \omega d\omega. \end{aligned}$$



The 3D equivalent is [? , p. 163]

$$dE_\omega = \frac{VT}{\pi^2 c^3} \omega^2 d\omega.$$

Comparing the leading terms, the Rayleigh-Jeans limit seems to follow

$$dE_\omega \propto \frac{L^d T}{2c^d} \omega^{d-1} d\omega.$$

The Wien limit is  $\hbar\omega \gg T$ . In this limit,  $e^{\hbar\omega/T} - 1 \approx e^{\hbar\omega/T}$ . For each case, then,

$$dE_\omega = \frac{\hbar L}{2\pi c} \omega e^{-\hbar\omega/T} d\omega \quad (d=1), \quad dE_\omega = \frac{\hbar A}{2\pi c^2} \omega^2 e^{-\hbar\omega/T} d\omega \quad (d=2).$$

The 3D equivalent is [? , p. 163]

$$dE_\omega = \frac{\hbar V}{\pi^2 c^3} \omega^3 e^{-\hbar\omega/T} d\omega,$$

which suggests

$$dE_\omega \propto \frac{\hbar L^d}{c^d} \omega^d e^{-\hbar\omega/T} d\omega$$

in the Wien limit.

## 5.2 Free energy and the Stefan-Boltzmann constant.

**Solution.** For a blackbody,  $\mu = 0$  [? , p. 163]. Since  $F = N\mu + \Omega$ , we have  $F = \Omega$  [? , p. 164]. For a Bose gas [? , p. 146],

$$\Omega = T \sum_k \ln(1 - e^{(\mu - \epsilon_k)/T}) = T \sum_k \ln(1 - e^{-\hbar\omega_k/T}),$$

since  $\epsilon_k = \hbar\omega_k$ . By a similar procedure as in Prob. 3.2, we can replace the sum by an integral via Eq. (6), and make the substitution  $u = \hbar\omega/T$  [? , p. 164]. So

$$\begin{aligned} (d=1) \quad F &= \frac{LT}{2\pi c} \int_0^\infty \ln(1 - e^{-\hbar\omega/T}) d\omega = \frac{LT^2}{2\pi\hbar c} \int_0^\infty \ln(1 - e^{-u}) du \\ &= \frac{LT^2}{2\pi\hbar c} \left( [u \ln(1 - e^{-u})]_0^\infty - \int_0^\infty \frac{u}{e^u - 1} du \right) = -\frac{LT^2}{2\pi\hbar c} \Gamma(2)\zeta(2) = -\frac{LT^2}{2\pi\hbar c} \frac{\pi^2}{6} = -\frac{\pi LT^2}{12\hbar c}, \end{aligned}$$

$$\begin{aligned} (d=2) \quad F &= \frac{AT}{2\pi c^2} \int_0^\infty \omega \ln(1 - e^{-\hbar\omega/T}) d\omega = \frac{AT^3}{2\pi\hbar^2 c^2} \int_0^\infty u \ln(1 - e^{-u}) du \\ &= \frac{AT^3}{2\pi\hbar^2 c^2} \left( \left[ \frac{u^2}{2} \ln(1 - e^{-u}) \right]_0^\infty - \frac{1}{2} \int_0^\infty \frac{u^2}{e^u - 1} du \right) = -\frac{AT^3}{2\pi\hbar^2 c^2} \Gamma(3)\zeta(3) = -\frac{0.601 AT^3}{\pi\hbar^2 c^2}, \end{aligned}$$

where we have used Eq. (5). The 3D equivalent is [? , p. 165]

$$F = -\frac{\pi^2 VT^4}{45\hbar^3 c^3},$$

which suggests

$$F \propto \frac{L^d T^{d+1}}{\hbar^d c^d}.$$

For the Stefan-Boltzmann constant  $\sigma$ , the Stefan-Boltzmann law in three dimensions is  $J^* = \sigma T^4$ , where  $J^*$  is the energy flux per unit area per unit time. This may be modeled by photons escaping through a small hole in the wall of the cavity. This escaping energy flux is given by [?, p. 169]

$$J^* = \langle c_{\perp} \rangle \frac{E}{V},$$

where  $E$  is the total energy of the gas and  $\langle c_{\perp} \rangle$  is the average component of the velocity perpendicular to the hole. In the 3D case, the cavity can be modeled as a sphere of volume  $V$  with a hole in the top at  $(x, y, z) = (0, 0, R)$ , where  $R$  is the sphere's radius. Then  $c_{\perp} = c \cos \theta$  in spherical polar coordinates. Only photons with a positive  $c_{\perp}$  can escape, so we integrate only over the upper hemispherical surface, and normalize by the angular area of the entire spherical surface, which is  $4\pi$  [?, p. 169]:

$$\langle c_{\perp} \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} c \cos \theta \sin \theta d\theta = \frac{1}{4\pi} (2\pi) \frac{1}{2} = \frac{c}{4} \quad (d = 3).$$

In the 2D case, we model the cavity as a circle of area  $A$  centered at the origin, with a hole in the top of the boundary at  $(x, y) = (0, R)$ . Then  $c_{\perp} = c \sin \theta$  in plane polar coordinates. We integrate only over the upper semicircular boundary and normalize by  $2\pi$ :

$$\langle c_{\perp} \rangle = \frac{c}{2\pi} \int_0^{\pi} \sin \theta d\theta = \frac{c}{\pi} \quad (d = 2).$$

In the 1D case, we imagine a system on a circle of circumference  $L$  with a hole at the origin. In this case, photons moving in either direction can access the hole from either side. Thus,  $c_{\perp} = 1$  for  $d = 1$ .

The total energy in each case is given by Eqs. (8–9). Using these results,

$$J^* = \frac{c}{L} \frac{\pi L T^2}{12\hbar} = \frac{\pi T^2}{12\hbar} \equiv \sigma T^2 \quad (d = 1), \quad J^* = \frac{c}{\pi A} \frac{1.202 A T^3}{\pi \hbar^2 c^2} = \frac{1.202 T^3}{\pi^2 \hbar^2 c} \equiv \sigma T^3 \quad (d = 2).$$

Thus, if  $T$  is measured in degrees,

$$\sigma = \frac{\pi k^2}{12\hbar} \quad (d = 1), \quad \sigma = \frac{1.202 k^3}{\pi^2 \hbar^2 c} \quad (d = 2),$$

where  $k$  is Boltzmann's constant. In 3D [?, p. 165],

$$\sigma = \frac{\pi^2 k^4}{60 \hbar^3 c^2},$$

which suggests

$$\sigma \propto \frac{k^{d+1}}{\hbar^d c^{d-1}}.$$

### 5.3 The relation between the free energy and energy (Boltzmann law).

**Solution.** The energy of the gas can be found from the free energy by  $E = F + TS$ , where  $S = -\partial F / \partial T$  is the entropy [?, p. 165]. For each case, the entropy is

$$S = -\frac{\partial}{\partial T} \left( -\frac{\pi L T^2}{12\hbar c} \right) = \frac{\pi L T}{6\hbar c} \quad (d = 1), \quad S = -\frac{\partial}{\partial T} \left( -\frac{0.601 A T^3}{\pi \hbar^2 c^2} \right) = \frac{1.803 A T^2}{\pi \hbar^2 c^2} \quad (d = 2).$$

Then the relationship between free energy and energy are

$$(d = 1) \quad E = -\frac{\pi L T^2}{12 \hbar c} + \frac{\pi L T^2}{6 \hbar c} = \frac{\pi L T^2}{12 \hbar c} = -F, \quad (8)$$

$$(d = 2) \quad E = -\frac{0.601 A T^3}{\pi \hbar^2 c^2} + \frac{1.803 A T^3}{\pi \hbar^2 c^2} = \frac{1.202 A T^3}{\pi \hbar^2 c^2} = -2F. \quad (9)$$

In 3D, the relationship is  $E = -3F$  [?, p. 165]. So the relationship appears to be  $E = -dF$ .

#### 5.4 Specific heat.

**Solution.** The specific heat is given by  $C_v = (\partial E / \partial T)_V$  [?, p. 165]. Then

$$E = \frac{\partial}{\partial T} \left( \frac{\pi L T^2}{12 \hbar c} \right) = \frac{\pi L T}{6 \hbar c} \quad (d = 1), \quad S = \frac{\partial}{\partial T} \left( \frac{1.202 A T^3}{\pi \hbar^2 c^2} \right) = \frac{3.606 A T^2}{\pi \hbar^2 c^2} \quad (d = 2).$$

In 3D, it is [?, p. 165]

$$C_v = \frac{16 \sigma V T^3}{c} = \frac{4 \pi^2 V T^3}{15 \hbar^3 c^3},$$

which suggests

$$C_v \propto \frac{\sigma L^d T^d}{c} \propto \frac{L^d T^d}{\hbar^d c^d}.$$

#### 5.5 Pressure.

**Solution.** The pressure can be found by  $P = -(\partial F / \partial V)_T$  [?, p. 165]:

$$S = -\frac{\partial}{\partial L} \left( -\frac{\pi L T^2}{12 \hbar c} \right) = \frac{\pi T^2}{12 \hbar c} \quad (d = 1), \quad S = -\frac{\partial}{\partial A} \left( -\frac{0.601 A T^3}{\pi \hbar^2 c^2} \right) = \frac{0.601 T^3}{\pi \hbar^2 c^2} \quad (d = 2).$$

In 3D, it is [?, p. 165]

$$P = \frac{4 \sigma T^4}{3 c} = \frac{\pi^2 T^4}{45 \hbar^3 c^3},$$

which suggests

$$P \propto \frac{\sigma T^{d+1}}{c} \propto \frac{T^{d+1}}{\hbar^d c^d}.$$

#### 5.6 The total number of photons in the cavity.

**Solution.** The total number of photons may be found by integrating Eq. (7) from  $\omega = 0$  to  $\infty$ . Changing variables to  $u = \hbar \omega / T$ , we find

$$(d = 1) \quad N = \frac{L}{2 \pi c} \int_0^\infty \frac{d\omega}{e^{\hbar \omega / T} - 1} = \frac{L T}{2 \pi \hbar c} \int_0^\infty \frac{du}{e^u - 1} = \frac{L T}{2 \pi \hbar c} \left[ \ln(1 - e^u) - u \right]_0^\infty \rightarrow \infty,$$

This integral's diverging suggests a 1D gas is not physical. However, in the high-frequency limit, equivalent to the high-energy limit  $\hbar \omega \gg T$ , the integrand approaches  $e^{-u}$ :

$$(d = 1) \quad \lim_{u \rightarrow \infty} N = \frac{L T}{2 \pi \hbar c} \int_0^\infty \frac{du}{e^u} = \frac{L T}{2 \pi \hbar c} \left[ -e^{-u} \right]_0^\infty = \frac{L T}{2 \pi \hbar c}.$$

In the 2D case, the integral converges. Making the same change of variable and using Eq. (??),

$$(d=2) \quad N = \frac{A}{2\pi c^2} \int_0^\infty \frac{\omega}{e^{\hbar\omega/T} - 1} d\omega = \frac{AT^2}{2\pi\hbar^2 c^2} \int_0^\infty \frac{u}{e^u - 1} du = \frac{AT^2}{2\pi\hbar^2 c^2} \Gamma(2)\zeta(2) = \frac{AT^2}{2\pi\hbar^2 c^2} \frac{\pi^2}{6} = \frac{\pi AT^2}{12\hbar^2 c^2}.$$

The 3D equivalent is

$$N = \frac{2\zeta(3)VT^3}{\pi^2\hbar^2 c^3} = \frac{2.404 VT^3}{\pi^2\hbar^2 c^3},$$

which suggests

$$N \propto \frac{L^d T^d}{\hbar^d c^d},$$

where this is an asymptotic limit in the 1D case.

**Problem 6. Thermodynamics of solids** Compute the following thermodynamic quantities for the harmonic photonic modes in a 1D and a 2D crystal at low temperatures (a.k.a. phonons) and compare with the textbook example of a 3D crystal.

**6.1** Free energy.

**6.2** Entropy.

**6.3** Energy.

**6.4** Specific heat.