

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 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 μ is the chemical potential of the gas. We may replace the sum by an integral from $p = 0$ to ∞ using Eq. (1), transform variables to ϵ , 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

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

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

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

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 Ω_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 Ω 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

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

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

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

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^* .

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.

5.2 Free energy and the Stefan-Boltzmann constant.

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

5.4 Specific heat.

5.5 Pressure.

5.6 The total number of photons in the cavity.

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.