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: $|\boldsymbol{\nabla}_x n| \ll \bar{n}^{4/3}$ ("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],

$$\frac{gL}{2\pi\hbar}\,dp \quad (d=1), \qquad \frac{2\pi g A}{(2\pi\hbar)^2}p\,dp \quad (d=2), \qquad \frac{4\pi g V}{(2\pi\hbar)^3}p^2\,dp \quad (d=3), \tag{1}$$

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,

$$(d=1) \quad N = \frac{gL}{2\pi\hbar}\int_0^{p_0} dp = \frac{gL}{2\pi\hbar}\Big[p\Big]_0^{p_0} = \frac{gLp_0}{2\pi\hbar},$$

$$(d=2) \quad N = \frac{2\pi g A}{(2\pi\hbar)^2}\int_0^{p_0} p\,dp = \frac{2\pi g A}{(2\pi\hbar)^2}\left[\frac{p^2}{2}\right]_0^{p_0} = \frac{gAp_0^2}{4\pi\hbar^2},$$

$$(d=3) \quad N = \frac{4\pi g V}{(2\pi\hbar)^3}\int_0^{p_0} p^2\,dp = \frac{4\pi g V}{(2\pi\hbar)^3}\left[\frac{p^3}{3}\right]_0^{p_0} = \frac{gVp_0^3}{6\pi^2\hbar^3}.$$

Solving each case for p_0, we find

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

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

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

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

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

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

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

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

$$\epsilon = \frac{p^2}{2m} \quad\Longrightarrow\quad 2m\,d\epsilon = 2p\,dp \quad\Longrightarrow\quad dp = \frac{m}{p}\,d\epsilon = \frac{m}{\sqrt{2m\epsilon}}\,d\epsilon = \sqrt{\frac{m}{2\epsilon}}\,d\epsilon\,. \tag{4}$$

Then in each case, we find

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

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

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

where we have used

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

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]

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$(d=2)\quad \Omega = P_0 + \frac{1}{V}\frac{\pi mgNT^2}{12\hbar^2\bar{n}} = P_0 + \frac{\pi mgT^2}{12\hbar^2},$$

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

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

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

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

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

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

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

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

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

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

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^*.

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

$$dN_\epsilon = \frac{gV}{\pi^2\hbar^3}\sqrt{\frac{m^3}{2}}\frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/T}-1}\,d\epsilon\,. \tag{5}$$

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

$$\bar{n} = \frac{g}{\pi^2\hbar^3}\sqrt{\frac{m^3}{2}}\int_0^\infty \frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/T}-1}\,d\epsilon\,. \tag{6}$$

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

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

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

$$\int_0^\infty \frac{z^{x-1}}{e^z-1}\,dz = \Gamma(x)\zeta(x), \tag{7}$$

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

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

and

$$\left(\frac{mT^*}{\pi}\right)^{3/2} = \frac{\bar{n}\hbar^3}{0.9235\,g} \quad\Longrightarrow\quad T^* = \frac{\pi}{m}\left(\frac{\bar{n}\hbar^3}{0.9235\,g}\right)^{2/3} = \frac{1.054\,\pi}{m\hbar^2}\left(\frac{\bar{n}}{g}\right)^{2/3}.$$

Define the function

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

and note that $\bar{n}^*(T^*) = \bar{n}$. Then we can rewrite Eq. (6) 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 μ, we find

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

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

$$\mu = -\frac{2\pi^2\hbar^6\bar{n}^2}{m^3g^2T^2}\left(\frac{T^{3/2}}{T^{*3/2}} - 1\right)^2 = -\frac{2\pi^2\hbar^6\bar{n}^2}{m^3g^2}\left(\frac{T^{1/2}}{T^{*3/2}} - \frac{1}{T}\right)^2. \tag{8}$$

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

4.2 Find the discontinuities in the derivatives of thermodynamic quantities (energy, entropy, thermodynamic potential, and specific heat) at the BEC transition. Which order is this phase transition?

Solution. Using Eq. (5), the energy of the Bose gas is

$$E = \int_0^\infty \epsilon\, dN_\epsilon = \frac{gV}{\pi^2\hbar^3}\sqrt{\frac{m^3}{2}}\int_0^\infty \frac{\epsilon^{3/2}}{e^{(\epsilon-\mu)/T}-1}\,d\epsilon\,.$$

The thermodynamic potential for a Bose gas is [? , p. 146]

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

Transforming the sum to an integral as in Prob. 3.2, we have [? , p. 149]

$$\begin{aligned}
\Omega &= \frac{gVT}{\pi^2\hbar^3}\sqrt{\frac{m^3}{2}}\int_0^\infty \sqrt{\epsilon}\ln\left(1-e^{(\mu-\epsilon)/T}\right)d\epsilon \\
&= \frac{gVT}{\pi^2\hbar^3}\sqrt{\frac{m^3}{2}}\left(\left[\frac{2}{3}\epsilon^{3/2}\ln\left(1-e^{(\mu-\epsilon_k)/T}\right)\right]_0^\infty - \frac{2}{3T}\int_0^\infty \frac{\epsilon^{3/2}}{e^{(\epsilon-\mu)/T}-1}\,d\epsilon\right) \\
&= -\frac{3gVT}{\pi^2\hbar^3}\left(\frac{m}{2}\right)^{3/2}\int_0^\infty \frac{\epsilon^{3/2}}{e^{(\epsilon-\mu)/T}-1}\,d\epsilon = -\frac{2}{3}E.
\end{aligned}$$

Note that $N = -(\partial\Omega/\partial\mu)_{T,V}$ [? , p. 24]. Then [? , p. 161]

$$\bar{n} = -\frac{1}{V}\frac{\partial\Omega}{\partial\mu} = \frac{2}{3V}\frac{\partial E}{\partial\mu} \approx \bar{n}^*,$$

since the contribution to $\bar{n}$ is small for $\mu \ll 1$. This gives us

$$\Omega = \Omega^* - \bar{n}^* V \mu, \qquad E = E^* + \frac{3}{2}\bar{n}^* V \mu,$$

where Ω^* and E^* are the thermodynamic potential and the energy at $\mu = 0$. Using Eq. (7),

$$\begin{aligned} E^* &= \frac{gV}{\pi^2\hbar^3}\sqrt{\frac{m^3}{2}}\int_0^\infty \frac{\epsilon^{3/2}}{e^{\epsilon/T}-1}\,d\epsilon = \frac{gV}{\pi^2\hbar^3}\sqrt{\frac{m^3T^5}{2}}\int_0^\infty \frac{z^{3/2}}{e^{z}-1}\,dz = \frac{gV}{\pi^2\hbar^3}\sqrt{\frac{m^3T^5}{2}}\Gamma(5/2)\zeta(5/2) \\ &= \frac{0.711\,gV}{\hbar^3}\sqrt{\frac{m^3T^5}{\pi^3}}, \end{aligned}$$

$$\Omega^* = -\frac{0.474\,gV}{\hbar^3}\sqrt{\frac{m^3T^5}{\pi^3}},$$

both of which are continuously differentiable in T. So the discontinuities in the T derivatives of Ω and E stem from μ, given by Eq. (8). Since

$$\frac{\partial\mu}{\partial T} \sim -\frac{\partial}{\partial T}\left(\frac{1}{T^2}\right) \propto -\frac{1}{T^3},$$

we conclude that

$$\frac{\partial\Omega}{\partial T} \sim \frac{1}{T^3}, \qquad \frac{\partial E}{\partial T} \sim -\frac{1}{T^3},$$

which both have infinite discontinuities at $T = 0$. In particular,

$$\lim_{T\to 0\pm}\frac{\partial\Omega}{\partial T} \sim \pm\infty, \qquad \lim_{T\to 0\pm}\frac{\partial E}{\partial T} \sim \mp\infty.$$

Entropy can be found by $S = -(\partial\Omega/\partial T)_{V,\mu}$ [? , p. 150], and the specific heat is given by $C_v = (\partial E/\partial T)_V$ [? , p. 165]. Since

$$S \sim -\frac{1}{T^3}, \qquad C_v \sim -\frac{1}{T^3},$$

then

$$\frac{\partial S}{\partial T} \sim -\frac{\partial}{\partial T}\left(\frac{1}{T^3}\right) \propto -\frac{1}{T^4}, \qquad \frac{\partial C_v}{\partial T} \sim -\frac{1}{T^4},$$

which both have infinite discontinuities at $T = 0$. Specifically,

$$\lim_{T\to 0\pm}\frac{\partial S}{\partial T} \sim -\infty, \qquad \lim_{T\to 0\pm}\frac{\partial C_v}{\partial T} \sim -\infty.$$

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

Solution. The ideal Bose gas can condense if the equivalent of Eq. (6) can be solved with $\mu = 0$ to obtain an expression for T^*. The number of quantum states in the interval dp is the same as for a Fermi gas, and so is given by Eq. (1) [**?** , p. 148]. Transforming this to the number of states in the interval $d\epsilon$ by Eq. (**??**), we obtain

$$\frac{gL}{2\pi\hbar}\sqrt{\frac{m}{2}}\frac{1}{\sqrt{\epsilon}}\,d\epsilon \quad (d=1), \qquad \frac{mgA}{2\pi\hbar^2}\,d\epsilon \quad (d=2), \qquad \frac{gV}{\pi^2\hbar^3}\sqrt{\frac{m^3}{2}}\epsilon^{3/2}\,d\epsilon \quad (d=3). \tag{9}$$

Applying the expression for the total number of particles in a Bose gas [**?** , p. 146],

$$N = \sum_k \frac{1}{e^{(\epsilon_k-\mu)/T}-1},$$

replacing the sum by an integral over $p \in (0,\infty)$, and transforming coordinates to $z = \epsilon/T^*$ as in Prob. 4.1, we obtain

$$(d=1) \quad \bar{n} = \frac{gL}{2\pi\hbar}\sqrt{\frac{m}{2}}\int_0^\infty \frac{d\epsilon}{\sqrt{\epsilon}(e^{\epsilon/T^*}-1)} = \frac{gL}{2\pi\hbar}\sqrt{\frac{mT^*}{2}}\int_0^\infty \frac{dz}{\sqrt{z}(e^z-1)} \to \infty,$$

$$(d=2) \quad \bar{n} = \frac{mgA}{2\pi\hbar^2}\int_0^\infty \frac{d\epsilon}{e^{\epsilon/T^*}-1} = \frac{mgAT^*}{2\pi\hbar^2}\int_0^\infty \frac{dz}{e^z-1} \to \infty.$$

Both integrals diverge, making it impossible to solve for T^* in either case.

However, these integrals will converge in the limit that $z \to \infty$, which is equivalent to $T \to 0$. In this limit,

$$(d=1) \quad \lim_{T\to 0}\bar{n} = \frac{gL}{2\pi\hbar}\sqrt{\frac{mT^*}{2}}\int_0^\infty \frac{dz}{e^z\sqrt{z}} = \frac{gL}{2\hbar}\sqrt{\frac{mT^*}{2\pi}},$$

$$(d=2) \quad \lim_{T\to 0}\bar{n} = \frac{mgAT^*}{2\pi\hbar^3}\int_0^\infty \frac{dz}{e^z} = \frac{mgAT^*}{2\pi\hbar^3}.$$

Thus, we conclude that, it is not possible for the 1D and 2D ideal Bose gases to condense above $T = 0$.

Referring back to Eq. (9), for $d = 1$ the number of states in the interval $d\epsilon$ diverges as $\epsilon \to 0$. For $d = 2$, the number of states is independent of ϵ. For $d = 3$, the number of states approaches 0 as $\epsilon \to 0$. It would seem that, in 1D and in 2D, there are many states with very low energy that may be occupied instead of $\epsilon = 0$, while this is not the case in 3D. Since the particles are therefore not "forced" into the ground state at nonzero temperature, the gas will not condense.

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:

$$\overline{n_k} = \frac{1}{e^{\hbar\omega_k/T}-1},$$

where ω_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]

$$\frac{L}{2\pi}\,df = \frac{L}{2\pi c}\,d\omega \quad (d=1), \qquad\qquad \frac{2\pi A}{(2\pi)^2} f\,df = \frac{A}{2\pi c^2}\omega\,d\omega \quad (d=2). \tag{10}$$

(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]

$$dN_\omega = \frac{L}{2\pi c}\frac{d\omega}{e^{\hbar\omega/T}-1} \quad (d=1), \qquad\qquad dN_\omega = \frac{A}{2\pi c^2}\frac{\omega}{e^{\hbar\omega/T}-1}\,d\omega \quad (d=2). \tag{11}$$

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

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

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

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

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

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,

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

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],

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

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. (10), and make the substitution $u = \hbar\omega/T$ [? , p. 164]. So

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

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

where we have used Eq. (7). The 3D equivalent is [? , p. 165]

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

which suggests

$$F \propto \frac{L^dT^{d+1}}{\hbar^dc^d}.$$

For the Stefan-Boltzmann constant σ, 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 4π [? , 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 2π:

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

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. (12–13). Using these results,

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

Thus, if T is measured in degrees,

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

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

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

Then the relationship between free energy and energy are

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

$$(d=2) \quad E = -\frac{0.601\, A T^3}{\pi \hbar^2 c^2} + \frac{1.803\, A T^3}{\pi \hbar^2 c^2} = \frac{1.202\, A T^3}{\pi \hbar^2 c^2} = -2F. \tag{13}$$

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

5.4 Specific heat.

Solution. The specific heat is given by $C_v = (\partial E/\partial T)_V$. Then

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

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]:

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

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

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

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. (11) from $\omega = 0$ to ∞. Changing variables to $u = \hbar\omega/T$, we find

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

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}:

$$(d=1) \quad \lim_{u\to\infty} N = \frac{LT}{2\pi\hbar c}\int_0^\infty \frac{du}{e^u} = \frac{LT}{2\pi\hbar c}\Big[-e^{-u}\Big]_0^\infty = \frac{LT}{2\pi\hbar c}.$$

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

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

The 3D equivalent is

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

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.

Solution. A crystal of N molecules is comprised of quantum harmonic oscillators that are free to oscillate in all spatial dimensions. We can count the number of states in the interval dk, where k is the wave number. For a crystal, it is related to the frequency of vibration by $k = d\omega/\bar{u}$, where $\bar{u}$ is the averaged velocity of sound for the particular crystal structure and d the number of spatial dimensions. The number of states in the interval is, for each case,

$$\frac{L}{2\pi}\,dk = \frac{L}{2\pi\bar{u}}\,d\omega \quad (d=1), \qquad \frac{2\pi A}{(2\pi)^2}k\,dk = \frac{A}{\pi\bar{u}^2}\omega\,d\omega\,,$$

where we have taken into account that there are d independent polarization directions in each case [**?** , pp.172–173].

The free energy is $F = N\epsilon_0 - T\ln Z$, where ϵ_0 is the energy per molecule when the system is at equilibrium, which depends on N and the volume V [**?** , pp. 87, 172]. The single-particle vibrational partition function is [**?** , p. 136]

$$Z_1 = \frac{1}{1-e^{-\hbar\omega/T}}.$$

The entire crystal can be modeled as $d\,N\nu$ independent oscillators with total free energy [**?** , p. 172]

$$F = N\epsilon_0 - T\sum_{\alpha=1}^{d\,N\nu}\ln\Big(1-e^{-\hbar\omega_\alpha/T}\Big).$$

For the entire crystal, the sum can be transformed to an integral over $\omega \in (0,\infty)$ [**?** , p. 173]. Referring to the similar integrals in Prob. 5.2, we have

$$(d=1) \quad F = N\epsilon_0 - \frac{LT}{2\pi\bar{u}}\int \ln\Big(1-e^{-\hbar\omega/T}\Big)\,d\omega = N\epsilon_0 - \frac{LT^2}{2\pi\hbar\bar{u}}\frac{\pi}{6} = N\epsilon_0 - \frac{LT^2}{12\hbar\bar{u}},$$

$$(d=2) \quad F = N\epsilon_0 - \frac{AT}{\pi\bar{u}^2}\int \omega\ln\Big(1-e^{-\hbar\omega/T}\Big)\,d\omega = N\epsilon_0 - \frac{AT^3}{\pi\hbar^2\bar{u}^2}\Gamma(3)\zeta(3) = N\epsilon_0 - \frac{1.202\,AT^3}{\pi\hbar^2\bar{u}^2}.$$

The 3D expression is [**?** , p. 173]

$$F = N\epsilon_0 - \frac{\pi^2 VT^3}{30\hbar^3\bar{u}^3},$$

suggesting

$$F = N\epsilon_0 - j(d)\,\frac{L^d T^{d+1}}{\hbar^d\bar{u}^d},$$

where $j(d)$ is a constant that depends on the number of dimensions, and we note that both ϵ_0 and $\bar{u}$ depend on the crystal structure and therefore d.

6.2 Entropy.

Solution. As in Prob. 5.3, $S = -\frac{\partial F}{\partial T}$:

$$S = -\frac{\partial}{\partial T}\left(N\epsilon_0 - \frac{LT^2}{12\hbar\bar{u}}\right) = \frac{LT}{6\hbar\bar{u}} \quad (d=1), \qquad S = -\frac{\partial}{\partial T}\left(N\epsilon_0 - \frac{1.202\,AT^3}{\pi\hbar^2\bar{u}^2}\right) = \frac{3.606\,AT^2}{\pi\hbar^2\bar{u}^2} \quad (d=2).$$

In 3D, the entropy is [**?** , p. 173]

$$S = \frac{2\pi^2 VT^3}{15\hbar^3\bar{u}^3},$$

which suggests

$$S \propto \frac{L^d T^d}{\hbar^d \bar{u}^d}.$$

6.3 Energy.

Solution. As in Prob. 5.3, $E = F + TS$:

$$(d=1) \quad E = N\epsilon_0 - \frac{LT^2}{12\hbar\bar{u}} + T\frac{LT}{6\hbar\bar{u}} = N\epsilon_0 + \frac{LT^2}{12\hbar\bar{u}},$$

$$(d=2) \quad E = N\epsilon_0 - \frac{1.202\,AT^3}{\pi\hbar^2\bar{u}^2} + T\frac{3.606\,AT^2}{\pi\hbar^2\bar{u}^2} = N\epsilon_0 + \frac{2.404\,AT^3}{\pi\hbar^2\bar{u}^2}.$$

The 3D equivalent is [**?** , p. 173]

$$E = N\epsilon_0 + \frac{\pi^2 T^4}{10\hbar^3\bar{u}^3},$$

which suggests

$$E = N\epsilon_0 + j(d)\frac{dT^{d+1}}{\hbar^d\bar{u}^d} = N - d\,F,$$

where $j(d)$ is a constant that depends on the number of dimensions, and is not necessarily the same as that in Prob. 6.1.

6.4 Specific heat.

Solution. As in Prob. 5.4, $C_v = (\partial E/\partial T)_V$. Then

$$C = \frac{\partial}{\partial T}\left(N\epsilon_0 + \frac{LT^2}{12\hbar\bar{u}}\right) = \frac{LT}{6\hbar\bar{u}} \quad (d=1), \qquad C = \frac{\partial}{\partial T}\left(N\epsilon_0 + \frac{2.404\,AT^3}{\pi\hbar^2\bar{u}^2}\right) = \frac{7.212\,AT^2}{\pi\hbar^2\bar{u}^2} \quad (d=2).$$

In 3D [**?** , p. 173]

$$C = \frac{2\pi^2 VT^3}{5\hbar^3\bar{u}^3},$$

which suggests

$$C \propto \frac{L^d T^d}{\hbar^d \bar{u}^d}.$$