

PHYS4101 Thermal Physics
(Fall 2021)

Final Exam

Thursday 9 Dec 2021

There are **five questions** and you are to work all of them. You are welcome to use your textbook, notes, or any other resources, but you may not communicate with another human. Of course, if you have questions, you are encouraged to ask the person proctoring the exam.

The five problems will be equally weighted but *they are not of equal difficulty*. If you are stuck on one, move on to another and come back if you have time.

Please start each problem on a new page in your exam booklet.

Good luck!

(1) Find an expression for the chemical potential μ of a degenerate ($T = 0$) Fermi gas with N highly relativistic fermions, that is energies $\epsilon = |\vec{p}|c$ for momentum \vec{p} , occupying a volume V . Then find the total energy, expressed in terms of N and μ . Compare the total energy in this case to the result we obtained for the non-relativistic case.

(2) Consider a “large” Einstein solid with N oscillators and q energy units. To a good approximation, as derived in your textbook Equation (2.18), the multiplicity Ω is given by

$$\log \Omega(N, q) = (q + N) \log(q + N) - q \log q - N \log N$$

Use this to find the entropy $S(N, q)$ of an Einstein solid. Next find the temperature T as a function of the energy $U = q\epsilon$, for some constant ϵ . Finally, find the specific heat at constant volume as a function of T . *Do not assume anything about the relative sizes of q and N .* Show that you get the answer you expect for $\epsilon \ll kT$.

(3) Use the thermodynamic identity for the energy U to write an expression for the pressure P as a partial derivative keeping the entropy S and number of particles N constant. Then use this result to calculate the pressure of a “photon gas” of energy density U/V , which can be written as a factor times U/V . Cite any equations you use from the textbook.

(4) Two solid blocks of dissimilar materials are initially at different temperatures and then brought into thermal contact with each other. Block #1 has a mass m and a specific heat capacity c , and is at temperature $T_1 = T$. Block #2 has mass $2m$ and specific heat capacity $3c/2$, and is at $T_2 = 3T$. Find the change in entropy ΔS of the two-block system after the joined pair of blocks comes to equilibrium, in terms of m and c . Show that $\Delta S > 0$.

(5) Calcium carbonate CaCO_3 exists in two phases, called calcite and aragonite, near the Earth’s surface. Use the thermodynamic data in the back of your textbook to determine which of these two is most stable on the surface of the Earth. Then calculate (numerically) the pressure at which the other becomes the most stable. Compare this to atmospheric pressure. You can assume constant temperature.

Solutions

(1) See Problem 7.22. This is very similar to the non-relativistic case that we covered in class. Following (7.36) we write

$$\epsilon = |\vec{p}|c = \frac{hc}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{hc}{2L} n$$

in which case $\mu = \epsilon_F = hc n_{\max}/2L$. We still have (7.38) $N = \pi n_{\max}^3/3$ so that

$$\mu = \frac{hc}{2L} \left(\frac{3N}{\pi} \right)^{1/3} = \frac{hc}{2} \left(\frac{3N}{\pi V} \right)^{1/3} = hc \left(\frac{3N}{8\pi V} \right)^{1/3}$$

which is the answer given in Problem 7.22. We also just follow (7.41) to get the total energy, that is

$$U = \pi \int_0^{n_{\max}} \epsilon(n) n^2 dn = \frac{\pi hc}{2L} \int_0^{n_{\max}} n^3 dn = \frac{\pi hc}{2L} \frac{1}{4} n_{\max}^3 n_{\max} = \frac{\pi hc}{2L} \frac{1}{4} \frac{3N}{\pi} \frac{2L}{hc} \mu = \frac{3}{4} N \mu$$

(I pointed out in class that it is easiest to “split” the powers of n_{\max} to get the energy in this form.) The non-relativistic result was (7.42) $U = (3/5)N\epsilon_F$, a bit less than for highly relativistic fermions.

(2) See Problem 3.25. We have $S = k \log \Omega$, and

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial U} = \frac{1}{\epsilon} \frac{\partial S}{\partial q} = \frac{k}{\epsilon} \frac{\partial}{\partial q} \{q[\log(q+N) - \log q] + N[\log(q+N) - \log N]\} \\ &= \frac{k}{\epsilon} \left\{ \log(q+N) + \frac{q}{q+N} - \log q - 1 + \frac{N}{q+N} \right\} = \frac{k}{\epsilon} \log \left(1 + \frac{N}{q} \right) \\ e^{\epsilon/kT} &= 1 + \frac{N}{q} = 1 + \frac{N\epsilon}{U} \quad \text{so} \quad U = \frac{N\epsilon}{e^{\epsilon/kT} - 1} \\ C_V &= \frac{\partial U}{\partial T} = -\frac{N\epsilon}{(e^{\epsilon/kT} - 1)^2} \left(-\frac{\epsilon}{kT^2} e^{\epsilon/kT} \right) = Nk \frac{(\epsilon/kT)^2 e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2} \end{aligned}$$

Note that in Equation (7.103), N is the number of atoms, and there are three oscillators (i.e. x , y , and z) for each atom. Now for $\epsilon/kT \ll 1$, we have

$$C_V = Nk \frac{(\epsilon/kT)^2 e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2} \approx Nk \frac{(\epsilon/kT)^2 (1 + \epsilon/kT)}{(1 + \epsilon/kT - 1)^2} = Nk$$

This is just what you expect. The high temperature limit means that each oscillator has many energy units, that is $q \gg N$. Thus $U = NkT$, i.e. (3.11), which is what you get from the equipartition theorem for the oscillator which has two quartic degrees of freedom. Of course, this gives $C_V = Nk$, i.e. (3.15).

(3) See Problem 7.45. The thermodynamic identity for energy is given in Equation (3.58) as

$$dU = TdS - PdV + \mu dN$$

Therefore we can write the pressure as

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S,N}$$

The energy (density) of a photon gas is given by (7.96), namely

$$\frac{U}{V} = \frac{8\pi^5 (kT)^4}{15 (hc)^3} = \alpha(kT)^4$$

where α is a constant. However, before we differentiate, we need it in a form that lets us keep S and N constant. From (7.89), and also (homework) Problem 7.46, the entropy is

$$S = \frac{32\pi^5}{45} V \frac{(kT)^3}{(hc)^3} k = \beta V (kT)^3$$

where β is a constant. The number of photons, from Problem 7.44 after doing the integral, is

$$N = 8\pi(2.40411)V \frac{(kT)^3}{(hc)^3} = k \frac{8\pi(2.40411)}{(32\pi^5)/45} S = (\text{Constant}) \times S$$

where a is a constant. Therefore, if S is constant then so is N . Now it is simple to write U in terms of S and V so that we can take the derivative:

$$U = \alpha V \left[\left(\frac{S}{\beta V} \right)^{1/3} \right]^4 = \gamma V^{-1/3}$$

where $\gamma \equiv \alpha \left(\frac{S}{\beta} \right)^{4/3}$ is a constant

$$\text{then } P = - \frac{\partial U}{\partial V} = \frac{1}{3} \gamma V^{-4/3} = \frac{1}{3} \frac{\gamma V^{-1/3}}{V} = \frac{1}{3} \frac{U}{V}$$

(4) First we need to find the final temperature T_f of the two blocks. Conservation of energy gives us

$$\begin{aligned} mc(T_f - T) &= (2m)(3c/2)(3T - T_f) \\ 4T_f &= 10T \\ T_f &= 5T/2 \end{aligned}$$

We know that the change in entropy for a block is $\Delta S = mc \log(T_f/T_i)$ so

$$\begin{aligned} \Delta S = \Delta S_1 + \Delta S_2 &= mc \log \left[\frac{5T/2}{T} \right] + (2m)(3c/2) \log \left[\frac{5T/2}{3T} \right] \\ &= mc \log \left[\frac{5}{2} \right] + mc \log \left[\left(\frac{5}{6} \right)^3 \right] \\ &= mc \log \frac{5^4}{2 \cdot 6^3} = mc \log \frac{625}{432} \end{aligned}$$

which is positive since the argument of the log is greater than unity.

(5) See Problem 5.28. This is almost identical to the problem we did for the phase transition between the graphite and diamond phases of elemental carbon. In this case, the Gibbs free energy of formation at atmospheric pressure and temperature, as given in the table on page 404 of Schroeder, of one mole of calcite and aragonite are -1128.8 kJ and -1127.8 kJ, respectively. Calcite has the lower Gibbs free energy so is the more stable of the two.

From Equation (5.41), the change in Gibbs free energy with pressure at constant temperature is given by

$$\left(\frac{\partial G}{\partial P} \right)_{T,N} = V$$

The table on page 404 also gives the volumes of calcite and aragonite as 36.93 cm^3 and 34.15 cm^3 . Setting $G_{\text{calcite}} = 0$ at atmospheric pressure and temperature, and converting everything to SI units, we have

$$\begin{aligned} G_{\text{calcite}} &= 36.93 \times 10^{-6} P \\ G_{\text{aragonite}} &= 34.15 \times 10^{-6} P + 1000 \end{aligned}$$

The Gibbs free energy for calcite grows more quickly with pressure than for aragonite, so at some positive pressure, aragonite will be the more stable form. To find this pressure, just equate the two Gibbs free energies. That is,

$$P = \frac{1000}{36.93 - 34.15} \times 10^6 = 3.6 \times 10^8 \text{ Pa} = 3600 \text{ bar}$$

which is close to 3600 times atmospheric pressure.