

Columbia University
Department of Physics
QUALIFYING EXAMINATION

Friday, January 18, 2019

10:00AM to 12:00PM

General Physics

Section 5. Thermodynamics and Statistical Mechanics

Two hours are permitted for the completion of this section of the examination. Choose 4 problems out of the 6 included in this section. (You will not earn extra credit by doing an additional problem). Apportion your time carefully.

Use separate answer booklet(s) for each question. Clearly mark on the answer booklet(s) which question you are answering (e.g., Section 5 (Thermodynamics and Statistical Mechanics), Question 2, etc.).

Do **NOT** write your name on your answer booklets. Instead, clearly indicate your **Exam Letter Code**.

You may refer to the single handwritten note sheet on $8\frac{1}{2}$ " \times 11" paper (double-sided) you have prepared on Modern Physics. The note sheet cannot leave the exam room once the exam has begun. This note sheet must be handed in at the end of today's exam. Please include your Exam Letter Code on your note sheet. No other extraneous papers or books are permitted.

Simple calculators are permitted. However, the use of calculators for storing and/or recovering formulae or constants is NOT permitted.

Questions should be directed to the proctor.

Good Luck!

1.

- (a) Using dimensional analysis, find the thermal energy U of an ultra-relativistic ideal gas (such as a photon gas) in a box of volume V at a temperature T , up to an overall constant.
- (b) Derive from the result in part (a) the dimensionless ratios CT/U , F/U and PV/U , where C is the heat capacity at constant volume, $F = U - TS$ is the free energy, and P is the pressure.
- (c) By what factor does the temperature increase when the volume of the box is adiabatically compressed to half its original volume?

2. Consider a long molecule which is composed of N ($N \gg 1$) monomers, each of which can reside in one of two states which have lengths a and b , with $b > a$. The energy of a monomer in the longer state is ε larger than a monomer in the shorter state (i.e. $\Delta E = \varepsilon$).

(a) Calculate the mean length of the molecule as a function of temperature, T .

(b) Calculate the standard deviation of the molecules' length.

Now, suppose the molecule is held at fixed length, L , where $Na < L < Nb$.

(c) Find the internal energy and entropy for the molecule.

(d) Calculate the force needed to keep the molecule held at length L .

3. In addition to the cosmic microwave background (CMB) of photons, the universe is permeated with an analogous background radiation of neutrinos, currently at an effective temperature of 1.95 K. In the hot early universe, neutrinos were in thermal equilibrium with photons: neutrino-antineutrino pairs were freely converted into photons and back. For the purposes of this problem, you may assume neutrinos are massless. Find the present total number of cosmic neutrinos plus anti-neutrinos per cubic meter, assuming there are three different neutrino species. (A precision of one significant digit suffices in your final result.)

The following integral formula may be useful:

$$\int_0^{\infty} dx \frac{x^n e^{-x}}{1 - a e^{-x}} = \sum_{k=0}^{\infty} \int_0^{\infty} dx x^n a^k e^{-(k+1)x} = n! \sum_{k=0}^{\infty} \frac{a^k}{(k+1)^{n+1}}.$$

Boltzmann's constant is $k = 8.6 \times 10^{-5}$ eV/K. Planck's constant is $\hbar = 6.6 \times 10^{-16}$ eV · s.

4. Consider two containers. One is of volume V_1 and contains N_1 oxygen atoms in thermal equilibrium at temperature T . The other is of volume V_2 and contains N_2 atoms of nitrogen, also in thermal equilibrium at temperature T . Suppose that the two containers are now connected so they can exchange particles and we have one system of volume $V = V_1 + V_2$ at temperature T .
- (a) Please find the pressure.
 - (b) Please find the entropy.
 - (c) Please state how your answers would change if both containers held oxygen initially.

5. Suppose that we have a gas of noninteracting particles moving in two dimensions with the dispersion

$$\varepsilon_k = v\sqrt{k_x^2 + k_y^2}$$

Please determine the following. *You may express your answers in terms of physical constants and integrals such as*

$$I(\zeta) = \int_0^\infty dx \frac{x^\zeta}{e^x - 1},$$

which evaluate to pure numbers. You do not need to give numerical values for the integrals.

- (a) the Bose-Einstein condensation temperature T_{BEC}
- (b) the specific heat at constant volume for temperatures $T < T_{BEC}$
- (c) the behavior of $dN/d\mu$ as the temperature approaches T_{BEC} from above.

6. Consider an ideal gas composed of N ${}^3\text{He}$ atoms contained in a vessel of volume V . The ${}^3\text{He}$ isotope has a nucleus consisting of two protons and one neutron. In the following, consider energy states of the ${}^3\text{He}$ atoms in a cubic box of volume $V = L^3$, where L is the length of the sides of the cube, and apply cyclic boundary conditions (*In cyclic boundary conditions the wavefunctions are unchanged under a translation of distance L along any coordinate*). Assume, for simplicity, that the system remains gaseous at all temperatures and assume that the ${}^3\text{He}$ atoms remain in their electronic ground state.

(a) Consider the limit of absolute zero of temperature ($T = 0$).

(i) Provide an expression specifying the possible energy states for single ${}^3\text{He}$ atoms.

(ii) What is the difference between the lowest and highest energy states of single ${}^3\text{He}$ atoms?

(iii) Obtain an expression for the total kinetic energy as function of N and V .

(iv) What would be the total kinetic energy for a gas composed of ${}^4\text{He}$ atoms?

(b) Assume that the temperature is raised slightly so that T remains small. The kinetic energy of the ${}^3\text{He}$ ideal gas can be written:

$$U(T) = U(0) + u(T),$$

where $u(T)$, to leading power in the temperature is proportional to T^n . Using qualitative and/or dimensional arguments, determine n .

Question 1 Solution

- (a) The thermal energy is extensive so it is proportional to V . Dimensional analysis then implies $\boxed{U = aVT^4}$, where a is some combination of powers of c , \hbar and k times a numerical constant. (To be precise, $a = a_0 k^4 / (c\hbar)^3$ where a_0 is a numerical constant.)
- (b) The heat capacity is $C = \partial_T U|_V = 4aVT^3$. The entropy is $S = \int C dT/T = \frac{4}{3}aVT^3$. The free energy is $F = U - TS = -\frac{1}{3}aVT^4$. The pressure is $P = -\partial_V F|_T = \frac{1}{3}aT^3$. Thus the dimensionless ratios are $\boxed{\frac{CT}{U} = 4, \frac{F}{U} = -\frac{1}{3}, \frac{PV}{U} = \frac{1}{3}}$.
- (c) Adiabatic compression means compression at constant entropy $S \propto VT^3$, so if the volume is reduced by a factor of 2, the temperature will increase by a factor of $\boxed{2^{1/3}}$.

Question 2 Solution

- (a) The single-monomer partition function Z_1 is $Z_1 = 1 + e^{-\beta\varepsilon}$ and since the monomers are uncoupled, the full molecule partition function is $Z = Z_1^N$, or

$$Z = (1 + e^{-\beta\varepsilon})^N.$$

The (average) number of monomers in the excited state, N_b , is just E/ε , so

$$\langle N_b \rangle = -\frac{1}{\varepsilon} \frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial (\beta\varepsilon)} = -N \left(\frac{-e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} \right) = \frac{N}{1 + e^{\beta\varepsilon}}.$$

Then, the average length is just

$$\langle L \rangle = Na + \langle N_b \rangle (b - a) = N \left(a + \frac{b - a}{1 + e^{\beta\varepsilon}} \right).$$

- (b) The mean squared length, $\langle L^2 \rangle$ expressed in terms of N_b is

$$\begin{aligned} \langle L^2 \rangle &= \langle (Na + N_b(b - a))^2 \rangle \\ &= \langle N^2 a^2 + 2NN_b a(b - a) + N_b^2 (b - a)^2 \rangle \\ &= N^2 a^2 + 2N \langle N_b \rangle a(b - a) + \langle N_b^2 \rangle (b - a)^2. \end{aligned}$$

Similarly, the mean length squared, $\langle L \rangle^2$, is

$$\langle L \rangle^2 = N^2 a^2 + 2N \langle N_b \rangle a(b - a) + \langle N_b \rangle^2 (b - a)^2,$$

with the result that the variance of the L distribution is

$$\text{Var } L = \langle L^2 \rangle - \langle L \rangle^2 = (b - a)^2 (\langle N_b^2 \rangle - \langle N_b \rangle^2) = (b - a)^2 \text{Var } N_b.$$

The variance of the N_b distribution can be obtained from the variance of the energy distribution,

$$\text{Var } N_b = \frac{1}{\varepsilon^2} \text{Var } E = \frac{1}{\varepsilon^2} \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{\partial^2 \ln Z}{\partial (\beta\varepsilon)^2} = \frac{N e^{\beta\varepsilon}}{(1 + e^{\beta\varepsilon})^2}.$$

Then, the standard deviation of the L distribution is

$$\sqrt{\langle L^2 \rangle - \langle L \rangle^2} = \sqrt{N} \left(\frac{b - a}{e^{\beta\varepsilon/2} + e^{-\beta\varepsilon/2}} \right) = \frac{2\sqrt{N}(b - a)}{\cosh(\beta\varepsilon/2)}.$$

- (c) If the length is fixed, then the average length per monomer, $l \equiv L/N$ is a useful quantify. Given L , the number of monomers in the excited state is

$$N_b = \frac{L - Na}{b - a} = N \left(\frac{l - a}{b - a} \right) \equiv N\gamma,$$

and $E = N_b \varepsilon = \varepsilon N \gamma$.

The entropy is given by $S = k \ln \Omega$ with $\Omega = \binom{N}{N_b} = \frac{N!}{N_b! (N - N_b)!}$. So,

$$S = k [\ln (N!) - \ln (N_b!) - \ln ((N - N_b)!)] .$$

Assuming N (and N_b) large and applying the Stirling approximation,

$$\begin{aligned} S &= k [N \ln N - N_b \ln N_b - (N - N_b) \ln (N - N_b)] \\ &= k \left[N_b \ln \left(\frac{N}{N_b} \right) + (N - N_b) \ln \left(\frac{N}{N - N_b} \right) \right] \\ &= -kN [\gamma \ln \gamma + (1 - \gamma) \ln (1 - \gamma)] . \end{aligned}$$

(d) The force is given by $F = \left. \frac{\partial F}{\partial L} \right|_T$, with $F = E - ST$ or

$$F = N_b \varepsilon - ST = N [\gamma \varepsilon + kT (\gamma \ln \gamma + (1 - \gamma) \ln (1 - \gamma))] .$$

The L dependence comes through the γ factor and

$$\begin{aligned} F &= \left. \frac{\partial F}{\partial \gamma} \right|_T \frac{d\gamma}{dL} = \left. \frac{\partial F}{\partial \gamma} \right|_T \frac{1}{N(b-a)} = \frac{1}{b-a} [\varepsilon + kT (\ln \gamma + 1 - \ln (1 - \gamma) - 1)] \\ &= \frac{1}{b-a} \left[\varepsilon + kT \ln \left(\frac{\gamma}{1 - \gamma} \right) \right] . \end{aligned}$$

Question 3 Solution

Since neutrinos are fermions, the average occupation number of a single-particle state of energy ϵ in the hot early universe at temperature T is given by the Fermi-Dirac distribution: $n_{\text{FD}} = \frac{1}{e^{\epsilon/kT} + 1}$. The chemical potential is zero here because the total number of neutrinos is not fixed, as neutrino-antineutrino pairs are freely created and annihilated. The energy of a massless particle of momentum p is $\epsilon = cp$. The number of neutrinos plus anti-neutrinos in a volume V is therefore

$$N = 3 \times 2 \times \frac{V}{(2\pi\hbar)^3} \int_0^\infty dp 4\pi p^2 \frac{1}{e^{cp/kT} + 1} = \frac{V}{2\pi^2} \left(\frac{kT}{\hbar c} \right)^3 \int_0^\infty dx \frac{x^2}{e^x + 1}. \quad (1)$$

Here $\frac{V}{(2\pi\hbar)^3} dp 4\pi p^2$ is the number of left-handed single-neutrino states with momentum between p and $p + dp$ in a volume V . The factor of 3 counts the neutrino species, and the factor of 2 counts the neutrinos and anti-neutrinos. Only left-handed neutrinos and right-handed antineutrinos are converted to photons and back, so there is no additional factor of 2 counting spin states. Using the formula given, the integral can be computed as

$$\int_0^\infty dx \frac{x^2}{e^x + 1} = 2 \sum_{n=0}^\infty \frac{(-1)^n}{(n+1)^3} \approx 1.8.$$

Summing the first few terms suffices to get a result to the required accuracy. The present number density of cosmic neutrinos is given by equation (1) with $T = 1.95$ K:

$$\frac{N}{V} \approx \frac{6}{2\pi^2} \left(\frac{1.95 \text{ K} \times 8.62 \times 10^{-5} \text{ eV/K}}{6.58 \times 10^{-16} \text{ eV} \cdot \text{s} \times 3 \times 10^8 \text{ m/s}} \right)^3 \times 1.8 \approx \boxed{3 \times 10^8 / \text{m}^3}.$$

Question 4 Solution

- (a) Our system has N_1 oxygen and N_2 nitrogen in a total volume $V = V_1 + V_2$. The free energy is

$$F = -N_1 T \left(\ln \left(\frac{V}{\lambda_O^3 N_1} \right) + 1 \right) - N_2 T \left(\ln \left(\frac{V}{\lambda_N^3 N_2} \right) + 1 \right); \quad \lambda_a = \left(\frac{2\pi\hbar^2}{m_a T} \right)^{\frac{1}{2}}.$$

Then $P = -\frac{\partial F}{\partial V}$ gives

$$P = \frac{(N_1 + N_2)T}{V}.$$

- (b) Using $S = -\frac{\partial F}{\partial T}$ gives

$$S = N_1 \left(\ln \left(\frac{V}{\lambda_O^3 N_1} \right) + \frac{5}{2} \right) + N_2 \left(\ln \left(\frac{V}{\lambda_N^3 N_2} \right) + \frac{5}{2} \right).$$

- (c) If both containers held oxygen initially then the final state would have $N = N_1 + N_2$ oxygen atoms in a volume V , so the pressure would not change and the entropy would become

$$S = N \left(\ln \left(\frac{V}{\lambda_O^3 N} \right) + \frac{5}{2} \right).$$

which is less than we found in part (b) because there is no entropy of mixing.

Question 5 Solution

- (a) The BEC temperature is given by setting the chemical potential equal to zero in the equation for the particle number:

$$N = V \int \frac{d^2k}{(2\pi)^2} \frac{1}{e^{\frac{\varepsilon_k}{T_{BEC}}} - 1},$$

or, using our specific form for ε_k

$$\frac{N}{V} = \frac{1}{2\pi v^2} \int_0^\infty d\varepsilon \frac{\varepsilon}{e^{\frac{\varepsilon}{T_{BEC}}} - 1} = \frac{T_{BEC}^2}{2\pi v^2} \int_0^\infty dx \frac{x}{e^x - 1} = \frac{T_{BEC}^2}{2\pi v^2} I(1)$$

so

$$T_{BEC} = \sqrt{\frac{2\pi v^2 N}{V I(1)}}.$$

- (b) Calculating the specific heat:

$$C = \frac{dE}{dT} = \frac{d}{dT} V \int \frac{d^2k}{(2\pi)^2} \frac{\varepsilon_k}{e^{\frac{\varepsilon_k - \mu(T)}{T}} - 1}$$

for $T < T_{BEC}$, $\mu = 0$ independent of T , so doing the angle integral and defining $x = v|k|/T$

$$C = \frac{dE}{dT} = \frac{d}{dT} V \int \frac{d^2k}{(2\pi)^2} \frac{\varepsilon_k}{e^{\frac{\varepsilon_k}{T}} - 1} = \frac{d}{dT} \frac{V}{2\pi v^3} T^3 \int_0^\infty dx \frac{x^2}{e^x - 1} = \frac{3VT^2}{2\pi v^3} I(2)$$

- (c) We find

$$\frac{dN}{d\mu} = \frac{d}{d\mu} V \int \frac{d^2k}{(2\pi)^2} \frac{1}{e^{\frac{\varepsilon_k - \mu(T)}{T}} - 1}$$

To simplify notation define

$$\lambda(T) = e^{\frac{\mu(T)}{T}}$$

so

$$\frac{d}{d\mu} = \frac{\lambda}{T} \frac{d}{d\lambda}$$

and

$$\frac{dN}{d\mu} = \frac{\lambda V}{T} \frac{d}{d\lambda} \int \frac{d^2k}{(2\pi)^2} \frac{\lambda}{e^{\frac{\varepsilon_k}{T}} - \lambda} = \frac{\lambda V}{T} \int \frac{d^2k}{(2\pi)^2} \left(\frac{1}{e^{\frac{\varepsilon_k}{T}} - \lambda} + \frac{\lambda}{\left(e^{\frac{\varepsilon_k}{T}} - \lambda\right)^2} \right).$$

Using $x = \varepsilon_k/T = v|k|/T$ we have

$$\frac{dN}{d\mu} = \frac{\lambda VT}{2\pi v^2} \int_0^\infty dx \left(\frac{x}{e^x - \lambda} + \frac{x\lambda}{(e^x - \lambda)^2} \right)$$

As $T \rightarrow T_{BEC}$, $\lambda \rightarrow 1$ from below. Writing $\lambda = 1 - \delta(T)$ we see that the second term gives the leading singular behavior which comes from $x \ll 1$ and is, to logarithmic accuracy,

$$\frac{dN}{d\mu} = \frac{VT_{BEC}}{2\pi v^2} \int dx \frac{x}{(x + \delta)^2} \rightarrow \frac{N}{T_{BEC}I(1)} \ln \left(\frac{1}{\delta} \right).$$

To find $\delta(T)$ we write

$$N = \frac{VT^2}{2\pi v^2} \int_0^\infty dx x \left(\frac{1 - \delta}{e^x - 1 + \delta} \right) \rightarrow \frac{VT^2}{2\pi v^2} \left(I(1) - \delta \ln \left(\frac{1}{\delta} \right) \right) + \dots.$$

Using the expression for T_{BEC} gives

$$T_{BEC}^2 = T^2 \left(1 - \frac{\delta}{I(1)} \ln \left(\frac{1}{\delta} \right) \right) + \dots$$

or

$$T^2 - T_{BEC}^2 = \frac{T^2}{I(1)} \delta \ln \left(\frac{1}{\delta} \right) + \dots,$$

implying

$$\delta \ln \left(\frac{1}{\delta} \right) = 2I(1)t,$$

where

$$t = \frac{(T - T_{BEC})}{T_{BEC}}.$$

Thus

$$\ln \delta + \ln \left(\ln \left(\frac{1}{\delta} \right) \right) = \ln (2I(1)t),$$

or

$$\ln \delta = \ln (2I_1 t) - \ln \left(\ln \left(\frac{1}{2I(1)t} \right) \right) + \dots,$$

implying

$$\frac{dN}{d\mu} = \frac{N}{T_{BEC}I(1)} \left[\ln \left(\frac{1}{2I(1)t} \right) + \ln \left(\ln \left(\frac{1}{2I(1)t} \right) \right) + \dots \right].$$

Question 6 Solution

- (a) (i) With cyclic boundary conditions and no interactions (an ideal gas) the possible momenta are:

$$p_i = \frac{2\pi m_i \hbar}{L},$$

where $i = x, y, z$ and m_i is a positive integer. The energy of single ${}^3\text{He}$ atoms is

$$\varepsilon(p_x, p_y, p_z) = \varepsilon_0 + \sum_i \frac{p_i^2}{2M},$$

where ε_0 is the ground state energy and M is the mass.

- (ii) Since ${}^3\text{He}$ atoms are fermions, the requested energy difference is the Fermi energy,

$$\varepsilon_F = \frac{p_F^2}{2M},$$

where the Fermi momentum is

$$p_F = \hbar \left(\frac{6\pi^2}{s_3 + 1} n \right)^{1/3},$$

where s_3 is the spin of the ${}^3\text{He}$ atoms and $n = N/V$. Thus

$$\varepsilon_F = \frac{\hbar^2}{2M} \left(\frac{6\pi^2}{s_3 + 1} n \right)^{2/3},$$

- (iii) The total kinetic energy is

$$E = \int_0^{\varepsilon_F} g(\varepsilon) \varepsilon d\varepsilon,$$

where $g(\varepsilon)$ is the density of states with energy ε in $d\varepsilon$ and is given by

$$g(\varepsilon) = (2s_3 + 1) \frac{V}{4\pi^2} \left(\frac{2M}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}$$

From the previous two equations, we find

$$E = (2s_3 + 1) \frac{V}{4\pi^2} \frac{2}{5} \varepsilon_F^{5/2},$$

which yields

$$E = \frac{3}{5} N \varepsilon_F.$$

- (iv) ${}^4\text{He}$ atoms are bosons. In the absence of interactions between atoms the kinetic energy of the atoms vanishes.

- (b) As the temperature is raised to a value $T > 0$, the ${}^3\text{He}$ atoms close to the Fermi level acquire an energy to move to higher energy states. A simple (qualitative) way to proceed to that on average atoms gain an energy $\delta u = k_B T$, where k_B is the Boltzmann constant. The number of atoms that change states is dictated by the Pauli exclusion principle. To obtain an estimate we may assume that the number of ${}^3\text{He}$ atoms that change state is $\Delta n \sim k_B T$. The estimate of the change in energy is $u(T) \sim \Delta n \delta u = (k_B T)^2$.