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Statistical Mechanics Spring, 2002

Problem Set IV Solutions

1) (Counts as 2 problems) Consider a single, non-relativistic quantum mechanical particle in a box of volume V (with infinite potential walls) as in problem 2 of set II. As you found there, the states can be labeled by integers (n_x, n_y, n_z).

a) Write down the formula for the energy, ϵ, of the particle as a function of V and (n_x, n_y, n_z). Now suppose that the volume V is changed by moving the walls of the box very slowly. In this case, (n_x, n_y, n_z) will remain fixed. Find the rate of change in energy, ϵ, with respect to volume, V, in this process, and thereby obtain a formula for the pressure, P, exerted by a single particle.

Solution: As we showed in HW#2, the energy of the particle is given by

$$\epsilon_{\vec{n}} = \frac{\pi^2\hbar^2\left(n_x^2 + n_y^2 + n_z^2\right)}{2mL^2} = \frac{\pi^2\hbar^2\vec{n}^2}{2mV^{\frac{2}{3}}}.$$

Hence the pressure, which is the rate of change of energy with respect to volume, is

$$P = -\left(\frac{\partial\epsilon}{\partial V}\right)_S = -\frac{\pi^2\hbar^2\vec{n}^2}{2m}\left(-\frac{2}{3}V^{-\frac{5}{3}}\right) = \frac{2\epsilon}{3V}. \quad \blacksquare$$

b) Now use the distribution function $n(\epsilon)$ derived in class to obtain the total pressure, P, exerted by a gas of N particles (with η spin states) as function of the quantities α and β for the cases in which particles are (i) distinguishable, (ii) bosons, and (iii) fermions. (You need not evaluate the integrals in the expression for P in cases (ii) and (iii).) Show that in all three cases, we have $PV = 2E/3$.

Solution: The total pressure will be the pressure exerted by a single particle integrated with respect to the number of particles in each state, i.e., $P_{\text{total}} = \int P(\epsilon)n(\epsilon)d\epsilon$, where $n(\epsilon)$ is the occupation number of each state. Independent of the kind of particle, we showed in part (a) that the pressure exerted by that particle is $2\epsilon/3V$. Thus, for cases (i), (ii) and (iii) the pressure is

$$P = \int P(\epsilon)n(\epsilon)d\epsilon = \int \frac{2\epsilon}{3V} n\left(\epsilon\right)d\epsilon = \frac{2}{3V}\int \epsilon n(\epsilon)d\epsilon = \frac{2E}{3V},$$

as desired. The occupation number number will be the density of states $g(\epsilon)$ times the appropriate "Boltzmann factor" $\left(e^{\alpha+\beta\epsilon} + k\right)^{-1}$, where $k = 0$ for "Boltzmanns", $k = -1$ for bosons, and $k = +1$ for fermions. As shown in class

$$g(\epsilon) = \frac{\eta V\sqrt{2m^3\epsilon}}{2\pi^2\hbar^3}.$$

Thus

$$P_{\text{total}} = \int d\epsilon \frac{2\epsilon}{3V} \frac{\eta V \sqrt{2m^3 \epsilon}}{2\pi^2 \hbar^3 \left(e^{\alpha+\beta\epsilon} + k\right)} = \int d\epsilon \frac{\eta \sqrt{2m^3} \epsilon^{\frac{3}{2}}}{3\pi^2 \hbar^3 \left(e^{\alpha+\beta\epsilon} + k\right)}$$

Evaluating the integral explicitly for the case of "Boltzmanns," we get

$$P_{\text{total}} = \frac{\eta\sqrt{2m^3}}{3\pi^2\hbar^3} e^{-\alpha} \beta^{-\frac{5}{2}} \Gamma\left(\frac{5}{2}\right) = \frac{\eta\sqrt{2\pi m^3}}{4\pi^2\hbar^3} \frac{e^{-\alpha}}{\beta^{\frac{5}{2}}}. \quad \blacksquare$$

c) For the case of fermions, show that when $\beta \to \infty$ (i.e., $T \to 0$) with N held fixed, the quantity $\mu \equiv -\alpha/\beta$ goes to a finite limit. Evaluate μ at $T = 0$ and use the result of part (b) to obtain the pressure exerted by a non-relativistic fermion gas at $T = 0$.

Solution: Using our above expression for $n(\epsilon)$ and rewriting it in terms of μ, we find that the total number of particles (which is held fixed) is

$$N = \frac{\eta V \sqrt{2m^3}}{2\pi\hbar^2} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)} + 1}.$$

As $\beta \to \infty$, all the states with energy less than μ will contribute as $\sqrt{\epsilon}$ because the exponential will go to zero, while those with energy greater than μ will have their contributions damped exponentially. Thus, we find

$$N = \frac{\eta V \sqrt{2m^3}}{2\pi\hbar^2} \int_0^\mu \sqrt{\epsilon} = \frac{\eta V \sqrt{2m^3}}{2\pi\hbar^2} \mu^{\frac{3}{2}} \Rightarrow \mu = \left(\frac{3\pi^2 N}{\eta V}\right)^{\frac{2}{3}} \frac{\hbar^2}{m\sqrt[3]{2}}.$$

To obtain the pressure, we first compute the energy by integrating $\epsilon^{\frac{3}{2}}$ (which is the fermi integrand obtained in part (b), again taking the $\beta \to \infty$ limit) up to energy μ, which yields

$$E = \frac{3N\mu}{5} = \frac{3^{\frac{5}{3}} N}{5} \left(\frac{3\pi^2 N}{\eta V}\right)^{\frac{2}{3}} \frac{\hbar^2}{m\sqrt[3]{2}}.$$

Finally, using the result of part (b), we find that

$$P = \frac{2E}{3V} = \frac{2N\mu}{5V} = \frac{\hbar^2}{5m} \left(\frac{6\pi^2}{\eta}\right)^{\frac{2}{3}} \left(\frac{N}{V}\right)^{\frac{5}{3}}. \quad \blacksquare$$

2) In class we derived criteria under which boson and fermion ideal gases behave classically. Significant departures from classical behavior for these gases occur at low temperatures and high densities on account of the "statistics" of indistinguishable particles. However, as also mentioned in class, a quantum ideal gas of distinguishable particles also will depart from classical behavior on account of the discreteness of energy levels. For a quantum gas of N distinguishable particles of mass m in a volume V, estimate the temperature at which non-classical behavior would become manifest. Evaluate this

temperature for the values of m and N/V typical of a gas at standard room temperature and pressure.

Solution: The particles will depart from classical behavior when the spacing of the energy levels is a significant fraction of the energy of most of the particles. As a (very) rough approximation, we can say this happens when the average energy of each particle is equal to the energy of the ground state. This gives

$$\frac{3}{2}kT = \frac{\pi^2\hbar^2}{mV^{\frac{2}{3}}} \Rightarrow T = \frac{\pi^2\hbar^2}{3kV^{\frac{2}{3}}}.$$

Plugging in $m = 30m_{\text{proton}}$ (our atmosphere is $O_2 - N_2$) and $V = 1\ m^3$ (since we've used that one a lot) gives

$$T \approx 5.6 \times 10^{-20}\text{K}.$$

Notice that the answer depends on V and not N/V. Since the particles are free, they don't care how many others are nearby. Since they're distinguishable, the thermal wavelength is irrelevant as they are occupying states in different Hilbert spaces. ■