
Homework Solutions 5 (Schroeder Chapter 6)

6 Say E_1 is the ground state ($n = 1$) energy, and E_2 is the energy for the $2^2 = 4$ first excited states. Since $kT \ll \Delta E$, all terms in the partition function for $n \neq 1$ are negligible. Therefore, for any one of the $n = 2$ states,

$$p_2 = \frac{e^{-E_2/kT}}{Z} \approx \frac{e^{-E_2/kT}}{e^{-E_1/kT}}$$

Since there are four of these states, and with $kT \approx \frac{1}{40}$ eV and $\Delta E = 10.2$ eV,

$$p(E_2) \approx 4 e^{(E_1 - E_2)/kT} \approx 10^{-171}$$

In other words, room temperature won't kick any H atoms into an excited state. But at 9500 K, $kT = 0.819$ eV, so $p(E_2) \approx 1.6 \times 10^{-5}$, which is not so negligible.

18 Second derivative:

$$\frac{\partial^2 Z}{\partial \beta^2} = \sum_n E_n^2 e^{-\beta E_n} = Z \sum_n E_n^2 \frac{e^{-\beta E_n}}{Z} = Z \bar{E}^2$$

Therefore

$$\bar{E}^2 = \frac{1}{Z} \frac{\partial}{\partial \beta} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \frac{\partial}{\partial \beta} (-Z \bar{E}) = -\frac{1}{Z} \left(\frac{\partial \bar{E}}{\partial \beta} + \bar{E} \frac{\partial Z}{\partial \beta} \right) = -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2$$

This means

$$\bar{E}^2 - \bar{E}^2 = -\frac{\partial \bar{E}}{\partial \beta} = -\frac{\partial T}{\partial \beta} \frac{\partial \bar{E}}{\partial T}$$

Now, $\partial T / \partial \beta = -kT^2$, and $\partial \bar{E} / \partial T = C_V$. So

$$\sigma_E = (\bar{E}^2 - \bar{E}^2)^{1/2} = kT \sqrt{C_V/k}$$

19 At high T , equipartition gives $\bar{E} = NkT$, and therefore $C_V = Nk$. This means

$$\sigma_E = kT \sqrt{N} \quad \text{and} \quad \frac{\sigma_E}{\bar{E}} = \frac{1}{\sqrt{N}}$$

In other words, the usual $1/\sqrt{N}$ for statistical fluctuations. For $N = 1$, this is 1—the average is unreliable. For $N = 10^4$, we get 1%. And at $N = 10^{20}$, the relative fluctuations are one part in 10^{10} . At this point, it's fine to say $U = \bar{E}$ and not worry about the fluctuations.

20 (not a)

- (a) It's an infinite geometric series, which you know.
- (b) Measuring energies relative to the ground state, $E_n = n\hbar\omega$. So

$$Z = \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

- (c)

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

- (d) If we have N identical, independent oscillators,

$$U = N\bar{E} = \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

- (e) You've done 3.25.

39

- (a) We need to integrate the Maxwell speed distribution with $v_{\text{esc}} = 1.1 \times 10^4$ m/s, the appropriate parameters for N_2 , and $T = 1000$ K:

$$p(v > v_{\text{esc}}) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{v_{\text{esc}}}^{\infty} dv v^2 e^{-mv^2/2kT} = 2.5 \times 10^{-88}$$

The Nitrogen is not going to escape.

- (b) Hydrogen is much lighter, so the same integral with H_2 parameters gives a probability of 2.2×10^{-6} . While small, over the lifetime of the Earth the H_2 molecules in a well-mixed atmosphere will all end up in the upper atmosphere repeatedly, and have a significant probability of escaping. So all the H_2 should vanish. He is only twice as massive as H_2 , and its probability ends up as 1.5×10^{-12} . He will similarly vanish, just more slowly.

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- (c) If we do the N_2 calculation with the new $v_{\text{esc}} = 2.4 \times 10^3$ m/s, we get a probability of 2.3×10^{-4} . So even the heavier gas molecules will escape quickly from the moon.

42

- (a) For a single oscillator,

$$F = -kT \ln Z = kT \ln(1 - e^{-\beta\hbar\omega})$$

For N independent oscillators, $F = NkT \ln(1 - e^{-\beta\hbar\omega})$.

- (b) The entropy is the derivative

$$S = - \left(\frac{\partial F}{\partial T} \right)_N = Nk \left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega}) \right]$$

47 A degree of freedom freezes out when $kT < \Delta E$. For a particle in a box, $E_n = n^2 E_1$, so

$$\Delta E \sim E_2 - E_1 = 3E_1 = 3 \frac{\hbar^2 \pi^2}{2mL^2} = 2.2 \times 10^{-19} \text{ eV}$$

Therefore

$$T = \frac{\Delta E}{k} = 2.6 \times 10^{-15} \text{ K}$$

This can't be reached currently for any gas.