Sample Solutions Exercise 9

Exercise 9.1: Canonical partition sum of the hydrogen atom (2P)

(a) Write down the partition sum $Z(\beta)$ of the electronic excitations of a hydrogen atom in the canonical ensemble. (1P)

(b) Show that the partition sum is divergent and try to explain why. (1P)

Sample Solution

(a) The energy levels of the hydrogen atom are $E_n = -R_y/n^2$. Each level is n^2-fold degenerate. Hence the partition sum reads (1P)

$$Z(\beta) = \sum_{n=1}^{\infty} n^2 e^{+\beta R_y/n^2}.$$

Correction advice: 0.5P for the correct setup with energies and 0.5P for the correct degeneracies.

(b) We have $n^2 \geq 1$ and $e^{+\beta R_y/n^2} \geq 1$, meaning that the summands are larger than 1, hence the sum diverges. (0.5P)

Where does this divergence come from? A wrong answer would be that we did not take translation into account, because this would only add additional configurations without removing the divergence. The correct answer, as already pointed out by Gibbs, is that for $n \to \infty$ the wave function occupy an infinite volume although they can be excited at almost no cost. This divergence is an example of what is known in as an **infrared divergence**, i.e., a divergence coming from the assumed unrestricted infinity of space. Restricting the atom to a finite volume cures this divergence. However, this task is technically non-trivial. (0.5P)

Exercise 9.2: Entropy of many harmonic oscillators (6P)

In this exercise we want to determine the entropy of N classical three-dimensional harmonic oscillators in the microcanonical ensemble as a function of the energy E.

(a) Compute the phase space volume

$$V(E,N) = \int_{\mathcal{H}\leq E} \prod_{i=1}^{3N} \mathrm{d}q_i \, \mathrm{d}p_i \quad \text{where} \quad \mathcal{H} = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{m\omega^2 q_i^2}{2} \right).$$

Hint: Relate this integral to the volume of a $6N$-dimensional sphere. (2P)

(b) Determine the phase space volume in an infinitesimal energy shell $[E, E + \delta E]$, given by (1P)

$$\delta V(E, N, \delta E) = \delta E \frac{\partial V(E, n)}{\partial E} .$$

(c) As a rough approximation, let us assume that each (quantum) state occupies a volume $(2\pi h)^{3N}$ in the shell. Use Stirlings formula to approximate the entropy of the states in the energy shell $H(E, N, \delta E) = k_B \ln |\Omega(E, N, \delta E)|$, keeping only the terms which grow at least linearly with N. (2P)

(d) Calculate the temperature of the system which is defined as $T^{-1} = \beta = \frac{\partial H}{\partial E}$. (1P)

Sample Solution

(a) We introduce $6N$ dimensionless coordinates by

$$x_i = \begin{cases} \frac{1}{\sqrt{2m}} p_i & \text{for } i = 1, \dots 3N \\ \sqrt{\frac{m\omega^2}{2}} q_{i-3N} & \text{for } i = 3N+1, \dots, 6N \end{cases}$$

turning the Hamilton function into

$$H = \sum_{i=1}^{3N} (x_i^2 + x_{i+3N}^2) = \sum_{i=1}^{6N} x_i^2 .$$

Since $\mathrm{d}x_i \, \mathrm{d}x_{i+3N} = \frac{\omega}{2} \, \mathrm{d}q_i \, \mathrm{d}p_i$ the volume turns into

$$V(E, N) = \left(\frac{2}{\omega}\right)^{3N} \int_{H \le E} \prod_{i=1}^{6N} \mathrm{d}x_i = \left(\frac{2}{\omega}\right)^{3N} \frac{\pi^{3N} E^{3N}}{\Gamma(3N+1)} = \frac{(2\pi E)^{3N}}{\omega^{3N} \, (3N)!} ,$$

where we used the formula for the volume of an n-dimensional sphere (see e.g. Wikipedia) which here has the radius $r = \sqrt{H} \le \sqrt{E}$.

(b) We simply take the derivative with respect to E:

$$\delta V(E, N, \delta E) = \delta E \frac{\partial V(E, n)}{\partial E} = \frac{3N\delta E}{E} \frac{(2\pi E)^{3N}}{\omega^{3N} \, (3N)!}$$

(c) The entropy in the energy shell is estimated by

$$H = k_B \ln |\Omega| = k_B \ln\left(\frac{\delta V(E, N, \delta E)}{(2\pi\hbar)^{3N}}\right) = k_B \ln\left(\frac{3N\delta E}{E} \frac{E^{3N}}{(\hbar\omega)^{3N} \, (3N)!}\right)$$

This can be rewritten as

$$H = k_B \left[\ln\left(\frac{3\delta E}{E}\right) + \ln N + 3N \ln\left(\frac{E}{\hbar\omega}\right) - \ln\big((3N)!\big) \right]$$

We now apply Stirling's formula $n! \approx \sqrt{2\pi n} (n/e)^n$

$$H = k_B \left[\ln\left(\frac{3\delta E}{E}\right) + \ln N + 3N \ln\left(\frac{E}{\hbar\omega}\right) - \frac{1}{2} \ln(6\pi N) - 3N \ln(3N/e) \right].$$

We sort the terms by their significance:

$$H = k_B\left[3N\left(\ln\left(\frac{E}{3N\hbar\omega}\right)+1\right)+\frac{1}{2}\ln N+\ln\left(\frac{3\delta E}{E}\right)-\frac{1}{2}\ln(6\pi)\right].$$

In the large N limit, the last three terms can be neglected, leading to the approximation

$$H \approx 3Nk_B\left[\ln\left(\frac{E}{3N\hbar\omega}\right)+1\right],$$

where the '$+1$' comes from the 'e' in the last term.

(d) Compute the partial derivative:

$$T^{-1} = \beta = \left(\frac{\partial H}{\partial E}\right)_N = \frac{3Nk_B}{E}.$$

This confirms that the average energy per 3D oscillator is indeed $3k_BT$.

Exercise 9.3: Legendre transformation - Extreme values (4P)

Let $f(x)$ be a strictly convex (concave) function on $\mathbb{R}$ with the local slope $m(x) = f'(x)$ and let $f^*(m)$ be the corresponding Legendre transform (see Lecture Notes).

(a) Show that $f(x)+f^*(m) = mx$, highlighting the symmetry between f and f^*. (1P)

(b) Suppose that $f(x)$ has an extremum at x_{ext} and that $f^*(m)$ has likewise an extremum at m_{ext}. Confirm that (1P)

$$x_{ext} = f^{*\prime}(0)\,, \qquad m_{ext} = f'(0)$$

and that (1P)

$$f(x_{ext}) = -f^*(0)\,, \qquad f^*(m_{ext}) = -f(0)\,.$$

(c) Prove that the curvatures of f and f^* are always reciprocal to each other, i.e. (1P)

$$f''(x)f^{*\prime\prime}(m) = 1 \qquad \forall x \text{ and } m = f'(x).$$

Sample Solution

(a) Simply insert the definition:

$$f(x)+f^*(m) \;=\; f(x)+\Big(m\,g(m)-f\big(g(m)\big)\Big) \;=\; f(x)+mx-f(x) \;=\; mx.$$

(b) • We first show that $x_{ext} = f^{*\prime}(0)$. To this end we compute the derivative of $f^*(m) = m\,g(m)-f\big(g(m)\big)$:

$$f^{*\prime}(m) = g(m)+m\,g'(m)-f'\big(g(m)\big)g'(m).$$

We evaluate this expression at $m = 0$, keeping in mind that $g(0)$ is the x-value where $f'(x) = 0$, hence $g(0) = x_{ext}$:

$$f^*(x) = g(0) + 0\,g'(0) + f'\big(g(0)\big)g'(0) = x_{ext} + 0\,g'(0) - \underbrace{f'(x_{ext})}_{=0}g'(0) = x_{ext}.$$

The relation $m_{ext} = f'(0)$ can be proven in the same way.

- In order to prove the relation $f(x_{ext}) = -f^*(0)$ [and likewise $f^*(m_{ext}) = -f(0)$] we simply evaluate $f(x) = m\,g(x) - f^*\big(g(x)\big)$, keeping in mind that $g(x_{ext})$ is just the slope of f at the extremum, hence $g(x_{ext}) = 0$:

$$f(x_{ext}) = x\,g(x_{ext}) - f^*\big(g(x_{ext})\big) = -f^*(0).$$

(c) We know that $f'(x) = m$ and $f^{*\prime}(m) = x$. Hence if we differentiate both we find that

$$f''(x) = \frac{\mathrm{d}m}{\mathrm{d}x}\,, \qquad f^{*\prime\prime}(m) = \frac{\mathrm{d}x}{\mathrm{d}m}.$$

Hence $f''(x)f^{*\prime\prime}(m) = \frac{\mathrm{d}m}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}m} = 1$.

(Σ = 12P)