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Sample Solutions Exercise 8

Exercise 8.1: 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

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

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 Strilings 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

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

This can be rewritten as

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

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

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

We sort the terms by their significance:

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

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

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

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

(d) Compute the partial derivative:

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

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

Exercise 8.2: Free energy of a perturbed system (6P)

A classical system in thermal equilibrium with a heat bath at temperature T is described by an energy function $E^{(0)} : \Omega^{\text{sys}} \to \mathbb{R} : s \to E_s^{(0)}$. Let $Z^{(0)} = \sum_s e^{-\beta E_s^{(0)}}$ be the partition sum of the system.

(a) Assume that the energy function is perturbed by $E_s^{(0)} \to E_s = E_s^{(0)} + \lambda E_s^{(1)}$ with $\lambda \ll 1$. Compute the corresponding partition sum $Z(\lambda)$ as a power series in λ. (2P)

(b) What is the mathematical meaning of $Z(\lambda)$? Hint: Try to compute $\frac{\mathrm{d}^n}{\mathrm{d}\lambda^n} Z(\lambda)\big|_{\lambda=0}$ (1P)

(c) Prove the general statement that in the canonical ensemble the free energy $F = E - TH$ (more precisely: $\langle F\rangle = \langle E\rangle - T\langle H\rangle$) is given by $F = -T\ln Z$. (1P)

(d) Apply (c) to (a),(b) in order to compute $F(\lambda)$ as a power series in λ up to second order. What is the mathematical meaning of $F(\lambda)$? (2P)

Sample Solution

(a) In the canonical ensemble the partition sum reads $Z^{(0)} = \sum_s e^{-\beta E_s^{(0)}}$, where $\beta = 1/T$ is the inverse temperature and the sum runs over all system configurations $s \in \Omega^{\text{sys}}$. In the unperturbed case, the expectation value of an arbitrary random variable X is given by

$$\langle x \rangle_0 = \frac{1}{Z^{(0)}} \sum_s e^{-\beta E_s^{(0)}} x_s.$$

Setting $x_s = e^{-\beta\lambda E_s^{(1)}} = 1 - \beta\lambda E_s^{(1)} + \mathcal{O}(\lambda^2)$ we simply get

$$Z(\lambda) = \sum_s e^{-\beta E_s} = \sum_s e^{-\beta(E_s^{(0)} + \lambda E_s^{(1)})} = Z^{(0)} \left\langle e^{-\beta\lambda E^{(1)}} \right\rangle_0$$

$$\Rightarrow \quad Z(\lambda) = Z^{(0)} \left\langle \sum_{n=0}^{\infty} \frac{(-\beta\lambda E^{(1)})^n}{n!} \right\rangle_0 = Z^{(0)} \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} \left\langle (-\beta E^{(1)})^n \right\rangle_0 .$$

(b) We have

$$Z(\lambda) = Z^{(0)} \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} m_n = Z^{(0)} \, M(\lambda)$$

where $m_n = \left\langle (-\beta E^{(1)})^n \right\rangle_0$, thus $Z(\lambda)$ may be interpreted as the moment-generating function $M(\lambda)$ of the perturbation $-\beta E^{(1)}$ multiplied by $Z^{(0)}$.

(c) We start with the definition of the Shannon entropy

$$H = -\sum_s P_s \ln P_s = -\frac{1}{Z} \sum e^{-\beta E_s} \ln \frac{e^{-\beta E_s}}{Z}$$

$$= \frac{1}{Z} Z \ln Z + \frac{\beta}{Z} \sum_s e^{-\beta E_s} E_s = \ln Z + \beta \langle E \rangle .$$

This implies

$$\ln Z = H - \beta E = -\beta(E - TH) = -\beta F \quad \Rightarrow \quad F = -T \ln Z$$

(d) Writing down the free energy we realize that

$$F(\lambda) = -T \ln Z(\lambda) = -T \ln Z^{(0)} - T \ln \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} m_n = F^{(0)} - T\, K(\lambda) ,$$

where $K(\lambda)$ is the cumulant-generating function of the perturbation $-\beta E^{(1)}$. The zeroth cumulant is always zero, the first one is the mean, and the second cumulant is the variance. Thus we can conclude that

$$F(\lambda) = F^{(0)} - \frac{1}{\beta} \sum_{n=1}^{\infty} \frac{\lambda^n}{n!} \kappa_n$$

$$\Rightarrow \quad F(\lambda) = F^{(0)} + \lambda \langle E^{(1)} \rangle_0 - \frac{\beta\lambda^2}{2} \left\langle \left(E^{(1)} - \langle E^{(1)} \rangle \right)^2 \right\rangle + \mathcal{O}(\lambda^3).$$

So the free energy is basically the cumulant-generating function of $-\beta E^{(1)}$.

(Σ = 12P)