

SAMPLE SOLUTIONS EXERCISE 9

EXERCISE 9.1: QUANTUM PARTICLE IN A 1D POTENTIAL WELL (8P)

Let us consider a single quantum-mechanical particle in a one-dimensional infinite potential well of length L in contact with a thermal reservoir at temperature T .

- (a) Compute the energy eigenvalues and write down the partition sum. (1P)
- (b) Show that in the low-temperature limit $T \rightarrow 0$ the logarithm of the partition sum is given by leading and next-to-leading order by (2P)

$$\ln Z(\beta, L) = -\frac{\beta\gamma}{L^2} + e^{-3\frac{\beta\gamma}{L^2}} + \mathcal{O}(e^{-8\frac{\beta\gamma}{L^2}}) \quad \text{where} \quad \gamma = \frac{\pi^2 \hbar^2}{2m}.$$

- (c) Compute the average energy E , the heat capacity C , and the pressure P in the limit of low temperatures by calculating the corresponding derivatives of $\ln Z$. (1P)
- (d) Why is $P > 0$ in the limit $T \rightarrow 0$? (1P)
- (e) Approximate the partition sum in the high-temperature limit $T \rightarrow \infty$. (2P)
- (f) Compute E , C , and P in the limit of high temperatures. (1P)

SAMPLE SOLUTION

- (a) We are looking for the solutions of the stationary Schrödinger equation $-\frac{\hbar^2}{2m}\Delta\psi(x) = E\psi(x)$ obeying the Dirichlet boundary conditions $\psi(0) = \psi(L) = 0$ at the infinite potential well. With the ansatz $\psi(x) \propto \sin(kx)$ we find that the wave numbers are quantized in steps of $k = n\pi/L$ where $n = 1, 2, \dots$. Inserting this ansatz into the Schrödinger equation gives the energies

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}.$$

This allows us to formally write down the partition sum

$$Z(\beta, L) = \sum_{n=1}^{\infty} e^{-\frac{\beta\gamma n^2}{L^2}} \quad \text{where} \quad \gamma = \frac{\pi^2 \hbar^2}{2m}, \quad \beta = \frac{1}{T}.$$

Unfortunately, this partition sum cannot be evaluated explicitly, and this is why we will study approximations below.

- (b) In the limit $T \rightarrow 0$ we have $\beta \rightarrow \infty$, hence $e^{-\beta\gamma/L^2}$ is very small. Thus, the partition sum Z can be approximated to leading and next-to-leading order by

$$\begin{aligned} Z(\beta, L) &= e^{-\frac{\beta\gamma}{L^2}} + e^{-\frac{4\beta\gamma}{L^2}} + \dots = e^{-\frac{\beta\gamma}{L^2}} (1 + e^{-\frac{3\beta\gamma}{L^2}} + \dots). \\ \Rightarrow \ln Z(\beta, L) &= -\frac{\beta\gamma}{L^2} + \ln(1 + e^{-\frac{3\beta\gamma}{L^2}} + \dots) \approx -\frac{\beta\gamma}{L^2} + e^{-\frac{3\beta\gamma}{L^2}} + \dots \end{aligned}$$

where we used the approximation $\ln(1 + \epsilon) \approx \epsilon$.

- (c) These quantities are given by (see lecture notes, note that here L plays the role of the volume V)

$$E = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_L, \quad C = \beta^2 \left(\frac{\partial^2 \ln Z}{\partial \beta^2} \right)_L, \quad P = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial L} \right)_\beta.$$

Inserting the partition sum we obtain

$$E = \frac{\gamma}{L^2} \left(1 + 3e^{-\frac{3\beta\gamma}{L^2}} + \dots \right), \quad C = \frac{9\beta^2\gamma^2}{L^4} e^{-\frac{3\beta\gamma}{L^2}}, \quad P = \frac{2\gamma}{L^3} \left(1 + 3e^{-\frac{3\beta\gamma}{L^2}} + \dots \right)$$

- (d) We are dealing here with a quantum-mechanical particle. Such a particle has a non-vanishing ground state energy. Changing the volume (the length L) at zero temperature will also change the value of the ground state energy. This means that work has to be done when compressing the system which manifests itself as a nonzero pressure even at zero temperature.
- (e) In the limit $T \rightarrow \infty$ ($\beta \rightarrow 0$) the summands in the partition sum $Z(\beta, L) = \sum_{n=1}^{\infty} e^{-\frac{\beta\gamma n^2}{L^2}}$ vary only slowly with n so that we can approximate the partition sum by a continuous integral as follows. Setting $\Delta x = \sqrt{\beta\gamma}/L$ we rewrite

$$Z(\beta, L) = \sum_{n=1}^{\infty} e^{-\frac{\beta\gamma n^2}{L^2}} = \frac{1}{\Delta x} \sum_{n=1}^{\infty} \Delta x e^{-(n\Delta x)^2} \approx \frac{L}{\sqrt{\beta\gamma}} \int_0^{\infty} dx e^{-x^2} = \frac{L}{\hbar} \sqrt{\frac{m}{2\pi\beta}}.$$

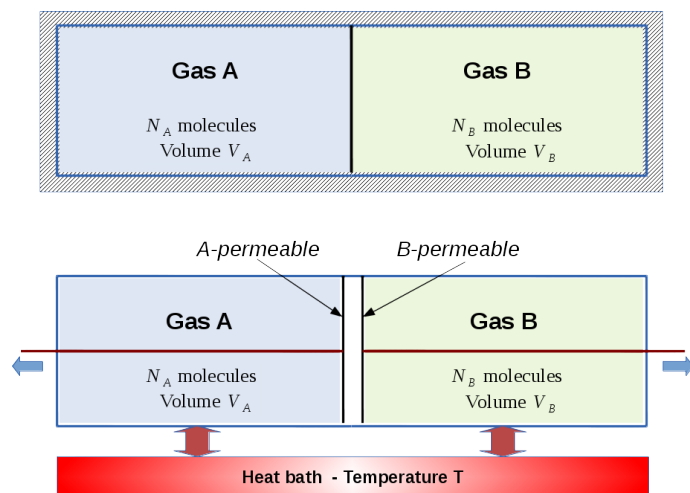
- (f) The results read

$$E = \frac{1}{2\beta}, \quad C = \frac{1}{2}, \quad P = \frac{1}{L\beta}.$$

EXERCISE 9.2: MIXING TWO GASES

(4P)

Let us consider two possibilities to mix two gases. In the first case an isolated container is divided into two chambers containing pure gases of two different types A and B , which are mixed by removing the separating wall in the middle. In the second case the container is connected to a heat bath of temperature T and the two gases are initially separated by two membranes which are permeable either exclusively to A or to B -particles. The mixing is carried out by moving the membranes quasi-statically to the left and to the right, as indicated in the figure.



- (a) Compute the change of system entropy in the first scenario.

(1P)

- (b) Compute the change of system entropy in the second scenario by relating it to the work needed to pull the membranes. The gases are assumed to be ideal, obeying the equation of state $pV = Nk_B T$. (2P)
- (c) Determine the entropy change in the heat bath in the second scenario. (1P)

SAMPLE SOLUTION

- (a) There are different ways to compute the entropy increase. One way is to argue on the basis of information gain. If the particle was in compartment A and now diffuses freely in AB , it gains the entropy of $\ln \frac{V_A+V_B}{V_A}$ about its position, and analogous for B -particles. This gain has to be multiplied with the particle numbers:

$$\Delta H = N_A \ln \frac{V_A + V_B}{V_A} + N_B \ln \frac{V_A + V_B}{V_B}.$$

- (b) Since the process is reversible, we can apply Clausius law $dH = \beta dQ$, hence

$$\Delta H = \int \beta dQ = \beta \left(\int_{V_A}^{V_A+V_B} p_A dV + \int_{V_B}^{V_A+V_B} p_B dV \right)$$

Using the equation of state $pV = Nk_B T = N/\beta$ we have $p_{A,B} = N_{A,B}/(\beta V)$ in the integrand:

$$\Delta H = N_A \int_{V_A}^{V_A+V_B} \frac{1}{V} dV + N_B \int_{V_B}^{V_A+V_B} \frac{1}{V} dV$$

Thus we retrieve the result obtained in (a).

- (c) Since the process of membrane moving is reversible, it cannot generate entropy in the total system. Therefore, the entropy change in the heat bath must be opposite of the system's entropy change, i.e. $\Delta H_{env} = -\Delta H_{sys}$.

($\Sigma = 12P$)