

Advanced Statistical Physics II – Problem Sheet 6

Problem 1 – Free expansion and mixing of ideal gases

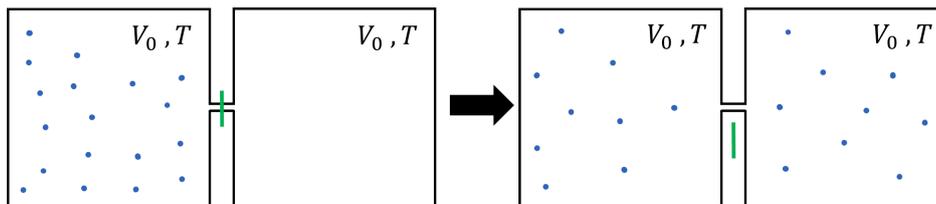


Figure 1: Free expansion of an ideal gas.

a) As depicted in Fig. 1, consider N_0 ideal gas particles initially in a volume V_0 and at temperature T . After opening the valve the gas expands into a volume $2V_0$ and is after this free expansion uniformly distributed at fixed T .

i) Calculate the work ΔW during the isothermal process $V_0 \rightarrow 2V_0$. For this use the ideal equation of state.

ii) By using the first and the second thermodynamic laws, find the entropy change $\Delta S = S_{2V_0} - S_{V_0}$.

iii) By using the Shannon entropy $S = -Nk_B \sum_i p_i \ln p_i$, calculate the entropy change ΔS . The p_i here refers to the probability of finding the particle in the left volume or in the right volume. These probabilities are different before and after the free expansion. You should get the same expression for ΔS .

iv) By using the Boltzmann entropy $S = k_B \ln w$ where $w = V^N / N!$ is the phase space volume, calculate the entropy change ΔS for $N \gg 1$.

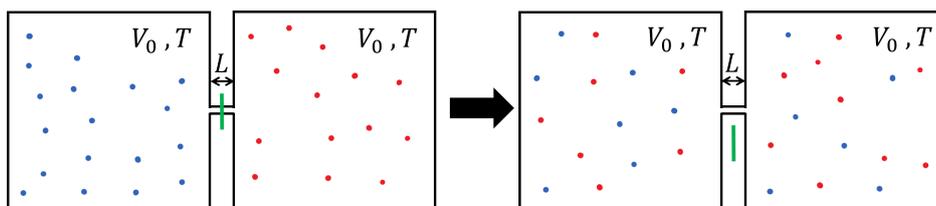


Figure 2: Mixing of ideal gases.

b) As depicted in Fig. 2, now consider two components of N_0 ideal gas particles initially separated in each volume V_0 and at temperature T . After opening the valve the gases interdiffuse throughout the volume $2V_0$ and are finally uniformly distributed at fixed T .

i) Write down the entropy production σ in terms of the particle flux $\vec{J}^{(l)}$, the chemical potential $\mu^{(l)}$, and the given parameters, where $l = 1, 2$ is the component index. Note that the mixing process is symmetric thus the center of mass velocity vanishes, $\vec{v} = \mathbf{0}$.

ii) From the above task you can rewrite the entropy production as $\sigma = \sigma^{(1)} + \sigma^{(2)}$. Now consider $\sigma^{(1)}$ only, where the component index "1" indicates the blue particles initially in the left volume. Show that $\mu^{(1)} = -T \frac{\partial S^{(1)}}{\partial N^{(1)}} = k_B T \ln n^{(1)}$ for $N \gg 1$, where $n^{(1)} = N^{(1)} / V_0$ is the time-dependent particle concentration in the left volume. Rewrite the entropy production $\sigma^{(1)}$.

iii) Assume that the compartments are much larger than the inter-connecting tube of length L and cross-section area A , so that the concentration $N^{(1)}(t)/V_0$ of the blue particles in the left compartment is uniform, where

$$N^{(1)}(t) = \begin{cases} N_0 & , \text{ for } t = 0 \text{ (beginning of diffusion),} \\ N_0/2 & , \text{ for } t = \tau \text{ (end of diffusion).} \end{cases} \quad (1)$$

Assume the concentration profile in the tube as $n^{(1)}(x, t) = [N^{(1)}(t) + (N_0 - 2N^{(1)}(t))x/L] / V_0$, where x is the position along the longitudinal axis of the tube. Rewrite the entropy production $\sigma^{(1)}$.

iv) Assume that the particle flux in the tube in x -direction is stationary, $J_x^{(1)} = -\dot{N}^{(1)}(t)/A$, due to continuity. Calculate the entropy change $\Delta S^{(1)} = \int dt \int_{\text{tube}} dV \sigma^{(1)}$.

Compare the entropy change $\Delta S^{(1)}$ obtained in the tasks a) and b). Interpret your result.