

Tutorial sheet 1

Discussion topics:

- What are “affinities” and “fluxes” in out-of-equilibrium systems? How do they relate to entropy production?
- How is local thermodynamic equilibrium defined?

1. Flow of a gas between two containers at different temperatures and pressures

Consider a composite system of two containers A and B with a classical ideal monoatomic gas of particles of mass m at temperatures T_A , T_B and pressures \mathcal{P}_A , \mathcal{P}_B respectively. Let $\Delta T \equiv T_B - T_A$ and $\Delta \mathcal{P} \equiv \mathcal{P}_B - \mathcal{P}_A$ denote the temperature and pressure differences.

i. Recall the expression of the Maxwell–Boltzmann distribution $p(\vec{v})$ for the velocities in an ideal gas at temperature T . Assuming that the particle density is uniform, write down the number density $f(\vec{r}, \vec{v}) d^3\vec{v}$ of particles per unit volume with a velocity between \vec{v} and $\vec{v} + d^3\vec{v}$.

ii. Particle flow

A small hole of cross section \mathcal{S} in the wall separating the containers allows gas to slowly flow from one container to the other. Where are at time t the gas particles which will traverse the hole with a given velocity \vec{v} between t and $t + dt$? Show that the number of particles flowing from container A to container B per unit time is

$$\mathcal{J}_N^{(A)} = \frac{\mathcal{P}_A \mathcal{S}}{\sqrt{2\pi m k_B T_A}}.$$

Deduce the overall particle flux $\mathcal{J}_N \equiv \mathcal{J}_N^{(A)} - \mathcal{J}_N^{(B)}$ and express it as a function of ΔT and $\Delta \mathcal{P}$, assuming those differences are small.

iii. Energy flow

Show that the flow of (kinetic) energy through the hole from container A to container B per unit time is

$$\mathcal{J}_E^{(A)} = \sqrt{\frac{2k_B T_A}{\pi m}} \mathcal{P}_A \mathcal{S}.$$

Deduce the overall energy flux $\mathcal{J}_E \equiv \mathcal{J}_E^{(A)} - \mathcal{J}_E^{(B)}$ and express it as a function of ΔT and $\Delta \mathcal{P}$.

iv. The chemical potential of a classical ideal gas is given by

$$\mu(T, \mathcal{V}, N) = -k_B T \ln \left[\frac{\mathcal{V}}{N} \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \right].$$

Express \mathcal{J}_N and \mathcal{J}_E as a function of the differences (beware the signs!)

$$\Delta \left(\frac{1}{T} \right) \equiv \frac{1}{T_B} - \frac{1}{T_A} \quad \text{and} \quad \Delta \left(-\frac{\mu}{T} \right) \equiv \frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}.$$

What do you recognize?

2. Energy fluctuations and heat capacity

The internal energy U of a system coupled to a heat reservoir, with which it can exchange energy, is a random variable. Give its variance as a function of the system heat capacity at constant volume.

Hint: Consider derivatives of the logarithm of the (canonical) partition function of equilibrium statistical mechanics.