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 $f(\vec{r},\vec{v})\,\mathrm{d}^3\vec{v}$ of particles per unit volume with a velocity between $\vec{v}$ and $\vec{v}+\mathrm{d}^3\vec{v}$.

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 $t+\mathrm{d}t$? 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

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

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

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

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.

Tutorial sheet 1: Solutions

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

(This exercise is an adaptation of Lachish, Am. J. Phys. **46** (1978) 1163–1164).

i. The Maxwell–Boltzmann velocity distribution reads

$$p(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \mathrm{e}^{-m\vec{v}^2/2k_B T},$$

which leads in a uniform gas at temperature T and pressure $\mathcal{P}$ to the single-particle phase-space distribution

$$f(\vec{r},\vec{v}) = \frac{N}{\mathcal{V}}\, p(\vec{v}) = \frac{\mathcal{P}}{k_B T}\left(\frac{m}{2\pi k_B T}\right)^{3/2} \mathrm{e}^{-m\vec{v}^2/2k_B T}.$$

ii. Particle flow

The particles with a given velocity $\vec{v}$ that traverse the hole between t and $t+\mathrm{d}t$ are those which were in an oblique cylinder with base $\mathcal{S}$ and axis of length $|\vec{v}|\,\mathrm{d}t$ along the direction of $\vec{v}$.

Denoting by x the direction perpendicular to the hole surface, with recipient A on the side of negative x, and by θ the angle of velocity with respect to this direction, one obtains

$$\mathcal{J}_N^{(A)} = \int_{v_x\geq 0} \mathcal{S}|\vec{v}|\cos\theta\, f(\vec{r},\vec{v})\,\mathrm{d}^3\vec{v} = \frac{\mathcal{P}_A\mathcal{S}}{k_B T_A}\left(\frac{m}{2\pi k_B T_A}\right)^{3/2} 2\pi\int_0^{\pi/2}\cos\theta\sin\theta\,\mathrm{d}\theta\int_0^\infty v^3\mathrm{e}^{-mv^2/2k_BT_A}\mathrm{d}v.$$

The integral over θ yields a factor $\frac{1}{2}$, while that over v can easily be performed using the change of variable $u = mv^2/2k_BT_A$

$$\int_0^\infty v^3\mathrm{e}^{-mv^2/2k_BT}\mathrm{d}v = \frac{2(k_BT_A)^2}{m^2}\int_0^\infty u\,\mathrm{e}^{-u}\,\mathrm{d}u = \frac{2(k_BT_A)^2}{m^2}.$$

All in all, one obtains $\mathcal{J}_N^{(A)} = \dfrac{\mathcal{P}_A\mathcal{S}}{\sqrt{2\pi m k_B T_A}}$. There follows

$$\mathcal{J}_N = \frac{\mathcal{S}}{\sqrt{2\pi m k_B}}\left(\frac{\mathcal{P}_A}{\sqrt{T_A}} - \frac{\mathcal{P}_B}{\sqrt{T_B}}\right) = \frac{\mathcal{P}_A\mathcal{S}}{\sqrt{2\pi m k_B T_A}}\left(1 - \frac{1+\Delta\mathcal{P}/\mathcal{P}_A}{\sqrt{1+\Delta T/T_A}}\right) \simeq \frac{\mathcal{P}_A\mathcal{S}}{\sqrt{2\pi m k_B T_A}}\left(\frac{\Delta T}{2T_A} - \frac{\Delta\mathcal{P}}{\mathcal{P}_A}\right). \tag{1}$$

iii. Energy flow

Using the same reasoning as in **ii.**, the energy flow per unit time from A to B is

$$\mathcal{J}_E^{(A)} = \int_{v_x\geq 0} \mathcal{S}|\vec{v}|\cos\theta\,\frac{1}{2}m\vec{v}^2 f(\vec{r},\vec{v})\,\mathrm{d}^3\vec{v} = \frac{\mathcal{P}_A\mathcal{S}}{k_BT_A}\left(\frac{m}{2\pi k_BT_A}\right)^{3/2}\frac{m}{2}\frac{4\pi(k_BT_A)^3}{m^3}\int_0^\infty u^2\,\mathrm{e}^{-u}\,\mathrm{d}u$$

The integral over u gives 2, so that $\mathcal{J}_E^{(A)} = \mathcal{P}_A\mathcal{S}\sqrt{\dfrac{2k_BT_A}{\pi m}}$ and thus

$$\mathcal{J}_E = \mathcal{S}\sqrt{\frac{2k_B}{\pi m}}\left(\mathcal{P}_A\sqrt{T_A} - \mathcal{P}_B\sqrt{T_B}\right) \simeq -\mathcal{P}_A\mathcal{S}\sqrt{\frac{2k_BT_A}{\pi m}}\left(\frac{\Delta T}{2T_A} + \frac{\Delta\mathcal{P}}{\mathcal{P}_A}\right). \tag{2}$$

iv. The chemical potential of the classical ideal gas can be rewritten as

$$\frac{\mu}{T} = -k_B \ln\left[\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} \frac{(k_B T)^{5/2}}{\mathcal{P}}\right].$$

This gives the total differential $\mathrm{d}\left(-\frac{\mu}{T}\right) = -k_B \frac{\mathrm{d}\mathcal{P}}{\mathcal{P}} + \frac{5k_B}{2}\frac{\mathrm{d}T}{T}$, and thus

$$\frac{\Delta\mathcal{P}}{\mathcal{P}} = -\frac{1}{k_B}\Delta\left(-\frac{\mu}{T}\right) + \frac{5}{2}\frac{\Delta T}{T}.$$

In addition, $\frac{\Delta T}{T} = -T\Delta\left(\frac{1}{T}\right)$, so that Eqs. (1) and (2) become

$$\mathcal{J}_N = \frac{\mathcal{P}_A \mathcal{S}}{\sqrt{2\pi m k_B T_A}}\left[\frac{1}{k_B}\Delta\left(-\frac{\mu}{T}\right) + 2T_A\Delta\left(\frac{1}{T}\right)\right] \equiv L_{NN}\Delta\left(-\frac{\mu}{T}\right) + L_{NE}\Delta\left(\frac{1}{T}\right), \tag{3a}$$

$$\mathcal{J}_E = \mathcal{P}_A \mathcal{S}\sqrt{\frac{2k_B T_A}{\pi m}}\left[\frac{1}{k_B}\Delta\left(-\frac{\mu}{T}\right) + 3T_A\Delta\left(\frac{1}{T}\right)\right] \equiv L_{EN}\Delta\left(-\frac{\mu}{T}\right) + L_{EE}\Delta\left(\frac{1}{T}\right). \tag{3b}$$

Identifying the response coefficients, one finds

$$L_{NE} = L_{NE} = \mathcal{P}_A \mathcal{S}\sqrt{\frac{2T_A}{\pi m k_B}},$$

so that the Onsager symmetry relation is fulfilled.

2. Energy fluctuations and heat capacity

If $Z_N(\beta, \mathcal{V})$ denotes the canonical partition function, then

$$\langle U\rangle = -\frac{\partial \ln Z_N}{\partial\beta} \quad \text{and} \quad \left\langle\left(U - \langle U\rangle\right)^2\right\rangle = \frac{\partial^2 \ln Z_N}{\partial\beta^2} = -\frac{\partial\langle U\rangle}{\partial\beta} = -\frac{\mathrm{d}T}{\mathrm{d}\beta}\frac{\partial\langle U\rangle}{\partial T} = k_B T^2 C_{\mathcal{V}}.$$