

## Tutorial sheet 3

**Discussion topic:** Reminder on equilibrium statistical mechanics: refresh your knowledge on the *phase space density* of a classical many-particle system and on the quantum mechanical *density operator*.

### 6. Adsorption and desorption

When a gas is in equilibrium with a solid wall, its molecules can adhere to that wall on special sites where they are trapped in a way which depends on the structure of the wall. This so-called “adsorption” is thus an equilibrium between two phases, the gas and the system of bound molecules, similar to a chemical equilibrium.

To model the phenomenon, Langmuir considered a wall with  $N_s$  sites, on each of which at most one molecule can get bound with a binding energy  $-E_b$ . The molecules which are not adsorbed form a perfect gas, and the adsorbed molecules do not interact with each other. One can show<sup>1</sup> that the average number of adsorbed particles is given by

$$N_{\text{av.}} = \frac{\mathcal{P}}{\mathcal{P} + \mathcal{P}_0(T)} N_s,$$

with  $\mathcal{P}$  the pressure of the gas and  $\mathcal{P}_0(T) \equiv (k_B T)^{5/2} \left( \frac{m}{2\pi\hbar^2} \right)^{3/2} e^{-E_b/k_B T}$ .

Assume that the adsorbed molecules and the gas are at different temperatures and chemical potentials, so that equilibrium is not attained.

- i. Show that the four kinetic coefficients associated with energy and particle exchanges are related to one another and express them in terms of  $L_{NN}$ .
- ii. Write down the evolution equation for the number  $N(t)$  of adsorbed molecules as a function of  $L_{NN}$ ,  $N_s$ ,  $\mathcal{P}$  and  $\mathcal{P}_0(T)$  and discuss the effects of the pressure  $\mathcal{P}$  and temperature  $T$  of the gas.

### 7. Stress tensor in a fluid

Let  $P_{ij}$  denote the Cartesian components of the stress tensor in a fluid. Consider an infinitesimal cube of fluid of side  $d\ell$ , where the sides are parallel to the axes of the coordinate system.

- i. Explain why the  $k$  component  $\mathcal{M}_k$  of the torque exerted on the cube by the neighboring regions of the fluid obeys  $\mathcal{M}_k \propto -\epsilon_{ijk} P_{ij} (d\ell)^3$ .
- ii. Using dimensional considerations, write down the dependence of the moment of inertia  $I$  of the cube on  $d\ell$  and on the fluid mass density  $\rho$ .
- iii. Using the results of the previous two questions, how does the rate of change of the angular velocity  $\omega_k$  scale with  $d\ell$ ? How can you prevent this rate of change from diverging in the limit  $d\ell \rightarrow 0$ ?

### 8. Continuity equation for particle number

The single-particle phase-space density  $f_1(t, \vec{r}, \vec{p})$  of a collection of  $N$  particles is the ensemble average

$$f_1(t, \vec{r}, \vec{p}) \equiv \left\langle \sum_{j=1}^N \delta^{(3)}(\vec{r} - \vec{r}_j(t)) \delta^{(3)}(\vec{p} - \vec{p}_j(t)) \right\rangle,$$

such that  $f_1(t, \vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p}$  is the number of particles in the phase space element  $d^3\vec{r} d^3\vec{p}$  about the point  $(\vec{r}, \vec{p})$ .

<sup>1</sup>Can you do it? For example by computing the grand partition function for the adsorbed molecules and using the expression of the chemical potential in an ideal gas as function of its pressure and temperature.

Show that the particle number density  $n(t, \vec{r})$  and the particle current density  $\vec{J}_N(t, \vec{r})$  are given by

$$n(t, \vec{r}) = \int f_1(t, \vec{r}, \vec{p}) d^3\vec{p}, \quad \vec{J}_N(t, \vec{r}) = \int f_1(t, \vec{r}, \vec{p}) \vec{v} d^3\vec{p},$$

with  $\vec{v}$  the velocity corresponding to momentum  $\vec{p}$ . Check that the continuity equation for particle number follows at once from these identities.