Home work week 7

1. We now consider N *interacting* atoms enclosed in volume V at temperature T. Assume that the Hamiltonian describing the potential energy of the interaction is harmonic in a suitable set of generalized coordinates (q_i, $i = 1, 2, ..., 3N$ (we will see later why this is in fact a rather good approximation):

$$V(q_i) = \frac{1}{2}k_i q_i^2 \tag{1}$$

with k_i the force constant of the harmonic potential (not to be confused with the Boltzmann constant k_B, even if we often omit the B). What is the average

- total energy?
- kinetic energy?
- potential energy?

What do you notice? This is the equipartition theorem.

2. Consider the uni-molecular reaction

$$\mathrm{A} \rightleftarrows \mathrm{B} \tag{2}$$

in the gas phase. This could for example be an *cis-trans* isomerization or a keto-enol reaction. We assume that the pressure is sufficiently low, and the temperature sufficiently high for the molecules to behave as an ideal classical gas. However, in contrast to previous examples, we now consider also the *intra-molecular* degrees of freedom (*i.e.* rotations, and vibrations). Their details don't matter a this point, but it is important to realize that these intra molecular degrees of freedom are *different* in A and B and so are the *intra-molecular* partition functions Z_A^{int} and Z_B^{int}. There is no need here to work these partition function out in this exercise! Starting from the partition functions ($Z = Z^{\mathrm{ideal}} Z^{\mathrm{int}}$), derive an expression for the free energy associated with the chemical reaction. What is the condition for equilibrium?

If you get stuck, don't get frustrated, because in that case we will start the next lecture from that point.