Thermodynamically Favorable State

The following three problems illustrate a very important idea of the thermodynamically favorable state of a system. Suppose a system can be in two qualitatively different states, like adsorbed and desorbed particle, associated and dissociated molecule, liquid or solid substance, etc. [Note that the word 'state' here is used in the macroscopic sense: it denotes a macroscopically large set of the quantum-mechanical eigenstates; for example, all the states of an adsorbed particle.] Which of the two state is the most probable one at a given temperature? Clearly, the one which contribution to the partition function is the largest: If \( Z_1 \) and \( Z_2 \) are the contributions of the two states to the partition function, then the total partition function is \( Z = Z_1 + Z_2 \), and the probabilities to find the system in the states 1 and 2 are given by

\[
P_1 = \frac{Z_1}{Z_1 + Z_2}, \quad P_2 = \frac{Z_2}{Z_1 + Z_2}.
\]  

(1)

If a problem like that involves macroscopically large parameters, then apart from some narrow crossover region we have either \( Z_1 \gg Z_2 \), or \( Z_2 \gg Z_1 \), and the system spends almost all its time in only one of the two states. This state is called thermodynamically favorable.

So, at fixed external parameters (like volume), the thermodynamically favorable state is the state with largest contribution to \( Z \). Correspondingly, this state has the smallest (in algebraic sense) contribution to the Helmholtz free energy \( F = -T \ln Z \). Recalling the formula

\[
F = E - TS,
\]  

(2)

we see an interesting interplay between the energy and entropy. At zero (or small enough) temperature, the main contribution to \( F \) is associated with energy, and the most favorable state is the state with lowest energy. But as the temperature increases, the entropy term starts to play more and more important part, and at large enough temperature can beat the energy term.

**Problem 31.** Consider a hydrogen atom in a cubic box of the linear size 1cm. Find the temperature \( T^* \) at which the probability to find the atom dissociated into proton and electron equals 1/2. Estimate characteristic width \( \Delta T \) of the crossover region where the probability to find the atom dissociated rapidly changes from the values considerably smaller than unity, to the values close to unity. Reminder: Binding energy of the hydrogen atom is 13 ev. Hint: You do not need to take into account the excited electronic states of the atom, because, as you will see, \( T^* \ll 10 \)ev, which implies that at dissociation temperatures the excited states has negligible probability to occur (effect Saha).

**Problem 32.** A particle is in a large cubic box of the size \( L \). It may be adsorbed on a surface and may fly in the bulk. Let us model the adsorption potential with a rectangular uniform potential well (in the perpendicular to the surface direction) of the depth \( u_0 \) and the size \( l_0 \ll L \). The parameters \( u_0 \) and \( l_0 \) are assumed to be large enough so that the motion of the adsorbed particle is all classical. Find the temperature \( T^* \) at which the probability to find the particle in the bulk equals 1/2. Estimate characteristic width \( \Delta T \) of the crossover region where the probability to find the particle adsorbed changes from values close to unity to the values much smaller than unity.

**Problem 33.** The same as Problem 32, but now the adsorption is quantum, which means that the motion of the adsorbed particle is essentially quantized in the direction perpendicular to the surface. To make the difference with the classical case most pronounced and, simultaneously, to significantly simplify the problem, consider the case when in the adsorption well there is only one bound state. In this case the motion of the
adsorbed particle is purely two-dimensional, and the only parameter characterizing the adsorption is the adsorption energy, $\varepsilon_0 > 0$, that should be subtracted from the energy of the adsorbed particle. To be specific, set $\varepsilon_0 = 1$ K, $L = 1$ cm, and the particle is the hydrogen atom (this value of $\varepsilon_0$ corresponds to the adsorption energy of hydrogen atom on the surface of the film of liquid $^4$He covering the surface of experimental cell). Caution: In the case of quantum adsorption the dimensionality of the adsorbed state is two. This means that one should take care of the kinetic energy as well, despite of the fact that the translational motion in both adsorbed and desorbed states is classical!