

Preparatory questions:

You should be able to answer these questions before doing the lab.

- In which chemical systems we can observe equal separation of energy levels ?
- What is "microstate" of a system ?
- What is "configuration" ?
- Is it correct to say that different microstates have always different configurations
- What can be said about probabilities of different microstates in a system with conserved total energy?
- How one can determine weight of a configuration?

What to do?

1. Start the program (the assistants will tell you how to login on the computer and start the program). Read the previous section and find all the described features. Try to perform several transitions manually. Check the agreement between state of the system (energy levels of molecules, displayed in the first graph) and occupation numbers in the second graph. Run simulation with default parameters. Observe results.

2. Start new run ("New run" command under "File" menu). Choose number of molecules $N=2$ and put both into first excited state. Start the simulation. Observe resulting average distribution. Start new run for 2 molecules again, but set them in somewhat higher energy levels. Observe average distribution. Explain the results. (Hint: pay attention to the behaviour of the statistical weight W . Write down all possible microstates and corresponding configurations. Deduce probability of each configuration, and determine average number of molecules in each state from that).

3. Run simulation for $N=3$. What is the shape of the average distribution? Can you explain the result? (Hint: analyse weight W for each of the possible configurations).

4. Repeat simulations with larger number of molecules. Choose 3-4 values of N in the range from 4 to 50. Note that the larger number of molecules is set, the longer simulations is needed to get reliable average distribution (a reasonable value of number of steps may be $200 \cdot N$). In each case, plot the final distribution over the energy levels in a logarithmic scale together with the "true" Boltzmann distribution. Observe how the calculated distribution approaches to the Boltzmann distribution with the growth of N . In each case, write down the average energy (which is set up by the initial conditions) and calculated (from the slope of the $\ln(P_{av}(n))$ curve) temperature. Compare with the exact result for the vibrational energy in a macroscopic system:

in dimensionless units:
$$E_{vib}/N = \frac{1}{\exp(1/T) - 1}$$

in real units:
$$E_{vib}/N = \frac{k_B \vartheta^v}{\exp(\vartheta^v/T) - 1}$$

where
$$\vartheta = \frac{hc \nu}{k_B}$$
 is the vibrational temperature

Present the data in a table form.

5. For a given diatomic gas and given temperature (ask assistant for the specific parameters), obtain average populations of the energy levels.

Hints: You cannot enter temperature in the program directly. You can only set up an initial state of some given total energy (which is also defines the average energy of a molecule), then the temperature will be calculated as a result of the simulation. So either use method of trials and errors, or evaluate the required energy by the analytic formula.

Vibrational wavenumbers of diatomic molecules:

molecule	ν (cm ⁻¹)
O ₂	1580
F ₂	892
Cl ₂	560
Br ₂	465
HCl	2991

6. Illustration of the thermodynamic second law.

Prepare initial state for $N=10$ molecules, and put the first molecule in a high energy state (for example, $n_1=12$), and other molecules in the ground state (enter line 12 0 0 0 0 0 0 0 0 0 into corresponding field). Write down statistical weight W and entropy $\ln(W)/N$. Press button "Next step" repeatedly and observe change of these quantities. Repeat for $N=20$. Describe and comment result.

7 (optional). For some fixed values of N and average energy (for example, $N=10$, $E/N=2$), try to prepare initial state: a) with minimal possible entropy; b) with maximal possible entropy.

Finally: Write an account of what have been done, your observations and comments. Insert printouts of the most important results.