Problem set 2: Computational Molecular Physics and Methods of Molecular Simulations

Petra Imhof, Antonia Mey, Burkhard Schmidt
Department of Physics // Mathematics and Computer Science
Freie Universität Berlin

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1. Dice game

(20 points) Suppose you have multiple three sided fair dice and you want to play three different games with these dice, where allowed dice rolls are treated differently in three different games. (i) The first game assumes that the different dice are distinguishable, i.e. all dice throws are legal (ii) The second game assumes that only those dice throws are legal, where $O(d_i) \leq O(d_{i+1})$..etc, where $O(d_i)$, is the outcome of the ith dice roll. (iii) The third game assumes that only those dice throws are legal, where $O(d_i) < O(d_{i+1})$, i.e. no die can have the same outcome.
In all cases, if a non-legal roll is obtained it is discarded and one starts over.

- rolling two dice, what is the probability of obtaining $O(d_1) + O(d_2) = 4$ in all three games?
- rolling three dice, what is the probability of obtaining $O(d_1) + O(d_2) + O(d_3) = 6$ in the third game?
- rolling three dice using the second game rule, there are 10 possible microstate outcomes, how many microstates are possible in a game of M dice with N sides.

2. Micro- and macrostates

(20 points) Consider a (quantum) system of 5 equally spaced energy levels, $E_n = nE_1$, $0 \leq n \leq 4$.

- Find all sets of occupation numbers with total energy $E = \sum_i N_i E_i = 6$ for the total number of particles $N = \sum_i N_i = 6$. Plot the occupation numbers versus the energies of the levels. Which case is (at least qualitatively) close to a Boltzmann distribution?
- Calculate the probabilities, i. e., the statistical weights Ω_n of the macrostates (using the general formula) and determine which macrostate is most probable, i. e., comprising most microstates. Connect this finding to the behavior of the occupation numbers discussed above. In which limit can we reach the Boltzmann distribution?

When counting the realisations (microstates), the following rules apply:

- exchanging two particles within the same energy level, does not generate a new microstate
- exchanging two particles between two different energy levels generates a new microstate
- putting one particle at a different energy level generates a new macrostate.

3. Thermodynamic quantities

(10 points) Use the partition function to derive the following thermodynamic functions

- Internal energy

$$U = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} \tag{1}$$

- Heat capacity

$$c_v = \frac{\partial}{\partial T} \left(k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right) \right)_{N,V} \tag{2}$$