Exercise 02

Name:	Matriculation number:
Name:	Matriculation number:

Results:

2.1	of 16 P
2.2	of 9 P
total	of 25 P

General instructions

- Submit your solution to Oliver Lemke (R. 35.17) before **Thursday 19. May at 8.15 am**.
- Fill out this cover sheet and submit it along with your solution.
- Show how you arrived at your answer.

2.1 Probability theory of alphabet pasta (16 P)

Table 1 shows the relative frequency (in percent) of letters in the English language. In a random experiment, N letters are drawn with probabilities given by this distribution. (Imagine sitting in front of a enormous bag of alphabet noodles and picking out noodles, one at a time.) The outcome of the experiment is a sequence L of letters, e.g.

$$L = \{\text{p, r, o, b, a, b, i, l, i, t, y}\}\,.$$

The composition C of a sequence denotes the how often a given letter occurs in the sequence

$$C = \text{p}_1\text{r}_1\text{o}_1\text{b}_2\text{a}_1\text{i}_2\text{l}_1\text{t}_1\text{y}_1\,.$$

Swapping letters changes the sequence, but not the composition. (e.g. $L' = \{\text{p, r, o, b, i, b, a, l, i, t, y}\}$)

(a) What is the most likely sequence of length N=5? (1 P)

(b) For an arbitrary sequence of letters, give general expressions for the number of possible sequences with the same composition, the probability of the sequence $\mathbb{P}(L)$, and the probability of the composition $\mathbb{P}(C)$. (3 P)

(c) Approximate $\mathbb{P}(C)$ by taking the logarithm, and applying Stirling's formula

$$\begin{aligned} \ln(N!) &\approx \ln\left(\frac{N^N}{e^N}\sqrt{2\pi N}\right) = N\ln N - N + \frac{1}{2}\ln(2\pi N) \\ &\approx N\ln N - N \end{aligned} \tag{1}$$

The resulting quantity is called the entropy $S(C)$. (2 P)

(d) For the words

- statistical
- thermodynamics
- statistical thermodynamics

Calculate the number of possible sequences with the same composition, the probability of the sequence $\mathbb{P}(L)$, the probability of the composition $\mathbb{P}(C)$, the logarithm of $\mathbb{P}(C)$, and the entropy $S(C)$. (7.5 P)

(e) Comment on the values for the entropy $S(C)$ and for $\mathbb{P}(C)$ (2.5 P)

Hint: disregarde the space in "statistical thermodynamics".

Letter	Frequency (%)	Letter	Frequency (%)	Letter	Frequency (%)	Letter	Frequency (%)
a	8.167	h	6.094	o	7.507	v	0.978
b	1.492	i	6.966	p	1.929	w	2.360
c	2.782	j	0.153	q	0.095	x	0.150
d	4.253	k	0.772	r	5.987	y	1.974
e	12.702	l	4.025	s	6.327	z	0.074
f	2.228	m	2.406	t	9.056		
g	2.015	n	6.749	u	2.758		

Table 1: Relative frequency of letters in the English language.

2.2 Partition function (9 P)

The partition function q is an important quantity which links the quantum energy levels of microscopic particles to the thermodynamic state functions. For a single particle the partition function is given as

$$q = \sum_{i=1}^{n} \exp\left(-\beta\epsilon_i\right) \tag{2}$$

The factor

$$\beta = \frac{1}{k_B T} \tag{3}$$

is called thermodynamic temperature, where the k_B is the Boltzmann constant and T is the absolute temperature. ϵ_i are the n accessible quantum energy levels which can be obtained by solving the stationary Schrödinger equation for the particle. Note that q is a sum over these energy levels and the contribution of each energy level to the total value of q is given by the exponential function $\exp(-\beta\epsilon_i)$. Let us consider a particle in a one-dimensional box of length L It's first n energy levels are given as

$$\epsilon_i = \frac{\hbar^2\pi^2}{2mL^2} i^2 \qquad i = 1, 2, ...n \tag{4}$$

(a) Caclulate the partition function for an electron ($m = 9.109 \cdot 10^{-31}$ kg) in a one-dimensional box of length $L = 500$ pm at $T = 300$ K. Assume that 10 energy levels are accessible. (1 P)

Next you will examine the sensitivity of the individual term $\exp(-\beta\epsilon_i)$ on various parameters. Use $m = 9.109 \cdot 10^{-31}$ kg, $L = 500$ pm and ϵ_{10} at $T = 300$ K as a starting point and vary one parameter at a time. Plot $\exp(-\beta\epsilon_i)$ as a function of

(b) i from $i = 1$ to $i = 100$ (1 P)

(c) T from $T = 1$ K to $T = 500$ K (1 P)

(d) β from $T = 1$ K to $T = 500$ K (1 P)

(e) L from 1 pm to 1 nm (logarithmic scale) (1 P)

(f) m from 10^{-31} kg to 10^{-26} kg (logarithmic scale) (1 P)

(g) Comment on the results. (3 P)