

Lösungen zum Übungsblatt 8

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Problem 1: Really big and small numbers 1: Unavoidable disturbances

At a distance of one light year (ly), the change of the gravitation field caused by the displacement of the mug arrives one year later. At this time, our experiment gets influenced. In this task we will estimate the impact of such disturbances to microcanonical systems.

At first, we compute the difference ΔU between the energy of the NaCl in the mug's gravitation field before and after its displacement of $\Delta r = 0.1\text{m}$:

$$\Delta U = -\gamma m_{\text{mug}} m_{\text{NaCl}} \left(\frac{1}{r} - \frac{1}{r + \Delta r} \right) = -\gamma m_{\text{mug}} m_{\text{NaCl}} \left(\frac{\Delta r}{r^2 + r \cdot \Delta r} \right) .$$

Setting in the values $r = 100\text{ly} = 100 \cdot 299792458\text{m/s} \cdot 315360000\text{s}$, $s = 0.1\text{m}$, $m_{\text{mug}} = 0.1\text{kg}$ and $m_{\text{NaCl}} = 58.44\text{g/mol}$, we get:

$$\Delta U = -4.362914603 \cdot 10^{-50} J .$$

As expected, this is a very small number. We come to the computation of the level distance in the NaCl probe. To do that, we need the amount of micro states Ω . We know that the specific entropy s is of order 1 in units of k_B thus $c \cdot k_B$ with a constant c . With entropy $S = k_B \cdot \ln \Omega$, this leads to:

$$s = c \cdot k_B = \frac{k_B \cdot \ln \Omega}{N} \Rightarrow \Omega = e^{cN} ,$$

where N is the number of particles. Since we have 1mol, this is the avogadro constant $N_A = 6.02214179 \cdot 10^{23}$. The level distance ΔE is the average energy difference between two neighbored micro states. We know that the energy interval of the probe is $\approx 1000\text{kJ}$, so ΔE is:

$$\Delta E = \frac{1000000 \text{ J}}{\Omega} = 1000000 \text{ J} \cdot e^{-cN_A} . \quad (1)$$

Since $\lim_{x \rightarrow -\infty} e^x = 0$ and N_A is a very large number, we cannot compute a numeric value different to 0. But we can make the following estimation: We look at the (fictitious) case $\Delta U = \Delta \tilde{E}$ and compute using (1) the belonging \tilde{N} that is obviously not N_A :

$$\Delta \tilde{E} = \Delta U = 1000000 \text{ J} \cdot e^{-c\tilde{N}} \Rightarrow \ln \left(\frac{\Delta U}{1000000} \right) = -c \cdot \tilde{N} = -127.5 .$$

Since obviously $\tilde{N} \ll N_A$, we conclude $\Delta E \ll \Delta U$. This justifies that the level distance ΔE is much smaller than the change of the potential energy ΔU caused by the mug's

displacement 1ly far away. This leads to the conclusion that we will never find a way to shield a probe from all external disturbances to get an energetically closed system.

Problem 2: Really big and small numbers 2: Width of the energy distribution in canonical states

We compute the partition sum

$$Z(E) = \int_0^{\infty} dE \exp(-\beta(E - TS(E))) \quad (2)$$

using the method of stationary point. We search the point E_0 with

$$\left. \frac{d}{dE}(E - TS(E)) \right|_{E_0} = 0 \ .$$

The entropy in an ideal gas is given by

$$S(E) = \frac{3}{2}k_B \ln(E) + c(x) \ ,$$

where the function $c(x)$ does not depend on E . We get:

$$\frac{d}{dE}(E - TS(E)) = \frac{d}{dE} \left(E - \frac{3}{2}Tk_B N \ln(E) + c(x) \right) = 1 - \frac{3}{2}Tk_B N \frac{1}{E} \ .$$

We continue:

$$1 - \frac{3}{2}Tk_B N \frac{1}{E_0} = 0 \quad \Rightarrow \quad E_0 = \frac{3}{2}Tk_B N \ .$$

We write the Taylor series of $E - TS(E)$:

$$\begin{aligned} f(E) &= (E - TS(E)) \\ &\approx f(E_0) + f'(E)|_{E=E_0} (E - E_0) + \frac{1}{2} f''(E)|_{E=E_0} (E - E_0)^2 + \mathcal{O}((E - E_0)^3) \\ &= \frac{3}{2}Tk_B N \left(1 - \ln \left(\frac{3}{2}Tk_B N \right) \right) + \frac{(E - E_0)^2}{3k_B TN} \ . \end{aligned}$$

By setting this into (2), we obtain with given $\beta := \frac{1}{k_B T}$ and by substituating $z := E - E_0$:

$$\begin{aligned}
Z(E) &\approx \int_0^\infty dE \exp\left(-\beta \left(Tk_B N \frac{3}{2} \left(1 - \ln\left(Tk_B N \frac{3}{2}\right)\right) + \frac{(E - E_0)^2}{3Tk_B N}\right)\right) \\
&= \exp\left(-\beta Tk_B N \frac{3}{2} \left(1 - \ln\left(Tk_B N \frac{3}{2}\right)\right)\right) \int_0^\infty dE \exp\left(-\beta \frac{(E - E_0)^2}{3Tk_B N}\right) \\
&= \exp\left(-\beta Tk_B N \frac{3}{2} \left(1 - \ln\left(Tk_B N \frac{3}{2}\right)\right)\right) \int_0^\infty dE \exp\left(-\beta \frac{(E - E_0)^2}{3Tk_B N}\right) \\
&= \exp\left(-\beta Tk_B N \frac{3}{2} \left(1 - \ln\left(Tk_B N \frac{3}{2}\right)\right)\right) \frac{1}{2} \int_{-\infty}^\infty dz \exp\left(-\beta \frac{z^2}{3Tk_B N}\right) \\
&= \exp\left(-\beta Tk_B N \frac{3}{2} \left(1 - \ln\left(Tk_B N \frac{3}{2}\right)\right)\right) \frac{1}{2} \sqrt{\frac{3\pi Tk_B N}{\beta}} .
\end{aligned}$$

Now we compute the variance:

$$\begin{aligned}
\text{var}(E) &= \frac{\partial^2 \ln(Z)}{\partial \beta^2} \\
&= \frac{\partial}{\partial \beta} \left(\frac{\partial \left(-\frac{3}{2} N \left(1 - \ln\left(\frac{3N}{2\beta}\right)\right) + \ln \frac{1}{2\beta} \sqrt{3\pi N} \right)}{\partial \beta} \right) \\
&= \frac{\partial}{\partial \beta} \left(-\frac{3}{2} \frac{N}{\beta} - \frac{1}{\beta} \right) \\
&= \frac{1}{\beta^2} \left(\frac{3}{2} N + 1 \right)
\end{aligned}$$

The energy per particle is given by $e = \frac{E}{N}$, so we get:

$$\text{var}(e) = \frac{1}{\beta^2 N} \left(\frac{3}{2} + \frac{1}{N} \right) .$$

We compute the the values of e :

N	$\text{var}(E) [J^2]$	$\text{var}(e) [J^2]$
10	$3.05 \cdot 10^{-41}$	$3.05 \cdot 10^{-43}$
100	$2.89 \cdot 10^{-40}$	$2.89 \cdot 10^{-44}$
1000	$2.86 \cdot 10^{-39}$	$2.86 \cdot 10^{-45}$
1mol	$1.72 \cdot 10^{-18}$	$4.74 \cdot 10^{-66}$

We look at the values of $\text{var}(e)$ for different N and see that the values decrease with growing N . So, e cannot be an extensive variable since the degree of freedom depends on N . In contrast, $\text{var}(E)$ grows with N , so E can be an extensive variable.

Problem 3: Barometric hight formula

Tasks:

- (i) Consider the atmosphere of the earth and calculate the average of the particle number density

$$n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (3)$$

for an ideal gas with N particles confined in an infinitely high cylinder of cross section A in a homogeneous gravitational field $U(\mathbf{r}) = U_1(z) = mgz$ (g is the gravitational acceleration). Plot the result by using the data of earth.

- (ii) Calculate the average distance and the variance of the distance of an oxygen molecule from Earth's surface.
- (ii) Calculate the pressure.

Methods:

- (i) We use, that the mean of a function $f(x)$ (in our case $n(\mathbf{r})$) in the canonical ensemble can be computed by ($\beta = \frac{1}{k_B T}$):

$$\langle f(\mathbf{p}, \mathbf{r}) \rangle = \frac{\int [d\mathbf{\Gamma}] f(\mathbf{p}, \mathbf{r}) e^{-\beta H(\mathbf{p}, \mathbf{r})}}{\int [d\mathbf{\Gamma}] e^{-\beta H(\mathbf{p}, \mathbf{r})}} \quad (4)$$

$H(\mathbf{p}, \mathbf{r}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_i)$ is the used Hamiltonian for the ideal gas.

- (ii) To compute the average height $\langle z_i \rangle$ of one (oxygen) molecule we insert $f(\mathbf{r}, \mathbf{p}) = z_i$ in (4) and obtain $\langle z_i \rangle$. The variance is defined by $\text{var}(z_i) = \langle z_i^2 \rangle - \langle z_i \rangle^2$. We have only to compute $\langle z_i^2 \rangle$.
- (iii) The ideal gas we consider (the atmosphere) can be described by (p : pressure, V : volume):

$$pV = Nk_B T \quad (5)$$

We need the result of (i) for the particle number density (6) and insert it in (5).

Results:

- (i) The number density in the homogeneous gravitational field in z -direction is (6):

$$\langle n(\mathbf{r}) \rangle = N_0 \cdot e^{-\frac{1}{k_B T} mgz}$$

Under the assumption that the air consists mostly of N_2 , you obtain a graph showing the dependence of the particle number density $\langle n(z) \rangle$ and the distance z from earth's surface (fig. 1).

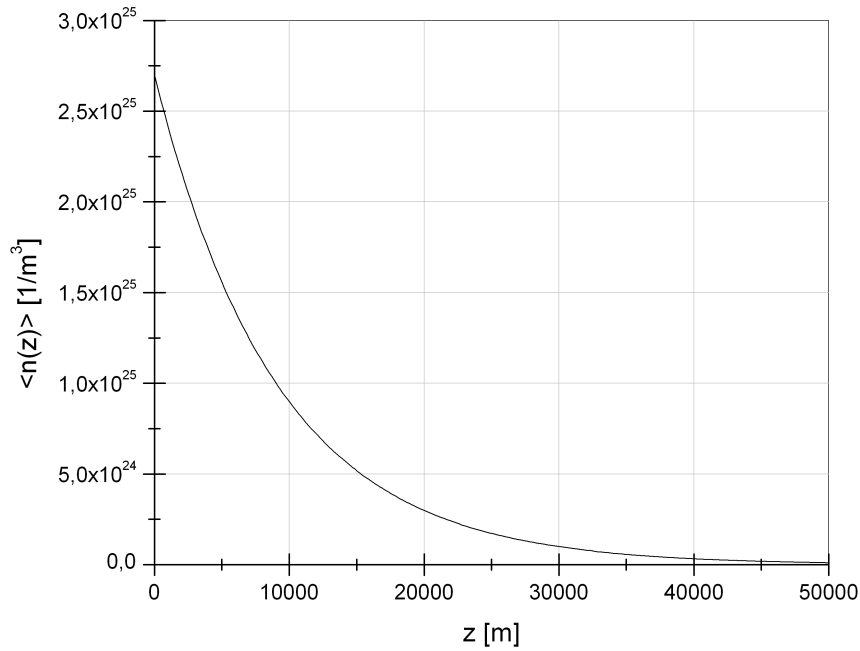


Figure 1: You can see the dependence of the particle number density $\langle n(z) \rangle$ and the distance z from earth's surface

- (ii) The average height of one particle is (7):

$$\langle z \rangle = \frac{k_B T}{mg}$$

The variance of a particle is (8):

$$\text{var}(z) = \frac{k_B^2 T^2}{m^2 g^2} = \langle z \rangle^2$$

For $T = 300\text{k}$ and a mass of one O_2 molecule $m_{O_2} = 5,3 \cdot 10^{-26}\text{kg}$ we obtain for the average height and the variance of one O_2 particle ($g = 9,81\text{m/s}^2$):

$$\begin{aligned}\langle z_{O_2} \rangle &\approx 7970\text{m} \\ \text{var}(z_{O_2}) &\approx 63500\text{m}\end{aligned}$$

(iii) The computed Barometric height formula is (9):

$$\begin{aligned}p(z) &= N_0 k_B T e^{-\frac{mgz}{k_B T}} \\ &= p_0 e^{-\frac{mgz}{k_B T}}\end{aligned}$$

Appendix:

(i) We want to calculate the average of the particle number density define by (3):

$$n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$$

We consider an ideal gas without interaction between the particles. $\mathbf{r}_i = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$ is the place of the i th particle (\mathbf{p}_i is the corresponding impulse). The gravitational potential is $U(\mathbf{r}) = U_1(z) = mgz$. In an canonical ensemble means can be computed by (4). In our case we obtain for $\langle n(\mathbf{r}) \rangle$:

$$\langle n(\mathbf{r}) \rangle = \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N \left(\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right) \exp \left(-\beta \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + U_1(z_j) \right)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N \exp \left(-\beta \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + U_1(z_j) \right)}$$

The result of the integrations over the N impulses \mathbf{p}_i in the numerator is the same as in the denominator. They cancel down and we obtain:

$$\begin{aligned}\langle n(\mathbf{r}) \rangle &= \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \left(\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right) \exp \left(-\beta \sum_{j=1}^N U_1(z_j) \right)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp \left(-\beta \sum_{j=1}^N U_1(z_j) \right)} \\ &= \frac{\sum_{i=1}^N \left[\int d\mathbf{r}_1 \dots d\mathbf{r}_N \delta(\mathbf{r} - \mathbf{r}_i) e^{-\beta U_1(z_i)} \exp \left(-\beta \sum_{\substack{j=1 \\ j \neq i}}^N U_1(z_j) \right) \right]}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp \left(-\beta \sum_{j=1}^N U_1(z_j) \right)}\end{aligned}$$

$$= \frac{\sum_{i=1}^N \left[e^{-\beta U_1(\mathbf{r})} \int d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N \exp \left(-\beta \sum_{\substack{j=1 \\ j \neq i}}^N U_1(z_j) \right) \right]}{\int d\mathbf{r}_i e^{-\beta U(\mathbf{r}_i)} \int d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N \exp \left(-\beta \sum_{\substack{j=1 \\ j \neq i}}^N U_1(z_j) \right)}$$

The first sum can be written as an multiplication with N , because the integrals are independent of i after the integration:

$$\langle n(\mathbf{r}) \rangle = \frac{N \cdot e^{-\beta U_1(\mathbf{r})}}{\int d\mathbf{r}_i e^{-\beta U(\mathbf{r}_i)}}$$

The integral in the denominator and the particle number N in the numerator are constant (inclusive the integration variable; so N_0 is the particle number density at the height $z = 0$):

$$\langle n(\mathbf{r}) \rangle = N_0 \cdot e^{-\frac{1}{k_b T} mgz} \quad (6)$$

To plot this result, we have to compute N_0 . We expect, that the atmosphere only consists of N_2 molecules with the weight $m_{N_2} = 4,6 \cdot 10^{-26} \text{kg}$ and a density on the earth's surface (by $T = 300\text{K}$) of $\varrho_{N_2} = 1,25 \frac{\text{kg}}{\text{m}^3}$. We obtain $N_0 = \frac{\varrho_{N_2}}{m_{N_2}} = 2,7 \cdot 10^{25} / \text{m}^3$.

(ii) \mathbf{r}_i and \mathbf{p}_i are defined as in (i). The average of the height of one oxygen molecule will be computed with (4). It's equal with oxygen molecule we consider. We take the i th:

$$\langle z_i \rangle = \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N z_i \exp \left(-\beta \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + U_1(z_j) \right)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N \exp \left(-\beta \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + U_1(z_j) \right)}$$

The integrations over all \mathbf{p}_i in the numerator is the same as in the denominator. We obtain:

$$\begin{aligned} \langle z_i \rangle &= \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N z_i \exp \left(-\beta \sum_{j=1}^N U_1(z_j) \right)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp \left(-\beta \sum_{j=1}^N U_1(z_j) \right)} \\ &= \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N z_i \exp \left(-\beta \sum_{j=1}^N U_1(z_j) \right)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp \left(-\beta \sum_{j=1}^N U_1(z_j) \right)} \end{aligned}$$

$$\begin{aligned}
& \frac{\int dz_i z_i e^{-\beta U(z_i)} \int d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N dx_i dy_i \exp\left(-\beta \sum_{\substack{j=1 \\ j \neq i}}^N U_1(z_j)\right)}{\int dz_i e^{-\beta U(z_i)} \int d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N dx_i dy_i \exp\left(-\beta \sum_{\substack{j=1 \\ j \neq i}}^N U_1(z_j)\right)} \\
&= \frac{\int_0^\infty dz_i z_i e^{-\beta mgz_i}}{\int_0^\infty dz_i e^{-\beta mgz_i}} \\
&= \frac{\left[-\frac{(1 + \beta mgz_i)e^{-\beta mgz_i}}{\beta^2 m^2 g^2} \right]_0^\infty}{\left[-\frac{e^{-\beta mgz_i}}{\beta mg} \right]_0^\infty} \\
&= \frac{1}{\beta mg} \\
&= \frac{k_B T}{mg}
\end{aligned} \tag{7}$$

The variance of the height of one oxygen molecule $\text{var}(z_i)$ is defined as:

$$\text{var}(z_i) = \langle z_i^2 \rangle - \langle z_i \rangle^2$$

With (7) we can compute the second part of this equation:

$$\langle z_i \rangle^2 = \frac{k_B^2 T^2}{m^2 g^2}$$

The first part is:

$$\begin{aligned}
\langle z_i^2 \rangle &= \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N z_i^2 \exp\left(-\beta \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + U_1(z_j)\right)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N \exp\left(-\beta \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + U_1(z_j)\right)} \\
&= \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N z_i^2 \exp\left(-\beta \sum_{j=1}^N U_1(z_j)\right)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp\left(-\beta \sum_{j=1}^N U_1(z_j)\right)}
\end{aligned}$$

$$\begin{aligned}
& \int dz_i z_i^2 e^{-\beta U_1(z_i)} \int d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N dx_i dy_i \exp\left(-\beta \sum_{\substack{j=1 \\ j \neq i}}^N U_1(z_j)\right) \\
= & \frac{\int dz_i z_i^2 e^{-\beta U_1(z_i)} \int d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N dx_i dy_i \exp\left(-\beta \sum_{\substack{j=1 \\ j \neq i}}^N U_1(z_j)\right)}{\int dz_i e^{-\beta U_1(z_i)} \int d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N dx_i dy_i \exp\left(-\beta \sum_{\substack{j=1 \\ j \neq i}}^N U_1(z_j)\right)} \\
= & \frac{\int_0^\infty dz_i z_i^2 e^{-\beta U_1(z_i)}}{\int_0^\infty dz_i e^{-\beta U_1(z_i)}} \\
= & \frac{\left[-\frac{(2 + 2\beta mg z_i + z_i^2 \beta^2 g^2 m^2) e^{-\beta mg z_i}}{\beta^3 m^3 g^3} \right]_0^\infty}{\left[-\frac{e^{-\beta mg z_i}}{\beta mg} \right]_0^\infty} \\
= & \frac{2}{\beta^2 m^2 g^2} \\
= & \frac{2k_B^2 T^2}{m^2 g^2} \\
\Rightarrow \text{var}(z_i) = & \frac{2k_B^2 T^2}{m^2 g^2} - \frac{k_B^2 T^2}{m^2 g^2} \\
= & \frac{k_B^2 T^2}{m^2 g^2} \tag{8}
\end{aligned}$$

(iii) (5) can be transformed to:

$$p(z) = \frac{N(z)}{V} k_B T$$

$N(z)/V = n(z)$ is the particle number density. With (6) we obtain:

$$\begin{aligned}
p(z) &= n(z) k_B T \\
&= N_0 k_B T e^{-\frac{mgz}{k_B T}} \\
&= p_0 e^{-\frac{mgz}{k_B T}} \tag{9}
\end{aligned}$$