

# Problems for the course FYS4130

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# Introduction to statistical methods. Simple random walks

## 0.1. Simple calculations with probabilities

Three people shoot the same target, partial probabilities to hit the target being  $p_1$ ,  $p_2$ , and  $p_3$ , respectively.

1. Find the probability that no one will hit the target.
2. Find the probability to find at least one bullet in the target.
3. Find the distribution function  $P_n$  to find  $n$  bullets in the target and check that  $\sum_n P_n = 1$ .
4. Find average value of the number of bullets in the target,  $\bar{n}$ , and mean square deviation,  $\overline{(\Delta n)^2} \equiv \overline{(n - \bar{n})^2}$ .
5. Find numerical values of  $P_n$ ,  $\bar{n}$ , and  $\overline{(\Delta n)^2}$  for  $p_1 = 0.8$ ,  $p_2 = 0.9$ ,  $p_3 = 0.7$ .

**Solution 0.1:** Independent event are those in which a shooter *misses* the target. Then the solutions are:

1.  $P_0 = (1 - p_1)(1 - p_2)(1 - p_3)$ .
2.  $P_{n \geq 1} = 1 - P_0 = 1 - (1 - p_1)(1 - p_2)(1 - p_3)$ .
3. The distribution has the form:

$$\begin{aligned} P_0 &= (1 - p_1)(1 - p_2)(1 - p_3), \\ P_1 &= p_1(1 - p_2)(1 - p_3) + p_2(1 - p_3)(1 - p_1) + p_3(1 - p_1)(1 - p_2), \\ P_2 &= p_1p_2(1 - p_3) + p_2p_3(1 - p_1) + p_3p_1(1 - p_2), \\ P_3 &= p_1p_2p_3. \end{aligned}$$

4.  $\bar{n} = \sum_{n=1}^3 p_n$ ,  $\overline{(\Delta n)^2} = \sum_{n=1}^3 p_n(1 - p_n)$ .

5. Numerical values are:  $P_0 = 0.006$ ,  $P_1 = 0.092$ ,  $P_2 = 0.398$ ,  $P_3 = 0.504$ ,  $\bar{n} = 2.4$ ,  $\overline{(\Delta n)^2} = 0.46$ .

The numerical results are obtained with the program Maple 6, see the file.

## 0.2. One-dimensional random walk. Binomial distribution

Consider a *asymmetric* random walk with the probability  $p$  for a hop to the right and  $q = 1 - p$  for a hop to the left. The probability  $W_N(m)$  for for  $m$  hops to the right from total number of hops  $N$  is given by the *binomial distribution* (??)

$$W_N(m) = \frac{N!}{m!(N-m)!} p^m (1-p)^{N-m}.$$

1. Find the probability  $P_N(M)$  for a total displacement  $M$  after  $N$  hops.
2. Find this probability for a symmetric case,  $p = 1/2$ .
3. Calculate average displacement  $\bar{M}$  after  $N$  hops. Hint: it is easier to use the equality  $\bar{M} = 2\bar{m} - N$  and calculate  $\bar{m}$ .
4. For the same situation calculate the dispersion  $\overline{(\Delta M)^2} = \overline{(M - \bar{M})^2}$ .
5. Compare  $\Delta^* M \equiv \sqrt{\overline{(\Delta M)^2}}$  and  $\bar{M}$ . What happens for symmetric random walk?
6. Two drunks start out together at the origin, each having equal probability of making a step to the left or to the right along the  $x$  axis. Find the probability that they meet again after each one makes  $N$  steps. It is understood that they make steps simultaneously. Hint: It is practical to consider their relative motion.

### Solution 0.2:

1. Since the total displacement  $M$  is the difference of number  $m$  of the hops to the *right* and  $N - m$  hops to the *left*, we have

$$m = (N + M)/2, \quad N - m = (N - M)/2.$$

As a result,

$$P_N(M) = \frac{N!}{[(N+M)/2]! [(N-M)/2]!} p^{(N+M)/2} (1-p)^{(N-M)/2}. \quad (1)$$

2. For  $p = 1/2$ ,

$$P_N(M) = \frac{N!}{2^N [(N+M)/2]! [(N-M)/2]!}. \quad (2)$$

3. Let us start with calculation of  $\bar{m}$ . We have

$$\begin{aligned}
\bar{m} &= \sum_{m=0}^N m W_N(m) = \sum_{m=0}^N m \frac{N!}{m!(N-m)!} p^m q^{N-m} \\
&= \sum_{m=0}^N \frac{N!}{m!(N-m)!} q^{N-m} \left[ p \frac{d}{dp} p^m \right] = p \frac{d}{dp} \left[ \sum_{m=0}^N \frac{N!}{m!(N-m)!} p^m q^{N-m} \right] \\
&= p \frac{d}{dp} (p+q)^N = pN(p+q)^{N-1} = pN.
\end{aligned}$$

Here we have used that  $p+q=1$ . Then

$$\bar{M} = 2\bar{m} - N = (2p-1)N = (p-q)N.$$

4. Again,

$$\begin{aligned}
\overline{M^2} &= \overline{(2m-N)^2} = 4\overline{m^2} - 4N\bar{m} + N^2 = 4\overline{m^2} + (1-4p)N^2, \\
\overline{M^2} - \bar{M}^2 &= 4\overline{m^2} + (1-4p)N^2 - (2p-1)^2 N^2 = 4\overline{m^2} - 4p^2 N^2.
\end{aligned}$$

Now we can use the same trick as in the previous problem to calculate  $\overline{m^2}$ .

$$\begin{aligned}
\overline{m^2} &= \sum_{m=0}^N m^2 W_N(m) = \sum_{m=0}^N m^2 \frac{N!}{m!(N-m)!} \\
&= \sum_{m=0}^N \frac{N!}{m!(N-m)!} \left( p \frac{d}{dp} \right)^2 p^m q^{N-m} = \left( p \frac{d}{dp} \right)^2 (p+q)^N \\
&= p [N(p+q)^{N-1} + p(N(N-1)(p+q)^{N-2})] \\
&= (Np)^2 + Np(1-p).
\end{aligned}$$

As a result, we obtain

$$\overline{M^2} = 4(Np)^2 + 4Np(1-p) - 4(pN)^2 = 4Np(1-p). \quad (3)$$

5. We have

$$\frac{\Delta^* M}{\bar{M}} = \sqrt{\frac{4Npq}{N^2(p-q)^2}} = \frac{1}{\sqrt{N}} \frac{\sqrt{2pq}}{|p-q|}.$$

6. The relative motion corresponds to  $2N$  steps, and the total displacement  $m=0$ . Thus, from Eq. (2) we get

$$P_{2N}(0) = \frac{(2N)!}{(2^N N!)^2}.$$

# Basic principles of thermostatics

## 0.3. Van der Waals gas

The fundamental relation for the Van der Waals gas is given by

$$s = s_0 + \mathcal{R} \ln[(v-b)/(v_0-b)] + (3/2)\mathcal{R} \ln \sinh[c(u+a/v)], \quad (4)$$

(all notations in this section are according the the book [?].

(i) Show that the corresponding equation of state is given by

$$(P + a/v^2)(v-b) = \mathcal{R}T. \quad (5)$$

(i) Expand the Van der Walls equation of state (5) in the form of virial expansion and determine 3 first virial coefficients.

### Solution 0.3:

(i) By definition  $T^{-1} = \left(\frac{\partial s}{\partial u}\right)_{v,N}$ . Consequently,

$$T^{-1} = \frac{3\mathcal{R}}{2} \frac{\cosh(u+a/v)}{\sinh(u+a/v)} \quad (6)$$

Following the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

we get

$$\frac{P}{T} = \left(\frac{\partial s}{\partial v}\right)_{u,N} = \frac{\mathcal{R}}{v-b} - \frac{3\mathcal{R}}{2} \frac{\cosh(u+a/v)}{\sinh(u+a/v)} \frac{a}{v^2} = \frac{\mathcal{R}}{v-b} - \frac{1}{T} \frac{a}{v^2}. \quad (7)$$

As a result, we obtaine the VdW equation (5).

(ii) Expanding Eq. (5) in powers of  $v^{-1}$  we get

$$P = \frac{T\mathcal{R}}{v} \left[ 1 + \frac{b - a/\mathcal{R}T}{v} + \frac{b^2}{v^2} + \dots \right].$$

Thus

$$B(T) = b - a/\mathcal{R}T, \quad C(T) = b^2.$$

**0.4.** Which of the following, offered as fundamental relations, are acceptable and which violate one or more of fundamental principles of thermostatics? ( $R, N_0, V_0$  and  $S_0$  are constants)

- (i)  $S = NR \left\{ 1 + \left[ (E/E_0)^{3/2} (V/V_0) (N/N_0)^{-5/2} \right] \right\}$
- (ii)  $S = R(EV/E_0V_0)^2 (N/N_0)^{-3}$
- (iii)  $S = \tan \left[ (E/E_0) (V/V_0)^2 (N/N_0)^{-3} \right]$
- (iv)  $S = R(EVN/E_0V_0N_0)^{1/3}$
- (v)  $S = NR \exp \left[ (E/E_0)^2 (V/V_0)^{-2} \right]$
- (vi)  $S = NR \coth \left[ (E/E_0)^2 (V/V_0) (N/N_0) \right]$
- (vii)  $S = R(EN/E_0N_0)^{1/2} \exp \left[ -(VN_0/V_0N)^2 \right]$
- (viii)  $S = R(NE/N_0E_0)^2 (V/V_0)^{1/5}.$

**Solution 0.4:** Main principle: the quantities  $S$  and  $V$  are *additive* in the particle number. Thus, the energy can be expressed as  $E = Nf(S/N, V/N)$ , or  $S/N = f_1(E/N, V/N) = f_1(u, v)$ . Let us put  $S = Ns$ ,  $E = Nu$ ,  $V = Nv$  and rewrite the equations as

- (i)  $s = R \left\{ 1 + \left[ (u/E_0)^{3/2} (v/V_0) N_0^{5/2} \right] \right\}$
- (ii)  $s = N_0^3 R (uv/E_0V_0)^2$
- (iii)  $s = N^{-1} \tan \left[ N_0^3 (u/E_0) (v/V_0)^2 \right]$
- (iv)  $s = N_0^{-1/3} R (uv/E_0V_0)^{1/3}$
- (v)  $s = R \exp \left[ (u/E_0)^2 (v/V_0)^{-2} \right]$
- (vi)  $s = R \coth \left[ (u/E_0)^2 (v/V_0) (N^4/N_0) \right]$
- (vii)  $s = R (u/E_0N_0)^{1/2} \exp \left[ -(vN_0/V_0)^2 \right]$

$$(viii) \quad s = N^{16/5} R (u/N_0 E_0)^2 (v/V_0)^{1/5}.$$

We observe that only Eqs. (i), (ii), (iv) (v) and (vii) meet the requirements. Thus, we are left with

$$(i) \quad s = R \left\{ 1 + \left[ (u/E_0)^{3/2} (v/V_0) N_0^{5/2} \right] \right\}$$

$$(ii) \quad s = N_0^3 R (uv/E_0 V_0)^2$$

$$(iv) \quad s = N_0^{-1/3} R (uv/E_0 V_0)^{1/3}$$

$$(v) \quad s = R \exp \left[ (u/E_0)^2 (v/V_0)^{-2} \right]$$

$$(vii) \quad s = R (u/E_0 N_0)^{1/2} \exp \left[ -(v N_0 / V_0)^2 \right]$$

For all these expression the entropy is an *increasing* function of the energy that is requires for the temperature to be positive, remember that  $T^{-1} = (\partial S / \partial E)_{V,N}$ .

Then, the pressure must also be positive, and the pressure is given by the relation  $P = -(\partial u / \partial v)_{s,N}$ . Thus, for a constant entropy the energy  $u$  must be *decreasing* function of volume. This requirement is met only for Eqs. (i), (ii) and (iv). Thus we are left with equations

$$(i) \quad s = R \left\{ 1 + \left[ (u/u_0)^{3/2} (v/v_0) \right] \right\}$$

$$(ii) \quad s = N_0^{-1} R (uv/u_0 v_0)^2$$

$$(iv) \quad s = N_0^{-1} R (uv/u_0 v_0)^{1/3}$$

where  $u_0 = E_0 / N_0$ ,  $v_0 = V_0 / N_0$ . These relations do not contradict general principles.

**0.5.** Consider an isolated composite system of constant total volume, which consists of two subsystems separated by a *movable* wall that permits flow of heat across it but is non-permeable by the flow of matter. Find out the condition of equilibrium between the two systems using

(a) the energy minimum principle

(b) the entropy maximum principle

**Solution 0.5:** Denote partial energies as  $E_i$ , partial entropies as  $S_i$ , and partial volumes as  $V_i$  for  $i = 1, 2$ . We have

$$E = E_1 + E_2 = \text{const}, \quad S = S_1 + S_2 = \text{const}, \quad V = V_1 + V_2 = \text{const}.$$

We have also

$$T = \left( \frac{\partial E}{\partial S} \right)_V = \left[ \left( \frac{\partial S}{\partial E} \right)_V \right]^{-1}, \quad P = - \left( \frac{\partial E}{\partial V} \right)_S = T \left( \frac{\partial S}{\partial V} \right)_E$$

(a) Minimum energy

$$\begin{aligned}\frac{\partial E}{\partial S_1} &= \frac{\partial E_1}{\partial S_1} + \frac{\partial E_2}{\partial S_2} \frac{\partial S_2}{\partial S_1} = \frac{\partial E_1}{\partial S_1} - \frac{\partial E_2}{\partial S_2} \rightarrow T_1 = T_2, \\ \frac{\partial E}{\partial V_1} &= \frac{\partial E_1}{\partial V_1} + \frac{\partial E_2}{\partial V_2} \frac{\partial V_2}{\partial V_1} = \frac{\partial E_1}{\partial V_1} - \frac{\partial E_2}{\partial V_2} \rightarrow P_1 = P_2.\end{aligned}$$

(b) Maximum entropy

$$\begin{aligned}\frac{\partial S}{\partial E_1} &= \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \rightarrow T_1 = T_2, \\ \frac{\partial S}{\partial V_1} &= \frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_2} \frac{\partial V_2}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \rightarrow P_1/T_1 = P_2/T_2.\end{aligned}$$

**0.6.** Now assume that the wall in the problem 0.5 is permeable to the flow of molecules. Find out the condition of equilibrium between the two systems using

- (a) the energy minimum principle
- (b) the entropy maximum principle

**Solution 0.6:**

(a) Remembering the expression for thermodynamic potential  $dE = T dS - P dV - \mu dN$  and using previous considerations we obtain the condition for the equilibrium as

$$\mu_1 = \mu_2.$$

(b) Following the previous considerations we get  $(\partial S_1/\partial N_1) = (\partial S_2/\partial N_2)$ . Since

$$dS = \frac{dE}{T} - \frac{\mu}{T} dN$$

we obtain the condition

$$\mu_1/T_1 = \mu_2/T_2 \rightarrow \mu_1 = \mu_2.$$

**0.7.** Prove the following consequences of the third law of thermodynamics

- (i)  $c_P$  and  $c_V$  of simple fluids must vanish at  $T = 0$ .
- (ii) Coefficient of thermal expansion  $\alpha$  vanishes at  $T = 0$

**Solution 0.7:**

- (i) For  $i = V, P$ , according to the definition,  $c_i = T (\partial s/\partial T)_i = (\partial S/\partial \ln T)_i$ . Since  $S$  tends to a finite limit (zero) and  $\ln T \rightarrow -\infty$ .
- (ii) The thermal expansion coefficient  $\alpha = (\partial V/\partial T)_P$  can be determined by the Maxwell relation  $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$ . Since  $S \rightarrow 0$  at  $T \rightarrow 0$  we observe that  $\alpha \rightarrow 0$ .



# Basic principles of statistical mechanics

**0.8.** The Hamiltonian of a collection of  $N$  non-interacting one-dimensional classic harmonic oscillators is given by

$$H = \frac{1}{2M} \sum_{i=1}^N p_i^2 + \frac{k}{2} \sum_{i=1}^N x_i^2.$$

Calculate the internal energy of the system using the rules of calculation for isolated systems. Hint: Apply the law of equipartition of the energy.

**Solution 0.8** According to the equipartition law, the average energy for each degree of freedom is the same. Here we have  $2N$  degrees of freedom. The average energy for one degree of freedom is

$$E_1 = \frac{\int_{-\infty}^{\infty} dp (p^2/2M) e^{-p^2/2MkT}}{\int_{-\infty}^{\infty} dp e^{-p^2/2MkT}} = \frac{kT}{2}.$$

The total energy is

$$E = 2NE_1 = NkT.$$

**0.9.** Model for rubber elasticity.

The rubber is assumed to consist of a polymer chain of  $N$  rod-like monomers, each of length  $a$  and is subjected to a force  $F$  in the  $+X$  direction. Each monomer can point independently along any of  $X, Y, Z$  axes, in either the  $+$  or  $-$  direction. The energy is only  $X$ -dependent;  $\epsilon = aF$  for the monomer pointing along  $-X$ ,  $\epsilon = -aF$  for the monomer pointing along  $+X$ ,  $\epsilon = 0$  for the monomer along  $\pm Y$  and  $\pm Z$ .

- Calculate the partition function for the  $N$ -monomer chain.
- Show that the linear thermal expansivity is negative, as for the real rubber. Interpret the result physically.

**Solution 0.9** .

(a) Each monomer has the partition function

$$Z_1 = 2 + 2 + e^{-\beta Fa} + e^{\beta Fa} = 4 + 2 \cosh(\beta Fa)$$

the total partition function being

$$Z = Z_1^N = 2^N [2 + \cosh(\beta Fa)]^N .$$

(b) If  $N\xi_+$  states point on the average to  $+X$ ,  $N\xi_-$  states point to  $-X$ , etc., then

$$\langle L_X \rangle = Na(\xi_+ - \xi_-), \quad \langle L_Y \rangle = Na(\eta_+ - \eta_-), \quad \langle L_Z \rangle = Na(\zeta_+ - \zeta_-),$$

We immediately obtain that  $\langle L_Y \rangle = \langle L_Z \rangle = 0$ . Furthermore,

$$\xi_{\pm} = e^{\pm\beta aF} / Z_1, \quad \rightarrow \quad \langle L_X \rangle = Na \frac{\sinh \beta aF}{2 + \cosh \beta aF} .$$

We immediately get  $\partial \langle L_X \rangle / \partial \beta > 0$ . Consequently,  $\partial \langle L_X \rangle / \partial T < 0$ . Rubber contracts upon heating.

**0.10.** The partition function for a system of some kind of particles is

$$Z_N = [(V - Nb)/\lambda^3]^N \exp(\beta aN^2/V),$$

where

$$\lambda = \sqrt{2\pi\hbar^2/mk_B T}$$

and  $a$  and  $b$  are constants,  $V$  is the volume and  $N$  is the number of particles; all other symbols have their usual meaning.

(a) Find the internal energy  $E(N, T, V)$ .

(b) Find the pressure  $P(N, T, V)$ .

(c) Find the entropy  $S(N, T, V)$ .

(d) Is this expression for  $S$  a valid fundamental relation, except perhaps at  $T = 0$ ? If not, what is wrong, and how can  $Z_N$  be appropriately corrected?

Hint: Recall Gibbs paradox.

**Solution 0.10**

(a) Since  $E = -\partial \ln Z / \partial \beta$  with  $\beta \equiv (k_B T)^{-1}$  we rewrite the partition function as

$$\ln Z_N = N \ln(V - Nb) - 3N \ln \lambda + \beta a N^2 / V$$

with  $\lambda = \sqrt{\beta \hbar^2 / m}$ . Having in mind that  $\partial \lambda / \partial \beta = 1/2\beta = k_B T / 2$  we get:

$$E = (3/2) N k_B T - a N^2 / V.$$

(b) Let us define the Helmholtz free energy

$$F = -k_B T \ln Z_N = -k_B T [N \ln(V - Nb) - 3N \ln \lambda + \beta a N^2 / V].$$

We have

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V - Nb} + \frac{a N^2}{V^2}.$$

(c)

$$\begin{aligned} S &= - \left( \frac{\partial F}{\partial T} \right)_{V, N} \\ &= N k_B \left[ \frac{3}{2} + \ln \frac{V - Nb}{\lambda^3} \right]. \end{aligned}$$

(d) Entropy is not an additive quantity. The states created by permutation of the particles are actually the same, so the partition function  $Z_N$  should be divided by  $N!$ . In the main approximation it will result in the expression

$$S = N k_B \left[ \frac{3}{2} + \ln \frac{v - b}{\lambda^3} \right], \quad v \equiv V/N.$$

Another point is that the entropy does not vanish as  $T \rightarrow 0$ . One cannot correct this property within classical statistics.

**0.11.** Calculate the partition function and the free energy for a ideal classical gas consisting of  $N$  molecules at temperature  $T$  contained in a vertical column of height  $H$  and cross-sectional area  $A$  in the presence of the of non-vanishing constant acceleration  $g$  due to gravity.

**Solution 0.11** The total energy of the molecule in the gravitational field is

$$E = \frac{p^2}{2m} + mgz$$

where  $z$ -axis is directed perpendicular to the Earth surface. Then,

$$\begin{aligned} Z_1 &= \int d^3r \int \frac{d^3p}{(2\pi\hbar)^3} e^{-\beta(p^2/2m + mgz)} \\ &= A \int_0^H dz e^{-\beta mgz} \int \frac{d^3p}{(2\pi\hbar)^3} e^{-\beta p^2/2m}. \end{aligned}$$

The first integral is equal to  $(\beta mg)^{-1} [1 - e^{-\beta mgH}]$ . The second integral can be calculated in the spherical coordinates. Since  $d^3p = p^2 dp d\theta d\phi$  and kinetic energy depends only on  $p$  we can write:

$$\frac{d^3p}{(2\pi\hbar)^3} = \frac{p^2 dp}{2\pi^2\hbar^3} = \frac{m\sqrt{2m\varepsilon} d\varepsilon}{2\pi^2\hbar^3} \equiv g(\varepsilon) d\varepsilon, .$$

Here  $\varepsilon \equiv p^2/2m$ , while

$$g(\varepsilon) = g_0 \varepsilon^{1/2}, \quad g_0 = \frac{(2m)^{3/2}}{4\pi^2\hbar^3}$$

is the *density of states*. Thus the second integral is

$$g_0 \int_0^\infty d\varepsilon \varepsilon^{1/2} e^{-\beta\varepsilon} = g_0 \beta^{-3/2} \int_0^\infty x^{1/2} e^{-x} dx = \frac{\sqrt{\pi}}{2} g_0 \beta^{-3/2}.$$

Collecting all the factors we obtain

$$Z_1 = Z \frac{1 - e^{-\beta mgH}}{\beta mgH}, \quad Z = V \frac{\sqrt{\pi}}{2} \frac{(2m)^{3/2}}{4\pi^2\hbar^3 \beta^{3/2}} = \frac{V}{\lambda^3}.$$

Finally,

$$Z_N = \frac{Z_1^N}{N!} = \frac{V^N}{\lambda^{3N} N!} \left[ \frac{1 - e^{-\beta mgH}}{\beta mgH} \right]^N.$$

**0.12.** Calculate the partition function and the free energy for an ideal classical gas consisting of  $N$  molecules at temperature  $T$  contained in a vessel and subjected to a centrifugal force  $-M\omega^2 z^2/2$ , where  $z$  is the distance of the particle from the axis of rotation and  $\omega$  is the angular velocity of rotation of the centrifuge.

**Solution 0.12:** When the external field is present, the integrand in the partition function contains an extra factor  $e^{-\beta U}$  where  $U \equiv -M\omega^2 z^2/2$ . Then one has to replace volume in the usual expression for the partition function by  $\int d^3r e^{-\beta U}$ . This procedure yields an extra factor

$$\begin{aligned} \frac{1}{V} \int d^3r e^{-\beta U} &= \frac{2\pi L}{\pi R^2 L} \int_0^R z dz e^{\beta M\omega^2 z^2/2} \\ &= \frac{2}{\beta M\omega^2 R^2} \int_0^{\beta M\omega^2 R^2/2} d\eta e^\eta = \frac{2}{\beta M\omega^2 R^2} \left( e^{\beta M\omega^2 R^2/2} - 1 \right). \end{aligned}$$

Thus,

$$Z = \frac{2Z_0}{\beta M\omega^2 R^2} \left( e^{\beta M\omega^2 R^2/2} - 1 \right), \quad F = F_0 - Nk_B T \ln \frac{2k_B T}{M\omega^2 R^2} \left( e^{M\omega^2 R^2/2k_B T} - 1 \right).$$

**0.13.** Consider an ideal monoatomic gas of  $N$  molecules in the presence of an external magnetic field  $H$ , where each molecule behaves as an Ising spin. Calculate the free energy, energy, and entropy and interpret the result physically. Find the limit of  $S$  at  $T \rightarrow 0$ .

**Solution 0.13:** The energy of the Ising spin  $S$  in magnetic field can be written as  $U = -\mu S_H H$  where  $S_H$  acquires the values  $\pm S$ . Consequently, the partition function can be written as

$$Z_1 = Z_0 \cdot \sum_{\pm} e^{\mp \beta \mu S H} = 2 \cosh(\beta \mu S H).$$

Here  $Z_0$  allows for non-magnetic degrees of freedom. Consequently,

$$\begin{aligned} Z &= Z_1^N / N! = (Z_0^N / N!) [2 \cosh(\beta \mu S H)], \\ F - F_0 &= -(N/\beta) \ln [2e \cosh(\beta \mu S H)], \\ E - E_0 &= -\partial Z / \partial \beta = -N \mu S H \tanh(\beta \mu S H), \\ (S - S_0)/k_B &= \beta(E - F) = N \ln [2e \cosh(\beta \mu S H)] - \beta N \mu S H \tanh(\beta \mu S H). \end{aligned}$$

**0.14.** Evaluate the contribution of a one-dimensional *anharmonic* oscillator having a potential

$V(x) = cx^2 - gx^3 - fx^4$  to the heat capacity. Discuss the the dependence of the mean value of the position  $x$  of the oscillator on the temperature  $T$ . Here  $c, g, f$  are positive constants. Usually,  $g \ll c^{3/2}(k_B T)^{-1/2}$  and  $f \ll c^2/k_B T$ .

**Solution 0.14.** Since  $g$  and  $f$  are small let us try to apply perturbation theory. Since the typical value of the displacement  $\bar{x} = (k_B T/c)^{1/2}$  we obtain

$$g\bar{x}^3/k_B T = (k_B T)^{1/2} c^{-3/2} \ll 1, \quad f\bar{x}^4/k_B T = fk_B T/c^2 \ll 1.$$

Thus one can expand the exponential to obtain

$$e^{-\beta V(x)} \approx e^{-\beta c x^2} (1 - \beta g x^3 - \beta f x^4).$$

As a result,

$$Z = Z_0 \int_{-\infty}^{\infty} dx e^{-\beta V(x)} \approx \sqrt{\frac{\pi}{\beta c}} \left( 1 + \frac{3f}{4\beta c^2} \right).$$

Here  $Z_0$  is the contribution of kinetic energy. Consequently,

$$\begin{aligned} \ln Z &= \ln Z_0 + (1/2) \ln(\pi/c) - (1/2) \ln \beta + \ln(1 + 3f/4\beta c^2) \\ &= \ln Z_0 + (1/2) \ln(\pi/c) - (1/2) \ln \beta + 3f/4\beta c^2, \\ E &= -\partial \ln Z_0 / \partial \beta - \partial \ln Z / \partial \beta \\ &= 1/2\beta + 1/2\beta + 3f/4\beta^2 c^2 \\ &= k_B T + 3f(k_B T)^2 / 4c^2, \\ C &= k_B (1 + 3fk_B T / 2c^2). \end{aligned}$$

To estimate  $\langle x \rangle$  we calculate

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x e^{-\beta V(x)}}{\int_{-\infty}^{\infty} dx e^{-\beta V(x)}} \approx -\beta g \frac{\int_0^{\infty} x^4 dx e^{-\beta c x^2}}{\int_0^{\infty} dx e^{-\beta c x^2}} = \frac{3}{4} \frac{g}{\beta c^2} = -\frac{3}{4} \frac{g \bar{x}}{\beta^{1/2} c^{3/2}} \ll \bar{x}.$$

We have  $\langle x \rangle \propto T$ . **0.15.** The energy of *anharmonic* oscillator is given by

$$H = p^2/2m + bx^{2n}$$

where  $n$  is a positive integer and  $n > 1$ . Consider a thermodynamic system consisting of a large number of these identical noninteracting oscillators.

- (a) Derive the single oscillator partition function.
- (b) Calculate an average kinetic energy of an oscillator.
- (c) Calculate an average potential energy of an oscillator.
- (d) Show that the heat capacity is

$$C = (Nk_B/2)(1 + 1/n).$$

**Solution 0.15.**

(a)

$$Z_1 = \int \frac{dp}{2\pi\hbar} e^{-\beta p^2/2m} \int dx e^{-\beta b x^{2n}} \equiv Z_k \cdot Z_p,$$

$$Z_k = \frac{m^{1/2}}{\hbar(2\pi\beta)^{1/2}},$$

$$Z_p = \frac{\Gamma(1/2n)}{n(\beta b)^{1/2n}}.$$

(b)

$$E_k = -\partial \ln Z_k / \partial \beta = k_B T / 2.$$

(c)

$$E_p = -\partial \ln Z_p / \partial \beta = k_B T / 2n.$$

(d) Straightforward.

**0.16.** Suppose the expression  $S = -k_B \sum_r P_r \ln P_r$  is accepted as a definition of the entropy. Imagine that a system  $A_1$  has probability  $P_r^{(1)}$  of being in a state  $r$  and a system  $A_2$  has probability  $P_s^{(2)}$  of being in a state  $s$ . Then

$$S_1 = -k_B \sum_r P_r^{(1)} \ln P_r^{(1)}, \quad S_2 = -k_B \sum_s P_s^{(2)} \ln P_s^{(2)}.$$

Each state of a composite system  $A$  consisting of  $A_1$  and  $A_2$  can then be labeled by the pair of numbers,  $r, s$ . Let the probability of  $A$  being found in the state  $r, s$  be denoted by  $P_{rs}$ , and the corresponding entropy is  $-k_B \sum_{r,s} P_{rs} \ln P_{rs}$ .

(a) If  $A_1$  and  $A_2$  are weakly interacting so they are statistically independent, then  $P_{rs} = P_r^{(1)} P_s^{(2)}$ . Show that under such circumstances the entropy is simply additive, i. e.  $S = S_1 + S_2$ .

(b) Suppose that  $A_1$  and  $A_2$  are *not* weakly so that  $P_{rs} \neq P_r^{(1)} P_s^{(2)}$ . One has, of course, the general, relations  $\sum_s P_{rs} = P_r^{(1)}$ ,  $\sum_r P_{rs} = P_s^{(2)}$ , and  $\sum_{r,s} P_{rs} = 1$ . Show that

$$S - (S_1 + S_2) = k_B \sum_{rs} P_{rs} \ln \frac{P_r^{(1)} P_s^{(2)}}{P_{rs}}.$$

Moreover, by using the inequality

$$-\ln x \geq 1 - x,$$

show that  $S \leq S_1 + S_2$ , where the equality holds only if  $P_{rs} = P_r^{(1)} P_s^{(2)}$  for all  $r$  and  $s$ . This means that the existence of correlation between the systems leads to a situation less random than where the systems are completely independent of each other.

**Solution 0.16:** Let us start from the part (b), and the 1st part will be a limiting case. We have

$$\begin{aligned}
 -(S_1 + S_2)k_B &= \sum_r P_r^{(1)} \ln P_r^{(1)} + \sum_r P_r^{(2)} \ln P_r^{(2)} \\
 &= \sum_{r,s} P_{rs} \ln(P_r^{(1)}) + \sum_{s,r} P_{rs} \ln P_s^{(2)} \\
 &= \sum_{r,s} P_{rs} \ln \left( P_r^{(1)} P_s^{(2)} \right).
 \end{aligned}$$

If  $P_{rs} = P_r^{(1)} P_s^{(2)}$  then  $S = S_1 + S_2$ . Now

$$\begin{aligned}
 S - (S_1 + S_2) &= k_B \sum_{r,s} P_{rs} \ln \frac{P_r^{(1)} P_s^{(2)}}{P_{rs}} \\
 &\leq k_B \sum_{r,s} P_{rs} \left[ \frac{P_r^{(1)} P_s^{(2)}}{P_{rs}} - 1 \right] \\
 &= k_B \sum_{r,s} \left[ P_r^{(1)} P_s^{(2)} - P_{rs} \right] = 0.
 \end{aligned}$$

**0.17.** Consider a system distributed over its accessible states  $r$  in accordance with a probability distribution  $P_r$ , and let its entropy be defined by the relations

$$S = -k_B \sum_r P_r \ln P_r, \quad \sum_r P_r = 1.$$

Compare this distribution with the canonical distribution

$$P_r^{(0)} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

corresponding to the same mean energy  $\langle E \rangle$ , i. e.

$$\sum_r P_r E_r = \sum_r P_r^{(0)} E_r = \langle E \rangle.$$

The entropy of the canonical distribution is

$$S_0 = -k_B \sum_r P_r^{(0)} \ln P_r^{(0)}.$$

(a) Show that

$$S - S_0 = k_B \sum_r P_r \ln \frac{P_r^{(0)}}{P_r}.$$

(b) Using the inequality  $\ln x \leq x - 1$  show that  $S_0 \geq S$ ; the equality sign holds only if  $P_r = P_r^{(0)}$  for all states  $r$ . This shows that, for a specific value of mean energy, the entropy  $S$  is a maximum for the canonical distribution.



**Solution 0.17:**

(a)

$$\begin{aligned}
(S - S_0)/k_B &= -\sum_r \left[ P_r \ln P_r - P_r^{(0)} \ln P_r^{(0)} \right] \\
&= -\sum_r \left[ P_r \ln P_r - P_r^{(0)} (-\beta E_r - \ln \mathcal{N}) \right] \\
&= -\ln \mathcal{N} - \beta \langle E \rangle - \sum_r P_r \ln P_r \\
&= \sum_r P_r \ln \frac{P_r^{(0)}}{P_r}.
\end{aligned}$$

(b) We have

$$\sum_r P_r \ln \frac{P_r^{(0)}}{P_r} \leq \sum_r P_r \left( \frac{P_r^{(0)}}{P_r} - 1 \right) = \sum_r [P_r^{(0)} - P_r] = 0.$$

**0.18.** A one-dimensional normal distribution of zero mean and standard deviation  $\sigma$  is given by

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2}.$$

(a) Show that its entropy is  $(k_B/2) \ln(2\pi e\sigma^2)$ .

(b) show that for given

$$\int_{-\infty}^{\infty} x^2 P(x) dx = \sigma^2$$

, the normalized probability distribution having the largest entropy in the one-dimensional normal distribution.

**Solution 0.18:**

(a) By definition,

$$S/k_B = -\langle \ln P \rangle = -\int_{-\infty}^{\infty} \left[ -\frac{x^2}{2\sigma^2} - \frac{1}{2} \ln(2\pi\sigma^2) \right] P(x) dx = \frac{1}{2} \ln(2\pi e\sigma^2).$$

(b) Let us construct the functional

$$\mathcal{F}[P(x), \lambda_1, \lambda_2] = -\int_{-\infty}^{\infty} dx P(x) \ln P(x) + \lambda_1 \left( \int_{-\infty}^{\infty} dx x^2 P(x) - \sigma^2 \right) + \lambda_2 \left( \int_{-\infty}^{\infty} dx P(x) - 1 \right).$$

Maximizing entropy under these two constraints implies that the variational derivation  $\delta\mathcal{F}/\delta[P(x)] = 0$  or equivalently:

$$-\ln P(x) - 1 + \lambda_1 x^2 + \lambda_2 = 0,$$

where the constants  $\lambda_1$  and  $\lambda_2$  are determined from the constraints:  $\lambda_1 = -\frac{1}{2\sigma^2}$  and  $\lambda_2 = 1 - \ln\sqrt{2\pi\sigma^2}$ . Hence, the Gaussian distribution:

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}.$$

**0.19.** Using the method of canonical ensemble. calculate the partition function, average energy and specific heat of a system consisting of  $N$  noninteracting quantum harmonic oscillators and show that these expressions do reduce to the corresponding classical results in the appropriate classical limit.

**Solution 0.19:** Since  $\varepsilon_n = \hbar\omega(n + 1/2)$  we obtain

$$\begin{aligned} Z_1 &= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = [2 \sinh(\beta\hbar\omega/2)]^{-1}, \quad Z = Z_1^N, \\ E &= N \frac{\hbar\omega}{2} + N \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}, \\ C/k_B &= \frac{\partial E}{\partial T} = N(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}. \end{aligned}$$

Classical limiting case at  $\beta\hbar\omega \ll 1$  is obvious.

**0.20.** Let us denote the average occupation of the  $n$ -th single-particle level by the symbol  $f_n$ . For fermions, consider the “variational entropy”

$$S_{\text{var}} = - \sum_n [f_n \ln f_n + (1 - f_n) \ln(1 - f_n)]$$

and for bosons, consider the “variational entropy”

$$S_{\text{var}} = - \sum_n [f_n \ln f_n + (1 + f_n) \ln(1 + f_n)].$$

Show that if  $S_{\text{var}}$  is maximized, subject to the conditions

$$\sum_n f_n = N, \quad \sum_n f_n \varepsilon_n = E$$

then the resulting distribution is the FD distribution in the 1st case and BE distribution in the 2nd case. Moreover, at the maximum  $S_{\text{var}}$  is equal to the equilibrium entropy of the FD and BE systems, respectively.

**Solution 0.20:** Let us construct the functional

$$\tilde{S} = S_{\text{var}} - \beta\mu N + \beta E = \sum_n [-f_n \ln f_n - (1 \mp f_n) \ln(1 \mp f_n) - \beta\mu f_n + \beta\epsilon_n f_n].$$

We have

$$\frac{\partial \tilde{S}}{\partial f_n} = \ln \frac{1 \mp f_n}{f_n} - \beta\mu + \beta\epsilon_n = 0 \quad \rightarrow \quad \frac{1 \mp f_n}{f_n} = e^{\beta(\epsilon_n - \mu)}.$$

Consequently,

$$f_n = \frac{1}{e^{\beta(\epsilon_n - \mu)} \pm 1}.$$

Substituting these solutions to the expressions for the variational entropy we find the equilibrium values of the entropy.

# Chapter 1

## Fluctuations, correlations and response

**1.1.** Consider a closed system consisting of  $N$  noninteracting classical one-dimensional harmonic oscillators at a temperature  $T$ . Using the canonical ensemble, show that the most probable energy of the system is identical to its average energy.

**Solution 1.1:** Let us start with the density of states for one-dimensional classical oscillator with the Hamiltonian  $\mathcal{H} = p^2/2m + m\omega^2 x^2/2$ . We have

$$D(\varepsilon) = \int \frac{dp dx}{2\pi\hbar} \delta\left(\varepsilon - \frac{p^2}{2m} - \frac{m\omega^2 x^2}{2}\right).$$

To calculate this integral let us first recall the relation

$$\int_a^b dx \delta[f(x)] = \sum_s \frac{1}{|f'(x_s)|}$$

where  $x_s$  are roots of equation  $f(x) = 0$  belonging to the interval  $(a, b)$ . In our case,

$$x_s = \pm \sqrt{\frac{2}{m\omega^2} \left(\varepsilon - \frac{p^2}{2m}\right)}, \quad |f'(x_s)| = m\omega^2 |x_s| = \sqrt{2m\omega^2 \left(\varepsilon - \frac{p^2}{2m}\right)}$$

Consequently,

$$D(\varepsilon) = \frac{2}{2\pi\hbar\sqrt{2m\omega^2}} \int_0^{\sqrt{2m\varepsilon}} \frac{dp}{\sqrt{\varepsilon - p^2/2m}} = \frac{2}{2\pi\hbar\sqrt{2m\omega^2}} \pi\sqrt{2m} = \frac{1}{\hbar\omega}.$$

Consequently, the number of states per particle is  $\varepsilon/\hbar\omega$ . The thermodynamical weight is then  $(\varepsilon/\hbar\omega)^N = (E/N\hbar\omega)^N$ . The entropy to be maximized is then

$$S = k_B N \ln \frac{E}{N} - \frac{E}{T}$$

that yields for the most probable  $E$  the equation

$$\frac{\partial S}{\partial E} = k_B \frac{N}{E} - \frac{1}{T} = 0 \quad \rightarrow \quad E = Nk_B T.$$

**1.2.** Calculate the mean-square fluctuation in energy, and the mean-square fractional fluctuation in the energy of

- (a) a quantum harmonic oscillator,
- (b) a collection of  $N$  identical quantum harmonic oscillators.

Examine the results in the high-temperature limit.

**Solution 1.2:**

- (a) Let us count the energy from the ground state energy  $E_0 = \hbar\omega/2$ . Then

$$\begin{aligned} Z_1 &= \sum_{n=1}^{\infty} e^{-\beta n \hbar \omega} = \frac{1}{1 - e^{-\beta \hbar \omega}}, \\ \langle E \rangle &= -\frac{\partial \ln Z_1}{\partial \beta} = \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} = \hbar \omega \mathcal{N}(\omega), \\ \langle E^2 \rangle &= \frac{1}{Z_1} \frac{\partial^2 Z_1}{\partial \beta^2} = \hbar^2 \omega^2 \mathcal{N}(\omega) [2\mathcal{N}(\omega) + 1], \\ \langle (\Delta E)^2 \rangle &= (\hbar \omega)^2 \mathcal{N}(\omega) [\mathcal{N}(\omega) + 1], \\ \langle (\Delta E)^2 \rangle / \langle E \rangle^2 &= [\mathcal{N}(\omega) + 1] / \mathcal{N}(\omega). \end{aligned}$$

- (b) In the case of  $M$  oscillators one has to multiply both  $\langle E \rangle$  and  $\langle (\Delta E)^2 \rangle$  by  $M$ . Thus,  $\langle (\Delta E)^2 \rangle = [\mathcal{N}(\omega) + 1] / M \mathcal{N}(\omega)$ . At high temperature, this ratio is approximately  $1/M$ .

**1.3.** Show that for an ideal classical Ising magnet

- (a) the thermal fluctuation in the magnetization  $\langle (\Delta M)^2 \rangle$  is related to the thermal energy  $k_B T$  and the corresponding response function, namely susceptibility  $\chi$  through

$$\langle (\Delta M)^2 \rangle = k_B T N \chi,$$

- (b) and

$$\langle (\Delta M)^2 \rangle^{1/2} / \langle M \rangle \propto 1 / \sqrt{N}.$$

**Solution 1.3:**

(a) The energy is  $\varepsilon = -\mu H$ . Then,

$$\begin{aligned} Z_1 &= 2 \cosh(\beta\mu H), \\ \langle M \rangle &= \frac{1}{H} \frac{\partial \ln Z_1}{\partial \beta} = \mu \tanh(\beta\mu H), \\ \chi &= \frac{\partial \langle M \rangle}{\partial H} = \frac{\beta\mu^2}{\cosh^2(\beta\mu H)}, \\ \langle M^2 \rangle &= \frac{1}{H^2} \frac{\partial^2 Z_1}{\partial \beta^2} = \mu^2, \\ \langle (\Delta M)^2 \rangle &= \mu^2 [1 - \tanh^2(\beta\mu H)] = \frac{\mu^2}{\cosh^2(\beta\mu H)}. \end{aligned}$$

Thus

$$\langle (\Delta M)^2 \rangle = k_B T N \chi.$$

(b) Follows from statistical independence of different spins.

**1.4.**  $V_1$  is the volume of a small subsystem of a very large container of volume  $V$ , which is filled with  $N$  atoms of an ideal classical monoatomic gas. Denote the probability of finding a particular gas particle in the subsystem volume by  $p = V_1/V$ . Find an expression for the Probability  $P(N_1)$  that there are  $N_1$  particles in the subsystem. From this expression, find the relative variance  $\langle (N_1 - \langle N_1 \rangle)^2 \rangle$ . Show that the relative variance vanishes in the thermodynamic limit, i. e. when  $V \rightarrow \infty$ ,  $N \rightarrow \infty$  with  $N/V = \text{const}$  and simultaneously  $V_1 \rightarrow \infty$  with  $p = \text{constant}$ .

**Solution 1.4:** Let us use the binomial distribution

$$P(N_1) = \frac{N!}{N_1!(N-N_1)!} \left(\frac{V_1}{V}\right)^{N_1} \left(1 - \frac{V_1}{V}\right)^{N-N_1} = \frac{N!}{N_1!(N-N_1)!} p^{N_1} (1-p)^{N-N_1}.$$

Assuming  $N_1 \ll N$  we write  $N! \approx (N-N_1)! N^{N_1}$  to get the *Poisson* distribution.

$$P(N_1) = \frac{(Np)^{N_1}}{N_1!} (1-p)^N \rightarrow \frac{(Np)^{N_1}}{N_1!} e^{-Np}.$$

We have

$$\begin{aligned} \langle N_1 \rangle &= e^{-Np} \sum_{N_1=0}^{\infty} \frac{N_1 (Np)^{N_1}}{N_1!} = Np e^{-Np} \sum_{N_1=1}^{\infty} \frac{(Np)^{N_1-1}}{(N_1-1)!} = Np, \\ \langle N_1^2 \rangle &= e^{-Np} \sum_{N_1=0}^{\infty} \frac{N_1^2 (Np)^{N_1}}{N_1!} = Np e^{-Np} \sum_{N_1=1}^{\infty} \frac{N_1 (Np)^{N_1-1}}{(N_1-1)!} \\ &= Np e^{-Np} \sum_{N_1=1}^{\infty} \frac{[1 + (N_1-1)] (Np)^{N_1-1}}{(N_1-1)!} = Np + (Np)^2, \\ \langle (\Delta N_1)^2 \rangle &= Np, \quad \langle (\Delta N_1)^2 \rangle / \langle N_1 \rangle^2 = (Np)^{-1}. \end{aligned}$$