Problem 1

Consider a classical particle in one dimension that is described by the Hamiltonian

$$H = c_1 \, |q|^{\alpha_1}$$

with q being a generalized coordinate, and c_1,$\alpha_1 > 0$.

a) Compute the partition function of the particle.

b) Compute the free energy F, the total internal energy, U, and the entropy S of the system.

c) Consider next a classical particle in two dimensions that is described by the Hamiltonian

$$H = c_1 \, |q_1|^{\alpha_1} + c_2 \, |q_2|^{\alpha_2}$$

with $q_{1,2}$ being generalized coordinates. Under which conditions for the parameters c_1, c_2, α_1, and α_2 does the equipartition theorem hold? Explain your result.

Solutions:

a)

$$Z(T,V,1) = \int_{-\infty}^{\infty} dq \exp\left[-\beta H\right] = \int_{-\infty}^{\infty} dq \exp\left[-\beta c_1 \, |q|^{\alpha_1}\right]$$

Using the transformation

$$x = \beta^{1/\alpha_1} c_1^{1/\alpha_1} q$$

I obtain

$$Z(T,V,1) = \frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}} \int_0^{\infty} dx \exp\left[-x^{\alpha_1}\right] = \frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}} \Gamma\left(1 + \frac{1}{\alpha_1}\right)$$

b) The free energy is thus given by

$$\begin{aligned} F &= -k_B T \ln Z(T,V,1) \\ &= -k_B T \ln\left[\frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}} \Gamma\left(1 + \frac{1}{\alpha_1}\right)\right] \end{aligned}$$

The entropy is given by

$$\begin{aligned} S &= -\frac{\partial F}{\partial T} = \frac{\partial}{\partial T}\left\{k_B T \ln\left[\frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}} \Gamma\left(1 + \frac{1}{\alpha_1}\right)\right]\right\} \\ &= \frac{\partial}{\partial T}\left\{k_B T \ln\left[\frac{2}{c_1^{1/\alpha_1}} \Gamma\left(1 + \frac{1}{\alpha_1}\right) (k_B T)^{1/\alpha_1}\right]\right\} \end{aligned}$$

$$
\begin{aligned}
&= k_B \ln\left[\frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}}\Gamma\left(1+\frac{1}{\alpha_1}\right)\right] + k_B T \frac{1}{\alpha_1}\frac{1}{T} \\
&= k_B \left\{\ln\left[\frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}}\Gamma\left(1+\frac{1}{\alpha_1}\right)\right] + \frac{1}{\alpha_1}\right\}
\end{aligned}
$$

and we have for the internal energy

$$
\begin{aligned}
U &= -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\ln\left[\frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}}\Gamma\left(1+\frac{1}{\alpha_1}\right)\right] \\
&= \frac{1}{\alpha_1}\frac{1}{\beta} = \frac{1}{\alpha_1}k_B T
\end{aligned}
$$

Equivalently

$$
\begin{aligned}
U &= F + TS = -k_B T \ln\left[\frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}}\Gamma\left(1+\frac{1}{\alpha_1}\right)\right] + T k_B \left\{\ln\left[\frac{2}{\beta^{1/\alpha_1} c_1^{1/\alpha_1}}\Gamma\left(1+\frac{1}{\alpha_1}\right)\right] + \frac{1}{\alpha_1}\right\} \\
&= \frac{1}{\alpha_1}k_B T
\end{aligned}
$$

c) We have for the internal energy

$$
U = \frac{1}{\alpha_1}k_B T + \frac{1}{\alpha_2}k_B T
$$

Thus the equipartition theorem only holds for

$$
\frac{1}{\alpha_1} = \frac{1}{\alpha_2}
$$

since only in this case is the energy equally distributed between the two degrees of freedom.

Problem 2)

Consider two coupled quantum mechanical harmonic oscillators with Hamiltonian

$$H = \hbar\omega_0 \left(n + \frac{1}{2}\right) + \hbar\omega_0 \left(m + \frac{1}{2}\right) + \alpha\hbar\omega_0 nm$$

where the harmonic oscillators can only be in the states with $n, m = 0, 1$

a) Compute the partition function
b) Compute the free energy of the system.

c) Compute the entropy. Is the entropy increased or decreased by the coupling-term with $\alpha > 0$? Explain your result.

Solutions:
a) The partition function is given by

$$\begin{aligned} Z &= \sum_{n,m=0}^{1} \exp\left[-\beta H\right] \\ &= \exp[-\beta \left(\hbar\omega_0 \frac{1}{2} + \hbar\omega_0 \frac{1}{2}\right)] + \exp\left[-\beta \left(\hbar\omega_0 \frac{3}{2} + \hbar\omega_0 \frac{1}{2}\right)\right] \\ &\quad + \exp\left[-\beta \left(\hbar\omega_0 \frac{3}{2} + \hbar\omega_0 \frac{1}{2}\right)\right] + \exp\left[-\beta \left(\hbar\omega_0 \frac{3}{2} + \hbar\omega_0 \frac{3}{2} + \alpha\hbar\omega_0\right)\right] \\ &= \exp\left[-\beta\hbar\omega_0\right] \left\{1 + 2\exp\left[-\beta\hbar\omega_0\right] + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\} \end{aligned}$$

b) The free energy is given by

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -k_B T \ln\left[\exp\left[-\beta\hbar\omega_0\right] \left\{1 + 2\exp\left[-\beta\hbar\omega_0\right] + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\}\right] \\ &= \hbar\omega_0 - k_B T \ln\left\{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\} \end{aligned}$$

c) The entropy is given by

$$\begin{aligned} S &= -\frac{\partial F}{\partial T} = \frac{\partial}{\partial T}\left[k_B T \ln\left\{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\}\right] \\ &= k_B \ln\left\{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\} \\ &\quad + k_B T \frac{\partial}{\partial T} \ln\left\{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\} \\ &= k_B \ln\left\{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\} \\ &\quad + k_B T \frac{\partial\beta}{\partial T}\frac{\partial}{\partial\beta} \ln\left\{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\} \end{aligned}$$

$$
\begin{aligned}
&= k_B \ln\left\{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\} \\
&\quad + k_B T\left(-\frac{1}{k_B T^2}\right)\frac{2\exp\left(-\beta\hbar\omega_0\right)\left(-\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\left[-\left(2+\alpha\right)\hbar\omega_0\right]}{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]} \\
&= k_B \ln\left\{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]\right\} \\
&\quad + k_B\left(\frac{\hbar\omega_0}{k_B T}\right)\frac{2\exp\left(-\beta\hbar\omega_0\right) + \left(2+\alpha\right)\exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]}{1 + 2\exp\left(-\beta\hbar\omega_0\right) + \exp\left[-\beta\left(2+\alpha\right)\hbar\omega_0\right]}
\end{aligned}
$$

The entropy is increased since the state with $n = m = 1$ of the system is pushed to higher energies.

Problem 3)

a) Blackbody radiation can be treated as a macroscopic thermodynamic system. Its energy density if given by

$$U = \frac{4}{c} V \sigma T^4$$

where σ is the Stefan-Boltzmann constant. Determine the form of the fundamental relation whose independent variables are V amd T, and obtain expressions for the pressure and specific heat (note that the entropy S for the systems vanishes at $T = 0$).

b) Starting from the entropy

$$S = N k_B \left[\frac{5}{2} + \ln \left\{ \frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right\} \right]$$

and internal energy

$$U = \frac{3}{2} N k_B T$$

of the ideal gas, compute its free energy and the grandcanonical potential.

Solutions:

a) We need to calculate the free energy F which is a function of T and V. Since

$$F = U - TS$$

we need to obtain the entropy S which we can get from

$$\left. \frac{\partial S}{\partial U} \right|_{V,N} = \frac{1}{T}$$

or

$$S = \int_0^T dU \frac{1}{T_1} = \int_0^T dT_1 \frac{1}{T_1} \frac{16 V \sigma}{c} T_1^3 = \frac{16 V \sigma}{c} \int_0^T dT_1 T_1^2 = \frac{16 V \sigma}{3c} T^3$$

and thus

$$\begin{aligned} F &= U - TS \\ &= \frac{4}{c} V \sigma T^4 - T \frac{16 V \sigma}{3c} T^3 \\ &= \frac{1}{c} V \sigma T^4 \left(4 - \frac{16}{3} \right) = -\frac{4}{3c} V \sigma T^4 \end{aligned}$$

To obtain the pressure, we use

$$p = -\frac{\partial F}{\partial V} = \frac{4}{3c} \sigma T^4$$

and the specific heat is given by

$$c_V = \frac{\partial U}{\partial T} = \frac{16}{c} V \sigma T^3$$

Legendre transformation

$$G = F + pV = -\frac{4}{3c} V \sigma T^4 + \frac{4}{3c} \sigma T^4 V = 0$$

b) The entropy of a system is given by

$$S = N k_B \left[\frac{5}{2} + \ln \left\{ \frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right\} \right]$$

Using that

$$U = \frac{3}{2} N k_B T$$

we find

$$\begin{aligned} F &= U - TS = \frac{3}{2} N k_B T - N T k_B \left[\frac{5}{2} + \ln \left\{ \frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right\} \right] \\ &= -N T k_B \left[1 + \ln \left\{ \frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right\} \right] = -N T k_B \left[1 + \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \right] \\ &= F(T, V, N) \end{aligned}$$

Next, we have to perform a Legendre transformation to and T, V, μ, where

$$\begin{aligned} \mu &= \frac{\partial F}{\partial N} = -\frac{\partial F}{\partial N} \left(N k_B T \left[1 + \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \right] \right) \\ &= -k_B T \left[1 + \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \right] + N k_B T \frac{1}{N} \\ &= -k_B T \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \end{aligned}$$

or

$$\begin{aligned} \mu &= -k_B T \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \\ \exp\left(-\frac{\mu}{k_B T} \right) &= \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \\ N &= V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \exp\left(\frac{\mu}{k_B T} \right) \end{aligned}$$

and hence

$$\begin{aligned}
\Phi(T, V, \mu) &= F(T, V, N) - \mu N \\
&= -N k_B T \left[1 + \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \right] + N k_B T \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \\
&= -N k_B T \\
&= -k_B T \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V \exp\left(\frac{\mu}{k_B T} \right)
\end{aligned}$$

Problem 4)

Consider the earth's atmosphere as an ideal gas with molecular weight μ in a gravitational field with g being the acceleration due to gravity.

a) If z denotes the height above sea level, show that the change in the atmospheric pressure p with height is given by

$$\frac{dp}{p} = -\frac{\mu g}{N_A k_B T} dz$$

where T is the temperature at height z.

b) If the decrease in pressure is due to an adiabatic expansion, i.e., using

$$pV^\gamma = const.$$

show that

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{dT}{T}$$

c) From a) and b) calculate dT/dz, the change in temperature with increasing z.

d) If the pressure and temperature at sea-level are given by p_0 and T_0 respectively, and the atmosphere is considered to be adiabatic, find the pressure p at height z.

Solutions:

a) We have

$$\begin{aligned}
p(z + dz)A - p(z)A &= -nAdzmg \\
p(z + dz) - p(z) &= -ndzmg \\
\frac{dp}{dz} dz &= -ndz \frac{\mu}{N_A} g \\
\frac{dp}{dz} &= -\frac{p}{k_B T} \frac{\mu}{N_A} g \\
\frac{dp}{p} &= -\frac{1}{k_B T} \frac{\mu}{N_A} g dz
\end{aligned}$$

where I used

$$pV = N k_B T \Longrightarrow p = n k_B T$$

b) We have

$$pV^\gamma = const.$$

Using next

$$V = \frac{Nk_BT}{p}$$

we obtain

$$T^\gamma p^{1-\gamma} = const.$$

Thus

$$\begin{aligned} d\left(T^\gamma p^{1-\gamma}\right) &= 0 \\ \gamma T^{\gamma-1} p^{1-\gamma} dT + (1-\gamma) T^\gamma p^{-\gamma} dp &= 0 \end{aligned}$$

and hence

$$\begin{aligned} \gamma T^{\gamma-1} p^{1-\gamma} dT &= (\gamma - 1) T^\gamma p^{-\gamma} dp \\ \frac{dp}{p} &= \frac{\gamma}{\gamma - 1} \frac{dT}{T} \end{aligned}$$

c) Combining the above equations,

$$\begin{aligned} \frac{dp}{p} &= -\frac{1}{k_BT} \frac{\mu}{N_A} g dz \\ \frac{dp}{p} &= \frac{\gamma}{\gamma - 1} \frac{dT}{T} \end{aligned}$$

I obtain

$$\begin{aligned} \frac{\gamma}{\gamma - 1} \frac{dT}{T} &= -\frac{1}{k_BT} \frac{\mu}{N_A} g dz \\ \frac{dT}{dz} &= -\frac{1-\gamma}{\gamma} \frac{\mu}{k_B N_A} g \end{aligned}$$

d) From

$$\frac{dT}{dz} = -\frac{1-\gamma}{\gamma} \frac{\mu}{k_B N_A} g$$

we obtain via integration

$$\begin{aligned} \int_{T_0}^{T} dT' &= -\int_0^z \frac{1-\gamma}{\gamma} \frac{\mu}{k_B N_A} g dz' \\ T &= T_0 - \frac{\gamma - 1}{\gamma} \frac{\mu}{k_B N_A} g z \end{aligned}$$

and hence using

$$\frac{dp}{p} = -\frac{1}{k_BT} \frac{\mu}{N_A} g dz$$

we obtain

$$
\begin{aligned}
\int_{p_0}^{p} \frac{dp'}{p'} &= -\int_0^z \frac{1}{k_B T} \frac{\mu}{N_A} g dz' = -\frac{\mu g}{k_B N_A} \int_0^z \frac{1}{T_0 - \frac{\gamma-1}{\gamma} \frac{\mu}{k_B N_A} g z'} dz' \\
\ln \frac{p}{p_0} &= -\frac{\mu g}{k_B N_A T_0} \int_0^z \frac{1}{1 - \frac{\gamma-1}{\gamma} \frac{\mu}{k_B N_A T_0} g z'} dz' = \frac{\mu g}{k_B N_A T_0} \frac{1}{\frac{\gamma-1}{\gamma} \frac{\mu}{k_B N_A T_0} g} \ln \left[1 - \frac{\gamma-1}{\gamma} \frac{\mu}{k_B N_A T_0} g z' \right] \Bigg|_0^z \\
\ln \frac{p}{p_0} &= \frac{\gamma}{\gamma - 1} \ln \left[1 - \frac{\gamma-1}{\gamma} \frac{\mu}{k_B N_A T_0} g z \right] \\
p(z) &= p_0 \left[1 - \frac{\gamma-1}{\gamma} \frac{\mu}{k_B N_A T_0} g z \right]^{\frac{\gamma}{\gamma-1}}
\end{aligned}
$$

Problem 5)

N identical classical particles occupy a square lattice with $2N$sites, with at most one particle per site. Alternate sites are labeled A and B.

Denote by c the fraction of particles on the A sites, N_A, i.e.,

$$c = \frac{N_A}{N} \Longrightarrow N_A = cN$$

Since $N_A + N_B = N$ I obtain

$$\frac{N_B}{N} = \frac{N - N_A}{N} = 1 - c$$

Note that

$$0 \leq N_A, N_B \leq N$$

a) Compute the entropy for fixed c.

b) When two objects are on neighboring A and B sites, there is a repulsive interaction energy E_0. For fixed c, and assuming that all configurations at

fixed c are equally likely, show that the average total energy of the system is

$$E(c) = 4NE_0c(1 - c)$$

c) In thermal equilibrium at temperature T, c is determined by minimizing the free energy

$$F(c) = E(c) - TS(c)$$

This system exhibits a second order phase transition at a temperature T_c.

(i) Describe the state of the system at very high temperatures. What is the observed value of c?

(ii) Describe the state of the system at very low temperatures. What are the possible values of c?

(iii) Determine T_c.

Solutions:

a) The entropy is given by

$$S = k_B \ln \Omega$$

where Ω is the number of microstates given a certain value of c. The total number of microstates if equal to

$$\Omega = \Omega_A(N_A)\Omega_B(N_B)$$

where $\Omega_A(N_A)$ is the number of microstates which can be obtained by distributing N_A particles over N sites, which is thus given by

$$\Omega_A(N_A) = \frac{N!}{N_A!\,(N - N_A)!}$$

and thus

$$\Omega = \Omega_A(N_A)\Omega_B(N_B) = \frac{N!}{N_A!\,(N-N_A)!}\frac{N!}{N_B!\,(N-N_B)!} = \frac{N!}{N_A!N_B!}\frac{N!}{N_B!N_A!} = \left(\frac{N!}{N_B!N_A!}\right)^2$$

and thus

$$\begin{aligned}
\frac{S}{k_B} &= \ln\Omega = 2\ln\left[\frac{N!}{N_A!N_B!}\right] \\
&\approx 2N\ln N - 2N - 2N_A\ln N_A + 2N_A - 2N_B\ln N_B + 2N_B \\
&= 2N\ln N - 2N_A\ln N_A - 2N_B\ln N_B \\
&= 2N\ln N - 2cN\ln[cN] - 2N(1-c)\ln[N(1-c)] \\
&= 2N\ln N - 2cN\ln N - 2cN\ln c - 2N(1-c)\ln N - 2N(1-c)\ln[1-c] \\
&= 2N\ln N - 2N\ln N - 2cN\ln c - 2N(1-c)\ln[1-c] \\
&= -2cN\ln c - 2N(1-c)\ln(1-c)
\end{aligned}$$

b) There are N sites labelled A. Each site is surrounded by 4 B sites (neglecting boundary effects). The probablity that the A site is occupied is c, and that one of the four neighboring B sites is occupied is $(1-c)$. Hence is the average energy is

$$E(c) = E_0 N 4c(1-c)$$

c) At large T, the entropy of the system is maximized, implying that

$$\frac{S(c)}{k_B} = -2cN\ln c - 2N(1-c)\ln(1-c)$$

should be at a maximum. Hence

$$\begin{aligned}
\frac{d}{dc}\frac{S(c)}{k_B} &= \frac{d}{dc}\left[-2cN\ln c - 2N(1-c)\ln(1-c)\right] = 0 \\
\frac{d}{dc}\left[c\ln c + (1-c)\ln(1-c)\right] &= 0 \\
\ln c + 1 - \ln(1-c) - 1 &= 0 \\
\ln\frac{c}{1-c} &= 0 \\
\frac{c}{1-c} &= 1 \Longrightarrow c = 1-c \Longrightarrow c = \frac{1}{2}
\end{aligned}$$

d) At low T the free energy is minimized by minimizing the energy $E(c)$. The latter is minimized for either $c=0$ or $c=1$, implying that either all particles are on the A or on the B sites.

e) To obtain T_c we need to minimize the free energy

$$F(c) = E(c) - TS(c) = E_0 N 4c(1-c) - k_B T \left[-2cN \ln c - 2N(1-c)\ln(1-c)\right]$$

Minimizing the free energy w.r.t. c yields

$$\begin{aligned}
\frac{d}{dc}F(c) &= \frac{d}{dc}\left\{4NE_0 c(1-c) + 2Nk_B T\left[c\ln c + (1-c)\ln(1-c)\right]\right\} \\
&= 4NE_0(1-2c) + 2Nk_BT\left[\ln c - \ln(1-c)\right] = 0
\end{aligned}$$

The phase transition will occur when

$$c = \frac{1}{2} \pm \delta$$

and hence

$$\begin{aligned}
0 &= (1 - 2\left[\frac{1}{2}+\delta\right]) + \frac{k_BT}{2E_0}\left[\ln\left[\frac{1}{2}+\delta\right] - \ln\left(1 - \left[\frac{1}{2}+\delta\right]\right)\right] \\
&= -2\delta + \frac{k_BT}{2E_0}\left[\ln\left[\frac{1}{2}+\delta\right] - \ln\left(\frac{1}{2}-\delta\right)\right] = \\
&= -2\delta + \frac{k_BT}{2E_0}\left[\ln\left[1+2\delta\right] - \ln(1-2\delta)\right] \\
&= -2\delta + \frac{k_BT}{2E_0}\left[2\delta - \frac{(2\delta)^2}{2} + \frac{(2\delta)^3}{3} + 2\delta + \frac{(2\delta)^2}{2} + \frac{(2\delta)^3}{3}\right] \\
&= -2\delta + \frac{k_BT}{2E_0}4\delta\left[1 + \frac{(2\delta)^2}{3}\right] = 0
\end{aligned}$$

which implies

$$\delta = 0$$

or

$$\begin{aligned}
\frac{k_BT}{E_0}\left[1 + \frac{(2\delta)^2}{3}\right] &= 1 \\
k_BT_c &= E_0
\end{aligned}$$