Theoretical Statistical Physics Solution to Exercise Sheet 6

1 Ideal gas in a harmonic potential

(4 points)

An ideal gas is trapped in a three-dimensional harmonic potential

$$V(\boldsymbol{x}) = a\,\boldsymbol{x}^2 = a(x_1^2 + x_2^2 + x_3^2), \qquad a > 0.$$
(1)

- a) What is the equilibrium distribution at temperature T?
- b) Calculate the density of the gas and its pressure and their dependence on x.
- c) Calculate the internal energy U (as the expected value of the energy), and the heat capacity.
- d) Define the volume of the gas as the expected value of $\frac{4\pi}{3}|\boldsymbol{x}|^3$. Calculate the volume and the thermal expansion coefficient of the gas.
- a) As we showed in exercise 3 on sheet 5, the stationary Boltzmann equation

$$\frac{\boldsymbol{p}}{m} \cdot \boldsymbol{\nabla}_{\boldsymbol{x}} f(\boldsymbol{x}, \boldsymbol{p}) = -\boldsymbol{F}(\boldsymbol{x}) \cdot \boldsymbol{\nabla}_{\boldsymbol{p}} f(\boldsymbol{x}, \boldsymbol{p})$$
(2)

admits solutions of the form of the Maxwell-Boltzmann distribution

$$f(\boldsymbol{x}, \boldsymbol{p}) = \mathcal{N} e^{-\beta E(\boldsymbol{x}, \boldsymbol{p})},\tag{3}$$

where $\beta = 1/k_{\rm B}T$ and $E(\boldsymbol{x}, \boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} + a \boldsymbol{x}^2$ is the system's total energy. Since equilibrium must be stationary (although the converse is not always true), we know that the gas is described by a distribution of this type. The normalization \mathcal{N} is fixed by requiring that the phase space density integrate to the total number of particles N that make up the gas,

$$\iint f(\boldsymbol{x}, \boldsymbol{p}) \,\mathrm{d}^3 x \,\mathrm{d}^3 p = \mathcal{N} \int e^{-a\,\beta\,\boldsymbol{x}^2} \,\mathrm{d}^3 x \int e^{-\beta\,\frac{\boldsymbol{p}^2}{2m}} \,\mathrm{d}^3 p = \mathcal{N} \Big(\frac{\pi}{a\,\beta}\Big)^{\frac{3}{2}} \Big(\frac{2\pi\,m}{\beta}\Big)^{\frac{3}{2}} \stackrel{!}{=} N. \tag{4}$$

We used a > 0 above. Thus,

$$\mathcal{N} = \frac{a^{\frac{3}{2}} \beta^3}{(2m)^{\frac{3}{2}} \pi^3} N, \tag{5}$$

and the equilibrium distribution at temperature T reads

$$f(\boldsymbol{x}, \boldsymbol{p}) = \frac{a^{\frac{3}{2}} \beta^3 N}{(2m)^{\frac{3}{2}} \pi^3} \exp\left[-\beta\left(\frac{\boldsymbol{p^2}}{2m} + a\,\boldsymbol{x}^2\right)\right].$$
 (6)

b) To find the spatial density n(x) of the trapped gas, we integrate the phase space density over all momenta,

$$n(\boldsymbol{x}) = \int f(\boldsymbol{x}, \boldsymbol{p}) \,\mathrm{d}^3 p = \frac{a^{\frac{3}{2}} \,\beta^3 \,N}{(2m)^{\frac{3}{2}} \,\pi^3} \,(2\pi \,m/\beta)^{\frac{3}{2}} \,e^{-a\,\beta\,\boldsymbol{x}^2} = \left(\frac{a\,\beta}{\pi}\right)^{\frac{3}{2}} N \,e^{-a\,\beta\,\boldsymbol{x}^2}. \tag{7}$$

It is instructive to verify that the units work out. Since the exponent $a \beta x^2$ must be dimensionless, $a\beta$ has dimensions of inverse area and so $N/(a\beta)^{3/2}$ is indeed a number density. Due to the rapidly decaying exponential, the gas is strongly localized. Defining the oscillation amplitude $\ell = 1/\sqrt{a\beta} = \sqrt{k_{\rm B}T/a}$, we see that for increased temperature, the gas has a wider density profile. This is consistent with the kinetic gas theory interpretation that particles of higher temperature will have higher average energy and are able to climb further up the trap walls.

To derive the pressure, we assume local equilibrium, i.e. the ideal gas law should hold locally at every \boldsymbol{x} . Thus

$$p(\boldsymbol{x}) = n(\boldsymbol{x}) R T = NR T \left(\frac{a\beta}{\pi}\right)^{\frac{3}{2}} e^{-a\beta \boldsymbol{x}^2}$$
(8)

c) The internal energy is the expectation value

$$U = \iint E(\boldsymbol{x}, \boldsymbol{p}) f(\boldsymbol{x}, \boldsymbol{p}) d^{3}x d^{3}p$$

$$= \left(\frac{\pi}{a\beta}\right)^{\frac{3}{2}} \mathcal{N} \int \frac{\boldsymbol{p}^{2}}{2m} e^{-\beta \frac{\boldsymbol{p}^{2}}{2m}} d^{3}p + (2\pi m/\beta)^{\frac{3}{2}} \mathcal{N} \int a\boldsymbol{x}^{2} e^{-a\beta \boldsymbol{x}^{2}} d^{3}x$$

$$= -\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} N \partial_{\beta} \int e^{-\beta \frac{\boldsymbol{p}^{2}}{2m}} d^{3}p - \left(\frac{a\beta}{\pi}\right)^{\frac{3}{2}} N \partial_{\beta} \int e^{-a\beta \boldsymbol{x}^{2}} d^{3}x \qquad (9)$$

$$= -\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} N \partial_{\beta} (2\pi m/\beta)^{\frac{3}{2}} - \left(\frac{a\beta}{\pi}\right)^{\frac{3}{2}} N \partial_{\beta} \left(\frac{\pi}{a\beta}\right)^{\frac{3}{2}}$$

$$= \frac{3}{2} \frac{N}{\beta} + \frac{3}{2} \frac{N}{\beta} = 3N k_{\rm B} T.$$

The equipartition theorem is able to shed some light on this result. It states that in thermal equilibrium, energy is shared equally amongst all accessible degrees of freedom, which is just another way of saying that an equilibrated system will maximize its entropy. Distributing the available energy evenly amongst all accessible modes maximizes the number of microstates consistent with the observed macrostate.

However, the equipartition theorem also makes a quantitative prediction. It states that each quadratic degree of freedom will, on average, possess an energy $\frac{1}{2} k_{\rm B} T$. In this case, we indeed have 6N quadratic degrees of freedom since the kinetic energy of each of the N particles is $\propto p^2$ while the potential energy is $\propto x^2$.

The heat capacity immediately follows from (9) as

$$C = \frac{\partial U}{\partial T} = 3Nk_{\rm B},\tag{10}$$

which is twice the heat capacity of an ideal gas contained in a potential-free box. d) The expectation value of $|x|^3$ is

$$\langle |\mathbf{x}|^{3} \rangle = \int |\mathbf{x}|^{3} n(\mathbf{x}) \,\mathrm{d}^{3} x \stackrel{(7)}{=} \left(\frac{a\,\beta}{\pi}\right)^{\frac{3}{2}} N \int |\mathbf{x}|^{3} e^{-a\,\beta\,\mathbf{x}^{2}} \,\mathrm{d}^{3} x$$

$$= \frac{4\pi}{2} \left(\frac{a\,\beta}{\pi}\right)^{\frac{3}{2}} N \int_{0}^{\infty} u^{2} e^{-a\,\beta\,u} \,\mathrm{d} u = \frac{4\pi}{2} \left(\frac{a\,\beta}{\pi}\right)^{\frac{3}{2}} N \,\partial_{a\beta}^{2} \int_{0}^{\infty} e^{-a\,\beta\,u} \,\mathrm{d} u$$

$$= \frac{4\pi}{2} \left(\frac{a\,\beta}{\pi}\right)^{\frac{3}{2}} N \,\partial_{a\beta}^{2} \frac{1}{a\beta} = \frac{4\pi}{2} \left(\frac{a\,\beta}{\pi}\right)^{\frac{3}{2}} N \frac{2}{(a\beta)^{3}} = \frac{4\pi\,N}{(\pi\,a\,\beta)^{\frac{3}{2}}}.$$

$$(11)$$

where we used the transformation $u = x^2$, du = 2|x| dx. Thus the gas fills a sphere of volume

$$V = \frac{4\pi}{3} \langle |\mathbf{x}|^3 \rangle = \frac{16\sqrt{\pi}}{3} \frac{N}{(a\beta)^{\frac{3}{2}}}.$$
 (12)

The thermal expansion coefficient is given by

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_{a,N} = \frac{3}{2T}.$$
(13)

2 Equilibrium distribution

Let $N \in \mathbb{N}$ be large and $g_i \ge 0 \quad \forall i \in \{1, \dots, N\}$ with $\sum_{i=1}^{N} g_i = 1$. We define the probability distribution

$$p(n_1, \dots, n_N) = g_1^{n_1} \dots g_N^{n_N} \frac{(n_1 + \dots + n_N)!}{n_1! \dots n_N!}.$$
(14)

Determine the most probable distribution of n_i (assuming that $n_i \gg 1$ for all i), and compute the deviations $\langle n_i^2 \rangle - \langle n_i \rangle^2$ from this distribution asymptotically for large n_i . (Here $\langle \cdot \rangle$ is the expectation value with respect to the probability distribution given by p.)

First, note that we can rewrite the distribution (14) more compactly,

$$p(n_1, \dots, n_N) = N_{\text{tot}}! \prod_{i=1}^N \frac{g_i^{n_i}}{n_i!},$$
 (15)

where $N_{\text{tot}} = \sum_{i=1}^{N} n_i$. Since $n_i \gg 1 \ \forall i \in \{1, \dots, N\}$, we can take the logarithm of (15) and use Stirling's approximation for large factorials, $\ln(n!) = n \ln(n) - n + \mathcal{O}(\ln n)$ to get

$$\ln(p) = \ln(N_{\text{tot}}!) + \sum_{i=1}^{N} \left[n_i \ln(g_i) - \ln(n_i!) \right]$$

$$\sim N_{\text{tot}} \ln(N_{\text{tot}}) - N_{\text{tot}} + \sum_{i=1}^{N} n_i \ln(g_i) - \sum_{i=1}^{N} [n_i \ln(n_i) - n_i] \qquad (16)$$

$$= N_{\text{tot}} \ln(N_{\text{tot}}) + \sum_{i=1}^{N} n_i \ln\left(\frac{g_i}{n_i}\right).$$

This asymptotic form of $\ln(p)$ becomes exact as $n_i \to \infty \forall i$. Differentiating (16) w.r.t n_i gives

$$\frac{\partial \ln(p)}{\partial n_i} = \frac{\partial}{\partial n_i} \Big[N_{\text{tot}} \ln(N_{\text{tot}}) \Big] + \frac{\partial}{\partial n_i} \Big[\sum_{j=1}^N n_j \ln\left(\frac{g_j}{n_j}\right) \Big]$$

$$= \ln(N_{\text{tot}}) + 1 + \ln\left(\frac{g_i}{n_i}\right) - 1$$

$$= \ln\left(N_{\text{tot}} \frac{g_i}{n_i}\right),$$
(17)

where we used $\partial N_{\text{tot}}/\partial n_i = 1$. To find the extremum distribution, we require that (17) be zero for all $i \in \{1, \ldots, N\}$.¹ This results in

$$\ln\left(N_{\text{tot}} \frac{g_i}{n_i}\right) \stackrel{!}{=} 0 \qquad \Rightarrow \qquad n_i^{\text{ext}} = g_i N_{\text{tot}} \quad \forall i \in \{1, \dots, N\}.$$
(18)

As can be seen from the plot below, x and $-x \log(x)$ are both concave functions. Since $\ln(p)$ decomposes into sums of these two components, it too must be concave. Any extremum of a concave function is a maximum, so we can infer that $n_i^{\text{ext}} = n_i^{\text{max}}$ in (18).

(4 points)

¹Here, we use that the logarithm is strictly monotonic on $(0, \infty)$ since $\partial_x \ln(x) = 1/x > 0 \quad \forall x \in (0, \infty)$ and so the maximum of $\ln(p)$ will also be the maximum of p.



Next we consider deviations from this distribution. First, note that by the multinomial theorem

$$1 = \left(\sum_{i=1}^{N} g_i\right)^{N_{\text{tot}}} = \sum_{n_1,\dots,n_N} p(n_1,\dots,n_N),$$
(19)

meaning the probabilities sum to one as they should for any distribution. Using (19), we calculate the first and second moment of our distribution.

where the last equality holds in the asymptotic regime $n_i \gg 1 \quad \forall i$ we are interested in. Similarly,

$$\langle n_i^2 \rangle = \sum_{n_1,\dots,n_N} n_i^2 p(n_1,\dots,n_N) = \sum_{n_1,\dots,n_N} g_i \frac{\partial}{\partial g_i} g_i \frac{\partial}{\partial g_i} p(n_1,\dots,n_N)$$

$$= g_i \frac{\partial}{\partial g_i} g_i \frac{\partial}{\partial g_i} \left(\sum_{j=1}^N g_j\right)^{N_{\text{tot}}} = g_i \left(N_{\text{tot}} + g_i N_{\text{tot}}(N_{\text{tot}} - 1)\right)$$

$$= n_i^{\max} + g_i n_i^{\max}(N_{\text{tot}} - 1) \approx n_i^{\max} + (n_i^{\max})^2,$$

$$(21)$$

where again, the last result holds asymptotically. (20) and (21) yield a deviation

$$\Delta n_i = \langle n_i^2 \rangle - \langle n_i \rangle^2 = n_i^{\text{max}}.$$
(22)

3 n-Ball

Compute the volume of a sphere of radius R in *n*-dimensional space. For n = 100, compare the volume of a sphere of radius 1 with one of radius 0.99.

The volume of an n-ball can be calculated without ever parametrizing an infinitesimal volume element in n-dimensional spherical coordinates by invoking properties of the Gauss integral and the Gamma function

$$\int_{-\infty}^{\infty} e^{-x^2} \mathrm{d}x = \sqrt{\pi}, \qquad \int_{0}^{\infty} x^{n-1} e^{-x} \,\mathrm{d}x = \Gamma(n).$$
(23)

(2)

To this end, note that

$$\pi^{\frac{n}{2}} = \prod_{i=1}^{n} \int_{-\infty}^{\infty} e^{-x_{i}^{2}} \mathrm{d}x_{i} = \int_{\mathbb{R}^{n}} e^{-x^{2}} \mathrm{d}^{n}x.$$
 (24)

Since the integrand depends only on the magnitude of the vector \boldsymbol{x} , this integral factorizes into a purely radial part and an angular integration,

$$\pi^{\frac{n}{2}} = \left(\int_0^\infty |\boldsymbol{x}|^{n-1} e^{-\boldsymbol{x}^2} \mathrm{d}|\boldsymbol{x}|\right) \left(\int \mathrm{d}^{n-1} \Omega_{n-1}\right) = \frac{1}{2} \Gamma\left(\frac{n}{2}\right) \int \mathrm{d}^{n-1} \Omega_{n-1}, \tag{25}$$

where we used the transformation $u = |\mathbf{x}|^2$, $du = 2\sqrt{u} d|\mathbf{x}|$ to bring the radial integration into the form of the Gamma function,

$$\int_0^\infty |\boldsymbol{x}|^{n-1} e^{-\boldsymbol{x}^2} \mathrm{d}|\boldsymbol{x}| = \int_0^\infty u^{\frac{1}{2}(n-1)} e^{-u} \frac{\mathrm{d}u}{2\sqrt{u}} = \frac{1}{2} \int_0^\infty u^{\frac{n}{2}-1} e^{-u} \mathrm{d}u = \frac{1}{2} \Gamma\left(\frac{n}{2}\right).$$
(26)

From (25), we gather that the surface area of the (n-1)-dimensional unit sphere is given by

$$A_{n-1}(1) = \int d^{n-1}\Omega_{n-1} = \frac{2\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2})}.$$
(27)

Since $\Gamma(n) = (n-1)!$ for $n \in \mathbb{N}$, $\Gamma(\frac{1}{2}) = \sqrt{\pi}$, and $\Gamma(n+1) = n \Gamma(n)$, this indeed gives the familiar results for the circumference of the unit disk in two and the surface of a unit ball in three dimensions,

$$A_1(1) = \frac{2\pi}{\Gamma(1)} = 2\pi, \qquad A_2(1) = \frac{2\pi^{\frac{3}{2}}}{\Gamma(\frac{3}{2})} = \frac{2\pi^{\frac{3}{2}}}{\frac{1}{2}\Gamma(\frac{1}{2})} = 4\pi.$$
(28)

The *n*-ball of radius R is the union of all concentric (n-1)-spheres up to radius R. Its volume thus follows from the surface of the unit sphere by a simple polynomial integration,

$$V_n(R) = \int_0^R A_{n-1}(1) r^{n-1} dr = \frac{2\pi^{\frac{n}{2}}}{n \Gamma(\frac{n}{2})} r^n \Big|_0^R = \frac{\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2}+1)} R^n.$$
(29)

In n = 100 dimensions, we get a ratio of the volume of the unit sphere to one with radius R = 0.99 of

$$\frac{V_{100}(1)}{V_{100}(0.99)} = \frac{1}{0.99^{100}} \approx 2.732.$$
(30)

Alternative solution We may also employ the more hands-on approach of parametrizing \mathbb{R}^n using *n*-dimensional spherical coordinates. We can then construct volume and surface elements via Jacobian determinants and integrate these to determine the volume of the whole *n*-ball. Let $r \in [0, \infty)$ be the radial coordinate and $\phi_1, \ldots, \phi_{n-2} \in [0, \pi]$ and $\phi_{n-1} \in [0, 2\pi)$ the angular coordinates. Then

$$x_{1} = r \cos(\phi_{1})$$

$$x_{2} = r \sin(\phi_{1}) \cos(\phi_{2})$$

$$x_{3} = r \sin(\phi_{1}) \sin(\phi_{2}) \cos(\phi_{3})$$

$$\vdots$$

$$x_{n-1} = r \sin(\phi_{1}) \dots \sin(\phi_{n-2}) \cos(\phi_{n-1})$$

$$x_{n} = r \sin(\phi_{1}) \dots \sin(\phi_{n-2}) \sin(\phi_{n-1})$$
(31)

provides a one-to-one mapping from Cartesian to spherical coordinates for all of \mathbb{R}^n (except for the origin which we define as $r = 0, \phi_i = 0 \quad \forall i \in \{1, \ldots, n-1\}$. Also it is easily checked that $\sum_{i=1}^{n} x_i x_i = r^2$, as it should for spherical coordinates. The Jacobian matrix $\frac{\partial(x_i)}{\partial(r,\phi_j)}$ associated with the coordinate transformation $(x_i) \to (r, \phi_i)$ reads

$$\begin{pmatrix} \cos(\phi_1) & -r\sin(\phi_1) & 0 & 0 & \cdots & 0 \\ \sin(\phi_1)\cos(\phi_2) & r\cos(\phi_1)\cos(\phi_2) & -r\sin(\phi_1)\sin(\phi_2) & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \sin(\phi_1)\dots\sin(\phi_{n-2})\cos(\phi_{n-1}) & \cdots & \cdots & -r\sin(\phi_1)\dots\sin(\phi_{n-2})\sin(\phi_{n-1}) \\ \sin(\phi_1)\dots\sin(\phi_{n-2})\sin(\phi_{n-1}) & r\cos(\phi_1)\dots\sin(\phi_{n-1}) & \cdots & r\sin(\phi_1)\dots\sin(\phi_{n-2})\cos(\phi_{n-1}) \end{pmatrix}$$

Computing the absolute value determinant of this matrix for small values of n, one finds

$$n = 2: \quad \left| \det \left(\frac{\partial(x, y)}{\partial(r, \phi)} \right) \right| = r,$$

$$n = 3: \quad \left| \det \left(\frac{\partial(x_1, x_2, x_3)}{\partial(r, \phi_1, \phi_2)} \right) \right| = r^2 \sin(\phi_1),$$

$$n = 4: \quad \left| \det \left(\frac{\partial(x_1, x_2, x_3, x_4)}{\partial(r, \phi_1, \phi_2, \phi_3)} \right) \right| = r^3 \sin^2(\phi_1) \sin(\phi_2).$$
(32)

One can already guess from these findings that the result for arbitrary $n \in \mathbb{N}$ is

$$\left|\frac{\partial(x_i)}{\partial(r,\phi_i)}\right| = r^{n-1}\sin^{n-2}(\phi_1)\sin^{n-3}(\phi_2)\dots\sin(\phi_{n-2}).$$
(33)

We will not prove this but simply postulate it.² Thus, the volume element is

$$d^{n}V = r^{n-1} \sin^{n-2}(\phi_{1}) \dots \sin(\phi_{n-2}) dr d\phi_{1} \dots d\phi_{n-1}.$$
 (34)

Hence, the volume of the n-ball is

$$V_n(R) = \int_0^r \mathrm{d}r \int_0^\pi \mathrm{d}\phi_1 \dots \int_0^\pi \mathrm{d}\phi_{n-2} \int_0^{2\pi} \mathrm{d}\phi_{n-1} r^{n-1} \sin^{n-2}(\phi_1) \dots \sin(\phi_{n-2}).$$
(35)

In order to perform the angular integrals, we need to compute $I_k = \int_0^{\pi} \sin^k(\phi) \, d\phi$. Integrating by parts and using $\sin^2(\phi) = 1 - \cos^2(\phi)$, we find the recursion relation

$$I_k = \frac{k-1}{k} I_{k-2},$$
(36)

with initial conditions $I_0 = \pi$ and $I_1 = 2$. Remembering that the Gamma function satisfies the recursion relation $\Gamma(x+1) = x \Gamma(x)$, we infer that a general solution of (36) is

$$I_k = \alpha \, \frac{\Gamma(\frac{k+1}{2})}{\Gamma(\frac{k}{2}+1)} \tag{37}$$

with some constant $\alpha \in \mathbb{R}$. Using $\Gamma(1/2) = \sqrt{\pi}$ and $\Gamma(1) = 1$, we identify α as $\sqrt{\pi}$. Since the solution to a linear second-order difference equation such as (36) is unique given two initial conditions, we have found I_k . For the volume of the *n*-ball, this implies

$$V_n(R) = \frac{2}{n} \pi^{n/2} R^n \frac{\Gamma(\frac{n-1}{2}) \Gamma(\frac{n-2}{2}) \dots \Gamma(\frac{3}{2}) \Gamma(1)}{\Gamma(\frac{n}{2}) \Gamma(\frac{n-1}{2}) \dots \Gamma(\frac{3}{2})} = \frac{\pi^{n/2} R^n}{\Gamma(\frac{n}{2}+1)},$$
(38)

since all Gamma functions cancel apart from $\frac{n}{2}\Gamma(\frac{n}{2}) = \Gamma(\frac{n}{2}+1)$ in the denominator and $\Gamma(1) = 1$ in the enumerator. The result is the same as in (29). We can recover from this the area of the (n-1)-ball by differentiation,

$$A_{n-1}(R) = \frac{\partial}{\partial R} V_n(R) = \frac{n}{R} V_n(R) = \frac{2\pi^{n/2}}{\Gamma(\frac{n}{2})} R^{n-1}.$$
(39)

²Unfortunately, induction cannot be used in this case because the Jacobian in n dimensions does not contain the (n-1)-dimensional Jacobian as a submatrix. This renders the proof a bit involved. The general idea is to factor out most of the r and ϕ_i dependent terms from the matrix and use Gauss elimination to bring the matrix into diagonal form. For further details, see here.