

**Problem 1. Central limit theorem** Consider a one-dimensional system consisting of a large number of non-interacting particles on a circle of circumference  $L$ . Assume that the positions of the particles are independent random variables (i.r.v.) uniformly distributed on the circle.

**1.1** Find the probability  $p_N(t, \alpha)$  of observing exactly  $\alpha N$  of the  $N$  particles in a fixed arc of length  $tL$ , where  $t, \alpha \in [0, 1]$ . (For  $\alpha = 0$  this is called *gap* (or *void*) *formation probability*.)

Find the leading behavior of the result in the limit  $N \rightarrow \infty$  with  $t, \alpha$  fixed. (You may use the Stirling formula  $n! \approx n^n e^{-n} \sqrt{2\pi n}$ . A good sanity check for the answer is that  $\int_0^1 p_N(t, \alpha) d\alpha$  evaluated with a computer should be 1.)

Make a plot of this leading term as a function of  $\alpha \in [0, 1]$  for  $N = 100$  and  $t = 0.1$ , overlaid with the exact discrete distribution. Describe any qualitative changes in the plot as  $N$  and  $t$  change, and whether the asymptotic approximation breaks down anywhere.

**Solution.** Consider a single particle  $i$  on the circle. The probability of observing it in an arc of length  $tL$  is  $p = t$ . This is equivalent to a Bernoulli trial with failure probability  $q = 1 - p = 1 - t$ . The binomial distribution gives the probability of obtaining exactly  $k$  successes out of  $N$  such trials [1]:

$$P_p(k | N) = \binom{N}{k} p^k q^{N-k} = \frac{N!}{k! (N-k)!} p^k (1-p)^{N-k}. \quad (1)$$

Assuming  $k = \alpha N$  is an integer, the probability of observing  $\alpha N$  of the  $N$  particles in this arc is given by

$$p_N(t, \alpha) = \frac{N!}{(\alpha N)! (N - \alpha N)!} t^{\alpha N} (1-t)^{N-\alpha N}. \quad (2)$$

To find the leading behavior as  $N \rightarrow \infty$ , we use Stirling's approximation for  $N!$ ,  $(\alpha N)!$ , and  $(N - \alpha N)!$ . In doing so, we assume  $N, \alpha N, (1 - \alpha)N \gg 1$ . This yields

$$\begin{aligned} p_N(t, \alpha) &\approx \frac{N^N e^{-N} \sqrt{2\pi N}}{(\alpha N)^{\alpha N} e^{-\alpha N} \sqrt{2\pi \alpha N} (N - \alpha N)^{N-\alpha N} e^{-(N-\alpha N)} \sqrt{2\pi (N - \alpha N)}} t^{\alpha N} (1-t)^{N-\alpha N} \\ &= \frac{N^{N-\alpha N}}{\alpha^{\alpha N} N^{N-\alpha N} (1-\alpha)^{N-\alpha N} \sqrt{2\pi \alpha (N - \alpha N)}} t^{\alpha N} (1-t)^{N-\alpha N} \\ &= \frac{1}{\sqrt{2\pi \alpha (1-\alpha) N}} \left(\frac{t}{\alpha}\right)^{\alpha N} \left(\frac{1-t}{1-\alpha}\right)^{N-\alpha N}. \end{aligned} \quad (3)$$

A plot comparing this approximation to the exact, discrete distribution is shown in Fig. 1 as a function of  $\alpha \in [0, 1]$  for  $N = 100$  and  $t = 0.1$ . Both distributions becomes broader and shorter as  $t$  is increased to 0.5, and then narrower and taller as  $t$  is increased from there. The area under the curve becomes smaller as  $N$  increases, although its shape does not change. This makes sense because  $p_N(t, \alpha)$  as a function of  $\alpha$  is not a PDF; the PDF is  $P_t(k|N)$  as a function of  $k = \alpha N$ . The area under the curve of  $p_N(t, \alpha)$  is  $1/N$ .

For  $t \lesssim 0.2$  and  $t \gtrsim 0.8$ , the approximate distribution has a slightly sharper and higher peak than the discrete distribution. This is slightly visible in Fig. 1 This discrepancy becomes more pronounced as  $N$  decreases. For  $N \lesssim 20$ , a discrepancy near the peak is visible even for  $t = 0.5$ . The approximation visibly diverges as  $\alpha \rightarrow 0$  for  $t \lesssim 0.2$  and as  $\alpha \rightarrow 1$  for  $t \gtrsim 0.8$ . This effect becomes more pronounced as  $N$  decreases. For  $N \lesssim 25$ , this divergence overtakes the expected behavior of the discrete distribution, and so the approximation becomes poor.

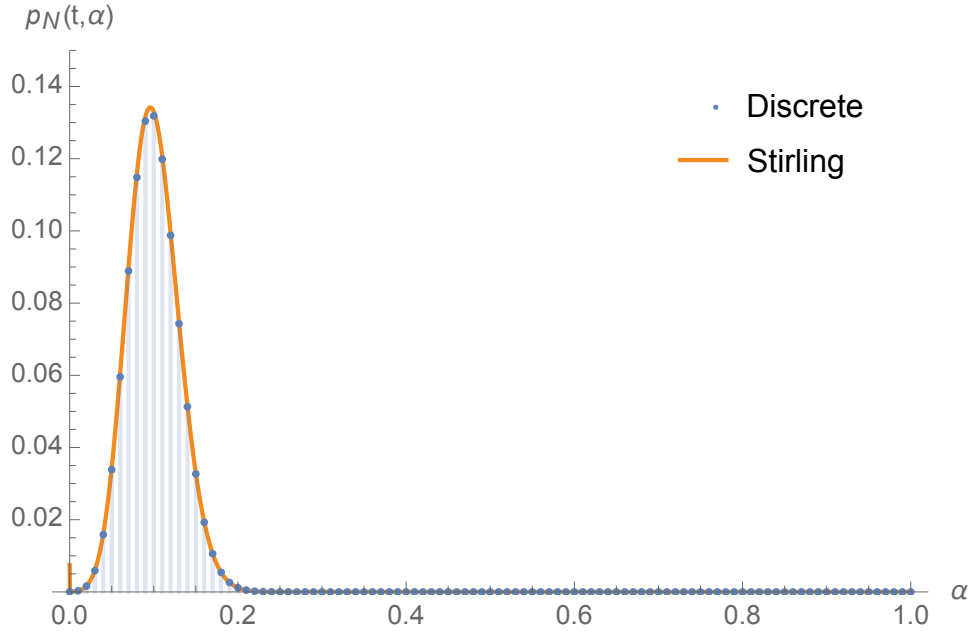


Figure 1: Comparison of the discrete expression (Eq. (2), blue) and Stirling's approximation to (Eq. (3), orange)  $p_N(t, \alpha)$  as functions of  $\alpha \in [0, 1]$  for  $N = 100$  and  $t = 0.1$ .

**1.2** In the large- $N$  limit, find the average number  $k$  (or the fraction  $\alpha = k/N$ ) of particles in the arc of length  $tL$  for a given  $t \in [0, 1]$ , and the fluctuation (variance) of this number, using the Central Limit Theorem. Plot the corresponding Gaussian distribution over  $\alpha \in [0, 1]$  and add it to the previous plot. How good is this approximation?

**Solution.** The mean of the binomial distribution is  $\mu = Np$ , and the variance is  $\sigma^2 = Npq$  [1]. Thus, the mean and variance of Eq. (2) are,

$$\mu_B = Nt, \quad \sigma_B^2 = Nt(1-t),$$

which correspond to the average number of particles in  $tL$  and the variance of that number, respectively.

By the Central Limit Theorem, we may approximate Eq. (2) by a Gaussian distribution [2]

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

with mean  $\mu_G = \mu_B = Nt$  and standard deviation  $\sigma_G = \sigma_B/\sqrt{N} = \sqrt{t(1-t)}$  [3]. (The factor of  $1/N$  in the variance is necessary because  $p_N(t, \alpha)$  is not normalized.) Since  $x$  is equivalent to  $k = \alpha N$ , this gives us the Gaussian distribution

$$p_N(t, \alpha) \approx \frac{e^{-N^2(\alpha-t)^2/2t(1-t)}}{\sqrt{2\pi t(1-t)}}. \quad (4)$$

This distribution is shown overlaid with the discrete distribution and Stirling's approximation in Fig. 2. The CLT approximation, being Gaussian, is perfectly symmetrical for all  $t$ , unlike the discrete function and Stirling's approximation, which both become more skew as  $t \rightarrow 0$  and  $t \rightarrow 1$ . This effect is visible in Fig. 2. The CLT is a worse approximation than Stirling in these cases, except when  $N$  is very large ( $\gtrsim 1000$ ). In this limit, the quality of both approximations is about the same. However, the CLT approximation has no singularities, making it a better approximation when  $\alpha, t \approx 0$  and  $\alpha, t \approx 1$ .

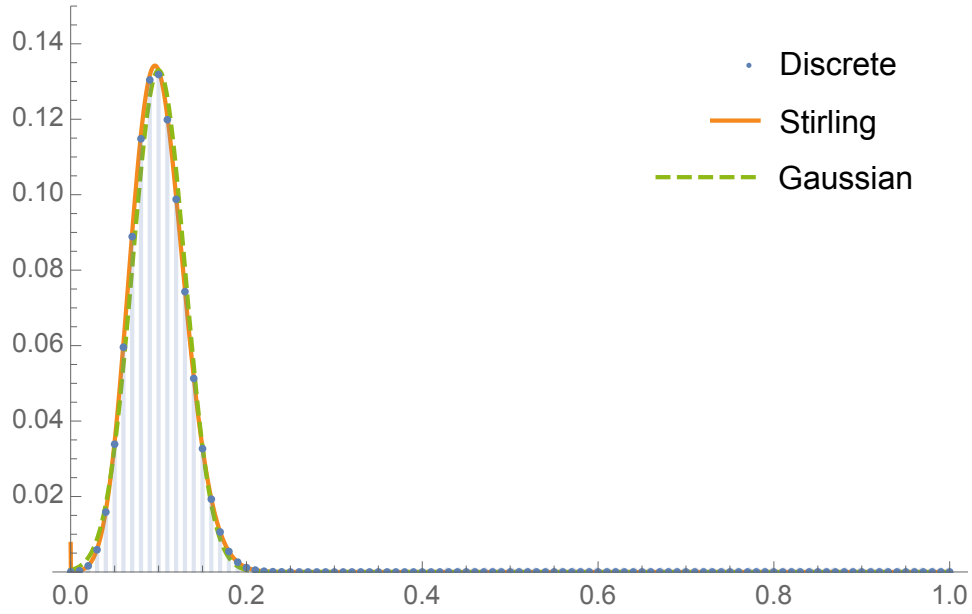


Figure 2: Comparison of the discrete expression (Eq. (2), blue), Stirling's approximation to (Eq. (3), orange), and CLT approximation to (Eq. (4), green)  $p_N(t, \alpha)$  as functions of  $\alpha \in [0, 1]$  for  $N = 100$  and  $t = 0.1$ .

**1.3** Defining the number density  $n(x) = \sum_{i=1}^N \delta(x - x_i)$ , compute the two-point correlation function

$$C(x, y) = \langle \delta n(x) \cdot \delta n(y) \rangle, \quad \delta n(x) = n(x) - \langle n \rangle,$$

which describes the fluctuations of the density.

**Solution.** Firstly, the mean  $\langle n \rangle$  is found by

$$\langle n \rangle = \frac{1}{L} \int_0^L n(x) dx = \frac{1}{L} \int_0^L \sum_{i=1}^N \delta(x - x_i) dx = \frac{1}{L} \sum_{i=1}^N \int_0^L \delta(x - x_i) dx = \frac{N}{L}.$$

Then

$$\begin{aligned} C(x, y) &= \frac{1}{L^2} \int_0^L \int_0^L \delta n(x) \delta n(y) dx dy = \frac{1}{L^2} \int_0^L \left( \sum_{i=1}^N \delta(x - x_i) - \frac{N}{L} \right) dx \int_0^L \left( \sum_{i=1}^N \delta(y - y_i) - \frac{N}{L} \right) dy \\ &= \frac{1}{L^2} \left( \sum_{i=1}^N \int_0^L \delta(x - x_i) dx - \frac{N}{L} \int_0^L dx \right) \left( \sum_{i=1}^N \int_0^L \delta(y - y_i) dy - \frac{N}{L} \int_0^L dy \right) \\ &= \frac{1}{L^2} \left( N - \frac{N}{L} \left[ x \right]_0^L \right) \left( N - \frac{N}{L} \left[ y \right]_0^L \right) \\ &= 0. \end{aligned}$$

This result suggests that the positions of different particles on the circles are not correlated [4, p. 360]. This is sensible since the locations of the particles are random and uniformly distributed, and the particles do not interact with one another.

## Problem 2. Entropy of simple systems

**2.1 Two-level systems** Consider a gas consisting of an even number  $N$  of non-interacting atoms with spins  $\sigma_i$ ,  $i = 1, \dots, N$ . The spin of each atom can take on the values  $\sigma_i = \pm 1$  with equal probability.

**2.1.1** What is the probability of a state with zero total magnetization? Determine the leading approximation for this probability in the limit  $N \rightarrow \infty$ .

**Solution.** The spins of the atoms are distributed binomially. The probability for atom  $i$  to have be spin up (i.e.  $\sigma_i = +1$ ) is  $p = 1/2$ . Let  $N = N_+ + N_-$ , where  $N_{\pm}$  is the number of atoms with  $\sigma = \pm 1$ . Then, from (1), the probability that  $N_+$  of the  $N$  atoms are spin up is given by

$$P_{1/2}(N_+ | N) = \frac{N!}{N_+!(N - N_+)!} \frac{1}{2^{N_+}} \frac{1}{2^{N-N_+}} = \frac{N!}{N_+!N_-!} \frac{1}{2^{N_+}} \frac{1}{2^{N_-}}.$$

The state has zero total magnetization if  $N_+ = N_- = N/2$ . This is the same as Prob. 1.1 with  $\alpha = t = 1/2$ . Feeding these into Eq. (3), we find in the large  $N$  limit

$$P_{1/2}(N/2 | N) = \frac{1}{\sqrt{2\pi(1/2)(1 - 1/2)N}} \left(\frac{1/2}{1/2}\right)^{N/2} \left(\frac{1 - 1/2}{1 - 1/2}\right)^{N/2} = \sqrt{\frac{2}{\pi N}}.$$

**2.1.2** Let us place the atoms in a magnetic field  $h$ , so that the Hamiltonian becomes

$$H = -h \sum_{i=1}^N \sigma_i.$$

Find the total number of states at a fixed energy  $E$  and the entropy per atom in the limit  $N \rightarrow \infty$  assuming that the energy per atom  $\epsilon = E/N$  is kept fixed.

**Solution.** The total energy of the system is  $E = h(N_- - N_+)$ . The total number of states at this energy is,

$$\Omega = \binom{N}{N_+} = \frac{N!}{N_+!N_-!} \approx \frac{N^N e^{-N} \sqrt{2\pi N}}{N_+^{N_+} e^{-N_+} \sqrt{2\pi N_+} N_-^{N_-} e^{-N_-} \sqrt{2\pi N_-}} = \frac{N^N}{N_+^{N_+} N_-^{N_-}} \sqrt{\frac{N}{2\pi N_+ N_-}},$$

in the limit that  $N, N_+, N_- \gg 1$

The total entropy is given by  $S = \ln \Omega$ . Here we will use Stirling's approximation as  $\ln n! \approx n \ln n - n$  [5]. Then

$$\begin{aligned} S &= \ln N! - \ln N_+! - \ln N_-! \approx N \ln N - N - N_+ \ln N_+ + N_+ - N_- \ln N_- + N_- \\ &= N \ln N - N_+ \ln N_+ - N_- \ln N_-, \end{aligned} \tag{5}$$

so the entropy per atom is

$$s = \frac{S}{N} = \frac{N \ln N - N_+ \ln N_+ - N_- \ln N_-}{N} = \ln N - \frac{N_+}{N} \ln N_+ - \frac{N_-}{N} \ln N_-.$$

**2.1.3** Compute the temperature of this system using  $1/T = (\partial S/\partial E)_N$ . Show that this result determines  $\epsilon$ , the average energy per atom, as a function of temperature.

**Solution.** By the chain rule,

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_N = \left( \frac{\partial S}{\partial N_+} \frac{\partial N_+}{\partial E} \right)_N.$$

Rewriting Eq. (5) in terms of  $N$  and  $N_+$ ,

$$S = N \ln N - N_+ \ln N_+ - (N - N_+) \ln(N - N_+) = N \ln N - N_+ \ln N_+ - N \ln(N - N_+) + N_+ \ln(N - N_+),$$

so

$$\frac{\partial S}{\partial N_+} = -\frac{N_+}{N_+} - \ln N_+ + \frac{N}{N - N_+} - \frac{N_+}{N - N_+} + \ln(N - N_+) = \ln(N - N_+) - \ln N_+ = \ln\left(\frac{N_-}{N_+}\right).$$

Also, since  $E = h(N_- - N_+) = h(N - 2N_+) = h(2N_- - N)$ ,  $\partial E/\partial N_+ = -2h$ . Then the temperature can be found by

$$\frac{1}{T} = -\frac{1}{2h} \ln\left(\frac{N_-}{N_+}\right) \implies T = -\frac{2h}{\ln(N_-/N_+)}. \quad (6)$$

To find  $\epsilon$  as a function of  $T$ , we first write  $N_+$  and  $N_-$  as functions of  $E$ :

$$N_+ = \frac{N}{2} - \frac{E}{2h}, \quad N_- = \frac{N}{2} + \frac{E}{2h}.$$

Then, substituting into Eq. (6) and solving for  $E$ ,

$$\frac{1}{T} = -\frac{q}{2h} \ln\left(\frac{N + E/h}{N - E/h}\right) \implies e^{-2h/T} = \frac{N + E/h}{N - E/h} \implies N(1 - e^{-2h/T}) = \frac{E}{h}(1 + e^{-2h/T}),$$

which implies

$$E = Nh \frac{1 - e^{-2h/T}}{1 + e^{-2h/T}} = -Nh \tanh\left(-\frac{2h}{T}\right) = -Nh \tanh\left(\frac{2h}{T}\right). \quad (7)$$

Then the average energy per atom is

$$\epsilon = \frac{E}{N} = -h \tanh\left(\frac{2h}{T}\right).$$

**2.1.4** Finally, compute the specific heat  $C(T, h)$ .

**Solution.** The Hamiltonian implies that the atoms have no kinetic energy; thus, pressure and volume are both constant, so the specific heat at constant pressure and at constant volume are identical. The specific heat is then given by [6, p. 9],

$$C = T \left( \frac{\partial S}{\partial T} \right)_N = \left( \frac{\partial E}{\partial T} \right)_N.$$

From Eq. (7),

$$C(T, h) = -Nh \frac{\partial}{\partial T} \tanh\left(\frac{2h}{T}\right) = \frac{2Nh^2}{kT^2} \sec^2\left(\frac{2h}{T}\right).$$

**2.2 Trapped atoms** Calculate the volume of the phase space for  $N$  classical non-interacting massive particles placed in a harmonic trap (i.e. a potential  $V(r) = m\omega^2 r^2/2$ ) with energies of at most  $E$ . Use it to calculate the entropy and the temperature.

**Solution.** The Hamiltonian of this system is

$$H(q_i, p_i) = \sum_{i=1}^N \left( \frac{p_i^2}{2m} + \frac{m\omega^2 r_i^2}{2} \right), \quad (8)$$

where  $p_i^2 = p_{1i}^2 + p_{2i}^2 + p_{3i}^2$  and  $r_i^2 = q_{1i}^2 + q_{2i}^2 + q_{3i}^2$ . For a particular energy  $E$ , the system is confined to a surface in phase space described by  $E = H(q_i, p_i)$  [6, p. 26]. For Eq. (8), this looks similar to the equation for an ellipsoid, which can be transformed into a sphere by the appropriate coordinate transformation. Let

$$\begin{aligned} \tilde{q}_{1i} &= \sqrt{m\omega} q_{1i}, & \tilde{q}_{2i} &= \sqrt{m\omega} q_{2i}, & \tilde{q}_{3i} &= \sqrt{m\omega} q_{3i}, \\ \tilde{p}_{1i} &= \frac{p_{1i}}{\sqrt{m\omega}}, & \tilde{p}_{2i} &= \frac{p_{2i}}{\sqrt{m\omega}}, & \tilde{p}_{3i} &= \frac{p_{3i}}{\sqrt{m\omega}}. \end{aligned}$$

Then

$$\begin{aligned} \tilde{r}_i^2 &= \frac{\tilde{q}_{1i}^2}{m\omega} + \frac{\tilde{q}_{2i}^2}{m\omega} + \frac{\tilde{q}_{3i}^2}{m\omega} = \frac{r_i^2}{m\omega}, \\ \tilde{p}_i^2 &= m\omega \tilde{p}_{1i}^2 + m\omega \tilde{p}_{2i}^2 + m\omega \tilde{p}_{3i}^2 = m\omega p_i^2, \end{aligned}$$

and so Eq. (8) becomes

$$H(\tilde{q}_i, \tilde{p}_i) = \sum_{i=1}^N \left( \frac{m\omega \tilde{p}_i^2}{2m} + \frac{m\omega^2 \tilde{r}_i^2}{2m\omega} \right) = \frac{\omega}{2} \sum_{i=1}^N (\tilde{p}_i^2 + \tilde{r}_i^2).$$

Then the surface is described by

$$\frac{2E}{\omega} = \sum_{i=1}^N (\tilde{p}_i^2 + \tilde{r}_i^2),$$

which is a  $6N$ -dimensional sphere of radius  $R = \sqrt{2E/\omega}$ . An  $n$ -dimensional sphere has volume

$$V_n = \frac{S_n R^n}{n}, \quad \text{where } S_n = \frac{2\pi^{n/2}}{(n/2 - 1)!},$$

for  $n$  even [7]. For  $6N$  dimensions,

$$S_{6N} = \frac{2\pi^{3N}}{(3N - 1)!}.$$

Finally, the phase space volume is

$$\Delta p \Delta q = \Delta \tilde{p}_i \Delta \tilde{q}_i = \frac{2\pi^{3N}}{(3N - 1)!} \frac{\sqrt{2E/\omega}^{6N}}{6N} = \frac{(4\pi E/\omega)^{3N}}{6N(3N - 1)!},$$

where  $\Delta p \Delta q = \Delta \tilde{p}_i \Delta \tilde{q}_i$  by Liouville's theorem.

The entropy may be found from the phase space volume by [4, p. 24]

$$S = \ln \left( \frac{\Delta p \Delta q}{(2\pi\hbar)^s} \right),$$

where  $s = 6N$  is the number of degrees of freedom of the system. For this system,

$$S = \ln \left( \frac{(4\pi E/\omega)^{3N}}{(2\pi\hbar)^{6N} 6N(3N-1)!} \right) = \ln \left( \frac{(E/\pi\hbar^2\omega)^{3N}}{6N(3N-1)!} \right).$$

The temperature is then given by

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_N = \frac{\partial}{\partial E} [3N \ln E - 3N \ln(\pi\hbar^2\omega) - \ln 6N - \ln(3N-1)!] = \frac{3N}{E} \implies T = \frac{E}{3N}.$$

**2.3 Three-level system** Consider a system of  $N$  independent atoms. Each atom may be in one of three states with energies  $-\epsilon, 0, \epsilon$ . Assume that the total energy of the gas is  $E = M\epsilon$ ,  $|M| \leq N$ . Calculate the entropy of the system and find the relation between the temperature and the energy. Also expand the results in the two special limits  $T \ll \epsilon$  and  $T \gg \epsilon$ .

**Solution.** We will use the partition function  $Z_i = \sum_n \exp(\epsilon_n/T)$  [4, p. 87]. This is admissible even for a classical system because the energy levels in this problem are discrete. For one particle in the three-level system, the partition function is

$$Z_i = e^{-\epsilon/T} + 1 + e^{\epsilon/T} = 1 + 2 \cosh\left(\frac{\epsilon}{T}\right),$$

so the total partition function for the system is

$$Z = \prod_i^N Z_i = \left[ 1 + 2 \cosh\left(\frac{\epsilon}{T}\right) \right]^N.$$

The Helmholtz free energy can be found by  $F = -T \ln Z$  [4, p. 87].  $F$  relates to the entropy by [4, p. 47]

$$S = - \left( \frac{\partial F}{\partial T} \right)_V.$$

This gives us an expression for the entropy:

$$\begin{aligned} S &= \frac{\partial}{\partial T} (T \ln Z) = \ln Z + T \frac{\partial}{\partial T} (\ln Z) = N \ln \left( 1 + 2 \cosh\left(\frac{\epsilon}{T}\right) \right) + NT \frac{\partial}{\partial T} \ln \left( 1 + 2 \cosh\left(\frac{\epsilon}{T}\right) \right) \\ &= N \ln \left( 1 + 2 \cosh\left(\frac{\epsilon}{T}\right) \right) - NT \frac{\epsilon}{T^2} \frac{2 \sinh(\epsilon/T)}{1 + 2 \cosh(\epsilon/T)} = N \left[ \ln \left( 1 + 2 \cosh\left(\frac{\epsilon}{T}\right) \right) - \frac{2\epsilon}{T} \frac{\sinh(\epsilon/T)}{1 + 2 \cosh(\epsilon/T)} \right]. \end{aligned}$$

The total energy of the system at equilibrium is, according to the lecture notes,

$$E = - \frac{\partial}{\partial \beta} \ln Z,$$

where  $\beta = 1/T$ . Then we have

$$E = -N \frac{\partial}{\partial \beta} \ln(1 + 2 \cosh(\beta\epsilon)) = -N \frac{2\epsilon \sinh(\beta\epsilon)}{1 + 2 \cosh(\beta\epsilon)},$$

so the relationship between energy and temperature is

$$E = -2N\epsilon \frac{\sinh(\epsilon/T)}{1 + 2 \cosh(\epsilon/T)}.$$

Let  $u = \epsilon/T$ . Then

$$S(u) = N \left[ \ln(1 + 2 \cosh u) - 2u \frac{\sinh u}{1 + 2 \cosh u} \right], \quad E(u) = -2N\epsilon \frac{\sinh u}{1 + 2 \cosh u}.$$

For the limit  $T \gg \epsilon$ , we expand about  $u = 0$ :

$$\begin{aligned} S(u) &= S(0) + u \left. \frac{\partial S(u)}{\partial u} \right|_{u=0} + \frac{u^2}{2} \left. \frac{\partial^2 S(u)}{\partial u^2} \right|_{u=0} + \mathcal{O}(u^3) \\ &= N \ln 3 - 2Nu \left[ u \frac{2 + 2 \cosh u}{(1 + 2 \cosh u)^2} \right]_{u=0} - N \left[ \frac{\cosh(2u) + 5 \cosh u - u \sinh(2u) - 7u \sinh u + 3}{(1 + 2 \cosh u)^2} \right]_{u=0} + \mathcal{O}(u^3) \\ &= N \left( \ln 3 - \frac{u^2}{3} + \mathcal{O}(u^3) \right), \end{aligned}$$

$$\begin{aligned} E(u) &= E(0) + u \left. \frac{\partial E(u)}{\partial u} \right|_{u=0} + \frac{u^2}{2} \left. \frac{\partial^2 E(u)}{\partial u^2} \right|_{u=0} + \frac{u^3}{6} \left. \frac{\partial^3 E(u)}{\partial u^3} \right|_{u=0} + \mathcal{O}(u^4) \\ &= -2N\epsilon u \left[ \frac{2 + \cosh u}{(1 + 2 \cosh u)^2} \right]_{u=0} + \frac{2N\epsilon}{3} u^2 \left[ \frac{\sinh(2u) + 7 \sinh u}{(1 + 2 \cosh u)^3} \right]_{u=0} \\ &\quad - \frac{N\epsilon}{3} u^3 \left[ \frac{\cosh(3u) + 12 \cosh(2u) - 12 \cosh u - 28}{(1 + 2 \cosh u)^4} \right]_{u=0} + \mathcal{O}(u^4) \\ &= N\epsilon \left( -\frac{2u}{3} + \frac{u^3}{9} + \mathcal{O}(u^4) \right). \end{aligned}$$

For the limit  $T \ll \epsilon$ , we take the limit as  $u \rightarrow \infty$ :

$$\begin{aligned} \lim_{u \rightarrow \infty} S(u) &= N \lim_{u \rightarrow \infty} \left[ \ln(1 + e^{-u} + e^u) - 2u \frac{\sinh u}{1 + 2 \cosh u} \right] = N \lim_{u \rightarrow \infty} \left[ \ln(e^u) - 2u \frac{\sinh u}{2 \cosh u} \right] = N \left[ u - 2u \frac{1}{2} \right] = 0, \\ \lim_{u \rightarrow \infty} E(u) &= -2N\epsilon \lim_{u \rightarrow \infty} \left[ \frac{\sinh u}{1 + 2 \cosh u} \right] = -2N\epsilon \lim_{u \rightarrow \infty} \left[ \frac{\sinh u}{2 \cosh u} \right] = -N\epsilon. \end{aligned}$$

**Problem 3. Quantum diatomic ideal gas** An ideal diatomic gas consists of non-interacting identical molecules  $H = \sum_{i=1}^N h_i$  which have three independent degrees of freedom  $h = h_K + h_V + h_R$ . The first one is the kinetic energy of translational motion  $h_K = \mathbf{p}^2/2m$ . The second is vibrational, i.e. each molecule is an oscillator with  $h_V = \pi^2/2 + \omega^2 q^2/2$ . The third is rotational  $h_R = \mathbf{L}^2/2I$ , where  $\mathbf{L}$  is the angular momentum. These three d.o.f. can be treated independently. Treat them as independent subsystems.

**3.1** Compute for each d.o.f. the equilibrium value of entropy as a function of energy.

**3.2** Compute for each d.o.f. the equilibrium value of energy as a function of entropy.

**3.3** Compute for each d.o.f. the equilibrium value of entropy as a function of temperature.

**3.4** Compute for each d.o.f. the equilibrium value of free energy as a function of temperature.



**3.5** Now consider all systems as quantum and repeat the calculations. This means that the momentum  $\mathbf{p}$  is quantized, each component of momentum taking the values  $p_k = (2\pi\hbar/L)k$ , where  $k$  is an arbitrary integer and  $L$  is the linear size of the box. Similarly, the energy of the vibrational modes is quantized as  $E_n = \hbar\omega(n + 1/2)$ , and the square of the angular momentum as  $L^2 = \hbar^2 l(l + 1)$ , where  $l$  is a non-negative integer. Discuss the quantum (low temperature) and the classical (high temperature) limits.

## References

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