

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 αN 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, α 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 αN 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 α 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.

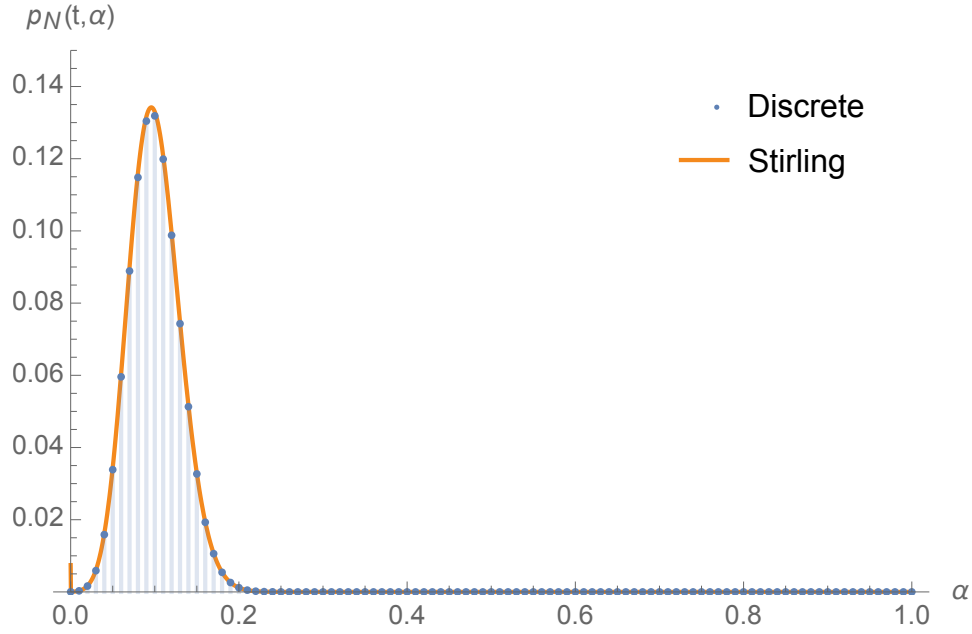


Figure 1: Comparison of the discrete expression (Eq. (2), blue) and Stirling's approximation to (Eq. (3), orange) $p_N(t, \alpha)$ as functions of $\alpha \in [0, 1]$ for $N = 100$ and $t = 0.1$.

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 $\alpha, t \approx 1$.

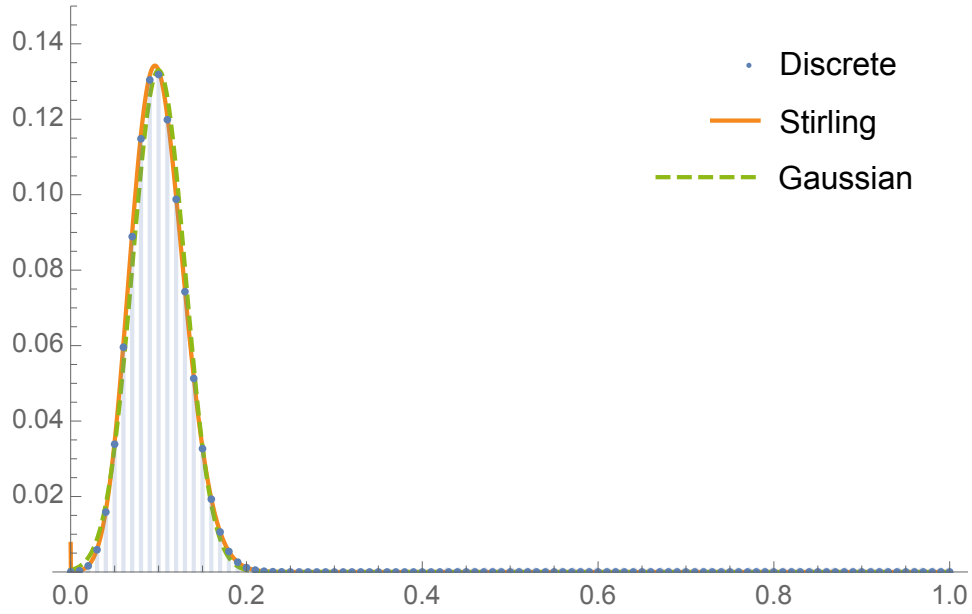


Figure 2: Comparison of the discrete expression (Eq. (2), blue), Stirling's approximation to (Eq. (3), orange), and CLT approximation to (Eq. (4), green) $p_N(t, \alpha)$ as functions of $\alpha \in [0, 1]$ for $N = 100$ and $t = 0.1$.

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 σ_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,

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

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 ϵ , 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 ϵ 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),

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

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 single-atom 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]. The free energy relates to the entropy by $S = -(\partial F / \partial T)_V$ [4, p. 47]. This gives us an expression for the entropy:

$$S = \frac{\partial}{\partial T} (T \ln Z). \quad (9)$$

For the three-level system,

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

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

$$E = -\frac{\partial}{\partial \beta} \ln Z, \quad (10)$$

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

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

We note also that

$$S = N \ln \left(1 + 2 \cosh \left(\frac{\epsilon}{T} \right) \right) + \frac{E}{T}.$$

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

3.1 Classical system 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.

Solution. Let $(\pi, q) \rightarrow (p_V, q_V)$ to avoid confusion. For the rotational degrees of freedom, we will use the coordinates θ, ϕ and the corresponding momenta p_θ, p_ϕ . The coordinates are distinct since they concern different subsystems. The Hamiltonians for each of the subsystems are

$$H_K = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}, \quad H_V = \sum_{i=1}^N \frac{p_{V_i}^2}{2} + \frac{\omega^2 q_{V_i}^2}{2}, \quad H_R = \sum_{i=1}^N \frac{1}{2I} \left(p_{\theta_i}^2 + \frac{p_{\phi_i}^2}{\sin^2 \theta_i} \right)$$

All three subsystems have per-particle energies that are not quantized. The general expression for the partition function in this case is [6, p. 55-56]

$$Z = \frac{1}{N!} \prod_i^N Z_i = \frac{1}{N!} \left(\frac{1}{(2\pi\hbar)^s} \iint e^{-\beta h} d^s p d^s q \right)^N,$$

where s is the number of degrees of freedom of the particle. The kinetic subsystem has three d.o.f., the vibrational subsystem has one d.o.f., and the rotational subsystem has two d.o.f. (since a diatomic molecule is azimuthally symmetric).

For each of the three subsystems, we find the single-particle partition functions [6, p. 55-56, 65] [8, p. 160]

$$Z_{Ki} = \frac{1}{(2\pi\hbar)^3} \iint e^{-p^2/2mT} d^3 p d^3 q = \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty p^2 e^{-p^2/2mT} d^3 p = \frac{V}{(2\pi\hbar)^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} = \frac{V}{\hbar^3} \left(\frac{mT}{2\pi} \right)^{3/2},$$

$$Z_{Vi} = \frac{1}{2\pi\hbar} \iint \exp\left(-\beta \frac{p_V^2 + \omega^2 q_V}{2}\right) dp_V dq_V = \frac{1}{2\pi\hbar} \sqrt{\frac{2\pi}{\beta\omega^2}} \sqrt{\frac{2\pi}{\beta}} = \frac{T}{\hbar\omega},$$

$$Z_{Ri} = \frac{1}{(2\pi\hbar)^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \iint \exp\left[-\frac{\beta}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right)\right] dp_\theta dp_\phi = \frac{2\pi I}{\beta} \frac{4\pi}{(2\pi\hbar)^2} = \frac{2IT}{\hbar^2},$$

so the partition functions for each system are

$$Z_K = \frac{1}{N!} \left[\frac{V}{\hbar^3} \left(\frac{mT}{2\pi} \right)^{3/2} \right]^N, \quad Z_V = \frac{1}{N!} \left(\frac{T}{\hbar\omega} \right)^N, \quad Z_R = \frac{1}{N!} \left(\frac{2IT}{\hbar^2} \right)^N.$$

Let E_K , E_V and E_R be the total energies of the respective subsystems. The energy at equilibrium can be found by Eq. (10). This yields

$$E_K = -\frac{\partial}{\partial\beta} \ln Z_K = -\frac{\partial}{\partial\beta} \left[N \ln \left(\frac{V}{\hbar^3} \right) + \frac{3N}{2} \ln \left(\frac{m}{2\pi} \right) - \frac{3N}{2} \ln \beta - \ln N! \right] = -\frac{3}{2} \frac{N}{\beta} = \frac{3}{2} NT, \quad (11)$$

$$E_V = -\frac{\partial}{\partial\beta} \ln Z_V = -\frac{\partial}{\partial\beta} (-N \ln(\hbar\omega) - N \ln \beta - \ln N!) = \frac{N}{\beta} = NT, \quad (12)$$

$$E_R = -\frac{\partial}{\partial\beta} \ln Z_R = -\frac{\partial}{\partial\beta} \left(N \ln \left(\frac{2I}{\hbar^2} \right) - N \ln \beta - \ln N! \right) = \frac{N}{\beta} = NT. \quad (13)$$

3.1.1 Compute for each subsystem the equilibrium value of entropy as a function of energy.

Solution. The entropy can be found by Eq. (9). For each subsystem, we find

$$\begin{aligned} S_K &= \frac{\partial}{\partial T} (T \ln Z_K) = \ln Z_K + T \frac{\partial}{\partial T} (\ln Z_K) \\ &= N \ln \left(\frac{V}{\hbar^3} \left(\frac{mT}{2\pi} \right)^{3/2} \right) - \ln N! + T \frac{\partial}{\partial T} \left[N \ln \left(\frac{V}{\hbar^3} \right) + \frac{3N}{2} \ln \left(\frac{m}{2\pi} \right) + \frac{3N}{2} \ln T - \ln N! \right] \\ &\approx N \ln \left(\frac{V}{\hbar^3} \left(\frac{mT}{2\pi} \right)^{3/2} \right) - N \ln N + N + T \frac{3N}{2T} = N \ln \left(\frac{V}{N\hbar^3} \left(\frac{mE_K}{3N\pi} \right)^{3/2} \right) + \frac{5N}{2}, \end{aligned} \quad (14)$$

$$\begin{aligned}
S_V &= \frac{\partial}{\partial T}(T \ln Z_V) = \ln Z_V + T \frac{\partial}{\partial T}(\ln Z_V) = N \ln\left(\frac{T}{\hbar\omega}\right) - \ln N! + T \frac{\partial}{\partial T}[N \ln(T) - N \ln(\hbar\omega) - \ln N!] \\
&\approx N \ln\left(\frac{T}{\hbar\omega}\right) - N \ln N + N + T \frac{N}{T} = N \ln\left(\frac{E_V}{N^2 \hbar\omega}\right) + 2N,
\end{aligned} \tag{15}$$

$$\begin{aligned}
S_R &= \frac{\partial}{\partial T}(T \ln Z_R) = \ln Z_R + T \frac{\partial}{\partial T}(\ln Z_R) = N \ln\left(\frac{2IT}{\hbar^2}\right) - \ln N! + T \frac{\partial}{\partial T}\left(N \ln\left(\frac{2I}{\hbar^2}\right) + N \ln T - \ln N!\right) \\
&\approx N \ln\left(\frac{2IT}{\hbar^2}\right) - N \ln N + N + T \frac{N}{T} = N \ln\left(\frac{2IE_R}{N^2 \hbar^2}\right) + 2N,
\end{aligned} \tag{16}$$

where we have eliminated T using Eqs. (11–13).

3.1.2 Compute for each subsystem the equilibrium value of energy as a function of entropy.

Solution. We need to solve Eqs. (14–16) for E_K , E_V , and E_R :

$$\begin{aligned}
e^{S_K/N-5/2} &= \frac{V}{N\hbar^3} \left(\frac{mE_K}{3N\pi}\right)^{3/2} \implies E_K = \frac{3N\pi}{m} \left(\frac{N\hbar^3}{V} e^{S_K/N-5/2}\right)^{2/3}, \\
e^{S_V/N-2} &= \frac{E_V}{N^2 \hbar\omega} \implies E_V = N^2 \hbar\omega e^{S_V/N-2}, \\
e^{S_R/N-2} &= \frac{2IE_R}{N^2 \hbar^2} \implies E_R = \frac{N^2 \hbar^2}{2I} e^{S_R/N-2}.
\end{aligned}$$

3.1.3 Compute for each subsystem the equilibrium value of entropy as a function of temperature.

Solution. We already did this work in Prob. 3.1.1, where we found

$$S_K \approx N \ln\left(\frac{V}{N\hbar^2} \left(\frac{mT}{2\pi}\right)^{3/2}\right) + \frac{5N}{2}, \quad S_V \approx N \ln\left(\frac{T}{N\hbar\omega}\right) + 2N, \quad S_R \approx N \ln\left(\frac{2IT}{N\hbar^2}\right) + 2N.$$

3.1.4 Compute for each subsystem the equilibrium value of free energy as a function of temperature.

Solution. Recall from Prob. 2.1 that $F = -T \ln Z$. Then we have

$$\begin{aligned}
F_K &= -T \left[N \ln\left(\frac{V}{\hbar^3} \left(\frac{mT}{2\pi}\right)^{3/2}\right) - \ln N! \right] \approx NT \left[\ln\left(\frac{N\hbar^3}{V} \left(\frac{mT}{2\pi}\right)^{3/2}\right) - 1 \right], \\
F_V &= -T \left[N \ln\left(\frac{T}{\hbar\omega}\right) - \ln N! \right] \approx NT \left[\ln\left(\frac{N\hbar\omega}{T}\right) - 1 \right], \\
F_R &= -T \left[N \ln\left(\frac{2IT}{\hbar^2}\right) - \ln N! \right] \approx NT \left[\ln\left(\frac{N\hbar^2}{2IT}\right) - 1 \right].
\end{aligned}$$

3.2 Quantum system 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.

3.2.1 Compute for each subsystem the equilibrium value of entropy as a function of energy.

3.2.2 Compute for each subsystem the equilibrium value of energy as a function of entropy.

3.2.3 Compute for each subsystem the equilibrium value of entropy as a function of temperature.

3.2.4 Compute for each subsystem the equilibrium value of free energy as a function of temperature.

3.2.5 Discuss the quantum (low temperature) and the classical (high temperature) limits.

References

- [1] E. W. Weisstein, “Binomial Distribution.” From MathWorld—A Wolfram Web Resource.
<https://mathworld.wolfram.com/BinomialDistribution.html>.
- [2] E. W. Weisstein, “Normal Distribution.” From MathWorld—A Wolfram Web Resource.
<https://mathworld.wolfram.com/NormalDistribution.html>.
- [3] E. W. Weisstein, “Central Limit Theorem.” From MathWorld—A Wolfram Web Resource.
<https://mathworld.wolfram.com/CentralLimitTheorem.html>.
- [4] L. D. Landau and E. M. Lifshitz, “Statistical Physics”, volume 5. Pergamon Press, 2nd edition, 1970.
- [5] E. W. Weisstein, “Stirling’s Approximation.” From MathWorld—A Wolfram Web Resource.
<https://mathworld.wolfram.com/StirlingsApproximation.html>.
- [6] R. K. Pathria and P. D. Beale, “Statistical Mechanics”. Elsevier, 3rd edition, 2011.
- [7] E. W. Weisstein, “Hypersphere.” From MathWorld—A Wolfram Web Resource.
<https://mathworld.wolfram.com/Hypersphere.html>.
- [8] M. Kardar, “Statistical Physics of Particles”. Cambridge University Press, 1st edition, 2007.