

Module Title: Introduction to Entropy in the Physical World ©UNIVERSITY OF LEEDS

School of Mathematics

Semester Two 201819

Calculator instructions:

- You are allowed to use a calculator which has had an approval sticker issued by the School of Mathematics.

Dictionaries:

- You are not allowed to use your own dictionary in this exam. A basic English dictionary is available to use: raise your hand and ask an invigilator, if you need it.

Exam information:

- There are 6 pages to this exam.
- There will be **2 hours 30 minutes** to complete this exam.
- You must answer **four** questions.
If you attempt more than four questions, only the best four results will be used in the final marks.
- All questions are worth equal marks.
- You must show all your calculations

1. (a) For a particular macrostate, the microstates of a system are fully characterized by a single, continuous, real variable x , drawn stochastically from a probability density function $p(x)$. In such cases, the Gibbs Entropy is obtained from $S = -k \int p(x) \log p(x) dx$. Supposing that:

$$p(x) = \begin{cases} c & \text{for } 0 \leq x \leq m \\ 0 & \text{otherwise.} \end{cases}$$

- i. Find an expression for c in terms of m . Hence eliminate c from any of your answers below, expressing the results in terms of the single remaining parameter m only.
 - ii. Evaluate the mean and variance of the distribution.
 - iii. Evaluate the entropy of the system, in units of Boltzmann's constant, S/k . You may assume that $p \log p \rightarrow 0$ as $p \rightarrow 0$.
 - iv. If m is allowed to vary, would you expect it to increase or decrease with time? Justify your answer in terms of the entropy just derived.
- (b) A general expression for the number of ways of distributing N indistinguishable particles amongst M boxes is:

$$W(N, M) = \frac{(N + M - 1)!}{N!(M - 1)!}.$$

- i. For the particular case of distributing 4 indistinguishable particles amongst 3 boxes, explicitly list the number of particles in each box for every state of the system, and so confirm the above formula is correct in that case. In how many of those states are the four particles confined to just the first two boxes? Again, confirm the above formula is correct.
- ii. How many ways are there of distributing 4 *distinguishable* particles amongst 3 boxes? (i.e. where swapping two particles from two different boxes gives a different microstate).
- iii. For the particular case of a large number N of indistinguishable particles distributed amongst an even larger number M of boxes, such that $M \gg N \gg 1$, use Stirling's formula $\log N! = N \log N - N$ to obtain an expression for $\log W(N, M)$. Using the fact that $N/M \ll 1$ show that:

$$\log W(N, M) \approx N \log M - N \log N + N,$$

and hence (or otherwise) obtain an approximation for the ratio $\frac{W(N, M/2)}{W(N, M)}$. Briefly comment on how your result relates to the expected probability of finding all the particles in just half of the boxes.

2. (a) By considering the change in total entropy when a small amount of heat energy ΔE flows from System 1 (with entropy S_1) to System 2 (with entropy S_2), explain why the statistical definition of temperature T , as

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

accounts for heat always flowing from warmer systems to colder systems. You may assume temperature is positive.

- (b) System A contains $N \gg 1$ objects, each of which can exist in four possible states, a single state with zero energy, and three excited states each with energy ε .

- i. If the total energy of System A is $E_A = n\varepsilon$, explain why the number of ways of arranging the energy quanta in System A is:

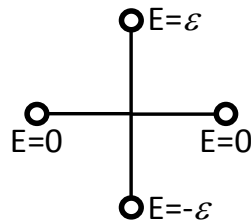
$$W = 3^n \frac{N!}{n!(N-n)!}.$$

- ii. Using Stirling's formula ($\log N! \approx N \log N - N$), obtain the entropy of System A, and hence show that:

$$E_A = \frac{3N\varepsilon}{3 + q}$$

where $q = \exp(\beta\varepsilon)$, and $\beta = (kT)^{-1}$.

- (c) A "quantum rotor" can exist in 4 rotated states, as shown in the figure below: one state with energy ε , one with energy $-\varepsilon$, and two with energy 0.



- i. Write down the partition function for one such quantum rotor.
 ii. Hence obtain the average energy for one quantum rotor at fixed temperature, T , and demonstrate that, for System B, which contains N quantum rotors, the average energy is:

$$\langle E_B \rangle = \frac{N\varepsilon(1 - q)}{1 + q}$$

where $q = \exp(\beta\varepsilon)$.

- (d) Systems A and B are prepared in initial states such that $E_A = E_B = 0$. They are then brought into thermal contact with each other. Find the final energy of each system in units of $N\varepsilon$.

3. (a) A 'sticky' bond in a molecule is of length zero when in its stuck state, and requires an energy ε to become unstuck, in which case its length is b . It is constrained to lie along 1-dimension, and subjected to a force $f > 0$ along that dimension. Hence, it can exist in three states $i = \{1, 2, 3\}$ with length $x = x_i$ and energy E_i such that:

$$\begin{aligned} x_1 &= -b, & E_1 &= \varepsilon + fb, \\ x_2 &= 0, & E_2 &= 0, \\ x_3 &= b, & E_3 &= \varepsilon - fb. \end{aligned}$$

The temperature parameter is $\beta = (kT)^{-1}$.

- Obtain normalised probabilities p_i of finding the bond in each of the three states $i = \{1, 2, 3\}$.
- Derive an expression for the mean bond length $\langle x \rangle$ and show that, in the limit $\beta fb \gg 1$,

$$\langle x \rangle = \frac{b}{1 + \exp[\beta(\varepsilon - fb)]}.$$

For this limit, and assuming also $\beta\varepsilon \gg 1$, discuss how the mean bond length behaves for both $fb \ll \varepsilon$ and $fb \gg \varepsilon$, referring to the probabilities that the bond is found in different states in each case.

- (b) A particle of mass m is constrained to move in one dimension vertically with position $0 < h < \infty$, so that its total potential energy is $V = G + U$ where $G = mgh$ is the gravitational potential energy and $U(h)$ is an additional potential energy independent of mass. Its partition function can thus be written as

$$Z = \int_0^\infty \exp[-\beta(mgh + U)] dh,$$

where $\beta = (kT)^{-1}$.

- Write down the normalised probability density function $p(h)$ that a particle is found at height h .
- Hence, show that

$$-\frac{m}{\beta} \frac{\partial \log Z}{\partial m} = \langle G \rangle.$$

where the angle brackets represent averages over $p(h)$.

- The potential energy is $U(h) = \beta^{-1}[Ah/h_0 - \log(h/h_0)]$, where A and h_0 are positive constants. Find h_{min} , which is the value of h that minimises the total potential energy V .
- By explicitly evaluating the integral for Z , or otherwise, obtain $\langle G \rangle$. Hence show that $\langle h \rangle = ah_{min}$ where you are required to find the constant a .

4. A simple model of a lattice gas consists of $n \gg 1$ identical gas particles distributed across $N \gg 1$ lattice sites. Each site is of volume v_0 . Hence, the total volume is $V = Nv_0$. The temperature is T .

- (a) First assume there are no interactions at all between particles (the energy is zero) and that the particles are dilute so that $n \ll N$. The number of ways of arranging the particles is approximately

$$W = \frac{N^n}{n!}.$$

By making use of Stirling's Formula ($\log N! = N \log N - N$) obtain the entropy and free energy F of the gas as a function of V , n , v_0 , T and Boltzmann's constant k . Demonstrate that the pressure $P = -\frac{\partial F}{\partial V}$ obeys the ideal gas law $PV = nkT$.

- (b) Now assume that no two particles can occupy the same lattice site, but that particles do not interact in any other way. Write down the number of ways of arranging the n particles across the N sites. By making use of Stirling's Formula obtain the entropy of the gas as a function of V , n , v_0 and Boltzmann's constant k .

- (c) Now, assume that, in addition, gas particles are attractive, so that each nearest-neighbour contact (where particles occupy adjacent lattice sites) gives a contribution $-\varepsilon$ to the energy, where $\varepsilon > 0$. By considering the fraction $\phi = \frac{nv_0}{V}$ of sites occupied by gas particles, demonstrate that a mean-field estimate for the total energy of the gas is:

$$E = -\frac{\varepsilon z n^2 v_0}{2V}$$

where z is the co-ordination number of the lattice. Hence, combining the expressions for energy and entropy from part (b), obtain the total free energy, F , of the gas.

- (d) Obtain the pressure $P = -\frac{\partial F}{\partial V}$ of the gas, and eliminate V from your expression for P by writing V in terms of ϕ , n and v_0 . Show that in the limit of small ϕ the ideal gas pressure is obtained. What happens to the pressure as $\phi \rightarrow 1$?
- (e) By considering solutions to $\frac{dP}{d\phi} = 0$, or otherwise, show that P does not monotonically increase with ϕ if $\frac{\varepsilon z}{kT} > a$, where a is a critical value to be determined.

5. In a persistent polymer chain, adjacent bonds pointing in the same direction have low energy, whilst adjacent bonds pointing in different direction have higher energy. A 1-dimensional model of such a polymer chain consists of N bonds. The i th bond makes a step of length l_i where each l_i takes the values $+1$ or -1 . The polymer chain is subjected to a force f along its length. In terms of these variables, the Hamiltonian of the polymer chain is:

$$E = -\varepsilon \sum_{i=1}^N l_i l_{i+1} - f \sum_{i=1}^N l_i.$$

where (for simplicity) we assume periodicity in the bond vectors: $l_{N+1} \equiv l_1$ and ε is an energy parameter.

- (a) Write a detailed expression for the partition function Z of the persistent polymer, taking care to specify the values of any variables that are summed over. Cast it into a form that allows it to be written in terms of the trace $\text{Tr}(\mathbf{T})$ of a transfer matrix \mathbf{T} , and hence write down \mathbf{T} , showing all of its components.
- (b) Find the eigenvalues of \mathbf{T} and show that, for $f = 0$, the largest eigenvalue is $2 \cosh \beta \varepsilon$ where β is the temperature parameter. Hence obtain the partition function Z and free energy F of the chain in the limit of large N both for $f \neq 0$ and $f = 0$.
- (c) For the case $f = 0$ in the limit of large N , evaluate the average energy $\langle E \rangle = -\frac{\partial \log Z}{\partial \beta}$, where β is the temperature parameter. Using your results for free energy and average energy, obtain the entropy of the chain. Evaluate the entropy in the limit $\varepsilon \beta \rightarrow 0$ and briefly comment on why this is the expected result in the high temperature limit.

May/June 2019 CHECK-LIST SOLUTIONS

MATH342401

Introduction to Entropy in the Physical World

1. (a)

(i) $c = 1/m$

(ii) $\langle x^2 \rangle = m/2, \sigma^2 = m^2/12$

(iii) $S/k = \log m$

(iv) Expect entropy to increase with time, hence m increases.

(b)

(i) Should find 15 states in all three boxes, 5 with all in first two boxes.

(ii) $3^4 = 81$.

(iii) $\frac{W(N, M/2)}{W(N, M)} \approx 1/2^N$.

2. (c) i. $Z = 2 + e^{\varepsilon\beta} + e^{-\varepsilon\beta}$

(d) $E_A = N\varepsilon/2, E_B = -N\varepsilon/2$.

3. (a)

(i) $p_1 = \exp(-\beta(\varepsilon + fb))/Z, p_2 = 1/Z, p_3 = \exp(-\beta(\varepsilon - fb))/Z$ where $Z = 1 + \exp(-\beta(\varepsilon + fb)) + \exp(-\beta(\varepsilon - fb))$.

(ii)

$$\langle x \rangle = \frac{2b \sinh(\beta fb) e^{-\beta\varepsilon}}{1 + 2 \cosh(\beta fb) e^{-\beta\varepsilon}}.$$

For $fb \ll \varepsilon, \langle x \rangle \approx be^{-\beta\varepsilon}$ (i.e. v. small).For $fb \gg \varepsilon, \langle x \rangle \approx b$.

(b)

(i) $p(h) = \exp[-\beta(mgh + U)]/Z$.

(iii) $h_{min} = h_0/(\beta mgh_0 + A)$.

(iv) $\langle G \rangle = 2mgh_0/(\beta mgh_0 + A), \langle h \rangle = 2h_{min}$.

4. (b) $W = N!/n!(N - n)!$

$S/k = (V/v_0) \log(V/v_0) - n \log n - (V/v_0 - n) \log(V/v_0 - n).$

(c) $F = -\frac{\varepsilon z n^2 v_0}{2V} - kT [(V/v_0) \log(V/v_0) - n \log n - (V/v_0 - n) \log(V/v_0 - n)].$

(d) $P = -\frac{\varepsilon z \phi^2}{2v_0} - \frac{kT}{v_0} \log(1 - \phi).$

(e) $a = 4$ [HINT... where are solutions of quadratic equation real?].

5. (a)

$$\begin{pmatrix} e^{\beta(\varepsilon+f)} & e^{-\beta\varepsilon} \\ e^{-\beta\varepsilon} & e^{\beta(\varepsilon-f)} \end{pmatrix}$$

or (alternatively)

$$\begin{pmatrix} e^{\beta(\varepsilon+f)} & e^{\beta(-\varepsilon+f)} \\ e^{-\beta(\varepsilon+f)} & e^{\beta(\varepsilon-f)} \end{pmatrix}$$

(b) Eigenvalues are $e^{\beta\varepsilon} \cosh \beta f \pm \sqrt{e^{2\beta\varepsilon} \cosh^2 \beta f - e^{2\beta\varepsilon} + e^{-2\beta\varepsilon}}$.

$$F = -NkT \log(e^{\beta\varepsilon} \cosh \beta f + \sqrt{e^{2\beta\varepsilon} \cosh^2 \beta f - e^{2\beta\varepsilon} + e^{-2\beta\varepsilon}}) \text{ for } f \neq 0.$$

$$F = -NkT \log(2 \cosh \beta\varepsilon) \text{ for } f = 0.$$

$$(c) \langle E \rangle = -N\varepsilon \tanh \beta\varepsilon.$$

$$S = Nk \log 2 \text{ as } \beta\varepsilon \rightarrow 0.$$