Statistical Mechanics

Handout 1:

In this course we introduce the subject of *statistical mechanics*. This is a thermodynamic theory in which account is taken of the microscopic properties of individual atoms or molecules analysed in a statistical fashion. Statistical mechanics allows macroscopic properties to be calculated from the statistical distribution of the microscopic behaviour of individual atoms and molecules.

Synopsis of course (as it appears in the syllabus)

Boltzmann factor. Partition function and its relation to internal energy, entropy, Helmholtz function, heat capacities and equations of state. *Quantum states and the Gibbs hypothesis (non-examinable).* Density of states. Application to: the spin-half paramagnet; simple harmonic oscillator (Einstein model of a solid); perfect gas; vibrational excitations of a diatomic gas; rotational excitations of a heteronuclear diatomic gas. Equipartition of energy. Bosons and fermions: Fermi-Dirac and Bose-Einstein distribution functions for non-interacting, indistinguishable particles. *Partition function for bosons and fermions when the particle number is not restricted and when it is: microcanonical, canonical and grand canonical ensemble (non-examinable).* Chemical potential. High-temperature limit and the Maxwell-Boltzmann distribution. *Simple treatment of fluctuations (non-examinable).* Low-temperature limit for fermions: Fermi energy and low-temperature limit of the heat capacity; application to electrons in metals and degenerate stars. Low-temperature limit for boson gas: Bose-Einstein condensation: calculation of the critical temperature of the phase transition; heat capacity; relevance to superfluidity in helium. The photon gas: Planck distribution, Stefan-Boltzmann law. *Kirchhoff's law (non-examinable).*

Plan of the lectures

1. Probability
2. Equipartition
3. Single-particle partition function
4. Partition function of a gas
5. Distinguishability
6. Photon gas
7. Chemical potential
8. Fermions and bosons
9. Fermions
10. Bosons
11. Examples
12. Information and entropy

Books: Consult your tutor for recommendations, but good treatments may be found in:

- Concepts in thermal physics: S. J. Blundell and K. M. Blundell (OUP, 2006) [£22.95; 464 pages]
  (this book has been designed to cover the relevant material for the Oxford courses on kinetic theory, thermodynamics and statistical mechanics; it also contains some applications in astrophysics, atmospheric physics, atomic physics and condensed matter physics)
- Thermal physics: R. Baierlein (CUP, 1999) [£40; 442 pages]
  (very clear and readable style, with lots of good insights)
- Statistical mechanics: a survival guide: M. Glazer and J. Wark (OUP, 2001) [£24; 142 pages]
  (pithy summary of statistical mechanics, it does exactly what it says on the tin)

- Fundamentals of Statistical and Thermal Physics: F. Reif (McGraw Hill, 1965) [£44; 578 pages]
  (a rather traditional treatment of statistical mechanics, but very reliable)
- Thermal Physics: C. Kittel and H. Kroemer (2nd edition, 1980). [£63; 473 pages]
  (an interesting treatment of statistical mechanics that might make good background reading)

This handout contains some background information that will be used in Lectures 1 and 2.

Binomial theorem

$$(x+y)^n = \sum_{k=0}^{n} {}^nC_k\, x^k y^{n-k} \text{ where } {}^nC_k = \frac{n!}{k!(n-k)!}. \tag{1}$$

Bernoulli trial

A *Bernoulli trial* is an "experiment" with two possible outcomes. One outcome (which we will call "success") occurs with probability p and the other outcome (which we will call "failure") occurs with probability $1-p$. An example is coin tossing.

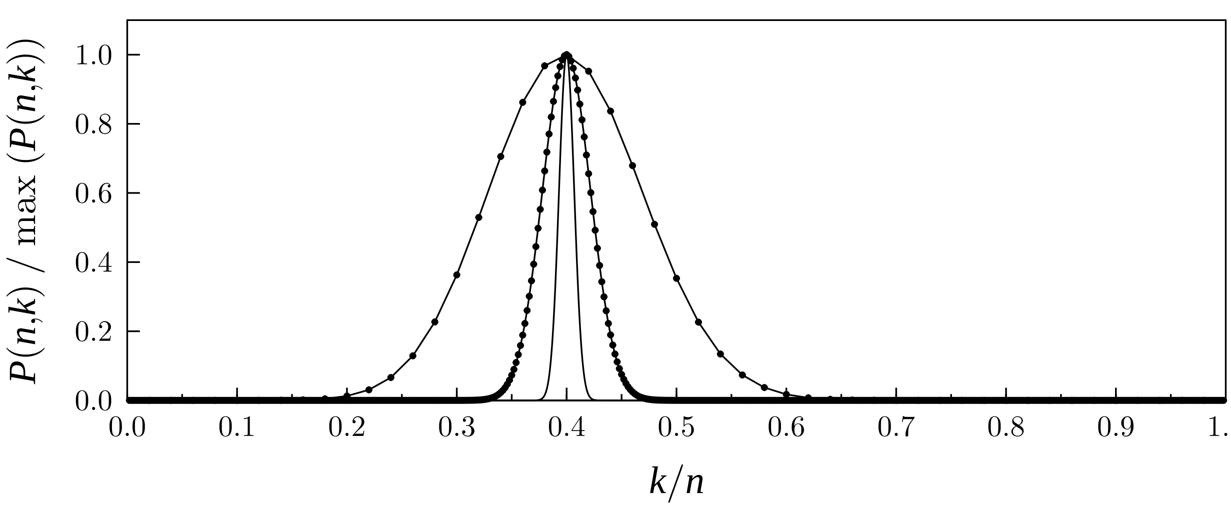
Let x be a random variable which takes the value 1 for success and 0 for failure. Then

$$\langle x \rangle = 0 \times (1-p) + 1 \times p = p \tag{2}$$
$$\langle x^2 \rangle = 0^2 \times (1-p) + 1^2 \times p = p \tag{3}$$
$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{p(1-p)}. \tag{4}$$

Binomial distribution

The *binomial distribution* governs the probability $P(n,k)$ of getting k successes from n independent Bernoulli trials. Thus

$$P(n,k) = {}^nC_k\, p^k (1-p)^{n-k}. \tag{5}$$



Binomial probability for $p = 0.4$. The plots are for $n = 50$, $n = 500$ and $n = 5000$ and are scaled so that their maximum amplitudes are the same. This demonstrates that as n increases, the *fractional width* decreases.

Since the binomial distribution is the sum of n *independent* Bernoulli trials, then

$$\langle k \rangle = np \tag{6}$$

$$\sigma_k = \sqrt{np(1-p)}. \tag{7}$$

Thus the fractional width of the distribution, $\frac{\sigma_k}{\langle k \rangle}$ is proportional to $\frac{\sqrt{n}}{n} = \frac{1}{\sqrt{n}}$.

Example: Coin tossing with a fair coin. In this case, $p = \frac{1}{2}$.

- For $n = 16$ tosses, the expected number of heads is $np = 8$. The standard deviation is $\sqrt{np(1-p)} = 2$.
- For $n = 10^{20}$ tosses, the expected number of heads is $np = 5 \times 10^{19}$. The standard deviation is $\sqrt{np(1-p)} = 5 \times 10^{9}$, ten orders of magnitude smaller than the expected value.

Microstates and macrostates

Tossing a coin n times produces a particular result, such as

$$0010100110110100111101\ldots$$

where 1 corresponds to heads and 0 corresponds to tails. We will refer to this particular sequences as a **microstate**. If you want to specify the microstate you have to enumerate the sequence of 1's and 0's *in order* and (somewhat tediously) *in detail*.

Usually, we only care about the fact that a particular coin-tossing experiment produces k heads and $n-k$ tails. We don't care which order they come in. This information can be summarised using a single number: k. This number (rather succinctly) specifies the **macrostate**.

In this case, the single macrostate described by k corresponds to ${}^nC_k$ microstates. This number can be very big! For example, if $n = 100$ and $k = 50$, then ${}^nC_k \approx 4 \times 10^{27}$

- For a gas in equilibrium in a container of volume V, one could attempt to specify the system in detail as follows: atom number 1 is at position $\mathbf{r}_1$, travelling with velocity $\mathbf{v}_1$, atom number 2 is at position $\mathbf{r}_2$, etc, etc. This describes a particular *microstate*. It is however a very time-consuming and tedious (and fundamentally impossible) way to describe a large system!

- Usually we just care that the gas has an average pressure p and an average temperature T. This is a particular *macrostate*, which corresponds to a huge number of different microstates.

Stirling's formula

To work out factorials of big numbers, one can use **Stirling's formula**:

$$\boxed{\ln n! \approx n \ln n - n.} \tag{8}$$

n	$\ln(n!)$	$n \ln n - n$
10	15.10	13.026
100	363.74	360.52
1000	5912.1	5907.8
10000	82109	82103
100000	1.0513×10^{6}	1.0513×10^{6}
1000000	1.2816×10^{7}	1.2816×10^{7}

(all numbers quoted to 5 significant figures)

Conditional probability

The conditional probability $P(A|B)$ is the probability that event A occurs *given* that event B has happened.

The joint probability $P(A \cap B)$ is the probability that event A and event B both occur.

$$P(A|B) = \frac{P(A \cap B)}{P(B)}. \tag{9}$$

Bayes theorem is stated as follows:

$$P(A|B) = \frac{P(B|A)P(A)}{P(B)}. \tag{10}$$

$P(A)$ is called the **prior** probability, since it is the probability of A occurring without any knowledge as to the outcome of B.

Boltzmann factor

In statistical mechanics, the probability that a system is in some particular state α is proportional to the Boltzmann factor $\mathrm{e}^{-\beta E_\alpha}$ (where $\beta = 1/(k_\mathrm{B}T)$). The partition function, Z, is defined by

$$\boxed{Z = \sum_\alpha \mathrm{e}^{-\beta E_\alpha}} \tag{11}$$

where the sum is over all states of the system (each one labelled by α). Thus, the probability that a system is in some particular state α is equal to $\mathrm{e}^{-\beta E_\alpha}/Z$.

Equipartition (a result of classical statistical physics)

Let the energy E of a particular system be given by $E = \alpha x^2$, where α is some positive constant and x is some variable. Let us also assume that x could in principle take any value with equal probability. The probability $P(x)$ of the system having a particular energy αx^2 is proportional to the Boltzmann factor $\mathrm{e}^{-\beta\alpha x^2}$, so that after normalizing, we have

$$P(x) = \frac{\mathrm{e}^{-\beta\alpha x^2}}{\int_{-\infty}^{\infty} \mathrm{e}^{-\beta\alpha x^2}\,\mathrm{d}x}, \tag{12}$$

and the mean energy is

$$\langle E \rangle = \int_{-\infty}^{\infty} E\,P(x)\,\mathrm{d}x = \frac{\int_{-\infty}^{\infty} \alpha x^2 \mathrm{e}^{-\beta\alpha x^2}\,\mathrm{d}x}{\int_{-\infty}^{\infty} \mathrm{e}^{-\beta\alpha x^2}\,\mathrm{d}x} = \frac{1}{2\beta} = \frac{1}{2}k_\mathrm{B}T. \tag{13}$$

Equipartition theorem:
If the energy of a classical system is the sum of n quadratic modes, and that system is in contact with a heat reservoir at temperature T, the mean energy of the system is given by $n \times \frac{1}{2}k_\mathrm{B}T$.

The equipartition theorem expresses the fact that energy is ‘equally partitioned’ between all the separate modes of the system, each mode having a mean energy of precisely $\frac{1}{2}k_\mathrm{B}T$.

SJB
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