Thermodynamics and statistical mechanics

Javier Junquera

UC

UNIVERSIDAD
DE CANTABRIA

Bibliography
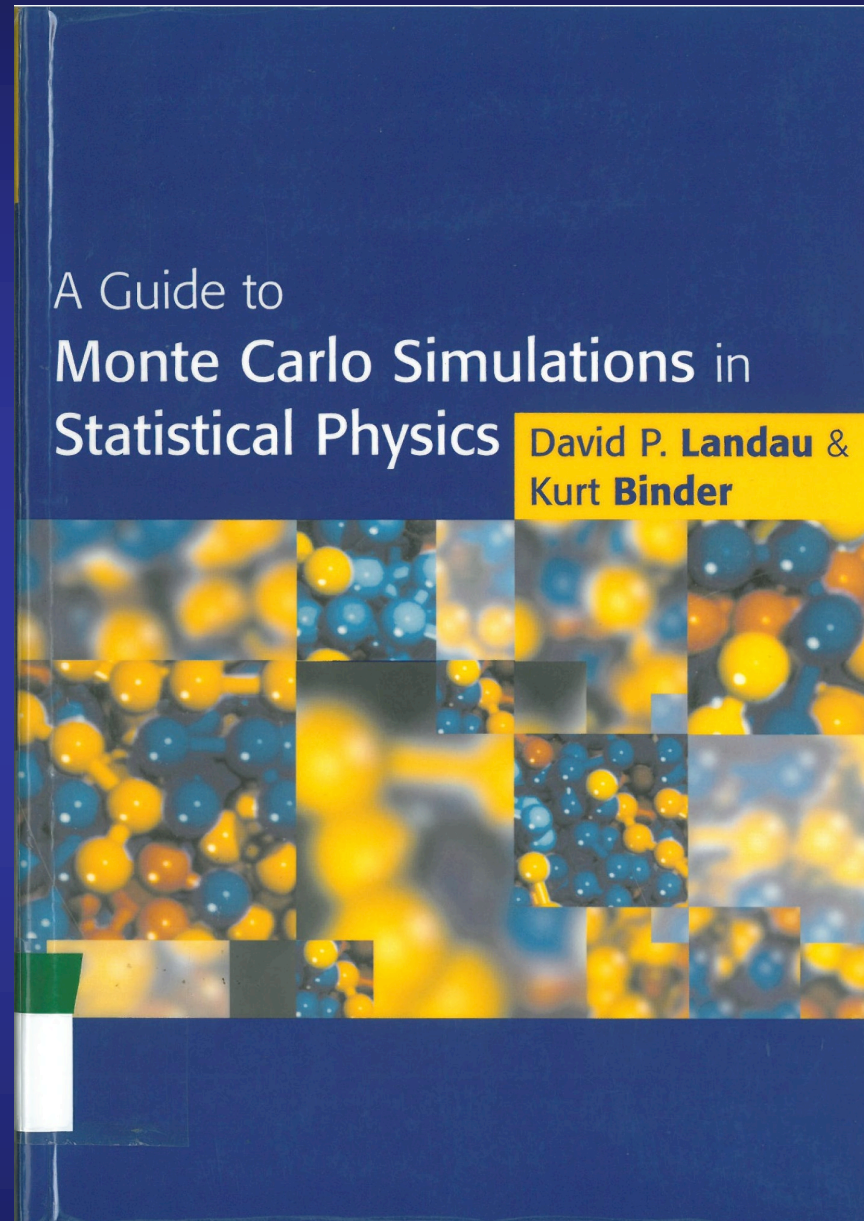
The Boltzmann factor

Let us imagine a quantum mechanical sample, that might be, for instance:
- a single atom,
- a molecule
- a box of a perfect gas
- …

This quantum mechanical system is in thermal contact with a large body of matter (a temperature bath) at temperature T

It has some probability of being found in any of its possible quantum states. Let us call any single microscopic state α , and its energy ε_α

This energy might involve:
- Kinetic energy
- Rotational energy
- Internal vibrational energy
- Magnetic energy
- Electronic excited energy
- …

What is the probability of finding the sample in state α

The Boltzmann factor

First, let us imagine the sample and the bath together to constitute an isolated system from the rest of the Universe, with total energy U_0

In equilibrium, the system has Γ_0 possible states and entropy S_0

$$S_0 = k_{\mathrm{B}} \log \Gamma_0 \qquad \text{(in equilibrium)}$$

Γ_0 is the product of possible states of the sample, Γ_{sample} , and the number of possible states of the bath Γ_{bath} when the system is in equilibrium with total energy U_0

$$\Gamma_0 = \Gamma_{\mathrm{sample}} \Gamma_{\mathrm{bath}} \qquad \text{(in equilibrium)}$$

In equilibrium, and with a total energy U_0 , the quantum sample might be in different quantum states with different energies

The Boltzmann factor

Now, instead of being in equilibrium, let us instead specify that the
sample is in state α with energy ε_α.

The bath is always internally in equilibrium,
In this case with an energy $U_0 - \varepsilon_\alpha$

The number of possible states for the bath when the sample is in state α is $\Gamma^\alpha_{\text{bath}}$

Since the sample is in state α, its number of possible states is

$$\Gamma_{\text{sample}} = 1$$

Therefore

$$\Gamma^\alpha_{\text{system}} = \Gamma^\alpha_{\text{bath}} \Gamma_{\text{sample}} = \Gamma^\alpha_{\text{bath}}$$

The probability of finding the sample in state α, w_α, is simply
the number of states of the system in which the sample happens to
be in state α divided by the total number of states in equilibrium

$$w_\alpha = \frac{\Gamma^\alpha_{\text{system}}}{\Gamma_0} = \frac{\Gamma^\alpha_{\text{bath}}}{\Gamma_0}$$

(ratio of the favourable cases to the
whole number of cases possible)

The Boltzmann factor

The probability w_α plays a crucial role in statistical physics

The sample is always in some state, so

$$\sum_{\text{all states}} w_\alpha = 1$$

If a quantity, say f_α, has a definite value in each quantum state of the sample, then its average or thermodynamic value is given by

$$\overline{f} = \sum_\alpha f_\alpha w_\alpha$$

In particular, f might be the energy of the sample.
Then, the thermodynamic or average energy is

$$\overline{\varepsilon} = \sum_\alpha \varepsilon_\alpha w_\alpha$$

The Boltzmann factor

The probability w_α plays a crucial role in statistical physics

When the sample is in the definite state α, the bath has an entropy

$$S_{\text{bath}}^\alpha = k_{\text{B}} \log \Gamma_{\text{bath}}^\alpha$$

Substracting this energy from the equilibrium entropy of the system

$$S_0 - S_{\text{bath}}^\alpha = -k_{\text{B}} \log \left(\frac{\Gamma_{\text{bath}}^\alpha}{\Gamma_0} \right) = -k_{\text{B}} \log w_\alpha$$

We have therefore

$$\omega_\alpha = e^{-(S_0 - S_{\text{bath}})/k_{\text{B}}}$$

The Boltzmann factor

$$\omega_\alpha = e^{-(S_0 - S_{\mathrm{bath}})/k_{\mathrm{B}}}$$

Assumption:
The entropy of the bath only depends on its energy

$$U_{\mathrm{bath}} = U_0 - \varepsilon_\alpha$$

$$S_{\mathrm{bath}}^\alpha = S_{\mathrm{bath}}\left(U_0 - \varepsilon_\alpha\right)$$

Since ε_α is much smaller than U_0 , we can expand S_{bath} in a Taylor series

$$S_{\mathrm{bath}}^\alpha = S_{\mathrm{bath}}\left(U_0\right) - \frac{\partial S_{\mathrm{bath}}}{\partial U_{\mathrm{bath}}}\varepsilon_\alpha$$

But $\quad \dfrac{\partial S_{\mathrm{bath}}}{\partial U_{\mathrm{bath}}} = \dfrac{1}{T}$

$$S_{\mathrm{bath}}^\alpha = S_{\mathrm{bath}}\left(U_0\right) - \frac{\varepsilon_\alpha}{T}$$

The Boltzmann factor

$$\omega_\alpha = e^{-(S_0 - S_{\text{bath}})/k_{\text{B}}}$$

$$S_{\text{bath}}^\alpha = S_{\text{bath}}(U_0) - \frac{\varepsilon_\alpha}{T}$$

Replacing the second equation into the first one

$$w_\alpha = e^{-(S_0 - S_{\text{bath}}(U_0) + \varepsilon_\alpha/T)/k_{\text{B}}} = e^{-(S_0 - S_{\text{bath}}(U_0))/k_{\text{B}}} \; e^{-\varepsilon_\alpha/k_{\text{B}}}$$

$$= A e^{-\varepsilon_\alpha/k_{\text{B}}}$$

where $A = e^{-(S_0 - S_{\text{bath}}(U_0))/k_{\text{B}}}$ **that is independent of the microstate** α

Since $\displaystyle\sum_{\text{all states}} w_\alpha = 1$

$$A = \frac{1}{\sum_\alpha e^{-\frac{\varepsilon_\alpha}{k_{\text{B}}T}}}$$

In fact, $A = \dfrac{1}{Z}$ **, where** $Z = \displaystyle\sum_\alpha e^{-\frac{\varepsilon_\alpha}{k_{\text{B}}T}}$ **is the partition factor**

The Boltzmann factor

The probability w_α plays a crucial role in statistical physics

The probability of finding the sample in state α with energy ε_α at temperature T is given by

$$w_\alpha = \frac{e^{-\varepsilon_\alpha/k_{\mathrm{B}}T}}{Z}$$

$e^{-\frac{\varepsilon_\alpha}{k_{\mathrm{B}}T}}$ is called the Boltzman factor

First question about the Boltzmann factor

$$w_\alpha = \frac{e^{-\varepsilon_\alpha/k_\mathrm{B}T}}{Z}$$

We started with the assumption that all possible states are equally likely

However, the previous expression shows how the lowest energy states
are more likely than the highest energy states…
How is it possible?

All possible quantum states of an isolated system are equally likely

The system is divided in two parts:
- the sample (very small compared with the rest)
- the bath (the rest)

For all the possible quantum states of the system as a whole,
the lower the energy of the sample, the larger the energy available to the bath

Since the bath is much bigger than the sample, it has many more ways to
use up the extra energy than the sample would, i. e.
The more quantum states are available for the systema as a whole, the
therefore, the more probable the situation is

Second question about the Boltzmann factor

$$w_\alpha = \frac{e^{-\varepsilon_\alpha/k_{\mathrm{B}}T}}{Z}$$

The ground state (i.e. The lowest energy state) is always the most probable state

Why do not commonly find macroscopic samples in their ground states? How is it possible?

A macroscopic sample has just one, unique ground state.

At any higher energy, the sample may have many possible quantum states with the same energy.
Then, the sample will generally have many possible states at nearly the same energy

Each of these states is less probable than the ground state,
But there are so many of them that the sample is more likely to be found in one of those that it is to be found in the ground state.

Partition function

Equilibrium statistical mechanics is based on the idea that the there is a partition function which contains all of the essential information about the system under consideration

$$Z = \sum_{\text{all states}} e^{-\mathcal{H}/k_{\text{B}}T}$$

$\mathcal{H}$ **is the Hamiltonian of the system**

T **is the Temperature**

k_{B} **is the Boltzmann constant**

The sum is over all possible states of the system, that depends upon its size and the number of particles

In general, the partition function cannot be evaluated exactly

Exact evaluation of a partition function: a particular example
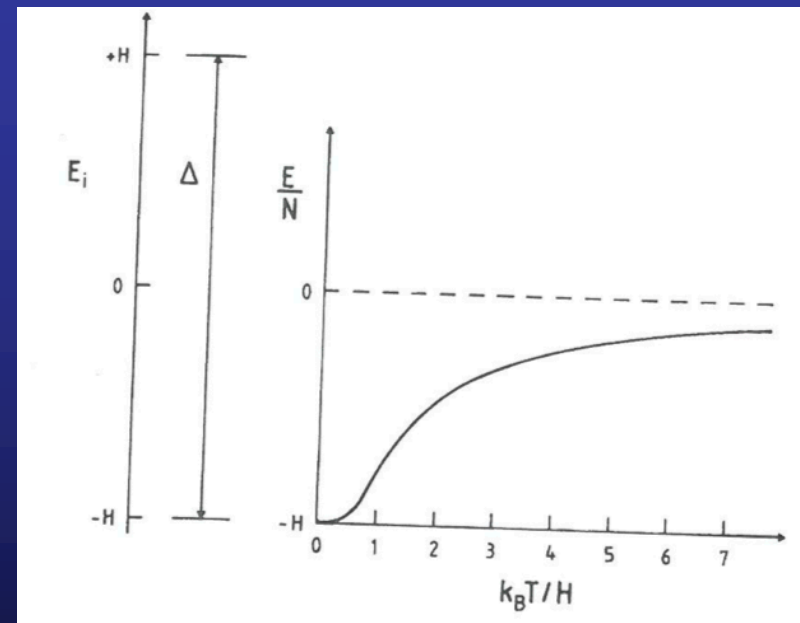
A system of N particles
Each of which has only two states (i.e. a non-interacting Ising model in an external magnetic field)

$$\mathcal{H} = -H \sum_i \sigma_i \qquad \sigma_i = \pm 1$$
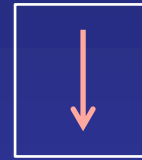
$$Z = \sum_{\text{all states}} e^{-\mathcal{H}/k_{\mathrm{B}}T}$$

$$Z = \left(e^{-H/k_{\mathrm{B}}T} + e^{H/k_{\mathrm{B}}T}\right)^N$$

Energies of the states and the temperature dependence of the internal energy in this case
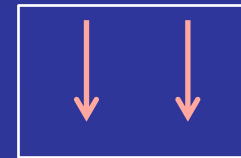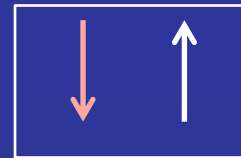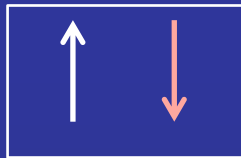
Exploring all the possible states: an impossible mission
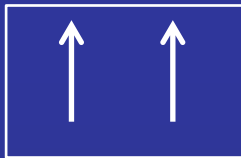
A system with **one-spin: 2^1 = 2 possible configurations**

A system with **two-spin: 2^2 = 4 possible configurations**

A system with **three-spin: 2^3 = 8 possible configurations**

A system with **10000-spin: 2^{10000} possible configurations**
(and this is only for a very small fraction of Avogadro's number and only for two possible states per particle!)

Probability of finding the system in a particular state

The probability of any particular state of the system is also determined by the partition function

The probability that the system is in state μ is

$$P_\mu = \frac{e^{-\frac{\mathcal{H}(\mu)}{k_\mathrm{B}T}}}{Z}$$

$\mathcal{H}(\mu)$ Hamiltonian when the system is in the μth state

We will take advantage of this property in evaluating the results for estimating probabilities with Monte Carlo methods

Thermodynamic potentials and their relation with the partition function

The free energy of a system can be determined from the partition function as

$$F = -k_{\mathrm{B}} T \ln Z$$

and all other quantities can be calculated by appropriate differentiation

The internal energy of a system can be obtained as

$$U = -T^2 \frac{\partial (F/T)}{\partial T}$$

This means that if the internal energy of a system can be measured, the free energy can be extracted by appropriate integration (assuming that the free energy is known as some reference temperature).
Free energy differences may be estimated by integration as

$$\frac{\partial (F/T)}{\partial T} = -\frac{U}{T^2} \Rightarrow d(F/T) = -U \frac{dT}{T^2} = U d(1/T) \Rightarrow \Delta(F/T) = \int d(1/T) U$$

Problem: determine the temperature dependence of the internal energy of the non-interacting Ising model

$$F = -k_{\mathrm{B}} T \ln Z \qquad\qquad U = -T^2 \frac{\partial \left(F/T \right)}{\partial T}$$

$$\frac{F}{T} = -k_{\mathrm{B}} \ln Z \Rightarrow \frac{\partial \left(F/T \right)}{\partial T} = -k_{\mathrm{B}} \frac{\partial \left(\ln Z \right)}{\partial T} = -k_{\mathrm{B}} \frac{\frac{\partial Z}{\partial T}}{Z}$$

$$\frac{\partial Z}{\partial T} = \frac{\partial}{\partial T} \left[\left(e^{-\frac{H}{k_{\mathrm{B}} T}} + e^{\frac{H}{k_{\mathrm{B}} T}} \right)^N \right]$$

$$= N \left(e^{-\frac{H}{k_{\mathrm{B}} T}} + e^{\frac{H}{k_{\mathrm{B}} T}} \right)^{N-1} \left(\frac{H}{k_{\mathrm{B}} T^2} e^{-\frac{H}{k_{\mathrm{B}} T}} - \frac{H}{k_{\mathrm{B}} T^2} e^{\frac{H}{k_{\mathrm{B}} T}} \right)$$

$$\frac{\partial \left(F/T \right)}{\partial T} = -k_{\mathrm{B}} \frac{\frac{\partial Z}{\partial T}}{Z} = -k_{\mathrm{B}} \frac{N \left(e^{-\frac{H}{k_{\mathrm{B}} T}} + e^{\frac{H}{k_{\mathrm{B}} T}} \right)^{N-1} \left(\frac{H}{k_{\mathrm{B}} T^2} e^{-\frac{H}{k_{\mathrm{B}} T}} - \frac{H}{k_{\mathrm{B}} T^2} e^{\frac{H}{k_{\mathrm{B}} T}} \right)}{\left(e^{-\frac{H}{k_{\mathrm{B}} T}} + e^{\frac{H}{k_{\mathrm{B}} T}} \right)^N}$$

$$= -\frac{NH}{T^2} \frac{\left(e^{-\frac{H}{k_{\mathrm{B}} T}} - e^{\frac{H}{k_{\mathrm{B}} T}} \right)}{\left(e^{-\frac{H}{k_{\mathrm{B}} T}} + e^{\frac{H}{k_{\mathrm{B}} T}} \right)}$$

Problem: determine the temperature dependence of the internal energy of the non-interacting Ising model

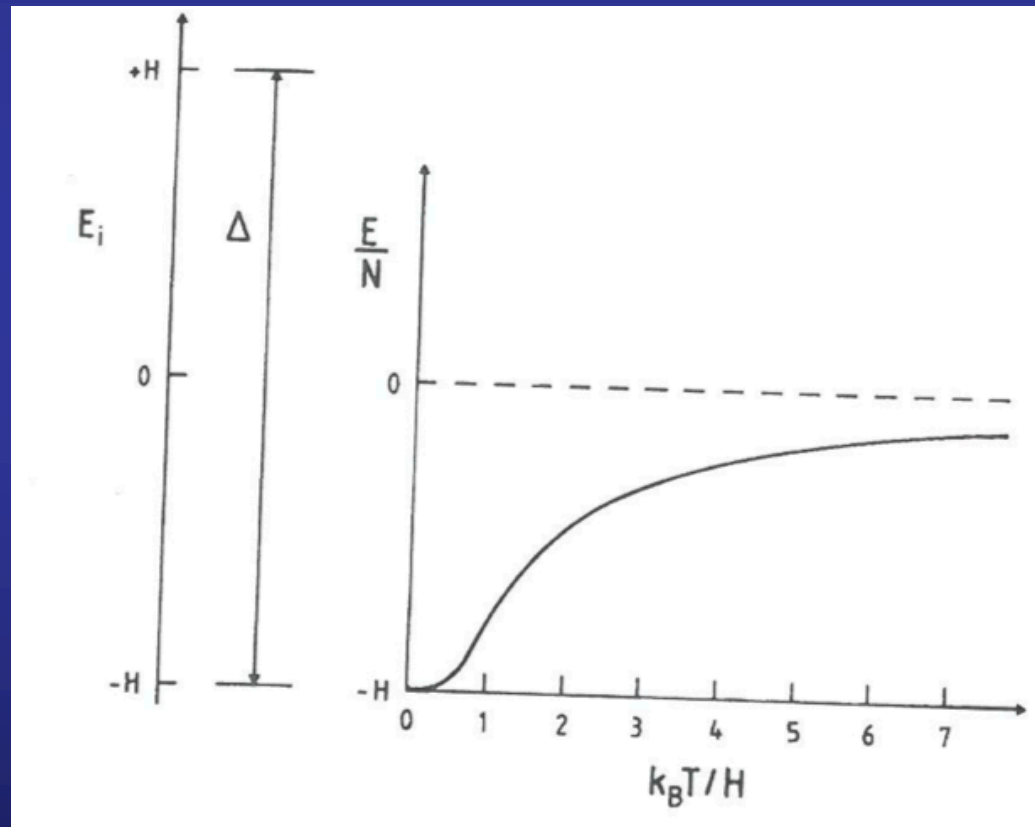$$F = -k_\mathrm{B} T \ln Z \qquad\qquad U = -T^2 \frac{\partial \left(F/T\right)}{\partial T}$$

$$\frac{\partial \left(F/T\right)}{\partial T} = -k_\mathrm{B} \frac{\frac{\partial Z}{\partial T}}{Z} = -k_\mathrm{B} \frac{N \left(e^{-\frac{H}{k_\mathrm{B} T}} + e^{\frac{H}{k_\mathrm{B} T}}\right)^{N-1} \left(\frac{H}{k_\mathrm{B} T^2} e^{-\frac{H}{k_\mathrm{B} T}} - \frac{H}{k_\mathrm{B} T^2} e^{\frac{H}{k_\mathrm{B} T}}\right)}{\left(e^{-\frac{H}{k_\mathrm{B} T}} + e^{\frac{H}{k_\mathrm{B} T}}\right)^N}$$

$$= -\frac{NH}{T^2} \frac{\left(e^{-\frac{H}{k_\mathrm{B} T}} - e^{\frac{H}{k_\mathrm{B} T}}\right)}{\left(e^{-\frac{H}{k_\mathrm{B} T}} + e^{\frac{H}{k_\mathrm{B} T}}\right)}$$

$$U = -T^2 \frac{\partial \left(F/T\right)}{\partial T} = NH \frac{\left(e^{-\frac{H}{k_\mathrm{B} T}} - e^{\frac{H}{k_\mathrm{B} T}}\right)}{\left(e^{-\frac{H}{k_\mathrm{B} T}} + e^{\frac{H}{k_\mathrm{B} T}}\right)}$$

$$\frac{U}{N} = -H \tanh\left(\frac{H}{k_\mathrm{B} T}\right) = -H \tanh\left[\left(\frac{k_\mathrm{B} T}{H}\right)^{-1}\right]$$

Problem: determine the temperature dependence of the internal energy of the non-interacting Ising model

$$\frac{U}{N} = -H \tanh\left(\frac{H}{k_{\mathrm{B}}T}\right) = -H \tanh\left[\left(\frac{k_{\mathrm{B}}T}{H}\right)^{-1}\right]$$

Fluctuations: how to compute probabilities of macroscopic quantities

We first form the moments, where $\beta \equiv \frac{1}{k_{\mathrm{B}}T}$ the average energy is denoted by $\overline{U}$ and U is a fluctuating quantity

$$\overline{U}(\beta) = \langle \mathcal{H}(\mu) \rangle \equiv \sum_{\mu} P_{\mu} \mathcal{H}(\mu) = \frac{\sum_{\mu} \mathcal{H}(\mu) e^{-\beta \mathcal{H}(\mu)}}{Z} = \frac{\sum_{\mu} \mathcal{H}(\mu) e^{-\beta \mathcal{H}(\mu)}}{\sum_{\mu} e^{-\beta \mathcal{H}(\mu)}}$$

$$\langle \mathcal{H}^2 \rangle = \frac{\sum_{\mu} \mathcal{H}^2(\mu) e^{-\beta \mathcal{H}(\mu)}}{\sum_{\mu} e^{-\beta \mathcal{H}(\mu)}}$$

We note the relationship

$$-\left. \frac{\partial U(\beta)}{\partial \beta} \right|_{\mathrm{V}} = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2$$

Since $\left. \frac{\partial U}{\partial T} \right|_{V} = C_V$, where C_V is the specific heat, then

$$k_{\mathrm{B}} T^2 C_V = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \langle (\Delta U)^2 \rangle_{NVT}, \qquad \Delta U \equiv \mathcal{H} - \langle \mathcal{H} \rangle$$

Fluctuations: the isothermal susceptibility

Similar fluctuation relations exist for many other quantities,
for example, the isothermal susceptibility

$$\chi = \frac{\partial \langle M \rangle}{\partial H}\bigg|_T$$

that is related to fluctuations of the magnetization $M = \sum_i \sigma_i$

Writing the Hamiltonian of the system in the presence of a magnetic field H

$$\mathcal{H} = \mathcal{H}_0 - HM$$

And knowing that the average magnetization can be written as

$$\langle M \rangle = \frac{\sum_\mu M(\mu) e^{-\beta \mathcal{H}(\mu)}}{\sum_\mu e^{-\beta \mathcal{H}(\mu)}}$$

Then

$$k_{\mathrm{B}} T \chi = \langle M^2 \rangle - \langle M \rangle^2 = \sum_{i,j} \left(\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \right)$$

Proof in next slide

Fluctuations: the isothermal susceptibility

**Similar fluctuation relations exist for many other quantities,
for example, the isothermal susceptibility**

$$\chi = \frac{\partial \langle M \rangle}{\partial H}\bigg|_T$$

$$\langle M \rangle = \frac{\sum_\mu M(\mu) e^{-\beta \mathcal{H}(\mu)}}{\sum_\mu e^{-\beta \mathcal{H}(\mu)}} \qquad\qquad \mathcal{H}(\mu) = \mathcal{H}_0(\mu) - H M(\mu)$$

Then

$$\chi = \frac{\partial \langle M \rangle}{\partial H} = \frac{\partial}{\partial H} \left[\frac{\sum_\mu M(\mu) e^{-\beta \mathcal{H}(\mu)}}{\sum_\mu e^{-\beta \mathcal{H}(\mu)}} \right]$$

$$= \frac{\left[\left(\sum_\mu M(\mu) e^{-\beta \mathcal{H}(\mu)} \beta M(\mu) \right) \left(\sum_\mu e^{-\beta \mathcal{H}(\mu)} \right) - \left(\sum_\mu M(\mu) e^{-\beta \mathcal{H}(\mu)} \right) \left(\sum_\mu e^{-\beta \mathcal{H}(\mu)} \beta M(\mu) \right) \right]}{\left(\sum_\mu e^{-\beta \mathcal{H}(\mu)} \right)^2}$$

$$= \beta \frac{\sum_\mu M^2(\mu) e^{-\beta \mathcal{H}(\mu)}}{\sum_\mu e^{-\beta \mathcal{H}(\mu)}} - \beta \left(\frac{\sum_\mu M(\mu) e^{-\beta \mathcal{H}(\mu)}}{\sum_\mu e^{-\beta \mathcal{H}(\mu)}} \right)^2$$

$$= \beta \left[\langle M^2 \rangle - \langle M \rangle^2 \right]$$

$$k_{\mathrm{B}} T \chi = \langle M^2 \rangle - \langle M \rangle^2 = \sum_{i,j} \left(\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \right)$$

Basic notions of probability theory

Equivalent notation

$$p(A_k) \equiv p_k$$

From its definition

$$p(A_i \ \text{or} \ A_j) \leq [P(A_i) + P(A_j)]$$

We call A_i **and** A_j **"mutually exclusive" events, if and only if the occurrence of** A_i **implies that** A_j **does not occur and vice versa**

$$p(A_i \ \text{and} \ A_j) = 0 \qquad p(A_i \ \text{or} \ A_j) = P(A_i) + P(A_j)$$

Basic notions of probability theory: conditional probability

Let us consider two events:
- **The first with outcomes** $\{A_i\}$ **and probabilities** p_{1i}
- **The second with outcomes** $\{B_j\}$ **and probabilities** p_{2j}

We consider now the outcome (A_i, B_j) **and consider the probability** p_{ij}
as a joint probability that both A_i **and** B_j **occur**

If the events are independents:

$$p_{ij} = p_{1i} \times p_{2j}$$

If they are not independent, we define the conditional probability $p(j|i)$
that B_j **occurs given that** A_i **occurs**

$$p(j|i) = \frac{p_{ij}}{\sum_k p_{ik}} = \frac{p_{ij}}{p_{1i}}$$

Of course, we have $\displaystyle\sum_j p(j|i) = 1$ **since some** B_j **must occur**

Basic notions of probability theory: some basic definitions

The outcome of such random effects might be logical variables or real numbers. These real numbers are calles random variables

We define the expectation value of the random variable as

$$\langle x \rangle \equiv E(x) \equiv \sum_i p_i x_i$$

Similarly, any real function $g(x_i)$ has the expectation value

$$\langle g(x) \rangle \equiv E(g, x) = \sum_i p_i g(x_i)$$

We define the nth moment as

$$\langle x^n \rangle = \sum_i p_i x_i^n$$

And the cumulants

$$\langle (x - \langle x \rangle)^n \rangle = \sum_i p_i (x - \langle x \rangle)^n$$

Of the greatest importance is the case $n = 2$, called the "variance"

$$\mathrm{var}(x) = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$$

Basic notions of probability theory: some basic definitions

Generalizing the definitions to two random variables (x_i and y_i) then the expectation value is

$$\langle xy \rangle = \sum_{i,j} p_{ij} x_i y_j$$

If x and y are independent, then $p_{ij} = p_{1i} p_{2j}$

$$\langle xy \rangle = \sum_i p_{1i} x_i \sum_j p_{2j} y_j = \langle x \rangle \langle y \rangle$$

As a measure of the degree of independence of the two random variables, we define the covariance

$$\mathrm{cov}(x,y) = \langle x, y \rangle - \langle x \rangle \langle y \rangle$$

Special probability distributions and the central limit theorem

Consider two events A_0 and A_1 that are mutually exclusive and exhaustive

$$P(A_1) = p, \qquad x = 1 \qquad\qquad P(A_0) = 1 - p, \qquad x = 0$$

Suppose now that N independent samples of these events occur.
Each outcome is 0 or 1.
We denote the sum X of these outcomes

$$X = \sum_{r=1}^{N} x_r$$

The probability that $X = n$ is the probability that n of the X_r were 1 and $(N - n)$ were 0.

$$P(X = n) = \binom{N}{n} p^n (1 - p)^{N-n}$$

Where $\binom{N}{n}$ is the binomial coefficients

This is called the binomial distribution

Special probability distributions: the binomial distribution

Consider two events A_0 and A_1 that are mutually exclusive and exhaustive

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Special probability distributions: the Poisson distribution

The binomial distribution

$$P(X = n) = \binom{N}{n} p^n (1 - p)^{N-n}$$

If the probability of "success" is very small, the binomial distribution can be approximated by the Poisson distribution

$$P(x = n) = \frac{\lambda^n}{n!} \exp(-\lambda), \qquad n = 0, 1, \dots$$

Special probability distributions:
the Gaussian distribution

The most important distribution we will encounter in statistical physics

$$p_{\mathrm{G}}(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(x - \langle x \rangle)^2}{2\sigma^2} \right]$$

If the number of random variables $x_1, x_2, x_3, \ldots, x_n$ are all independent of each other and drawn from the same distribution, the average value

$$\overline{X} = \sum_{i=1}^{N} \frac{x_i}{N}$$

In the limit $N \to \infty$ will always be distributed according to the gaussian distribution, irrespective of the distribution from which the x_i were drawn

This is known as the "central limit theorem"

The variance of $\overline{X}_N$ is σ^2

and $\sigma^2 \propto \dfrac{1}{N}$

Special probability distributions: the geometrical distribution

Suppose that we perform an experiment with two possible outcomes: 0 and 1

If the outcome is 0, the experiment is repeated
If the outcome is 1, we stop

Random variable of interest:
The number of experiments n until we get the outcome 1

$$P(x = n) = (1 - p)^{n-1} p \qquad\qquad n = 1, 2, 3 \ldots$$

This is called the geometrical distribution

Basic notions of probability theory:
Statistical errors

Suppose the quantity A is distributed according to a Gaussian with mean value $\langle A \rangle$ and width σ

We consider n statistically independent observations $\{A_i\}$ of this quantity A

Un unbiased estimator of the mean $\langle A \rangle$ of this distribution is

$$\overline{A} = \frac{1}{n} \sum_{i=1}^{n} A_i$$

And the standard error of this estimate

$$\mathrm{error} = \frac{\sigma}{\sqrt{n}}$$

But, how to estimate the variance from the observations?

Basic notions of probability theory: Statistical errors

But, how to estimate the variance from the observations?

Consider the variations

$$\delta A_i = A_i - \overline{A}$$

Obviously

$$\overline{\delta A_i} = 0$$

So we are interested in the mean square deviations

$$\overline{\delta A^2} = \frac{1}{n} \sum_{i=1}^{n} (\delta A_i)^2 = \overline{A^2} - \left(\overline{A} \right)^2$$

The expectation value of this quantity is easily related to $\sigma^2 = \langle A^2 \rangle - \langle A \rangle^2$

$$\langle \overline{\delta A^2} \rangle = \sigma^2 \left(1 - \frac{1}{n} \right) \Rightarrow \sigma = \sqrt{\frac{n \langle \overline{\delta A^2} \rangle}{n-1}}$$

Since $\mathrm{error} = \dfrac{\sigma}{\sqrt{n}}$ **we arrive to the usual formula for the computation of errors of averages from uncorrelated estimates**

$$\mathrm{error} = \frac{\sigma}{n} = \sqrt{\frac{\langle \overline{\delta A^2} \rangle}{n-1}} = \sqrt{\frac{\sum_{i=1}^{n} (\delta A_i)^2}{n(n-1)}}$$
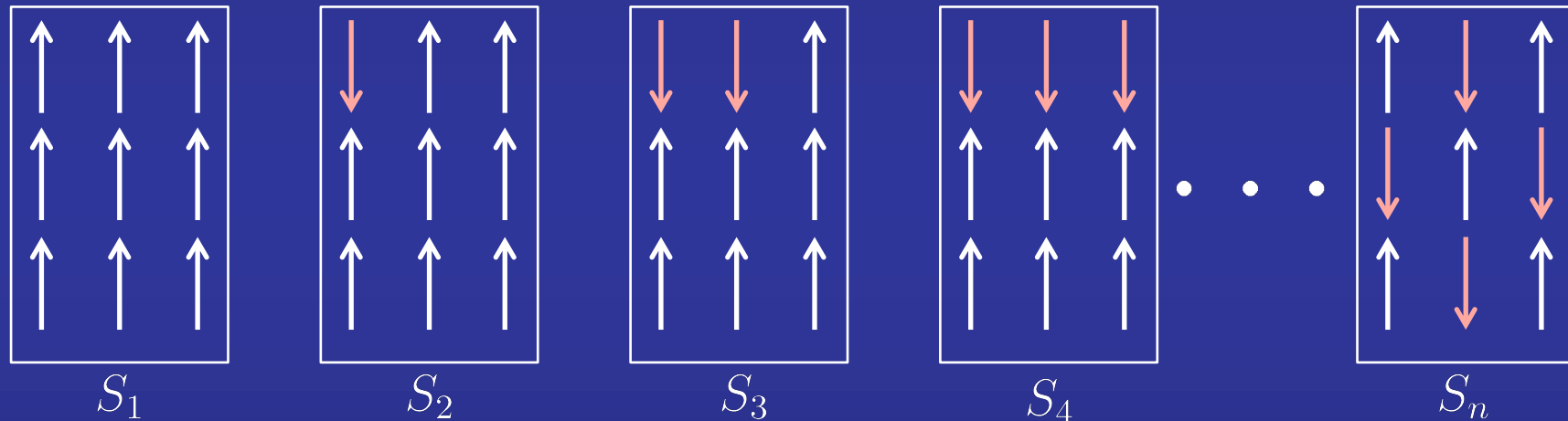
The concept of the Markov chain

We define a stochastic process at discrete times labeled consecutively $t_1, t_2, t_3, \ldots$

for a system with a finite set of possible states $S_1, S_2, S_3, \ldots$

This finite set of possible outcomes is called the state space

For instance, for a 2D Ising model

$$S_1 \qquad S_2 \qquad S_3 \qquad S_4 \qquad S_n$$

We denote by X_t the state the system is in at time t

We consider the conditional probability that $X_{t_n} = S_{i_n}$ given that at the preceeding time the system state $X_{t_{n-1}}$ was in state $S_{i_{n-1}}$, etc

$$P(X_{t_n} = S_{i_n} | X_{t_{n-1}} = S_{i_{n-1}} | X_{t_{n-2}} = S_{i_{n-2}} | \ldots | X_{t_1} = S_{i_1})$$

The concept of the Markov chain

We denote by X_t the state the system is in at time t

We consider the conditional probability that $X_{t_n} = S_{i_n}$ given that at the preceeding time the system state $X_{t_{n-1}}$ was in state $S_{i_{n-1}}$, etc

$$P(X_{t_n} = S_{i_n} | X_{t_{n-1}} = S_{i_{n-1}} | X_{t_{n-2}} = S_{i_{n-2}} | \ldots | X_{t_1} = S_{i_1})$$

Such a process is call a Markov process if this conditional probability is in fact independent of all states but the immediate predecessor

$$P = P(X_{t_n} = S_{i_n} | X_{t_{n-1}} = S_{i_{n-1}})$$

The corresponding sequence of states $\{X_t\}$ is called a Markov chain

The above conditional probability can be interpreted as the **transition probability** to move from state i to state j

$$W_{ij} = W(S_i \rightarrow S_j) = P(X_{t_n} = S_j | X_{t_{n-1}} = S_i)$$

Transition probabilities

The above conditional probability can be interpreted as the transition probability to move from state i to state j

$$W_{ij} = W(S_i \rightarrow S_j) = P(X_{t_n} = S_j | X_{t_{n-1}} = S_i)$$

As usual for transition probabilities, we require that

$$W_{ij} \geq 0, \qquad \sum_j W_{ij} = 1$$

We may construct the total probability $P(X_{t_n} = S_j)$ that at time t_n the system is in state S_j as

$$P(X_{t_n} = S_j) = P(X_{t_n} = S_j | X_{t_{n-1}} = S_i) P(X_{t_{n-1}} = S_i) = W_{ij} P(X_{t_{n-1}} = S_i)$$

The master equation (or "continuity equation")

The master equation considers the change of this probability with time t (treating time as a continuous variable rahter than discrete variable)

$$\frac{dP(S_j, t)}{dt} = -\sum_i W_{ji} P(S_j, t) + \sum_i W_{ij} P(S_i, t)$$

Probability to move away from state j to any other state i

Probability to move to state j coming from any other state i

Knowledge of the state at time t completely determines the future time evolution, there is no memory of the past (knowledge of behaviour of the systems at times earlier than t is not needed)

The master equation at the equilibrium probability

The equilibrium probability $P_{\text{eq}}(S_j)$ satisfies

$$\frac{dP_{\text{eq}}(S_j, t)}{dt} \equiv 0$$

Since

$$\frac{dP(S_j, t)}{dt} = -\sum_i W_{ji} P(S_j, t) + \sum_i W_{ij} P(S_i, t)$$

then

$$W_{ji} P_{\text{eq}}(S_j) = W_{ij} P_{\text{eq}}(S_i)$$