

Selected topics from statistical physics

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Chapter 1

Introduction

1.1 Some books

- F.Reif: Fundamentals of Statistical and Thermal Physics
- L.E.Reichl: A Modern Course in Statistical Physics
- C.Kittel: Elementary Statistical Physics
- J.Sethna Statistical Mechanics, mEntropy, Order Parameters and Complexity (free on internet)
- R.K.Pathria: Statistical Mechanics
- Gould, Tobochnik: Thermal and Statistical Physics (free on internet)
- S.K.Ma: Statistical Physics
- MIT Open course project (<http://ocw.mit.edu/OcwWeb/Physics/index.htm>)
- J.M.Yeomans Statistical Mechanics of Phase Transitions

Chapter 2

Supplements to the probability theory

2.1 Some definitions

Probability density

$$p(a < x < b) = \int_a^b \varrho(x) dx$$

Mean value

$$\overline{f(x)} = \int f(x) \varrho(x) dx$$

Independent variables

$$\varrho(x, y) = \varrho_1(x) \varrho_2(y)$$

Marginal distribution

$$\varrho_1(x) = \int \varrho(x, y) dy$$

Function of random variable

$$y = f(x)$$

$$\begin{aligned} \overline{g(y)} &= \int g(f(x)) \varrho(x) dx = \int g(y) \delta(y - f(x)) \varrho(x) dx dy = \\ &= \int g(y) \varrho(f^{-1}(\xi)) \delta(y - \xi) \frac{1}{f'(f^{-1}(\xi))} dy d\xi = \int g(y) \tilde{\varrho}(y) dy \\ \tilde{\varrho}(y) &= \int \delta(y - f(x)) \varrho(x) dx = \varrho(f^{-1}(y)) \frac{1}{f'(f^{-1}(y))} \end{aligned}$$

Sum of two independent variables

$$z = x + y$$

$$\varrho(z) = \int \delta(z - (x + y)) \varrho_1(x) \varrho_2(y) dx dy = \int \varrho_1(x) \varrho_2(z - x) dx$$

It is a convolution

Characteristic function

$$f(k) = \langle \exp(ikx) \rangle = \int dx \exp(ikx) \varrho(x) = \sum \frac{(ik)^n}{n!} \langle x^n \rangle$$

$$\varrho(x) = \frac{1}{2\pi} \int dk \exp(-ikx) f(k)$$

$$\langle x^n \rangle = (-i)^n \frac{d^n f}{dk^n}$$

Characteristic function of a function of a random variable

$$y = \varphi(x)$$

$$\varrho(y) = \int \varrho(x) \delta(y - \varphi(x)) dx$$

$$f(k) = \int dy e^{iky} \varrho(y) = \int dx dy e^{iky} \varrho(x) \delta(y - \varphi(x))$$

$$f(k) = \int e^{ik\varphi(x)} \varrho(x) dx$$

For the sum of two variables the density function is a convolution, so the characteristic function is a product, since the Fourier transform of a convolution is the product of Fourier transforms.

$$\int e^{ikz} \delta(z - (x + y)) \varrho_1(x) \varrho_2(y) dx dy dz = \int dx e^{ikx} \varrho_1(x) \int dy e^{iky} \varrho_2(y) = f_1(k) f_2(k)$$

Cumulants

$$\ln(f(x)) = \sum \frac{(ik)^n}{n!} C_n$$

$$C_1 = \langle x \rangle$$

$$C_2 = \langle x^2 \rangle - \langle x \rangle^2 \equiv \langle x^2 \rangle_C$$

$$C_3 = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + 2\langle x \rangle^3 \equiv \langle x^3 \rangle_C$$

Cumulant expansion

$$\begin{aligned} \langle x_1 x_2 x_3 x_4 \rangle &= \langle x_1 x_2 x_3 x_4 \rangle_C + \langle x_1 x_2 x_3 \rangle_C \langle x_4 \rangle_C + 3 \text{ terms} + \\ &+ \langle x_1 x_2 \rangle_C \langle x_3 x_4 \rangle_C + 2 \text{ terms} + \langle x_1 x_2 \rangle_C \langle x_3 \rangle_C \langle x_4 \rangle_C + 5 \text{ terms} + \\ &+ \langle x_1 \rangle_C \langle x_2 \rangle_C \langle x_3 \rangle_C \langle x_4 \rangle_C \end{aligned}$$

Normal distribution

$$\begin{aligned} \varrho(x) &= \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2}\right) \\ f(k) &= \exp\left(-\frac{k^2\sigma^2}{2}\right) \\ \ln(f(k)) &= -\frac{k^2\sigma^2}{2} \end{aligned}$$

only second cumulant non-zero, so all higher moments are expressible through the second cumulant.

Variance

$$\sigma^2 = \langle x^2 \rangle_C$$

Covariance

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

Correlation function

$$\text{cor}(x, y) = \frac{\text{cov}(x, y)}{\sigma_x \sigma_y}$$

Multivariate Gauss distribution

$$\begin{aligned} \varrho(x_1, \dots, x_n) &= \sqrt{\frac{\det(g)}{(2\pi)^n}} \exp\left(-\frac{1}{2} x^\top g x\right) \\ f(k_1, \dots, k_n) &= \langle \exp(i(k_1 x_1 + \dots + k_n x_n)) \rangle \\ \langle x_1 x_2 x_3 x_4 \rangle &= (-i)^4 \frac{\partial}{\partial k_1} \frac{\partial}{\partial k_2} \frac{\partial}{\partial k_3} \frac{\partial}{\partial k_4} f(k_1, \dots, k_n) \Big|_{k_i=0} = \\ &= \langle x_1 x_2 \rangle \langle x_3 x_4 \rangle + \langle x_1 x_3 \rangle \langle x_2 x_4 \rangle + \langle x_1 x_4 \rangle \langle x_2 x_3 \rangle \end{aligned}$$

Wick theorem

Generating function

$$f(u) = \sqrt{\frac{A}{2\pi}} \int dx \exp\left(-\frac{1}{2}Ax^2 + ux\right)$$

to be compared with characteristic function with $u = ik$

Technique: shift of variables

$$x = x' - \frac{u}{A}$$

$$f(u) = \exp\left(\frac{u^2}{2A}\right)$$

Taylor series generates moments

Another technique to calculate moments: Euler Gamma function

$$\Gamma(z) = \int_0^\infty t^{z-1} \exp(-t) dt$$

$$\Gamma(n) = (n-1)!$$

$$\Gamma(z+1) = z\Gamma(z)$$

$$\Gamma(1/2) = \sqrt{\pi}$$

$$\Gamma\left(\frac{n}{2}\right) = \sqrt{\pi} \frac{(n-2)!!}{2^{(n-1)/2}} \quad \text{for odd } n$$

$$\begin{aligned} \int dx x^n \exp\left(-\frac{1}{2}Ax^2\right) &= \left(\frac{A}{2}\right)^{-\frac{n+1}{2}} \int d\xi \xi^n \exp(-\xi^2) = \\ &= \left(\frac{2}{A}\right)^{\frac{n+1}{2}} \int \frac{1}{2} t^{-1/2} t^{n/2} \exp(-t) = \frac{1}{2} \left(\frac{2}{A}\right)^{\frac{n+1}{2}} \Gamma\left(\frac{n+1}{2}\right) \end{aligned}$$

2.2 n-dimensional sphere

$$(\sqrt{\pi})^n = \int dx \exp\left(-\sum x_i^2\right) = \int \exp(-r^2) S_n(r) dr$$

from here one easily calculates the surface of the n-dimensional sphere $S_n(r)$ assuming the form

$$S_n(r) = C_n r^{n-1}$$

$$S_n(r) = \frac{2\pi^{n/2}r^{n-1}}{\Gamma(n/2)}$$

and then also the volume of an n-dimensional sphere $V_n(r)$ via

$$V_n(r) = \int_0^r S_n(r)dr$$

$$V_n(r) = \frac{\pi^{n/2}r^n}{\Gamma(n/2 + 1)}$$

2.3 Laplace method

Also called steepest descent method or saddle point method is an approximation scheme which is used to evaluate the integral

$$\int \exp(Mf(x))dx \quad \text{for } M \rightarrow \infty$$

Let $f(x)$ has only one maximum at x_0 , then the integral is dominated by this maximum

$$f(x) = f(x_0) + \frac{1}{2}f''(x_0)(x - x_0)^2$$

$$\begin{aligned} \int \exp(Mf(x))dx &= \exp(Mf(x_0)) \int dx \exp\left(-\frac{1}{2}M|f''(x_0)|(x - x_0)^2\right) = \\ &= \exp(Mf(x_0)) \sqrt{\frac{2\pi}{M|f''(x_0)|}} \end{aligned}$$

The logarithm is dominated by the maximum

$$\ln(f(x)) = Mf(x_0)$$

Stirling formula

$$N! = \sqrt{2\pi N}N^N e^{-N}$$

$$\begin{aligned} N! = \Gamma(N + 1) &= \int x^N e^{-x} dx = \int e^{-Nz} (Nz)^N N dz = \\ &= N^{N+1} \int dz e^{(-Nz + N \ln z)} = N^{N+1} \int e^{N(\ln z - z)} dz \end{aligned}$$

Laplace method with

$$f(z) = \ln z - z$$

$$f'(z) = \frac{1}{z} - 1 \quad \text{maximum for } z = 1$$

$$f''(z) = -\frac{1}{z^2}$$

$$N! = N^{N+1} e^{-N} \sqrt{\frac{2\pi}{N}}$$

2.4 Central limit theorem

Let us investigate what happens with a general function by repeating convolutions. Expressed in the language of probabilities: if the probability distributions of the random variables x_i ($i = 1, \dots, N$) are given by the same function $f(x_i)$, what is the probability distribution of the sum of those variables. The question is answered by the central limit theorem, according to which in the limit $n \rightarrow \infty$ the variable

$$X_n = \frac{\sum_{i=1}^n (x_i - \mu)}{\sqrt{n}\sigma}$$

is distributed according to the standard normal distribution $\mathcal{N}(0, 1)$. Here $\mu < \infty$ is the mean of x_i , $\sigma < \infty$ is the root mean squared of $(x_i - \mu)$.

We shall now prove (not completely rigorously) the central limit theorem. The characteristic function for the probability distribution $f(x)$ is given by the following relation

$$\varphi_f(t) = \langle e^{itx} \rangle \equiv \int_{D(f)} f(x) e^{itx} dx,$$

for $t \in \mathbb{R}$. We see that $\varphi_f(t)$ is actually the Fourier transform of the probability density $f(x)$. An important formula holds

$$\langle x^n \rangle = -i^n \varphi_f^{(n)}(0) \equiv -i^n \left. \frac{d^n}{dt^n} \varphi_f(t) \right|_{t=0}.$$

Using this relation, we can write the Taylor series of the characteristic function of the probability density $f(x)$ with a mean 0 and variance 1 in the form

$$\varphi_f(t) = 1 - \frac{t^2}{2} + o(t^2) \quad (t \rightarrow 0).$$

We define new random variables $y_i = (x_i - \mu)/\sigma$. These variables have the mean value 0 and variance 1.

By convolution the characteristic functions get multiplied (they are the Fourier transforms). Since $X_n = \sum_i y_i / \sqrt{n}$, the characteristic function of its distribution

$g(X_n)$ is the product of the characteristic functions of the distribution $f(y/\sqrt{n})$ and can be written as

$$[\varphi_g(t/\sqrt{n})]^n = \left[1 - \frac{t^2}{2n} + o(t^2/n)\right]^n \xrightarrow{n \rightarrow \infty} e^{-t^2/2}.$$

The last function is the characteristic function of the standard normal distribution $\mathcal{N}(0, 1)$, we have proved that the distribution $g(X_n)$ converges to the standard normal distribution $\mathcal{N}(0, 1)$.

The prove (on our level of rigor) was not complicated. However, the proof does not show, that the convergence to the normal distribution is in many cases really very fast. An example of a different behavior of slow convergence is the Poisson distribution with a small mean, e.g. $\lambda = 10^{-3}$.

The central limit theorem can be generalized for the sum of random variables distributed according to different distributions from which no one dominates by its variance to their sum. Having in mind that many random variables around us are given by a simultaneous influence of many random contributions, it is clear why the normal distribution is exceptionally important¹. In this respect we remind here the standard lectures on experimental data processing, where the normal distribution is used to characterize measurement errors of practically all physical quantities.

Finally, we shall discuss so called law of large numbers. We begin by deriving the Thebyshev inequality which relates the variance of a distribution σ^2 with the probability that the corresponding random variable will differ from the mean value by $\epsilon > 0$. The variance is defined as

$$\sigma^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 f(x) dx.$$

If we leave out from the domain of integration the region $|x - \langle x \rangle| < \epsilon$, we can write

$$\sigma^2 \geq \int_{-\infty}^{\langle x \rangle - \epsilon} (x - \langle x \rangle)^2 f(x) dx + \int_{\langle x \rangle + \epsilon}^{\infty} (x - \langle x \rangle)^2 f(x) dx.$$

Since $|x - \langle x \rangle| \geq \epsilon$, we can replace the expressions $(x - \langle x \rangle)^2$ by ϵ^2 while the inequality still holds. We get

$$\sigma^2 \geq \epsilon^2 \left[\int_{-\infty}^{\langle x \rangle - \epsilon} f(x) dx + \int_{\langle x \rangle + \epsilon}^{\infty} f(x) dx \right] = \epsilon^2 P(|x - \langle x \rangle| \geq \epsilon).$$

¹Just a small terminological footnote. We see that the normal distribution had so many exceptional properties, that the attribute "normal" is rather inappropriate. Its another name, the Gaussian distribution, is also not very appropriate, because it was formulated already by de Moivre and its properties were studied by Laplace, when Gauss was six years old. Gauss own work from 1809, however, contained a simple derivation of the central limit theorem and the distribution itself became therefore popular.

This is the Tchebyshev inequality. It is usually written as

$$P(|x - \langle x \rangle| \geq \epsilon) \leq \frac{\sigma^2}{\epsilon^2}.$$

Now let us consider the sum of N independent identically distributed random variables $y_N = (x_1 + \dots + x_N)/N$. Clearly $\langle y \rangle = \langle x \rangle$. Since $\sigma_y^2 = \sigma_x^2/N$ (the reader can easily check this himself) the Tchebyshev inequality gives

$$P(|y_N - \langle x \rangle| \geq \epsilon) \leq \frac{\sigma_y^2}{\epsilon^2} = \frac{\sigma_x^2}{N\epsilon^2}.$$

Assuming $\sigma_x < \infty$ it is clear that for any chosen value ϵ we get

$$\lim_{N \rightarrow \infty} P(|y_N - \langle x \rangle| \geq \epsilon) = 0.$$

The probability that the arithmetic average y_N of independent identically distributed random variables x_i difference from $\langle x \rangle$, in the limit $N \rightarrow \infty$ declines to zero.

This fact justifies the experimental procedure to measure the probability as a ratio of the number favorable events to the total number of events. This ratio according to the law of large numbers converges to a certain value and this value we call the probability of the studied phenomenon.

Exercise

a) Show that in the limit $n \rightarrow \infty$ assuming $pn = \text{const.} \equiv \lambda$, the binomial distribution approaches the Poisson distribution

$$f(k) = \frac{\lambda^k}{k!} e^{-\lambda},$$

where λ is the mean value of the random variable k .

b) Show that in the limit $\lambda \rightarrow \infty$ the Poisson distribution approaches the normal distribution $\mathcal{N}(\lambda, \sqrt{\lambda})$.

• a) Using the assumptions $n \gg 1, p \ll 1$ and denoting $np \equiv \lambda$ we get

$$\begin{aligned} P(k) &= \binom{n}{k} p^k (1-p)^{n-k} \approx \frac{n(n-1)\dots(n-k+1)}{k!} p^k (1-p)^n = \\ &= \frac{n(n-1)\dots(n-k+1)}{k!} p^k \left(1 - \frac{\lambda}{n}\right)^n \approx \frac{n^k p^k}{k!} e^{-np} = \frac{\lambda^k}{k!} e^{-\lambda}. \end{aligned}$$

The fact that λ is also the mean value for the variable k , follows from the relation $\lambda = pn$ (since pn is the mean value of the binomial distribution). One can also

prove this fact by explicit substitution of $P(k)$ into the definition of the mean value. We get

$$\langle k \rangle = \sum_{k=0}^{\infty} k P(k) = \sum_{k=1}^{\infty} k \frac{\lambda^k}{k!} e^{-k} = \lambda \sum_{k=1}^{\infty} \frac{\lambda^{k-1}}{(k-1)!} e^{-k} = \lambda \sum_{l=0}^{\infty} P(l) = \lambda.$$

b) We shall investigate the limit $\lambda \gg 1$. Using the Stirling formula $\ln n! \approx n \ln n - n + \frac{1}{2} \ln n + \ln \sqrt{2\pi}$ and the expansion $\ln(1+y) \approx y - y^2/2$ ($y \ll 1$) we get

$$\begin{aligned} \ln P(k) &\approx k \ln \lambda - \lambda - k \ln k + k - \frac{1}{2} \ln k - \ln \sqrt{2\pi} = \\ &= (\lambda + x) \ln \lambda - \lambda - (\lambda + x) \ln [\lambda(1 + x/\lambda)] + \lambda + x - \frac{1}{2} \ln [\lambda(1 + x/\lambda)] - \\ &\quad - \ln \sqrt{2\pi} \approx -(\lambda + x) \left(\frac{x}{\lambda} - \frac{x^2}{2\lambda^2} \right) + x - \ln \sqrt{\lambda} - \frac{x}{2\lambda} + \frac{x^2}{4\lambda^2} - \ln \sqrt{2\pi} \approx \\ &\approx -\frac{x^2}{2\lambda} - \ln \sqrt{2\pi\lambda} = \ln \left\{ \frac{1}{\sqrt{2\pi\lambda}} \exp \left[-\frac{(k-\lambda)^2}{2\lambda} \right] \right\}. \end{aligned}$$

Here we have denoted $k = \lambda + x$ (we assume $x \ll \lambda$) and at the end of the calculation we neglected the terms x/λ , x^2/λ^2 and x^3/λ^2 . We see that the Poisson distribution in the limit $\lambda \rightarrow \infty$ approaches the normal distribution $\mathcal{N}(\lambda, \sqrt{\lambda})$. ■

Exercise

The matrix elements x_{ij} of the matrix X of the dimension $n \times n$ are equal to $+1$ or -1 with the same probability $1/2$, the matrix elements values are independent of each other. What is the mean value of the square $|X|^2$ of the determinat of that matrix?

2.5 Random numbers

Generic random number generator

```
i := (i*k) mod N
r := i;
r := r/N; //this is real number arithmetic
return(r)
```

Typically the procedure is called as a parameterless function like `RND()`. The value of i is kept locally inside the procedure for the next call, so each time the function is called a different value r is returned.

The initial value of i is called seed. The seed can be set during the initialization of the generator and this enables to get identical sequences of pseudo-random numbers.

Present day random number generator are more sophisticated then our generic example. But some features remain true

- existence of starting "seed value"
- finite number of generated numbers, random generators show cyclic behavior: our generic example can generate at most N different random numbers, then it cycles. Modern generators have extremely large cycles.

Default random number generators produces uniformly generated random numbers in the interval (0, 1). If one needs random numbers distributed according to some non-uniform probability density $\varrho(x)$, one has to perform a suitable software transformation.

The key is Monte Carlo integration

$$\bar{f} = \int_a^b f(x)dx$$

The mean value can be determined "experimentally"

$$\bar{f} = \frac{1}{N} \sum_1^N f(a + RND() * (b - a))$$

this is a default Monte Carlo integration algorithm.

We want to calculate by Monte Carlo the integral

$$\int_{-\infty}^{\infty} f(x)\varrho(x)dx$$

but we want to use random generator generating x distributed according to $\varrho(x)$
The key is the substitution to integral using "inverse to primitive"

$$x = F^{-1}(\xi)$$

where

$$F(x) = \int_{-\infty}^x \varrho(x')dx'$$

is the primitive function to probability density, so it is the cumulative probability distribution function. Its inverse is therefore defined on the interval

$$\xi \in (0, 1)$$

The substitution is

$$dx = \frac{1}{F'}d\xi = \frac{1}{\varrho(F^{-1}(\xi))}d\xi$$

and we get

$$\int_{-\infty}^{\infty} f(x)\varrho(x)dx = \int_0^1 d\xi f(F^{-1}(\xi))\varrho(F^{-1}(\xi))\frac{1}{\varrho(F^{-1}(\xi))} = \int_0^1 d\xi f(F^{-1}(\xi))$$

We see that the integral can be calculated by the following Monte Carlo

$$\int_{-\infty}^{\infty} f(x)\varrho(x)dx = \frac{1}{N} \sum_1^N f(F^{-1}(RND()))$$

So random variable x distributed according to the probability density $\varrho(x)$ is generated by the algorithm

$$x = F^{-1}(RND())$$

This, however, requires that we can analytically calculate the primitive function and its inverse, what is not always possible. In such a case we have to use numerical methods. The above described method is usually called "importance sampling". An obvious method is that we numerically tabulate the primitive function choosing some suitable set of points $\{x_i\}$:

$$y_i = F(x_i) = \int_{-\infty}^{x_i} \varrho(x')dx'$$

and we use some suitable interpolation method between the points. Now the procedure is as follows

- generate randomly $\xi = RND()$
- find i such that $y_i < \xi < y_{i+1}$
- find by inverse interpolation the value x , $x_i < x < x_{i+1}$ corresponding to ξ . That is the generated random number x .

Another method which can be used if $\varrho(x)$ is defined on the finite interval (a, b) if we know, that $\varrho(x)$ is majorized by some value M :

$$\forall x \in (a, b) : 0 < \varrho(x) < M$$

Then the algorithm for generating random numbers x distributed according to $\varrho(x)$ proceeds as follows

- we generate randomly a point (ξ, η) in the "bounding rectangle" that is $\xi = a + (b - a) \times RND()$ and $\eta = M \times RND()$
- if the generated point (ξ, η) is below the curve ϱ , that is if $\eta < \varrho(\xi)$ we accept value ξ as the generated value x

- otherwise we repeat the process by generating a new point (ξ, η)

It is obvious that we can in this way "experimentally" determine the area below the curve $\varrho(x)$ (what percentage of the bounding rectangle it occupies) and so the method correctly generates the points distributed according to density ϱ

Exercise

Design the random number generator for the normally distributed numbers using the uniformly distributed random number generators. (This can be done exactly even the normal distribution does not have cumulative distribution function which could be expressed analytically.)

- We cannot directly express analytically the primitive function to the most important probability distribution, the normal distribution (the primitive function to normal distribution is called the error function $\text{erf}(\cdot)$). Fortunately, it is possible to perform the importance sampling analytically for the two-dimensional Gauss distribution and then generate the one dimensional distribution as a projection of the two dimensional one.

The two-dimensional normal distribution has the form

$$\rho(x, y) = \frac{1}{2\pi\sigma^2} \exp\left(-\frac{x^2 + y^2}{2\sigma^2}\right)$$

The trick is to use the radial coordinates r, φ . The probability density expressed in these variables factorizes into two marginal distributions. For both of them we know the corresponding primitive function and also its inverse²

In the cylindrical coordinates we get

$$\tilde{\rho}(r, \varphi) = \frac{1}{\sigma^2} r \exp\left(-\frac{r^2}{2\sigma^2}\right) \frac{1}{2\pi}$$

The marginal distribution in the variable r is

$$\rho_r(r) = \frac{1}{\sigma^2} r \exp\left(-\frac{r^2}{2\sigma^2}\right)$$

The marginal distribution of the variable φ is

$$\rho_\varphi(\varphi) = \frac{1}{2\pi}$$

²The distribution factorizes also in Cartesian coordinates, but the marginal distributions are the one-dimensional normal distributions for which the primitive functions cannot be analytically expressed.

The primitive function to the marginal distribution $\rho_r(r)$ is

$$F_r(r) = \int_0^r dr' \frac{1}{\sigma^2} r' \exp\left(-\frac{r'^2}{2\sigma^2}\right) = 1 - \exp\left(-\frac{r^2}{2\sigma^2}\right)$$

and so the generator for of r will be its inverse

$$r = \sqrt{-2\sigma^2 \ln(1 - \text{RND}())}$$

The variable defined as $(1 - \text{RND}())$ is just another random variable uniformly distributed in the interval $(0, 1)$, so we can rewrite the last expression as

$$r = \sqrt{-2\sigma^2 \ln(\text{RND}())}$$

The generator for the variable φ is trivial

$$\varphi = 2\pi \text{RND}()$$

So the one-dimensional normally distributed variable can be generated as

$$x = \sqrt{-2\sigma^2 \ln(\text{RND}())} \cos(2\pi \text{RND}())$$

■.

Exercise

Bertrand's paradox

Seemingly well defined task may be to find the probability that the length of a randomly chosen circle chord is greater than the side of an equilateral triangle inscribed into that circle. Paradox is hidden in the fact, that the statement "randomly chosen circle chord" is not well defined. Different specification of its exact meaning lead to different results. Do find at least two such different specifications.

- If we randomly choose the chord by randomly choosing the angle between two points on the circle, the the result is $p_1 = 1/3$. If we randomly choose a point from the disk as a center of the chord the result is $p_2 = 1/4$. ■

Exercise

Benford's law

Let us consider a set of some data like lengths of rivers in the world, actual stock market prices, thermal capacities of different substances etc. Benford (1938) noticed that the probability distribution of a value of the first digit within the data set is not uniform as one would naively expect. The digits 1 to 9 appear with the probabilities $\{0.301, 0.176, 0.125, 0.097, 0.079, 0.067, 0.058, 0.051, 0.046\}$. The key observation is that this distribution has to be invariant with respect to the change of scale (for example the unit length in which the lengths are expressed or the currency in which the prices are expressed). Find the appropriate probability distribution.

- The probability distribution has to be scale invariant what means that changing $x \mapsto kx$ has to lead to $P(kx) = f(k)P(x)$ (the distribution $P(x)$ has the same shape). Since $\int P(x) dx = 1$, that the constrain $P(kx) d(kx) = 1$ leads immediately to $f(k) = 1/k$. Differentiating scaling expression with respect to k and setting $k = 1$ we get $xP'(x) = -P(x)$. This equation has the solution $P(x) = 1/x$. This is not a correct probability distribution, since the integral $\int P(x) dx$ diverges. However, one cannot take the expression literally, since in real situations each data set has a natural cut-offs both at high and at low values of x .

Now the probability of the digit C to be the first digit is

$$P_C = \frac{\sum_n \int_{C \times 10^n}^{(C+1) \times 10^n} P(x) dx}{\sum_n \int_{1 \times 10^n}^{10 \times 10^n} P(x) dx} = \log_{10} \left(1 + \frac{1}{C} \right),$$

what corresponds to Benford observations. ■

2.6 Selected items from statistics

We start with a normally distributed variable x .

$$\varrho(x) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{x^2}{2}\right)$$

Now we form a new random variable

$$y = x^2$$

Its probability density is

$$\varrho_y(y) = \int \varrho(x) \delta(y-x^2) dx = \Theta(y) \left(\frac{1}{\sqrt{2\pi}} \exp\left(-\frac{y}{2}\right) \frac{1}{2\sqrt{y}} + \text{term with the negative root} \right)$$

$$\varrho_y(y) = \frac{1}{\sqrt{y}} \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{y}{2}\right)$$

This is a special case of a more general " χ^2 distribution with n degrees of freedom"

$$\varrho_{\chi^2}(x) = \frac{1}{2^{n/2} \Gamma(\frac{n}{2})} x^{\frac{n}{2}-1} \exp\left(-\frac{x}{2}\right)$$

So we see that the square of a gaussian variable is distributed according to the χ^2 distribution with 1 degree of freedom.

Now we look for the characteristic function of the χ^2 distribution.

$$\begin{aligned}
 f_{\chi^2}(k) &= \int e^{ikx} \frac{1}{2^{n/2}\Gamma(\frac{n}{2})} x^{\frac{n}{2}-1} \exp(-\frac{x}{2}) dx = \\
 &= \frac{1}{2^{n/2}\Gamma(\frac{n}{2})} \int x^{\frac{n}{2}-1} \exp(-x(\frac{1}{2} - ik)) dx = \\
 &= \frac{1}{2^{n/2}\Gamma(\frac{n}{2})} \frac{1}{(\frac{1}{2} - ik)^{n/2}} \int_0^{(1/2-ik)\infty} d\xi \xi^{n/2-1} \exp(-\xi) = \\
 &= \frac{1}{(1 - 2ik)^{n/2}}
 \end{aligned}$$

In the derivation a manipulation with integration path in the complex ξ -plane was needed.

We see that the characteristic function is a n -fold product, so it is a Fourier transform of a n -fold convolution. So it is clear, that the probability density corresponds to n -fold sum of squares of gaussian variables.

If x_1, x_2, \dots, x_n are independent draws from a normal $N(0, 1)$ distribution, then the random variable

$$y_n = \sum_i x_i^2$$

is distributed as χ^2 with n degrees of freedom.

This fact is used to test statistical hypotheses. The model example looks as follows.

Suppose we have a container of random values x said to be distributed according to normal distribution $N(\mu, \sigma)$. We want to verify the fact experimentally. The procedure is

- We formulate a null-hypothesis according to which the assumed fact is true: that is we assume that the random values in the container are really distributed according to $N(\mu, \sigma)$.
- We perform an experiment: draw n independent samples x_1, \dots, x_n .
- We calculate the statistics

$$\chi^2 = \sum_1^n \frac{(x - \mu)^2}{\sigma^2}$$

According to the null-hypothesis this variable should be distributed as chi-squared with n degrees of freedom.

- The value of χ^2 obtained in the previous step is checked for probability. That is we evaluate the probability p that a chi-squared distribution can give value as observed or higher

$$p = \int_{\chi^2}^{\infty} \varrho_{\chi^2}(x) dx$$

- If the obtained value p is very small (like $\lesssim 0.001$) we say that it is very improbable that we have such a bad-luck that we observe such a big deviation from the expected null-hypothesis-behaviour. So we reject the null-hypothesis. If the value p is not small enough, we say that it may be that the value χ^2 we have observed is due to a fluctuation and we keep the null hypothesis as valid.

Another use of chi-squared distribution for statistical testing is given by the following Pearson theorem.

We have r histogram bins, and the expected probabilities for a random event to fall into the i -th bin are p_i . We observe n random events and the actual number of hits in the i -th bin are n_i . Then the statistics

$$\chi^2 = \sum_1^r \frac{(n_i - np_i)^2}{np_i}$$

is distributed as chi-squared with $(r - 1)$ degrees of freedom.

The use of this theorem for test is obvious.

- We assume we know the expected probabilities p_i and as the null hypothesis we assume they are true.
- We perform the experiment and observe the actual number of hits n_i and calculate the statistics χ^2 .
- We calculate what is the probability p to observe the value χ^2 as observed or even higher.
- If p is reasonably small we reject the null hypothesis and say that the true probabilities are different from those expected.

What we have just described is the use of the Pearson theorem for a goodness-of-fit test. The other often used possibility is the test-of-independence. We shall present the idea on the following example.

We consider a clinical study (experiment) the aim of which is to test which of the two available drugs (DRUG1, DRUG2) is better for treatment of a particular disease. The study is organized as follows. The patient having the disease are randomized (chosen randomly) for treatment either with DRUG1 or DRUG2. Then their health state is observed and classified into two categories RESPONSE (these are patients whose disease positively reacted to the treatment) and NO RESPONSE (those for whom the treatments did not have the required effect). Then a "contingency table" is created where number of patients of each category is entered. The contingency table for our case is a 2×2 matrix and is defined by the white fields in the following table

	DRUG1	DRUG2	Totals
RESPONSE	15	8	23
NO RESPONSE	7	5	12
Totals	22	13	35

What we have is objects (patients) categorized according to two "features". The first feature is "type of drug" and can have two discrete values (DRUG1, DRUG2). Two columns in the contingency table correspond to these two different values of the feature 1. The other feature is "type of response" and can also have two discrete values (RESPONSE, NO RESPONSE). Two rows of the contingency table correspond to two values of the feature 2. In a more general case we shall have two features, so the table will be again two dimensional, but there may be more values for both features, so the table can have more rows and/or columns. our aim is to recognize whether one of the two drugs is more efficient than the other. This is scientifically not quite well defined question. Science is methodologically more about disproving things than about proving. So we formulate a null hypothesis: the two drugs are equally efficient. In a more mathematical way the null hypothesis is formulated as: The feature 1 and the feature 2 are statistically independent.

What it means for the contingency table?

There are four categories of patients in our table (number of rows *times* number of columns). The actual number of entries in each category can be denoted as N_{ij} . So for example N_{21} is the observed number of patients in the second row and first column, that is it is the number of patients treated by the DRUG1 with status NO RESPONSE, so $N_{21} = 7$ in our table. The independence of features means that the probability for a patient to enter a particular row is independent on what column it enters and the probabilities to enter a particular cell factorize. If the null hypothesis holds, then a set of parameters r_1, r_2, c_1, c_2 must exist which give the probabilities to enter the rows 1 and 2 and columns 1 and 2, respectively. If there were no statistical fluctuations then the observed numbers of hits should be

$$N_{ij} = N r_i c_j$$

where N is the total number of patients. Now the task is twofold

- Estimate the optimal values of parameters r_1, r_2, c_1, c_2 which best describe the observed data provided the null hypothesis holds
- Test whether the optimal parameters really describe the observed data well or the description is so poor that we should abandon the null hypothesis.

To estimate the optimal parameters we introduce the following notation

$$N_{i+} = \sum_j N_{ij}$$

$$N_{+j} = \sum_i N_{ij}$$

These variables describe the number of hits of particular row (or column) and are entered as "totals" in the above contingency table. For the total number of patients we get

$$N = \sum_{i,j} N_{ij} = \sum_i N_{i+} = \sum_j N_{+j}$$

Now it is intuitively clear³ that

$$r_i = \frac{N_{i+}}{N} \quad c_j = \frac{N_{+j}}{N}$$

So the expected number of hits E_{ij} in the cell (i, j) , provided the null hypothesis holds and fluctuations are zero, is

$$E_{ij} = N r_i c_j = \frac{N_{i+} N_{+j}}{N}$$

So we create another contingency table containing not the observed but rather the expected numbers of hits. Here it is

	DRUG1	DRUG2	Totals
RESPONSE	14.457	8.543	23
NO RESPONSE	7.543	4.457	12
Totals	22	13	35

Now the question reads: are the differences between the two contingency tables (observed versus expected) so big, that it is improbable they are due to statistical fluctuations? We construct an obvious statistics

$$\chi^2 = \sum_{i,j} \frac{(N_{ij} - E_{ij})^2}{E_{ij}}$$

³The argumentation can be based on maximizing the likelihood, we shall discuss this method later in these lectures

This variable (for large enough values of entries in the contingency tables) should be distributed as chi-squared with $(r - 1) \times (c - 1)$ degrees of freedom⁴.

For our case the number of degrees of freedom is 1. The value of χ^2 we get is 0.16. In the suitable tables of cumulative distribution function for the chi-squared distribution we find that the probability to observe this value or greater is $p = 0.69$. So we see that we cannot reasonably reject the hypothesis that the two drugs are equally efficient, the number of patients is just not high enough to arrive at a significant conclusion.

Actually, we do not need tables of cumulative chi-squared distributions. In Excell there is a convenient statistical function CHITEST which returns the value of p , the usage is well documented in Excell's help.

We now describe without any details another common task of statistics which comes under logo "Student test".

The Student distribution with n degrees of freedom is defined by the probability density

$$\varrho_t(x) = \frac{\Gamma(\frac{n+1}{2})}{\Gamma(\frac{n}{2})\sqrt{\pi}\sqrt{n}} \left(1 + \frac{x^2}{n}\right)^{-(n+1)/2}$$

It can be shown that if we have $(n + 1)$ samples

$$x_0, x_1, x_2, \dots, x_n$$

from the normal $N(0, 1)$ distribution, then the statistics

$$t = \frac{x_0}{\sqrt{\frac{1}{n} \sum_{i=1}^n x_i^2}}$$

is distributed according to the Student distribution with n degrees of freedom

The generic example looks as follows. We have two containers said to contain normally distributed samples of the same gaussian distributions $N(\mu, \sigma)$ with unknown but equal values of the parameters μ and σ . We make n draws from the first container, getting the sequence of random values

$$x_1, x_2, \dots, x_n$$

and m draws from the second container getting the sequence

$$y_1, y_2, \dots, y_m$$

⁴We did not prove the statement. it is just intuitively clear that the table with r rows and c columns has just $(r - 1) \times (c - 1)$ independent degrees of freedom, since the sum of probabilities in each row and column should be equal to 1.

The null hypothesis is that the two containers are truly equivalent. The question is can we rule out the null hypothesis on basis of the observed events?

The procedure is as follows

- Calculate the sample means

$$\bar{x} = \frac{1}{n} \sum_i x_i \quad \bar{y} = \frac{1}{m} \sum_i y_i$$

- calculate sample variances

$$s_x^2 = \frac{1}{n-1} \sum_i (x_i - \bar{x})^2 \quad s_y^2 = \frac{1}{m-1} \sum_i (y_i - \bar{y})^2$$

- calculate the statistics t

$$t = \frac{\bar{x} - \bar{y}}{\sqrt{\frac{(n-1)s_x^2 + (m-1)s_y^2}{n+m-2} \left(\frac{1}{n} + \frac{1}{m} \right)}}$$

- the random variable t should have the Student distribution with $(n+m-2)$ degrees of freedom. Usually it is $|t|$ which matters and we ask what is the probability that the absolute value of a student-distributed variable is greater than the value we have observed. So we have to integrate both the left and the right tail of the distribution to get the probability which we consider for estimating the significance.

2.7 Bayesian statistics

See also [Jaynes], arXiv:hep-ph/9512295.

First works on mathematical statistics of authors as Gauss, Pascal, Bernoulli, Bayes significantly differ in spirit from the present day approach of, say Fisher, Pearson, and Neymann. The Bayesian statistics based on the Bayes relation for the conditional probability is a sort of come-back to the original approach. Its principle can be symbolically expressed by the following scheme

prior probability + data obtained \longrightarrow posterior probability

The prior probability here measures our complete knowledge obtained before the experiment considered, the posterior probability corresponds to our knowledge

after the process of the considered data evaluation. The scheme looks rather mysteriously. To understand it better we have to discuss its different parts.

For example we said that the prior probability measure our complete knowledge. How it is possible? If we understand the notion of probability as the ratio of the number favorable events to the number of all events, it cannot measure knowledge. As an alternative here we consider the probability to be the measure of our **confidence** of a realization of a particular event. The limiting values are 0 for the events we consider to be impossible and 1 for the events we consider to be certain. This approach seems to lack objectiveness, but otherwise it is reasonable that a plausible definition of a "measure of knowledge" fulfills the following axioms

- additivity for disjoint events: $A \cap B = \emptyset \implies P(A \cup B) = P(A) + P(B)$ (more exactly one should consider here the countable additivity)
- normalization: $P(\Omega) = 1$,
- nonnegativity: $P(X) \geq 0$
- continuity at zero: if the set series $X_1 \supseteq X_2 \supseteq X_3 \supseteq \dots$ approaches the empty set, then $P(X_i) \rightarrow 0$

These are, however the Kolmogorov axiom of probability theory⁵.

The advantage of understanding the probability as a measure of knowledge is the possibility to use it also in situations where the repetition of experiments is not possible, like the probability of the result of a particular football match. Moreover, in physics we often need to set confidence intervals for various quantities (these are intervals where the value lays with certain probability, like 95%). In this case the probability understood as a rate of favorable events does not have sense: the value either lays within the interval or not. What is questionable is our confidence for both possibilities. So saying it again in a short way: the probability need not be the result of a random process we model by it our knowledge (or ignorance).

The next reasoning is heavily based on the Bayes relation for the conditional probability, so we start by deriving it. Let A be some event and $\{B_i\}$ is a set of disjoint events such that $\cup B_i = \Omega$. The definition of conditional probability leads to the equality $P(A \cap B_i) = P(A)P(B_i|A)$ and in the same time

⁵A small side note. A useful test of the correctness of the probability assignment is to investigate the fairness of a bet (that is to check whether the mean win on both sides is zero). If we assign the probability of 20% to some event, we should be ready to bet 1\$ for the possibility to gain $1\$/20\% = 5\%$ when the event really happens. In a same way we should be ready to bet 1\$ for the possibility to gain $1\$/80\% = 1,25\%$ if that event does not happen

$P(A \cap B_i) = P(B_i \cap A) = P(B_i)P(A|B_i)$. Comparing these two relations we get

$$P(B_i|A) = \frac{P(B_i)P(A|B_i)}{P(A)}.$$

The event A may happen so that some of the events B_i happens and then with the probability $P(A|B_i)$ also the event A . This statement can be mathematically expressed as $P(A) = \sum_i P(B_i)P(A|B_i)$. Inserting this into the above equation we get

$$P(B_i|A) = \frac{P(B_i)P(A|B_i)}{\sum_i P(B_i)P(A|B_i)}.$$

Now we rename the entries in the Bayes formula to correspond more clearly to the context in which we shall use it

$$P(M_i|\mathcal{D}) = \frac{\pi(M_i)P(\mathcal{D}|M_i)}{\sum_i \pi(M_i)P(\mathcal{D}|M_i)}.$$

Here M_i denotes competing models, \mathcal{D} the data obtained, $\pi(M_i)$ the prior probability of the model M_i and $P(\mathcal{D}|M_i)$ the probability to observe the data assuming validity of the M_i . The left side of the relation, $P(M_i|\mathcal{D})$, is the posterior probability. We shall demonstrate the practical use of the formula by several examples.

Exercise

The basic exercise on conditional probability

We have two bags X and Y , both of them contain a large number of balls. The first bag contains 20% of white balls, the second one 40%. Now we draw 9 balls out of the same bag and it happens that 3 of them are white. What is the probability that we have been drawing from the bag X ?

- We have here two competing models, that is drawing from the bag X and drawing from the bag Y . We denote the ratios of white balls in the bags as $n(X)$ and $n(Y)$. Now the probabilities of drawing 3 white balls out of 9 drawn are

$$P(9G, 3B|X) = \binom{9}{3}n(X)^3(1 - n(X))^6 \doteq 0.176,$$

$$P(9G, 3B|Y) = \binom{9}{3}n(Y)^3(1 - n(Y))^6 \doteq 0.251$$

The random choice of the bag is described best by the prior probabilities $\pi(X) = \pi(Y) = 0.5$. Then

$$P(X|9G, 3B) \doteq 41\%, \quad P(Y|9G, 3B) \doteq 59\%.$$

We see that the data obtained do not provide much information which bag was chosen for drawing. ■

Exercise

Concerning conditional probability

The contestant in the TV competition is given the following task. He should choose one of three boxes, knowing that the win is hidden in one of them, the other two are empty. When he points to one box, the TV moderator (knowing which box contains the reward) opens one of the remaining boxes which he is sure is empty. Now he allows the competitor to make his mind again an change his choice if he wants. What the competitor should do, should he change his choice and point to the the closed box?

- At the first sight it seems that no relevant information was provided in the system and so it is no sense in changing the choice. However, more careful reasoning shows that the change of choice is really advantageous.

So at the beginning one box is chosen randomly. If the choice was a lucky one (this is with the probability $1/3$), the change of the choice is bad, we loose the win. However if the original choice was bad (and this is with the probability $2/3$), the change of choice leads to a sure win. So the strategy to change the choice leads to a win with the probability $1/3 \cdot 0 + 2/3 \cdot 1 = 2/3$. If we keep the original choice we win only with the probability $1/3$. ■

Exercise

We play a gambling game. If our opponent is fair, the probability of loosing the game is $P_0 = 1/2$. Before we start we estimate the prior probability that our opponent would be cheating as $\pi(C)$ The game begins and we loose in n consecutive rounds. To what extent do we trust our oponent now.

- The event which happened (n consecutive loses) we denote by L_n , an honest oponent will be denoted by \check{H} , cheater by C . The following relation holds $P(L_n|\check{H}) = (1/2)^n$, $P(L_n|C) = 1$. Then

$$P(C|L_n) = \frac{\pi(C) \times 1}{\pi(C) \times 1 + (1 - \pi(C)) \times (1/2)^n}.$$

It is worth to notice that for arbitrary $\pi(C) > 0$ the $\lim_{n \rightarrow \infty} P(C|L_n) = 1$. On the other hand if $\pi(C) = 0$ (it means that we absolutely trust our opponent) the posterior probability $P(C|L_n) = 0$ for arbitrary n . That means we shall trust the opponent whatever results we observe.

This example demonstrate in a very simplified way the development of knowledge in physics. Obtaining more data leads to changes of our knowledge about the observed system. However, we also see, that our prior knowledge is absolutely essential. In the gambling game it determines how we evaluate our strategy: it determines the number of lost rounds after which we accuse our oponent of cheating. ■

The generalization of the Bayes relation for the case of continuous class of models is obvious: we just substitute the sum by an integral.

Let us investigate its use in the simple example of fitting the data by a straight line. This simple example will also manifest better the relation between the classical and Bayesian statistics.

We have results of some measurement, the set of data points $\{x_i, y_i\}$ for $i = 1, \dots, N$. According to theory, the relation between x a y should be a linear one $y = Ax + B$. What values of A a B correspond best to the observed data?

If we measured absolutely exactly, we should obtain for each x_i the value $y_i^* = Ax_i + B$. Now let us assume, that the deviations from this value (measurement errors) are distributed normally with the standard deviation σ and the mean $\mu = 0$. This assumption is essential and is usually justified by the central limit theorem. The probability that for x_i we obtain the value y_i is

$$P(y_i|A, B) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{(y_i - Ax_i - B)^2}{2\sigma^2} \right].$$

The probability to obtain the whole observed set of values $\{y_i\}$ is

$$P(\{y_i\}|A, B) = \frac{1}{(\sqrt{2\pi}\sigma)^N} \exp \left[-\sum_{i=1}^N \frac{(y_i - Ax_i - B)^2}{2\sigma^2} \right].$$

This is so called likelihood function. Now let be non-Bayesian (frequentist) for a moment. Then the likelihood function is all we need and we estimate the best values for A a B by maximizing the likelihood function $P(\text{data}|\text{parameters})$. The above expression shows that the maximum is achieved when the sum of the squares of deviations is minimal. The estimates \hat{A} a \hat{B} are given as

$$\hat{A}, \hat{B} = \underset{A, B}{\operatorname{argmin}} \left\{ \sum_{i=1}^N (y_i - Ax_i - B)^2 \right\}.$$

So we have ended with the old good least squares method⁶.

⁶We have assumed, that we know the value of σ . For example, the value might be printed on the apparatus we use for measuring the y_i data values. It is easy to imagine, that we do not know σ a-priori. Then we can consider σ to be another parameter of the model describing the data, that is we now have three unknown parameters A, B, σ . And we can determine *sigma* by maximizing the likelihood

$$\hat{A}, \hat{B}, \hat{\sigma} = \underset{A, B, \sigma}{\operatorname{argmax}} \frac{1}{(\sqrt{2\pi}\sigma)^N} \exp \left[-\sum_{i=1}^N \frac{(y_i - Ax_i - B)^2}{2\sigma^2} \right]$$

Notice that in this case we did not get just the minimization of the square deviations, since the parameter σ appears also in the gaussian normalization factors which are essential to get the reasonable value for σ . Trying just to minimize the expression

$$\sum_{i=1}^N \frac{(y_i - Ax_i - B)^2}{2\sigma^2}$$

we would (wrongly) get $\sigma = \infty$.

Does this mean, that the least squares method is our golden calf? Not at all. We should notice the hidden assumptions. At first it was the assumption on normal distributions of the measurement errors. Within the Bayesian spirit, however, we should also consider the prior probability $\pi(A, B)$. Our main interest is not the likelihood function, but the posterior probability of the values of A and B after observing $\{y_i\}$. According to the Bayes formula it is given as

$$\begin{aligned} f(A, B|\{y_i\}) &= \frac{\pi(A, B) P(\{y_i\}|A, B)}{\int \pi(A, B) P(\{y_i\}|A, B) dAdB} = \\ &= \frac{\pi(A, B)}{C(\sqrt{2\pi}\sigma)^N} \exp \left[- \sum_{i=1}^N \frac{(y_i - Ax_i - B)^2}{2\sigma^2} \right]. \end{aligned}$$

The denominator of the fraction plays no role for the further consideration and is denoted simply by C . The maximum of the posterior probability differs in general from the maximum of the likelihood function.

So we briefly repeat the basic scheme. The Bayes formula contains $P(\mathcal{D}|M_i)$, what is the probability of observing the data assuming the model M_i is true. This object plays role also in classical statistics and is called the likelihood function. Classical statistics then estimates the values of the unknown parameters M_i based on the observed data \mathcal{D} by maximizing the likelihood function. In the case no prior information is available such a strategy is natural. An equivalent result is obtained within the Bayesian approach if we use equal prior probabilities for all models ($\pi(M_i) = C$).

However, it must be stressed that for continuous probabilities the notion of "equal probabilities" is not well defined, since it is heavily dependent on the used parametrization. Using a specific parametrization is equivalent to using a specific prior probability. Changing the parametrization, say from x to $y = x^2$, changes the location of the likelihood function maximum.

Problems with prior probabilities lead many people to consider the Bayesian statistic as inferior to the classical one. They do not like the "additional freedom" represented by the prior probability. We have seen, however, that the same freedom is implicitly hidden in the classical approach. The Bayesian approach just displays this freedom fairly in explicit way. On the other hand a certain relief of concern can be found in the fact that asymptotically (for infinite amount of observational data) the results do not depend on the prior probabilities⁷.

A final remark. The result of the Bayesian analysis is the posterior probability of models (in the continuous case it is the probability density). This complete information is sometimes felt as superfluous: people prefer to get a specific number

⁷This is strictly true only if the prior probability is not equal to zero in some region. In that case even a large amount of data cannot create a non-zero posterior probability in that region.

rather than the probability distribution. The posterior probability is therefore often used to get just its mean value or the point of its maximum, depending on a specific situation. Of course, a lot of information is lost by such a process. When further data gathering is expected, it is wise to keep the complete posterior probability and use it as a prior probability for the later analysis.

Exercise

Data analysis for the experiment measuring the mass m of some particle lead to the result $m = -0.3 \pm 1.0$ eV. Later it was realized that the mass is a positive quantity. What is the correct posterior probability distribution after including this fact into the analysis? What is the mean mass value?

- We represent the initial data analysis by the formula $f(D|m) \sim \exp[-(m + 0,3)^2/2]$, the prior probability⁸ $\pi(m) = \vartheta(m)$ ($\vartheta(m)$ is equal to zero for negative m and equal to 1 for positive m). Then

$$f(m|D) = \frac{\vartheta(m) \exp[-(m + 0,3)^2/2]}{\int \vartheta(m) \exp[-(m + 0,3)^2/2] dm} \implies \langle m \rangle \doteq 0,7 \text{ eV.}$$

The last value is a numerical estimate. ■

Exercise

We are performing an experiment measuring a dimensionless quantity b . According to our prior knowledge the value of b is 10 ± 7 (Gauss distribution is assumed here). We obtain two new experimental values $b_1 = 4$ and $b_2 = 6$. We assume our measurement has Gaussian error distribution with $\sigma = 4$.

- Express our final knowledge ($? \pm ?$) about b
- What would be the estimate for b in limiting cases $\sigma \rightarrow 0$ and $\sigma \rightarrow \infty$?

- The parameter to be determined is the value of b . Then

$$\pi(b) = \frac{1}{\sqrt{2\pi} \cdot 7} \exp \left[-\frac{(b - 10)^2}{2 \times 7^2} \right].$$

The probability that by one measurement the value x is obtained is

$$P(x|b) = \frac{1}{\sqrt{2\pi} \cdot 4} \exp \left[-\frac{(x - b)^2}{2 \times 4^2} \right].$$

Notice the different values for the standard deviations in the prior probability of b and in the probability describing the measurement process.

⁸More exactly we should use some normalized function for example by introducing cut-off at very large values of m .

a) Using Bayes formula we get (with the normalization factors canceled out)

$$P(b|\text{data}) = \frac{\exp \left[-\frac{(b-10)^2}{2 \times 7^2} - \frac{(4-b)^2}{2 \times 4^2} - \frac{(6-b)^2}{2 \times 4^2} \right]}{\int_{-\infty}^{\infty} \exp \left[-\frac{(b-10)^2}{2 \times 7^2} - \frac{(4-b)^2}{2 \times 4^2} - \frac{(6-b)^2}{2 \times 4^2} \right] db}.$$

The distribution $P(b|\text{data})$ is a normal distribution its maximum is in the same point as the mean value and the median We therefore do not need to consider various possibilities for expressing the estimate the result is $\hat{b} = 325/57 \doteq 5.7$. For the root mean squared we get $\hat{\sigma}^2 = 392/57$ a $b = 5,7 \pm 2,6$.

b) The limit $\sigma \rightarrow 0$ means that the measurement is extremely precise, therefore the final estimate should not depend on the prior probability. However, it is contradictory to get two different values for the same quantity if the measurement is absolutely precise. So this case is not self consistent. For the limit $\sigma \rightarrow \infty$ the new measurement has no significance at all and the posterior probability will be equal to the prior one.

2.8 Best fit. Parameter error estimation

We add here a section on fit-parameter error estimation. To simplify the discussion we consider a single parameter fit. If there are more parameters, parameter correlations should be taken into account⁹. We shall consider just a simple single parameter linear fit, but the linearity is not essential for the considerations here. So suppose we have a set of data points

$$\{y_i, x_i\}$$

The values x_i are supposed to be known precisely, the values y_i are measured with known error (variance) σ_i^2 . We want to find the best fit of the form

$$y = kx$$

with unknown parameter k to be determined by the fitting procedure. So in the language of the previous section k represents "the theory", The likelihood function (probability to obtain data for a given theory k) is

$$P(\{y_i\}|k) = \prod_i \frac{1}{\sqrt{2\pi\sigma_i^2}} \exp\left(-\sum_i \frac{(y_i - kx_i)^2}{2\sigma_i^2}\right) = C \exp\left(-\frac{1}{2}\chi^2(k)\right)$$

⁹Introductory discussion can be found in F. James, The Interpretation of Errors in Minuit <http://seal.cern.ch/documents/minuit/mnerror.pdf>

where C is a normalization constant¹⁰ and

$$\chi^2(k) = \sum_i \frac{(y_i - kx_i)^2}{\sigma_i^2}$$

is the standard chi-squared statistics we would use for hypothesis testing were the value of k given. See the correct normalization factor $1/2$ in the exponent in front of χ^2 . Now maximizing likelihood means minimizing chi-squared. So suppose we performed the minimization and found the optimal value k_0 . We want to know the precision of the fit parameter value k_0 , or said it differently, we want to know the fit-parameter error.

We shall use the Bayesian argumentation here. So let us consider some arbitrary fit-parameter value k . The relation of posterior probabilities will be

$$\frac{P(k|\{y_i\})}{P(k_0|\{y_i\})} = \frac{P(\{y_i\}|k)\pi(k)}{P(\{y_i\}|k_0)\pi(k_0)}$$

where $\pi(k)$ and $\pi(k_0)$ are the prior probabilities of parameter values k, k_0 . If the prior probability $\pi(\cdot)$ is reasonably flat in the vicinity of k_0 , then for k not too far from k_0 we have $\pi(k) \approx \pi(k_0)$ and the prior probabilities cancel. We get

$$\frac{P(k|\{y_i\})}{P(k_0|\{y_i\})} = \frac{P(\{y_i\}|k)}{P(\{y_i\}|k_0)} = \frac{\exp(-\frac{1}{2}\chi^2(k))}{\exp(-\frac{1}{2}\chi^2(k_0))} = \exp(-\frac{1}{2}\Delta\chi^2(k))$$

Now suppose we assume that the posterior probability is gaussian. Then

$$\frac{P(k|\{y_i\})}{P(k_0|\{y_i\})} = \exp(-\frac{(k - k_0)^2}{2\sigma_k^2})$$

Comparing the two formula we see that

$$\sigma_k^2 = (k_1 - k_0)^2$$

where k_1 is the parameter value for which

$$\Delta\chi^2(k_1) = 1$$

This is the reason for the general wisdom: $\Delta\chi^2 = 1$ corresponds to one standard deviation. The critical values for "more standard deviations" are found accordingly.

¹⁰Actually we are slightly cheating here. The gaussians are probability densities, not probabilities. We assume that the values y_i are not continuous variables. We consider y to be a binned (discretized) variable, the y_i are the central values of the corresponding bin and the bins have size Δy . We stress that Δy has nothing to do with the measurement errors σ_i^2 . We assume that the value Δy is small enough so that the gaussians are reasonably flat within the bins. The normalization constant C then comprises also a power of Δy .

2.9 Competition of two models

In physics we often meet situations when we have to choose between two alternative models. For example for the set of data points $\{x_i, y_i\}$ we have to decide whether the data support the two-parameters linear model

$$y_i = A + Bx_i$$

or an alternative three-parameters quadratic model

$$y_i = A + Bx_i + Cx_i^2$$

This is a question from the methodology of physics and within the Popper-like spirit it seems to be wrongly stated. Our basic belief is that in physics we cannot prove hypotheses, we can just disprove (reject) them. Here we have two hypotheses, linear and quadratic. If one of them can be rejected (by suitable statistical test) then we favor the other hypothesis. But what if neither of them can be disproved?

Then we usually use "The Occam razor". William of Ockham was the 14th century Franciscan friar who formulated a famous statement "entities should not be multiplied beyond necessity" which in physics is usually paraphrased as "All other things being equal, the simplest solution is the best". So in case neither of two competitive models can be rejected by statistics, we favor the simpler one. And we stay at the simpler one until, eventually, more precise data disprove it; then we switch to some alternative description.

This requires that we recognize which of the two models is the simpler one. We shall be more rigorous shortly, for the moment the intuitive view is enough. An it tells us that the linear model is simpler than the quadratic one.

So the "standard folklore" (non-Bayesian, frequentist) is the following.

- Choose the simplest model (here the linear one). Adjust its parameters (A, B) by maximizing the likelihood
- Having fixed the parameters of the model perform a statistical test. For example you can calculate the χ^2 statistics

$$\chi^2 = \sum \frac{(y_i - A - Bx_i)^2}{\sigma^2}$$

and calculate the probability to observe the value obtained if the null hypothesis (linear model is true) holds

- If you get a reasonable probability, accept the model until new analysis is forced by new data.

- If you get too small a probability, reject the model and repeat the analysis with a more complicated model

Now, the Bayesian approach to the same problem would be:

- Estimate the prior model probabilities $\pi(M_1)$ and $\pi(M_2)$. (M_1 is the linear model, M_2 is the quadratic model.) The model prior probabilities might depend on the model parameters.
- Express the posterior model probabilities through the model parameters for both models
- Maximize both posterior probabilities choosing the optimal values of the model parameters.
- Compare the two posterior model parameters calculating their ratio (so that the normalization factor from the denominator drops out)

$$\frac{P(M_1|data)}{P(M_2|data)} = \frac{\pi(M_1)P(data|M_1)}{\pi(M_2)P(data|M_2)}$$

- Accept the model for which the posterior probability is higher

It is clear that the Bayesian results heavily depends on the choice of the prior probabilities. This is the reason of bitter fights between Bayesians and frequentists. It is true, that the Bayesian approach goes somewhat beyond the Popper "reject philosophy" accepting the model out of two candidates whose posterior probability is perhaps only slightly higher than that of the other candidate. On the other hand the Popper approach can be taken literally only in situations where one of the models is considered as established (a paradigm in the Khun's sense) which should be first rejected and than only the alternative should be considered. And this can be well modeled by the Bayesian approach giving the paradigm model very high prior probability with respect to the alternative. Then the data must really disfavor the paradigm model for the alternative to win. The Bayesian approach can be, however, used also in the heuristic phase of "establishing the first paradigm" when no model has a large preference.

Anyhow, the difference between the Bayesians and the frequentists is not that big as one could naively think. The frequentist (in the heuristic phase of reasoning) also compare the models prior to considering the data. They just qualitatively estimate one of the models as "more simple" with respect to the other one. Bayesian prior probabilities do the same, in more explicit and quantitative way. The frequentists results can be always reproduced by the Bayesians if the choose the prior probabilities in a suitable way.

2.10 Model as data compression

According to the discussion in the previous section one might conclude, that the prior probabilities are completely arbitrary subjective measure. It is not quite so. There exist sound ideas how to give prior probabilities of models rather objective, even rigorous foundations. The key observation here is the idea that, an a very abstract level, model (or theory) is just a way of data compression.

Let us for the moment discuss the descriptive aspect of a physical model (or theory), forgetting about its predictive aspects.

Suppose we have some measured data. The data is represented by set of numbers. In a computer language the data nothing but a (perhaps very large) string of zeros and ones. At an abstract level a model is just a way hod to describe the corresponding data. Here the word "describe" is not a rigorous term. Speaking again a computer language we can say we have a model if we have a program which is able to reproduce (to write down, to print) the data string. By "program" we mean here program which does not need any "input data", just produces output by itself, out of nothing. This is no restriction. Actually we can hide any "input data" inside the program in the form of "initial value" of some string variable.

Understanding programs in this broad sense, we can always find (construct) a program ("model") which reproduces some particular observed data. We just hide the data string inside the program as the initial value of a string and then write just a single line statement "Print that string". And that is, the program reproduces the data string. Of course, there is no use for such a "model". The model being a program is just a string of zeros and ones. And this particular "copy model" is a string even a few bits longer than the "data string" it describes. So it all seems to be a trivial nonsense. Just wait a moment. There exists many programs: as many as are (finite, but perhaps large) strings of zeros and ones. It may well happen, that some of the programs, when started with a blank list of output, ends its run with just our "data string" printed at the output. And the program may be significantly shorter than the data string it outputs. We all know that it happens. The data string can be at least "zipped" into a shorter string, included into an unzip program and voila: here is the program shorter than the data string, which prints out the complete data string. This is called "data compression". Sometimes the data compression can be extremely efficient. The string of billion digits looking like

01 . . . ,

Can be reproduced by a very short program

```
for (i=0; i<10^9; i++) print ("01");
```

Such a strong compression can indeed be called "the theory" of the observed data

To summarize: there might exist many (even infinitely many) programs printing the desired data string. However, one of them must be the shortest. This program can be called "the theory" of the observed data. Actually the considerations must be a bit more precise taking into account different computers and different programming languages, but all this is just inessential complication: the basic idea was reproduced here quite well.

So is there an end for theoretical physics? For any data string let the computer find the shortest program capable to print the string down and we have got the theory. Fortunately (or unfortunately?) this idea cannot be realized. One can prove, that there is no universal computational (computer based) way how to find the shortest program capable to produce a given string.

This might sound surprising since a simple idea to accomplish the task seems to be obvious.

- Programs are just finite strings of zeros and ones. This is a countable set. This set can be even ordered according to the length of the string representing the program. So the set of all programs can be numbered giving number 1 to the shortest program, 2 to the next one etc.
- Begin with program No 1. Run it. Wait until it stops. If it prints the desired data string, you have found the shortest program, the "theory". If not, continue with program No.2. And so on.
- Some program eventually prints the desired data string, at least the "copy program" must do so.
- The first program (found in this way) which prints the data string is the shortest one doing so.
- So we can computationally find "the theory" for every "observed data string"

Nice but wrong. There is a flaw in the above argumentation. The flaw is in the words "Wait until it stops". We all know there are programs which never stop. For example programs which contain infinite loops. First program which starts but never ends breaks our "theory finding algorithm".

So we need a modification of the algorithm. Like the following. If you consider to run the program No.n, first check whether it stops after started. If not, do not start it and go to the next program in row.

Easy said, difficult to do. One should just by inspection (not running it) recognize whether some program stops after it starts. One needs an algorithm to do the inspection. An algorithm means a program. But there is so called halting theorem. It says such a program does not exist. So our "theory finding" search for the shortest program reproducing data cannot work¹¹.

It is quite instructing to prove the halting theorem. So far we considered only programs which do not need any inputs. Let us now consider more general programs which read some input string at their start, then run, stop and produce output string.

Input strings are again just sequences of zeros and ones. Without loss of generality we can say that each such string starts with one¹². So it is just a binary representation of some integer number, we shall denote it by m . Programs can be also denoted by numbers, say n . The output string of a program n given the input string m is again a binary number, let us denote it as $T(n, m)$. Well, with one exception. Maybe the program n given the input string m never stops, then it does not produce any number. In this case we define

$$T(n, m) = \square$$

So in principle we can imagine an infinite table with all the results of all the programs given all the possible input strings¹³. This table is the matrix $T(n, m)$. (In the n -th row and m -th column is the output $T(n, m)$). Some entries in the table are, of course \square .

We said "in principle" because we are not sure whether the matrix can really be constructed (computed). Well, the matrix is infinite, so it can never be constructed (computed) in totality. But we can define the matrix be computable if we can compute the entry in any given (n, m) position. Can we?

Yes if the halting problem can be solved. We need the program symbolically denoted as H which if given two¹⁴ numbers (n, m) (that is some program and its data) always halts and outputs 1 if the considered program n with data string m stops and outputs 0 if the program n with data m does not stop.¹⁵

With the help of the magic program H one can compute the matrix $T(n, m)$. Indeed: given the two numbers (n, m) we first run the H program with (n, m) as

¹¹It can be proved that no other algorithm can work either.

¹²We can always start the program by a statement "forget about the initial one from the input string".

¹³What about programs which do not need any input. We still can present them any input string, they simply do not consider it and their result does not depend on the input string at all. For such programs the result $T(n, m)$ would be the same for all the m

¹⁵Any two numbers (strings) can be artificially written as one string, say with digits on odd positions from the first string and on the even positions from the second string

input. If it writes 0, we know $T(n, m) = \square$ and that is all. If the H program ends with 1, it is safe to run the program n with data m and we get the result $T(n, m)$. So if the program H exists, the table $T(n, m)$ is computable.

Now we are going to show, that the table $T(n, m)$ cannot be computable. Suppose it is. Then its diagonal $T(n, n)$ is also computable. Then a vector $V(n)$ defined¹⁶ as $V(n) = T(n, n) + 1$ is also computable. It means there exists a program which computes this vector. There must be a number n_0 such that $T(n_0, m) = V(m)$ but then

$$T(n_0, n_0) = V(n_0) = T(n_0, n_0) + 1 \neq T(n_0, n_0)$$

We got contradiction. So the program H does not exist. The halting theorem is proven.

2.11 Coding theory

In this section we start to investigate deep relation between probability and information. We shall first need elements of the coding theory.

The goal of coding is to translate a given information into a sequence of symbols, possibly a short one. The basic symbols used by computers are zero and one. On the other hand the Morse code uses three symbols a dot, a dash and a gap. The last mentioned symbol has a special meaning, it separates different letters from each other.¹⁷ It is interesting to note, that it is possible to code a message by just using two symbols. At the first sight one would say that one needs two symbols to code for letters and something else to code gaps between letters. However it is possible to construct codes for letters such that no sequence of symbols which is a true code for some symbol appears as a prefix in the sequence of some other letter. Then a sequence of symbols without any gaps can be cut into pieces representing individual letters (the gaps can be introduced automatically). We read the sequence from the beginning symbol by symbol. After reading a symbol we check whether we already have a valid code for a letter. If not, we read the following symbol. If yes we break the reading, introduce a gap and start reading further as if from the first symbol. A code \mathcal{K} having the described property is called prefix-free code, sometimes shortly just a prefix code. The set of all letters is called alphabet \mathcal{A} . In what follows we shall assume that the symbols used are 0 and 1. Let us stress again, that the alphabet can be in principle very reach, containing a large number of letters.

¹⁶Well, some of the $T(n, n)$ might be \square . We define a "rule" $\square + 1 = 1$

¹⁷In this section we shall use the word "letter" in a general meaning of the smallest codable unit. Practically it may be a letter (in the usual meaning of the word) or it may be a group of letters, a word, or something representing a complicated prior agreed meaning. So a message would be just a sequence of letters

Let us denote the lengths of codes of letter of an m -letter alphabet as s_1, \dots, s_m . Let the corresponding code is prefix-free. Then the following (Kraft inequality) holds

$$\sum_i 2^{-s_i} \leq 1.$$

The inverse is also true, that is if the lengths of m sequences s_1, \dots, s_m fulfill the Kraft inequality, then a prefix-free code exists for an m -letter alphabet with the code sequences of the corresponding lengths.

Let us prove the theorem. Without a loose of generality we assume that the lengths are ordered and s_m is maximal. Any given prefix code can be represented by a binary tree of depth s_m where the branches from each node correspond code symbols (0 and 1) and each codeword is represented by a path to a leaf at depth s_i . This guarantees that no codeword is a prefix of another. For each leaf in such a code tree, consider the set of descendants A_i the leaf considered would have at depth s_m in a full binary tree. Then

$$A_i \cap A_j = \emptyset, \quad i \neq j$$

and

$$|A_i| = 2^{s_m - s_i}$$

Thus, given that the total number of nodes at depth s_m is 2^{s_m} ,

$$\left| \bigcup_{i=1}^m A_i \right| = \sum_{i=1}^m 2^{s_m - s_i} \leq 2^{s_m}$$

from which the Kraft inequality follows. For the converse, we just show the main idea. Given any ordered sequence of n integer numbers s_1, \dots, s_m , satisfying the Kraft's inequality, one can construct a prefix code with codeword lengths equal to s_i by pruning subtrees from a full binary tree of depth s_m in the following way. First choose any node from the full tree at depth s_1 and remove all of its descendants. Then iterate the procedure with the remaining nodes for $i = 2, \dots, m$.

It is useful to demand that the message should have the total length as small as possible. Let us denote the length of the code assigned to the letter x by $L(x)$ and the alphabet of all letter by \mathcal{A} . The mean length assigned to a letter is $\langle L \rangle = \sum P(x)L(x)$. We assume here that the probabilities $P(x)$ are known beforehand.

How to minimize this mean length? Clearly it is wise to assign short symbol sequences to very probable letters and longer sequences to improbable letters. (Morse himself went to a printing office to see how many pieces of different letters they have at their disposal.) Mathematically it is a constrained optimization, what are the optimal code lengths to minimize the mean length provided the Kraft

inequality is satisfied. Using the Lagrange multiplier technique, we get the unconstrained optimization problem with the cost function

$$\mathcal{L} = \sum_{x \in \mathcal{A}} P(x)L(x) - \lambda \left(\sum_{x \in \mathcal{A}} 2^{-L(x)} - 1 \right).$$

The solution is $L(x) = -\log_2 P(x)$. The optimal mean code length per letter is

$$H = - \sum_{x \in \mathcal{A}} P(x) \log_2 P(x)$$

This expression is called the entropy of the information source (when coding in the binary code). Since $\log_2 x = \ln 2 \cdot \ln x$, H differs only by a multiplicative factor from the expression for entropy $S = -k \sum p_i \ln p_i$ known in statistical physics.

We have so far neglected the problem that the expression $L(x) = -\log_2 P(x)$ leads to non-integer code lengths, what is nonsense. One possibility is to use the ceiling function (rounding to the nearest larger integer), such a coding is called Shannon-Fano. However, in extreme situations like when coding a two letter alphabet A, B with the probabilities $p_A = 0.9, p_B = 0.1$, we get $L_A = 1$ and $L_B = 4$, clearly a non-optimal solution with $\langle L \rangle = 1.3$. The trivial assignment $A \rightarrow 0$ and $B \rightarrow 1$ gives $\langle L \rangle = 1$. No better assignment exists, so the value of information source entropy $H \doteq 0.47$ cannot be achieved in this extreme situation. In practical situations we can get close to the entropy value.

An optimal solution (coding individual letters) is the Huffman code¹⁸. We start with two least probable letters and assign to them (as final symbols for their code sequences) 0 and 1. We sum their probabilities and count them together as if one letter the number of "effective letters" of the alphabet decreases by one. We iterate the procedure until all the letters have their code sequences assigned (see the figure).

The code sequences for the example in the above figure are $A \mapsto 11, B \mapsto 10, C \mapsto 01, D \mapsto 001, E \mapsto 000$. Huffman code is used in many applications like zip, mp3 and mpeg.

Of course there might be a better solution than coding the message letter by letter, as we demonstrate in the following exercise. **Exercise**

¹⁸In early times of the coding theory finding the optimal code was a prestigious challenge. The winner was (in 1952) an MIT student David Huffman who worked on the problem within a project related to the lecture on coding theory.

Let the probability of letter A be $p_A = 0.999$, the probability of the letter B be $p_B = 0.001$. Suggest a practically useful way to code messages of typically million letters. (Giving the typical message length just helps to estimate the efficiency of the coding scheme, asymptotically the efficiency does not depend on this number.)

- A message of the given length contains typically 1000 B letters sparsely distributed among the A letters. Therefore it is better not to code letter by letter, but to code the long sequences of A 's. A useful code may look as follows. We first give the total number of B 's in the message. Then we give the length of the first A -sequence, then the second sequence and so on. All the numbers used in the scheme are of the order of 1000, that is 11 binary digits. We shall need roughly 1000 such numbers, so 11000 binary digits. Actually we shall solve the problem of coding the delimiter between the numbers, but this does not change the order of magnitude of the estimate. Having a million letters, we need roughly 0.011 bit per letter. The information source entropy in this case is $H \doteq 0.011$, so our code is very good.

Chapter 3

Supplements to the foundations of statistical physics

3.1 Density matrix

Let us have an arbitrary macrostate of some system and the ensemble of microstates representing this macrostate. The macrostate considered need not be stationary. The ensemble is a set of microstates $|x\rangle$ and the set of their probabilities $p(x)$. Then the mean value of any physical quantity is

$$\bar{A} = \sum_x p(x) \langle x | \hat{A} | x \rangle$$

This can be written in a more compact form when we introduce the operator (density matrix)

$$\hat{\rho} = \sum_x |x\rangle p(x) \langle x|$$

as

$$\bar{A} = \text{Tr}(\hat{\rho}\hat{A})$$

Indeed, using any base $|n\rangle$ on can write

$$\begin{aligned} \text{Tr}(\hat{\rho}\hat{A}) &= \sum_n \langle n | \hat{\rho}\hat{A} | n \rangle = \sum_n \langle n | \sum_x |x\rangle p(x) \langle x | \hat{A} | n \rangle = \\ &= \sum_n \sum_x \langle n | x \rangle p(x) \langle x | \hat{A} | n \rangle = \\ &= \sum_n \sum_x p(x) \langle x | \hat{A} | n \rangle \langle n | x \rangle = \\ &= \sum_x p(x) \langle x | \hat{A} | x \rangle = \bar{A} \end{aligned}$$

The density matrix is evidently a hermitian operator, it can be expressed in any base (in general it would not be diagonal) as

$$\hat{\rho} = \sum_{m,n} |m\rangle \rho_{mn} \langle n|$$

The time evolution of a macrostate will be described by a time dependent density matrix

$$\begin{aligned} \hat{\rho}(t) &= \sum_x |x(t)\rangle p(x) \langle x(t)| = \\ &= \sum_x \exp(-\frac{i}{\hbar} \hat{H}t) |x\rangle p(x) \langle x| \exp(\frac{i}{\hbar} \hat{H}t) \end{aligned}$$

Differentiating with respect to time we get the equation of motion

$$i\hbar \frac{\partial}{\partial t} \hat{\rho}(t) = [\hat{H}, \hat{\rho}]$$

If the macrostate is stationary, then it will be described by a time independent density matrix. According to the equation of motion we see that such a density matrix commutes with the Hamiltonian. Therefore there exists a base of stationary states in which the density matrix will be diagonal having the form

$$\hat{\rho} = \sum_n |n\rangle \rho_{nn} \langle n|$$

This is the reason why in statistical physics of stationary macrostates we can limit ourselves to the ensembles composed of stationary states.

In the case of a canonical ensemble we get for the density matrix

$$\hat{\rho} = \sum_n |n\rangle \frac{1}{Z} \exp(-\frac{E_n}{kT}) \langle n|$$

which can be formally written as

$$\hat{\rho} = \frac{1}{Z} \exp(-\frac{\hat{H}}{kT})$$

3.2 Entropy

We want to discuss now the notion of information. Information concerns knowledge. More specifically information can change the state of knowledge. Information can change a complete unawareness to a partial or even complete knowledge.

One of the main messages of this section is the idea that the level of unawareness can be described (modeled) by the concept of probability. When the dice was thrown, but I do not know the result yet, then there is no genuine probability to speak about. The result is fixed, but I do not have the knowledge about it. However, I can measure the level of my unawareness by the probabilities of various events **before they happen**.

If the dice is thrown and somebody tells me the result, he communicates me some information. How to measure the quantity of information? The starting point is the requirement that the message saying an improbable event happened carries more information than a message reporting that a probable event happened. The quantity of information is therefore related to the probability of the message carrying the information. Information about the event is related to the probability of that event before it happened.

Now we require that the information can be communicated in parts. For example I can first announce that the unknown number is odd, and then only the number itself. It is natural to require that the information from partial messages should be added to get the total information. Having in mind that the probability of independent events combine multiplicatively, but the corresponding independent pieces of information should be combined additively it is natural to assume that the amount of information is given by the logarithm of the corresponding probability.

$$I = -\log(p)$$

Let us now consider a communication channel communicating the pieces of information. Each piece of information is a message that some event happened. Let the events are denoted by the index i and their probabilities p_i . Then the mean amount of information contained in one message is

$$S = -\sum_i p_i \log(p_i)$$

This expression is called the entropy of the information channel.

We have seen this expression in the previous section when we discussed the optimal coding. We came to the conclusion the having events with probabilities p_i it is optimal to assign to them codewords with the lengths $-\log_2(p_i)$ so that the mean message length would be

$$S = -\sum_i p_i \log_2(p_i)$$

Using the logarithms of different bases just changes the units in which we measure the amount of information. (Changing the base just multiplicatively renormalizes

the logarithm.) The unit corresponding to binary logarithm is called bit, the unit corresponding to natural logarithm is called nat.

Now we prove that the expression for entropy has the following important optimality property. Considering arbitrary sequences of positive numbers q_i satisfying the condition $\sum_i q_i = 1$ the following inequality holds

$$-\sum_i p_i \log(q_i) \geq -\sum_i p_i \log(p_i)$$

We shall prove it for natural logarithms, but the generalization to arbitrary logarithm base is trivial

$$\begin{aligned} \log(x) &\leq x - 1 \\ \log\left(\frac{q_i}{p_i}\right) &\leq \frac{q_i}{p_i} - 1 \\ p_i \log(q_i) - p_i \log(p_i) &\leq q_i - p_i \\ \sum_i (p_i \log(q_i) - p_i \log(p_i)) &\leq \sum_i (q_i - p_i) = 0 \\ -\sum_i p_i \log(p_i) &\leq -\sum_i p_i \log(q_i) \end{aligned}$$

q.e.d. By the way we have proved again the optimal coding theorem, that is that one should use the codewords of the length $\log(q_i) = \log(p_i)$.

Now, why all this is relevant to statistical physics?

A macrostate in statistical physics is represented by a statistical ensemble of microstates i , whose probabilities are p_i . Statistical entropy (of the macrostate) is defined as

$$S = -\sum_i p_i \log(p_i)$$

So we see that the statistical entropy can be interpreted in the following way.

Let us imagine that somebody gives us a sample of some macrostate. A macrostate is a virtual notion, he must actually give us some specific microstate. He just does not tell us which specific microstate from the corresponding ensemble he gave us. So our knowledge about the system considered just corresponds to its macrostate, we are completely unaware of the microstate actually delivered. Now imagine that someone tells us which particular microstate was actually delivered. Then our original unawareness is changed to a complete knowledge. The amount of information contained in the message was $-\log(p_i)$ where p_i is the probability

assigned in the statistical ensemble to the microstate actually delivered. So the mean amount of information needed to complete our knowledge from macrostate to microstate level is

$$S = - \sum_i p_i \log(p_i)$$

In statistical physics we use natural logarithm, therefore the units for entropy should be nats. Actually, however, a slightly different definition of entropy is used in physics, containing the Boltzmann constant k

$$S = -k \sum_i p_i \log(p_i)$$

and so we express entropy in units of energy/temperature (J/K).

Exercise

Information source entropy

We study the particle velocity in one-dimensional gas.

- What is the probability density distribution of velocity $f_1(v)$ which maximizes entropy $S = \langle \ln f_1 \rangle_{f_1}$, provided mean absolute value of a particle velocity is given $\langle |v| \rangle \equiv u$?
- How the result changes if the mean kinetic energy of a particle is given $\langle mv^2/2 \rangle = mu^2/2$?
- Which of these two specifications (mean absolute value of the velocity or mean kinetic energy) provides more information on the particle velocity. (Here we are interested, in fact in the difference of corresponding entropies.)

- a) We shall use the technique of Lagrange multipliers. The optimized function will be

$$\mathcal{L} = - \int_{-\infty}^{\infty} f_1(v) \ln f_1(v) dv + \alpha \left(1 - \int_{-\infty}^{\infty} f_1(v) dv \right) + \beta \left(u - \int_{-\infty}^{\infty} f_1(v) |v| dv \right).$$

Now we calculate the functional derivative¹ (sometimes called variation derivative) $\delta \mathcal{L} / \delta f_1$ and put it equal to zero.

$$\frac{\delta \mathcal{L}}{\delta f_1(v)} = 0 \implies \ln f_1(v) = -1 - \alpha - \beta |v| \implies f_1(v) = \frac{1}{2u} \exp\left(-\frac{|v|}{u}\right).$$

b) We proceed similarly as in the previous case and we get $f_2(v) = \exp(-v^2/2u^2) / \sqrt{2\pi u^2}$. The lesson is that the Maxwell distribution maximizes entropy at given mean kinetic energy.

c) More information is contained in the mean kinetic energy, the entropy difference is $(1 + \ln 2 - \ln \pi) / 2 \ln 2 \doteq 0,4$ bits. ■

¹If functional derivative is too abstract for the reader he/she can imagine a discretized problem and its continuum limit

Exercise

Weighting golden marbles

We have 9 golden marbles, 8 of them are from true gold, 1 is fake, therefore weighing less than the others. We have ordinary equal arms beam balance to find the fake marble. How many weighings do we need?

One can find the solution by trial and error method, but there is a nice way using the concept of information. Any weighing on a beam balance can lead to one of three results (the load on the left pan is equal to the one on the right pan, the left is heavier than the right, or the right is heavier than the left) $L < P$, $L = P$, $L > P$. Now how much information can we gain by one weighing. The mean information obtained in one weighing is

$$S = - \sum_{i=1}^3 p_i \log(p_i)$$

where the probabilities (of the three possible outcomes) satisfy the normalization condition. $p_1 + p_2 + p_3 = 1$. Finding the maximum is a constrained optimization problem and can be solved by the Lagrange multiplier method and look for an unconstrained optimum of the function

$$F(p_1, p_2, p_3) = - \sum_{i=1}^3 p_i \log(p_i) + \lambda \sum_{i=1}^3 p_i$$

Differentiating with respect to p_i we get

$$-\log(p_i) - 1 + \lambda = 0$$

So the value of p_i does not depend on the index i , so all the prior probabilities should be equal

$$p_i = \frac{1}{3}$$

It is useful for the case considered to use the base 3 for the logarithms, the corresponding unit of information is called one trit. Optimally we can gain one trit of information for one weighing since

$$S = - \sum_{i=1}^3 \frac{1}{3} \log_3\left(\frac{1}{3}\right) = 1$$

How much information do we need to identify the fake marble. It can be any of the 9 marbles, so the probability to randomly point to a fake one is $1/9$. The information needed is therefore

$$-\log_3\left(\frac{1}{9}\right) = 2$$

We need 2 trits of information, we can obtain maximally 1 trit per weighing, so we need at least 2 weighings to identify the fake marble. Actually it can be done. We

start by taking randomly three marbles and put them on the left pan and another random three marbles and put them on the right pan. If the pans are balanced, the fake marble is one of the remaining three marbles. Otherwise it is one of the three marbles with the smaller weight. So in the next weighing we have to identify as fake one of three marbles. We take randomly one and one, if they have equal weight the fake is the remaining one, otherwise the fake one is that with smaller weight.

3.3 Variation principles

We have already met the inequality

$$-\sum_i p_i \log(q_i) \geq -\sum_i p_i \log(p_i)$$

in terms of the density matrix it can be written in the following form

$$-Sp(\rho \ln(\rho)) \leq -Sp(\rho \ln(\rho'))$$

This inequality holds for arbitrary density matrix ρ' .

Let us consider the Hilbert space of some physical system and a subspace of this space corresponding to vectors with a given fixed energy. Let this subspace have the dimension N . This subspace corresponds to microcanonical ensemble with the density matrix given as

$$\rho = \frac{1}{N} \sum_n |n\rangle\langle n|$$

For arbitrary density matrix defined in the energy subspace we get (according to the above inequality)

$$S' = -Sp(\rho' \ln(\rho')) \leq -Sp(\rho' \ln(\rho)) = -Sp(\rho' \ln(\frac{\hat{1}}{N})) = \ln N$$

On the right hand side there is the entropy of the microcanonical distribution. We see that the microcanonical distribution has the largest entropy from all the distributions defined in the energy subspace considered.

Now let us consider the canonical density matrix

$$\rho = \frac{1}{Z} \exp(-\beta \hat{H})$$

and an arbitrary density matrix ρ' (defined on the whole Hilbert space). We get the inequality

$$\begin{aligned} S' = -Sp(\rho' \ln(\rho')) &\leq -Sp(\rho' \ln(\rho)) \\ S' &\leq -Sp(\rho'(-\ln(Z) - \frac{\hat{H}}{T})) = +\ln(Z) + \frac{1}{T}E' \\ E - TS &\leq E' - TS' \\ F &\leq F' \end{aligned}$$

We have got the variation principle which we formulate also in words now. If we have a system in contact with a heat reservoir at temperature T. The equilibrium (macro)state of the system is described by the canonical density matrix ρ . If the system is in (macro)stat described by some other density matrix ρ' , then it is in a non-equilibrium (macro)state. The mean energy in this non-equilibrium state is

$$E' = Sp(\rho' \hat{H})$$

and its entropy is

$$S' = -Sp(\rho' \ln(\rho'))$$

We can define free energy in this (non-equilibrium macro)state as

$$F' = E' - TS'$$

According to the above inequality this non-equilibrium free energy is smaller than the equilibrium entropy.

We can use the theorem in the following way. In the trial density matrix ρ' we introduce some free parameter α , and we tune it so that the corresponding **non-equilibrium** free energy $F'(\alpha)$ is at minimum.

Practically we use this variation principle in a special way. There are more than one "canonical density matrices" in the sense that the macrostates corresponding to them are macroscopically undistinguishable from each other. In the standard definition of the canonical density matrix

$$\rho = \frac{1}{Z} \exp(-\beta \hat{H})$$

we assume that calculating the traces (which we do to get physical predictions) we sum over the complete Hilbert space. However we can modify the density matrix that we do the traces only over some subspace of the complete Hilbert space. Formally we can write

$$\rho = \frac{1}{Z} \hat{P} \exp(-\beta \hat{H}) \hat{P}$$

where \hat{P} is the projection operator projecting to the subspace considered. Usually we choose the subspace as the subspace on which all the states have specific value

A of some (macroscopically measurable) variable \hat{A} . We denote the corresponding projection operators symbolically as

$$\hat{P}_{\hat{A}=A}$$

and we get

$$\rho_A = \frac{1}{Z_A} \hat{P}_{\hat{A}=A} \exp(-\beta \hat{H}) \hat{P}_{\hat{A}=A}$$

we mean by this notation that, for example

$$Z_A = \sum_{i, A_i=A} \exp(-\beta H_i)$$

We know that for a macroscopical system all sums are saturated by the subspace on which the value of some variable is equal to the macroscopical equilibrium value of that variable. In other words ρ is equivalent to ρ_A if $A = \langle A \rangle = Tr(\rho A)$.

Now we can use the value A as the variation parameter in the above described variation principle. So among the subspaces having specific fixed value A of the variable \hat{A} we look for the subspace for which the corresponding free energy is minimal. The value A_{min} for which the minimum is achieved is the equilibrium value of the quantity \hat{A}

$$A_{min} = \langle A \rangle = Sp(\rho A)$$

This is the way how equilibrium values are often calculated in statistical physics. We minimize the non-equilibrium free energy corresponding to a general non-equilibrium value of the quantity of interest. The value of this quantity for which the minimum is achieved is its equilibrium value.

So far we have considered a variation procedure based on the inequality saying that the non-equilibrium free energy is greater than the equilibrium free energy of **the same system**.

Now we formulate an alternative variation principle based on comparing two **equilibrium** free energies. We start from the previous inequality but now as a trial density matrix we shall choose canonical (equilibrium) matrix corresponding, however, to different Hamiltonian \hat{H}' . We keep the notation

$$E' = Sp(\rho' \hat{H})$$

so that E' is the mean energy corresponding to the original Hamiltonian \hat{H} in the trial state ρ . Now we introduce a new quantity

$$E'' = Sp(\rho' \hat{H}')$$

it is the mean energy corresponding to the trial Hamiltonian \hat{H}' in the trial state ρ' . Adding and subtracting the same term E'' to the previous inequality we get

$$\begin{aligned} E - TS &\leq E' - E'' + E'' - TS' \\ F &\leq (E' - E'') + F'' \end{aligned}$$

where F'' is the canonical (equilibrium) free energy of a trial system with the Hamiltonian \hat{H}' . Variation technology proceeds in a standard way. We introduce a free parameter α into the trial Hamiltonian \hat{H}' and we get a variable upper estimate

$$F \leq (E'(\alpha) - E''(\alpha)) + F''(\alpha)$$

We choose then the value of α so that the right hand side is at minimum.

The difference between the two alternatives of the variation principle is the following. The non-equilibrium free energy of a system is the upper estimate of the equilibrium free energy of the same system. However, the equilibrium free energy of some other system has no direct relation to the equilibrium energy of our system of interest. To get the upper estimate, we have to add to the trial equilibrium free energy the term

$$E' - E''$$

3.4 Classical and quantum statistics

We have seen in the section on density matrix that the statistical ensembles describing the equilibrium macrostates can be formed just from stationary states. Then all the calculations are (in principle) simple, because for discrete sets their elements can be just counted.

A different situation emerges in the classical physics. The microstate there is a point in a continuous phase space. Simply there are "too many points" in the continuum. We cannot speak about their probabilities, we have to use probability densities. We need for that, however, to introduce a suitable measure, in other words, we have to know how to integrate in the space considered. There is no prior (canonical) measure on a general manifold. Different measures, however, lead to different probabilities assignment. In particular, the notion of uniform probability (maximally unbiased probability) crucially depends on the choice of the probability measure. So "complete lack of knowledge" cannot be uniquely modeled on a general manifold. However, to build the statistical physics we desperately need the notion of unbiased probability, that is "the most democratic" probability which "gives a same importance" to everybody. It is easy to define the "democratic probability" on a discrete space: every state is assigned the same probability and the normalization condition then makes it unique. In a continuous space we run into difficulties. Sets which have equal measures for a particular integration measure, might get different measures for a different choice of the integration measure. There is no canonical prior probability on a general manifold.

Fortunately enough, we do not run into this problem in classical statistical physics, since we speak about a measure in phase space. Introducing different measure

essentially means introducing new coordinates in the space considered. And, in a phase space, we "are not allowed" to introduce new coordinates arbitrarily. We can limit ourselves to use only canonical coordinates, that is coordinates which do not change the form of Hamilton equations of motion. There are infinitely many sets of canonical coordinates in a phase space. WE shall show, however, that a substitution changing one canonical set of variables to another canonical set has the Jacobian equal to one, that is the two sets of coordinates lead to the same measure in the phase space. It means a phase space has the same measure in any canonical coordinates and the maximally unbiased (prior) probability can be canonically defined: it is the probability density which is uniform when expressed in (any) canonical coordinates.

So to the problem of canonical transformations.

Let us have canonical coordinates p, q . We shall omit indexes everywhere, so p, q can represent many (10^{23}) variables with indexes. We have Hamiltonian $H(p, q)$ and the equations

$$\dot{p} = -\frac{\partial H}{\partial q} \quad \dot{q} = \frac{\partial H}{\partial p}$$

We introduce new variables P, Q by transformations $P(p, q), Q(p, q)$. The new coordinates P, Q are called canonical, if

$$\dot{P} = -\frac{\partial \tilde{H}}{\partial Q} \quad \dot{Q} = \frac{\partial \tilde{H}}{\partial P}$$

where

$$\tilde{H}(P, Q) = H(p(P, Q), q(P, Q))$$

We get from definition of P

$$\dot{P} = \left(\frac{\partial P}{\partial q}\right)_p \dot{q} + \left(\frac{\partial P}{\partial p}\right)_q \dot{p} = \left(\frac{\partial P}{\partial q}\right)_p \left(\frac{\partial H}{\partial p}\right)_q + \left(\frac{\partial P}{\partial p}\right)_q \left(-\frac{\partial H}{\partial q}\right)_p$$

We should get

$$\dot{P} = -\frac{\partial \tilde{H}}{\partial Q} = \left(\frac{\partial H}{\partial p}\right)_q \left(\frac{\partial p}{\partial Q}\right)_P + \left(\frac{\partial H}{\partial q}\right)_p \left(\frac{\partial q}{\partial Q}\right)_P$$

Comparing the two expressions we get two conditions of canonicity

$$\left(\frac{\partial P}{\partial q}\right)_p = -\left(\frac{\partial p}{\partial Q}\right)_P$$

$$\left(\frac{\partial P}{\partial p}\right)_q = \left(\frac{\partial q}{\partial Q}\right)_P$$

The two other conditions of canonicity can be get similarly considering \dot{Q} .

Now the Jacobian can be calculated by dividing the total canonical transformation into two subsequent canonical transformations

$$J = \frac{\partial(Q, P)}{\partial(q, p)} = \frac{\partial(Q, P)}{\partial(q, P)} \frac{\partial(q, P)}{\partial(q, p)}$$

$$J = \left(\frac{\partial Q}{\partial q} \right)_P \left(\frac{\partial P}{\partial p} \right)_q$$

Substituting the second condition of canonicity we get

$$J = \left(\frac{\partial Q}{\partial q} \right)_P \left(\frac{\partial q}{\partial Q} \right)_P = 1$$

So the volume of a certain region of the phase space is invariant with respect to canonical transformation. So the notion of uniform probability distribution in the phase space is invariant with respect to canonical transformation.

We shall show now that the volume of the phase space is also invariant with respect to time development according to the equations of motion. So let we have initial point p, q , and the final point p', q' which is reached after an infinitesimal time development during the time dt .

$$q' = q + \frac{\partial H}{\partial p} dt$$

$$p' = p - \frac{\partial H}{\partial q} dt$$

The Jacobian will be

$$J = \begin{vmatrix} \frac{\partial p'}{\partial q} & \frac{\partial p'}{\partial p} \\ \frac{\partial q'}{\partial q} & \frac{\partial q'}{\partial p} \end{vmatrix} = \begin{vmatrix} -\frac{\partial^2 H}{\partial q^2} dt & 1 - \frac{\partial^2 H}{\partial p \partial q} dt \\ 1 + \frac{\partial^2 H}{\partial q \partial p} dt & \frac{\partial^2 H}{\partial p^2} dt \end{vmatrix}$$

$$|J| = 1 + O(dt^2)$$

And so

$$\frac{dJ}{dt} = 0 \Rightarrow |J| = 1 = \text{const}$$

Therefore the volume of a region of the phase space does is constant with respect to the flow according to equations of motion. This is so called Liouville theorem.

Now suppose we define a probability density in the phase space, which generally depends explicitly on time

$$\varrho(t, p, q)$$

Since probability has to be conserved, the continuity equation should be satisfied

$$\frac{\partial \varrho}{\partial t} + \frac{\partial}{\partial p}(\varrho \dot{p}) + \frac{\partial}{\partial q}(\varrho \dot{q}) = 0$$

Substituting from the equations of motion we get

$$\frac{\partial \varrho}{\partial t} - \frac{\partial}{\partial p}\left(\varrho \frac{\partial H}{\partial q}\right) + \frac{\partial}{\partial q}\left(\varrho \frac{\partial H}{\partial p}\right) = 0$$

The mixed derivatives drop out and we get

$$\frac{\partial \varrho}{\partial t} + \frac{\partial}{\partial p}\dot{p} + \frac{\partial}{\partial q}\dot{q} = 0$$

That means that if we insert into ϱ the solutions of the equations of motion

$$\varrho(t, p(t), q(t))$$

we get the total time derivative is zero

$$\frac{d}{dt}\varrho(t) = 0$$

This equation is also called the Liouville theorem.

If we just speak about probabilities, the choice of canonical coordinates makes things unique. If we want to introduce entropy we arrive at a problem of choosing the unit for the volume of the phase space. The discrete formula for the entropy

$$S = - \sum_i \ln(p_i) p_i$$

can be generalized to the case of continuous space and probability density as

$$S = - \int \ln(\rho) \rho d\Phi$$

where $d\Phi$ denotes the element of the phase space volume. However ρ is the probability density, that means probability divided by the phase space volume. So the normalization of the probability density depends on the choice of a unit for the phase space volume. In the integrals defining probabilities we get something like

$$P(\text{subset}) = \int_{\text{subset}} \rho d\Phi$$

and the unit of the volume of the space, being in the numerator in $d\Phi$ and in the denominator in ρ cancels. In the integral defining the entropy, the phase space volume unit is present also in ρ under the logarithm $\ln(\rho)$ and does not cancel in the

integral. Moreover, the phase space volume is not dimensionless, in one particle mechanics it has the dimension of distance *times* momentum what in the usual units is Js. The logarithm is, however, well defined only for dimensionless quantities. So we have to express the phase space volume in some prescribed unit and take for ρ just the numerical factor. Changing the unit of the phase space volume does not change the values of probabilities, but it does change the value of entropy. Since changing the volume unit renormalizes the probability density ρ multiplicatively, and ρ appears under logarithm, the entropy gets additively renormalized. So classical entropy is well defined up to an arbitrary additive constant.

To choose the unit for the phase space volume we look for something with the dimension Js. The obvious candidate is the Planck constant $\hbar = 1.055 \times 10^{-34}$ Js.

In quantum statistics we have discrete space of stationary states, their number can be counted in a unique way and it is a dimensionless quantity, so the quantum entropy is absolutely defined, without any additive arbitrariness².

We can ask whether we can choose the phase space volume unit in such a way that we get for the entropy in the classical case the same number as in the classical limit of quantum statistical physics. The answer is positive, the matching unit of the phase space can be found. We demonstrate it on the example of ideal gas.

In the classical limit of the quantum statistics of the ideal gas we get for entropy the well known Sackur-Tetrode formula

$$S_q = kN \ln \frac{V}{N} + kN \frac{3}{2} \ln kT + kN \frac{3}{2} \ln \frac{m}{2\pi\hbar^2} + \frac{5}{2}kN$$

In classical statistical physics we get the expression³

$$S_k = -k \int \frac{1}{N!} \prod_i d^3x_i d^3p_i \frac{N!}{V^N} C^{3N/2} \exp\left(-\sum_i \frac{p_i^2}{2mkT}\right) \ln\left(\frac{N!}{V^N} C^{3N/2} \exp\left(-\sum_i \frac{p_i^2}{2mkT}\right)\right)$$

where

$$C = \left(\frac{1}{2\pi mkT}\right)$$

²The only free choice is in the base of the logarithm (like natural versus binary logarithm). The base is arbitrary, but its change just renormalizes entropy multiplicatively, what means change of entropy units (nats versus bits). This has nothing to do with the classical arbitrary additive constant

³The $N!$ factor is the "Gibbs paradox" factor: we have to sum only through different (distinguishable) states, therefore we integrate over the whole phase space but divide by $N!$. But then the probability density must be properly normalized so we require that

$$\int \frac{1}{N!} \prod_i d^3x_i d^3p_i \frac{1}{Z} \exp\left(-\sum_i \frac{p_i^2}{2mkT}\right) = 1$$

and the factor $N!$ will appear in Z and therefore under the logarithm as well.

Then

$$S_k = -kN \ln N + kN + kN \ln V + \frac{3kN}{2} \ln(2\pi mkT) + \frac{3kN}{2}$$

$$S_k = kN \ln \frac{V}{N} + kN \frac{3}{2} \ln kT + kN \frac{3}{2} \ln(2\pi m) + \frac{5}{2} kN$$

The classical calculation and the classical limit of the quantum calculation differ by an additive term

$$S_q = S_k - 3kN \ln(2\pi\hbar)$$

The results will be identical if we write the integration measure as

$$\int \prod_i \frac{d^3 x_i d^3 p_i}{(2\pi\hbar)^3}$$

The natural unit of the one-particle phase space therefore is

$$(2\pi\hbar)^3$$

3.5 Volume of an n -dimensional sphere and the number of states of a classical ideal gas

In the previous section we were calculating the entropy of an ideal gas using the classical canonical distribution. In this section we will discuss the classical microcanonical distribution of an ideal gas. We start with a mathematical detour: we derive the formula for the volume of an n -dimensional sphere. We need the integral

$$V_n = \int \dots \int_{\sum_i x_i^2 < R} dx_1 \dots dx_n.$$

Actually, because of dimensional reasons, we know, that the result will have the form

$$V_n = C_n R^n$$

so we just need the unknown⁴ factor C_n . The trick is that we shall instead calculate a Gaussian integral in n -dimensional space both in Cartesian and in spherical coordinates. In Cartesian coordinates

$$I = \int_{-\infty}^{\infty} dx_1 \dots \int_{-\infty}^{\infty} dx_n \exp[-x_1^2 - \dots - x_n^2] = (\sqrt{\pi})^n = \pi^{n/2}.$$

Now to write it in spherical coordinates we need a volume of a spherical layer

$$dV_n = S_n(R) dR$$

⁴We of course know that $C_2 = \pi$, $C_3 = 4\pi/3$

where $S_n(R)$ is a surface of an n -dimensional sphere with radius R . From

$$V_n = C_n R^n$$

we get

$$dV_n = nC_n R^{n-1} dR$$

and the Gaussian integral in the spherical coordinates can be written as⁵

$$\begin{aligned} I &= \int_0^\infty \exp[-R^2] dV_n = \int_0^\infty \exp[-R^2] nC_n R^{n-1} dR = \\ &= \frac{nC_n}{2} \Gamma(n/2) = C_n \Gamma(n/2 + 1). \end{aligned}$$

Comparing the two expressions we get C_n and

$$V_n = \frac{\pi^{n/2}}{\Gamma(n/2 + 1)} R^n$$

High dimensional spaces behave quite opposite to intuitive expectation. Let us investigate n -dimensional spheres with radius 1 and calculate what part of their volume is contained in a thin surface spherical layer of the thickness $\delta \ll 1$. we get

$$\frac{V_n(1) - V_n(1 - \delta)}{V_n(1)} = \frac{C_n - C_n(1 - \delta)^n}{C_n} = 1 - (1 - \delta)^n.$$

So for large enough n the layer contains practically all the volume of the sphere.

In statistical physics we work with the phase space of N particles where N is very large, of the order 10^{23} . The number of dimensions of the corresponding phase space is proportional to N , so we work with spaces of a really large number of dimensions.

Let us consider now an ideal classical gas and calculate the "number of states" with the total energy less than the given value E . Here the notion "number of states" has to be understood in the classical limit of the quantum mechanics. Classically we have in mind the phase space volume expressed in units of $(2\pi\hbar)^{3N}$. The condition we consider is

$$\sum_i p_i^2 / 2m < E$$

what in the space of momenta is a $3N$ -dimensional sphere. Calculating the phase space volume, the spatial integral gives just V^N , where V is the volume of the

⁵A brief reminder of the Gamma function: $\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$, $\Gamma(1) = 1$, $\Gamma(1/2) = \sqrt{\pi}$, $\Gamma(z+1) = z\Gamma(z)$, $\Gamma(z)\Gamma(z+1/2) = 2^{1-2z} \sqrt{\pi} \Gamma(2z)$.

container. Using the formula for the volume of n-dimensional sphere we get for the "number of states" with energy less than E

$$\Omega(E) = \frac{1}{N!} \frac{\pi^{3N/2} (2mE)^{3N/2} V^N}{\Gamma(3N/2 + 1) h^{3N}} \approx \left(\frac{4\pi e m E}{3N} \right)^{3N/2} \frac{(V/N)^N}{h^{3N}}.$$

Let us stress that $\Omega \sim E^{3N/2}$ is (for macroscopic number of molecules) extremely rising function of E . Also if the maximal energy is E and the number of states is $\sim E^{3N/2}$ then the typical difference between the energies of two states is extremely small ($\sim e^{-N}$). So it is not possible to make a rigorously isolated system: it would require that we shield the system from interactions with a typical value of energy exchange of the order ($\sim e^{-N}$).

Exercise

Vertices of the n-dimensional cube (hypercube) (there is 2^n of them) have coordinates given by n-dimensional vectors $\vec{r}_i = (\pm 1, \dots, \pm 1)$. Let us take a pair of normalized orthogonal vectors \vec{e}_x and \vec{e}_y . The projection of the vector \vec{r}_i into the plane xy is

$$r_{ix} = \vec{r}_i \cdot \vec{e}_x, \quad r_{iy} = \vec{r}_i \cdot \vec{e}_y.$$

Draw a projection of a 3-dimensional cube so that no projections of two vertices overlap. Draw projections of a 4- and 5-dimensional cube. The pictures can provide some imagination on spaces of higher dimensions.

Chapter 4

Numerical methods

4.1 Metropolis algorithm

The goal of statistical physics is to calculate mean values of physical quantities. The mean value of a quantity A in the macrostate representing by the statistical ensemble of microstates i whose probabilities are $p(i)$ is given as

$$\bar{A} = \sum_i A_i p(i)$$

where A_i is the value (quantum mechanical mean) of the quantity A in the microstate i . In the canonical distribution the microstate probability is

$$p(i) = \frac{1}{Z} \exp\left(-\frac{E_i}{kT}\right)$$

The mean value of any quantity could be in principle calculated numerically by the Monte Carlo method if we constructed a generator uniformly generating microstates in the microstate space. Let us denote such a generator symbolically as $\text{rg}()$. Then the mean value of the quantity A can be calculated as

$$\bar{A} = \sum_{i=\text{rg}()} A_i p(i)$$

Such a program is unrealistic. The function $p(i)$ is rapidly changing in the subspace of microstates and so one has to look for an importance sampling generator, generating the states according to the probability $p(\cdot)$.

An efficient algorithm was invented as is known under the name Metropolis algorithm. It is a stepping algorithm generating (in an infinite loop) a sequence of

states. One step of the algorithm consists of generating a new microstate from the "current" state. The method is of the "accept-reject" type. At first a trial state is generated out of the actual state and then a decision is made whether the trial state is accepted as a new actual state or the trial state is rejected and a new trial is generated instead. The details can be symbolically written as

```

repeat{
 $\xi_{\text{trial}} := \text{Generate\_trial\_state\_near\_to\_the\_actual\_state}(\xi_{\text{current}})$ 
if ( $E(\xi_{\text{trial}}) < E(\xi_{\text{current}})$ )
  then  $\xi_{\text{current}} := \xi_{\text{trial}}$ 
  elseif ( $\text{rnd}() < \exp(-\frac{E(\xi_{\text{trial}})-E(\xi_{\text{current}})}{T})$ )
    then  $\xi_{\text{current}} := \xi_{\text{trial}}$ 
print( $\xi_{\text{current}}$ )
}

```

So we see, that the algorithm generates in principle infinite sequence of states. In the sequence one can generate identical states following each other. This corresponds to the situation where the trial state was rejected and the actual state is kept as the actual state for the next step. Since a random number generator is used, the process is a (discrete)random process.

"Random process" is a notion used to describe a function of one variable, "time", whose function values are random. One can imagine a random process that in each time moment a random value is drawn. The result of the process is a function which for each time moment gives a specific value of some random variable. This function is called "realization of a random process".

There is an alternative view on the whole thing. One can see a random process as an infinite-dimensional random variable whose components are indexed by (continuous or discrete) time index t . One realization of a random process corresponds then to one draw of such a infinite-dimensional random variable. Using the language of functions instead of the language of indices is something similar to the variational calculus as a generalization of the differential calculus of many variables.

It should be stressed that speaking about a random variable in each time moment might be misleading. There is nothing like a probability density of a variable $f(t)$ for each time moment. In general the probability density for the time t might depend on values which were realized in previous time moments (and strictly speaking even for the following time moments). Mathematically it means, that the probability density for that multi-dimensional variable does not factorize into a product of probability distributions for different time moments.

The Metropolis algorithm is a stepping algorithm, so it is a discrete-time random process. In quantum statistics also the random values for the process are discrete:

we are living in the space of discrete microstates.

The Metropolis algorithm is a special case of a Markov process. This is a name given to a random process where the probability distribution relevant for the n -th step depends only on the value drawn in the $(n - 1)$ -th step, and (generally) on the value n . If the probability does not depend on n , we speak about a homogenous Markov process.

The dynamics of a homogenous Markov process in discrete space is completely given by a transfer matrix

$$P_{ij}$$

The matrix element P_{ij} denotes¹ the probability that the actual state j is (in the actual step) changes into the state i . It is the probability of the transition $j \rightarrow i$.

The matrix elements P_{ij} are non-negative and satisfy the normalization condition

$$\sum_i P_{ij} = 1$$

In the course of elementary statistical physics the a classical Markov process "drunken sailor" random walk is usually investigated. We shall analyze the general Markov process using the same procedure: we shall investigate a statistical ensemble of various realizations of the Markov process By that we mean various realizations of the same random process (the process with the same dynamics, given by the same transfer matrix). We can imagine that all the realizations in the ensemble are performed in parallel, performing the n -th step synchronously in the same time moment. We can then statistically analyze the states drawn in different processes in the same moment for example by calculating various means "through the ensemble".

The ensemble probability that in the n -th step the i state will be generated we denote by $p_n(i)$. Then from the definition of the transfer matrix it is clear that the following relation holds.

$$p_n(i) = \sum_j P_{ij} p_{n-1}(j)$$

This recurrence relation can be explicitly solved and ensemble probability after n steps can be written in terms of the ensemble probability at the beginning².

$$p_n(i) = \sum_j (P^n)_{ij} p_0(j)$$

¹Here we use a physical notation, the right index gives the initial state. In mathematics often a reversed notation is used with the left index denoting the initial state.

²If one does not start with a random state described by some initial ensemble probability but rather from a fixed specific state, then the initial ensemble probability is given by the Kronecker delta

As usual in matrix linear algebra, investigation of the properties of the expression is based on the technique of eigenstates and eigenvalues. We shall not do a general analysis, we just demonstrate the procedure on the simple two-dimensional case. So let us have two states "1" and "2" with energies E_1 a E_2 , where the notation is chosen so that $E_1 < E_2$. Then the Metropolis algorithm is given by the probabilities

$$\begin{aligned} p(2 \rightarrow 1) &= 1 = P_{12} \\ p(2 \rightarrow 2) &= 0 = P_{22} \\ p(1 \rightarrow 2) &= p = \exp\left(-\frac{E_2 - E_1}{kT}\right) = P_{21} \\ p(1 \rightarrow 1) &= 1 - p = P_{11} \end{aligned}$$

The corresponding transfer matrix is

$$P = \begin{pmatrix} 1 - p & 1 \\ p & 0 \end{pmatrix}$$

Notice that the matrix is not symmetric, therefore the left eigenvectors are not equal to the right eigenvectors. We clearly need the right eigenvectors, they are easily found in this simple case. They are

$$\begin{pmatrix} \frac{p}{1+p} \\ \frac{1}{1+p} \end{pmatrix} \text{ with eigenvalue } 1$$

and

$$\begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ with eigenvalue } -p$$

Notice, that the first eigenvector has positive components and we have normalized it to the sum 1. So this vector can be interpreted as the ensemble probability vector. The second eigenvector does not have non-negative components, their sum is equal to zero. It is a "non-physical" vector, its components cannot be interpreted as ensemble probabilities. However, the vector is useful, since it is linearly independent from the first one and they together form a base in the space of ensemble probabilities. Each "physical" vector of ensemble probabilities can be written as a linear combination of the two eigenvectors.

$$\begin{pmatrix} p(1) \\ p(2) \end{pmatrix} = c_1 \begin{pmatrix} \frac{p}{1+p} \\ \frac{1}{1+p} \end{pmatrix} + c_2 \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

The coefficients are easily found

$$\begin{aligned} c_1 &= 1 \\ c_2 &= \frac{p(1) - pp(2)}{1 + p} \end{aligned}$$

So we express the initial ensemble probability in the base of the eigenvectors and after n steps we get

$$\begin{pmatrix} p_n(1) \\ p_n(2) \end{pmatrix} = 1^n \begin{pmatrix} \frac{p}{1+p} \\ \frac{1}{1+p} \end{pmatrix} + c_2(-p)^n \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

In the limit $n \rightarrow \infty$ we get

$$\begin{pmatrix} p_\infty(1) \\ p_\infty(2) \end{pmatrix} = \begin{pmatrix} \frac{p}{1+p} \\ \frac{1}{1+p} \end{pmatrix}$$

The ensemble probability distribution therefore converges to a limiting distribution. Taking into account the definition of the parameter p we easily see that the limiting distribution is the Boltzmann distribution. So if we start the Metropolis algorithm from any ensemble distribution then after enough long time we generate a (micro)state which is a good representative of the canonical Boltzmann distribution. If we repeat the procedure, we get, always after enough long time, another (independent) microstate representing the canonical distribution. In this way we can gather enough representative microstates and we can calculate the mean value of the physical quantity of interest. The potential problem is hidden in the words "enough long time".

Chapter 5

Supplements to thermodynamics

5.1 Basic notions and laws of thermodynamics

In thermodynamics the state of the system is what we call the macrostate in statistical physics.

We intuitively understand the notion of isolated system.

First postulate: an isolated system spontaneously changes its (macro)state until it arrives at a steady state which we call the equilibrium state. The typical time needed to arrive to the equilibrium state is called the relaxation time. In equilibrium state all the (macroscopic)parameters of the system are constant with time. Sometimes the equilibrium time to reach the true equilibrium state is unrealistically high, the system might for a very long time stay in a metastable state (like glass).

We have the notion of external parameters (like volume or external magnetic field). Intuitively these are parameters which can be externally set by the experimentalist.

Going beyond the thermodynamics these are the parameters which set the energy levels of the (quantum) system. The energy of the system in the microstate i depends on the value of some external parameter V like $E_i(V, \dots)$. Then the conjugate force is

$$p_i = -\frac{\partial E_i}{\partial V}$$

and the corresponding macroscopic parameter is

$$p = \langle p_i \rangle$$

where the average is done over the statistical ensemble of microstates representing the macrostate considered.

Staying at the level of phenomenological thermodynamics we have to identify the macroscopic parameter conjugate to the external parameter V for example by observing it as a force to be applied to the system from outside to keep the external parameter V constant at the set value. Then the work done by an external agent changing the set value of V by dV is

$$\delta A' = -p dV$$

and the work done by the system upon the external agent is

$$\delta A = p dV$$

Now we need the notion of thermal contact. It is a way of interaction of two systems such that non of their (individual) external parameter is changed (but they still can exchange energy. We shall discuss energy in detail when we shall speak on the first law of thermodynamics.

Then we need the notion of "two systems being in thermal equilibrium with each other". We say the two systems are in thermal equilibrium with each other when, after bringing them to thermal contact, nothing macroscopic happens, that is the compound system is immediately in thermal equilibrium.

Then there is the zeroth law of thermodynamics, definition of temperature. We experimentally find and then postulate: The notion of "being in thermal equilibrium with each other" is transitive.

The properties of reflexivity and symmetry are automatic by definition, so the zeroth law of thermodynamics effectively says "being in thermal equilibrium is equivalence (in mathematical sense). So all the systems can be classified into (not-overlapping) classes of equivalence. And the classes can be labeled. The label is called "the temperature". Temperature defined in this way is not unique: the only requirement is that different classes have different labels. We, however, usually require more, we need property of continuity in labeling the classes. We need to find some practical (experimental method) to label the classes.

To do that we had to choose a suitable "thermoscope". By that we mean some system which can be found in many equivalence classes (in each class the system is, of course, in a different (macro)state. Ideally the system should be found in states having the same values of external parameters, differing by the value of some internal parameter (like pressure) in different equivalence classes. The system (and its chosen external parameter) can be used as thermoscope: bringing it to thermal contact with any other system and reading the value of pressure we can recognize

to which equivalence class the "measured" system belongs. We can do more, we can use the readings of our thermoscope to label the classes: so we use it effectively as a thermometer. Most often we first choose some (arbitrary) calibration to define our temperature scale. Like this: we take the thermoscope of a defined prescribed size, put it into contact with a melt of ice and water and label the pressure reading by zero. Then we put it to contact with boiling water and label the pressure reading as 100. The other pressure readings are simply linearly interpolated or extrapolated. The temperature defined in this way is rather arbitrary but can serve our purposes and is "continuously defined". Topology is introduced into the space of equivalence classes: the two classes are considered to be close to each other if the thermoscope readings are close to each other.

Now we should recognize, that the macrostate (and its energy) can be changed by external influence even if no external parameter is changed and so no macroscopic work is done. We conclude some other form of work can be performed and we call it heat. In general we get the first law of thermodynamics

$$\delta Q = dE + \delta A$$

Going beyond the phenomenological thermodynamics the interpretation is easy, from the notion of microstate we now what are the external parameters and the corresponding conjugate variables and we know (from mechanics, say) what is the energy of the microstate, and therefore we also know what is the macroscopic energy E being the average over microstates

$$E = \langle E_i \rangle$$

.

Staying at the level of phenomenological thermodynamics the situation is more complicated. We can macroscopically well identify the macroscopic work, but we do not have direct access to neither macroscopic energy nor heat. We need more assumptions and usually we assume that we intuitively feel in which situations $\delta Q = 0$. More specifically we believe we can force the heat to be zero by applying suitable thermal insulation to the system. Then energy can be changed only at the cost of macroscopic work and we can in principle determine energy differences by measuring the external macroscopic work. The energy is defined only upon an additive constant, we have to choose some (macro)state of the system and set its energy to arbitrary reference value. Then applying the thermal insulation and going from the reference state to any state, we measure the required work to be done for that and we calculate the energy of the final state.

However, the situation is more subtle. we cannot use just quasistatic (reversible) processes to perform the program. The point is that an arbitrary final state cannot be reached from the reference state via the quasi-static adiabatic curve. At least a part of the process must be done irreversibly. That is not a serious problem, the

energy conservation law holds for irreversible processes as well. So we can measure in principle the energy of any macrostate. Then we can get rid of the thermal insulation and can determine the amount of heat for any process measuring the work and calculating the energy difference.

Historically the process was different, one determined the energy (better to say identified the notion of energy) by measuring heat. The idea is as follows. We first go from the reference state by adiabatic process to the state which has the same values of the external parameters as the desired final state, but is still a different state differing for example by the value of the conjugated parameters (practically it means by temperature). Now we keep the external parameters constant and perform heat to get to the desired final state. We perform "produce" heat by an irreversible process (Joule) performing mechanical work on some other (macroscopic but very small with respect to our system of interest) auxiliary system which is in contact with our system and exchanges heat with it, with the auxiliary system performing an irreversible process where external work is performed upon it. The auxiliary system is small, so even if its temperature is gradually increasing its energy increases by negligible amount. All the work performed on it is transferred as output heat to our system until it reaches the desired final state. Measuring the external work on the auxiliary system we effectively measure heat performed on our system of interest. Using this method we automatically measure heat in units of energy. Now the important point is that if we sum the mechanical work performed on our system and the heat performed we get some value, which we interpret as the increase of the energy between the initial and the final state. But this interpretation is possible only after we observe the fact that the sum of heat and work performed between two states is always the same irrespective of the specific path we choose. This independence of the sum of heat and work on the path is, in fact, the statement of the first law of thermodynamics. In phenomenological thermodynamics the statement is far less trivial than in the statistical thermodynamics. In statistical thermodynamics the "internal energy" of the system is the primary notion and is interpreted the (mechanical) energy of the microstate. We have the concept of energy conservation formulated before we start to speak of some macrostates. So in Statistical thermodynamics the first law of thermodynamics is rather trivial and can be, in fact, used as a definition of the concept of heat: We now what is energy and what is the macroscopic work and the difference of those two is heat.

Historically in fact the procedure was still different from the procedure using the Joule irreversible (work to heat transfer) process as described above.

The notion of heat was older than the fact that it can be measured using the units for work. The notion of heat developed in calorimetric measurements. A calorimeter is a device which enables us to bring two systems into thermal contact with each other without being in thermal contact with external surroundings. We also assume that both the systems in thermal contact have all their external parameters fixed so that no mechanical (macroscopic) work is performed on them. We have

already the notion of phenomenological temperature and the thermometer. We measure the initial temperatures of the two systems (t_1, t_2) , then the irreversible process of achieving the common equilibrium state starts and afterwards we measure the common final temperature t . Performing experiments with various pairs of systems we arrive at the empirical notion of heat capacity. Each system is characterized by unique quantity, the heat capacity c , so that the calorimetric equation holds

$$c_1(t_1 - t) = c_2(t - t_2)$$

the heat capacities can (and do) depend on temperature, so the statement concerns only infinitesimally close initial temperatures t_1, t_2 . The heat capacities defined in this way are, however, determined up to unknown multiplicative constant. Fixing the value of the heat capacity of some system (like one kilogram of water) at some chosen temperature, the system of heat capacities is fixed. We first determine the heat capacity of "water" at slightly higher temperature referring to the defined heat capacity at the reference temperature. Repeating the process we slowly go to higher and higher temperatures each time fixing the heat capacity of "water" at the higher temperature. Now we call the quantity $c_1(t_1 - t)$ as heat, measured, say, in kilocalories when the heat capacity was defined in kilocalories per degree of temperature. We now have a reference system with heat capacity defined in the whole energy range and use it "to measure heat" (in arbitrary units kilocalories).

Now the point is that we can get from one equilibrium state to an arbitrary other equilibrium state by various combinations of reversible adiabatic (thermal insulation) and irreversible isochoric (fixed external parameters) processes. For the adiabatic process we measure the performed work (in Joules), the irreversible isochoric process we perform in a calorimeter bringing our system into thermal contact with "hot water" of a suitable temperature (find by the trial and error method) such that the final temperature would be just the desired temperature of the final state. And we calculate heat in kilocalories. Choosing different paths we obtain different number of Joules and different number of kilocalories. Now the statement of the first law of thermodynamics would be

There exist a universal multiplicative constant by which we can multiply all the values expressed in the kilocalories with the property that when we sum Joules for work with "modified kilocalories" for heat we always get the same sum irrespective of the path between the same initial and final states. So we have every good reason to name the "modified kilocalories" as Joules and measure heat in Joules. And then get the statement that the sum of work and heat independent of the path. So we get a new state-characterizing quantity, the energy.

Well all this was a rather long characterization of the various aspects of the zeroth and the first law of thermodynamics just to demonstrate "the art or reasoning" in phenomenological thermodynamics where it is strictly forbidden to speak about molecules.

We shall not continue within this spirit with the second or third law of thermodynamics. We refer to their statistical thermodynamics versions defined in the introductory course of statistical physics.

5.2 Properties of thermodynamic potentials

The first thermodynamic potential is the entropy. It has the property that for an isolated system the equilibrium state has the largest entropy from all the macrostates satisfying the external constraints. Practically it means that the entropy is the function of energy and the external parameters.

We now investigate the situation when all the parameters are extensive quantities, we shall generically call them E and V . We are going to prove that the entropy

$$S(E, V)$$

is a concave function of its parameters.

Let us suppose, that we have the system of total energy $2E$ and total volume $2V$ and we divide the system into two equal subsystems with energies E and volume V . Let us suppose that the "piston" which separates the two systems is diathermic (not adiabatic, it means it allows for transfer of heat) and non-fixed (it can move to allow for the redistribution of volume between the two subsystems). Then the homogenous situation as described above when the two subsystem have same energies and volumes is (by experience) the equilibrium one. The total equilibrium entropy would be

$$2S(E, V) = S(E, V) + S(E, V)$$

Now suppose that we fix the position of the piston, so the volumes remain to be equal, but we somehow arrange redistribution of energy, so that one of the subsystem will have the energy $E - \Delta E$ and the other the energy $E + \Delta E$. By that we obtain a non-equilibrium overall state, which should have smaller entropy, so we get

$$S(E - \Delta E) + S(E + \Delta E) \leq 2S(E)$$

this is just the definition of the concave function of one variable.

Now let us suppose that the piston is not only diathermic but it can also move, so that the volume can be redistributed between the two subsystem. Reasoning in a similar way we get

$$S(E - \Delta E, V - \Delta V) + S(E + \Delta E, V + \Delta V) \leq 2S(E, V)$$

Expanding into Taylor serie we get

$$\frac{\partial^2 S}{\partial E^2} (\Delta E)^2 + \frac{\partial^2 S}{\partial V^2} (\Delta V)^2 + 2 \frac{\partial^2 S}{\partial E \partial V} \Delta E \Delta V \leq 0$$

The condition says, that the matrix

$$\begin{pmatrix} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E \partial V} \\ \frac{\partial^2 S}{\partial E \partial V} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix}$$

must be negative definite, so we get the conditions for the concavity

$$\frac{\partial^2 S}{\partial E^2} \leq 0, \quad \frac{\partial^2 S}{\partial V^2} \leq 0, \quad \left(\frac{\partial^2 S}{\partial E \partial V} \right)^2 - \frac{\partial^2 S}{\partial E^2} \frac{\partial^2 S}{\partial V^2} \leq 0$$

These conditions are also called conditions of stability.

Now the same way as entropy must be maximal for given fixed energy and volume, energy must be minimal for given fixed entropy and volume. Since entropy and volume are again extensive quantities, we can repeat the trick with piston dividing the system into two subsystem and we can derive conditions for the convexity of energy as a function of entropy and volume.

The Gibbs potential is defined by the Legendre transformation

$$G = E - TS + pV$$

and since the Legendre transformation written in this order changes convexity to concavity, we have the statement: Gibbs potential is a concave function of its variables p and T .

We remind the "statistical thermodynamics definitions"

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N}$$

$$\frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E,V}$$

differentiating the first equation by T we get

$$-\frac{1}{T^2} \left(\frac{\partial T}{\partial E} \right)_{V,N} = \left(\frac{\partial^2 S}{\partial E^2} \right)_{V,N} \leq 0$$

where we used the condition of concavity so we get

$$\left(\frac{\partial T}{\partial E} \right)_{V,N} \geq 0$$

So we proved that energy is an increasing function of temperature.

Now we go to prove that energy spontaneously flows from the hotter system to colder system.

Let us consider two systems (S_1, E_1, T_1) and (S_2, E_2, T_2) . Let put them into thermal contact, however with the wall between them that is only slightly diathermic, so the energy flow between the two system is small. Then, even the global process is irreversible, both subsystems individually are in equilibrium state. So the total entropy can be calculated as the sum of two equilibrium entropies. The system as a whole is isolated so the total energy is conserved. Therefore for the energy changes of the subsystems we get

$$dE_1 = -dE_2$$

The change of the total entropy will be

$$dS = \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_2}{\partial E_2} dE_2 = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) dE_1 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 > 0$$

If $T_2 > T_1$ then $dE_1 > 0$ so the energy flows from the hotter subsystem to the colder one.

Similarly one can prove, that the volume of the subsystem with bigger pressure increases.

Now about the derivation of the equation of state.

We start with the equation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

In the first equation the condition of convexity gives

$$\left(\frac{\partial^2 S}{\partial E^2} \right)_{V,N} < 0$$

so the first equation can be inverted and the energy can be expressed in terms of temperature and volume. This expression then can be inserted into the equation

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N}$$

Energy is eliminated and we get p in terms of V, T , that is the equation of state.

We remind here the definition of thermodynamic potentials

$$F = E - TS$$

$$G = E - TS + pV$$

$$\Omega = E - TS - \mu N$$

In the last equation we have introduced so called grand potential, which is relevant for the grand-canonical distribution: the grand statistical sum can be expressed in terms of the grand potential

$$\mathcal{Z} = \sum \exp\left(\frac{\mu N_i - E_i}{kT}\right) = \exp\left(-\frac{\Omega}{kT}\right)$$

The first and second law of thermodynamics give (for general, even irreversible) processes

$$TdS \geq dE + pdV - \mu dN$$

$$dE \leq TdS - pdV + \mu dN$$

$$dF \leq -SdT - pdV + \mu dN$$

$$dG \leq -SdT + Vdp + \mu dN$$

$$d\Omega \leq -SdT - pdV - Nd\mu$$

The Gibbs potential is a function of intensive variables p, T and one extensive variable N . So scaling the system by λ we get

$$\lambda G(p, T, N) = G(p, T, \lambda N)$$

Differentiating by λ and putting $\lambda = 1$ we get (for equilibrium potential)

$$G = N \frac{\partial G}{\partial N} = N\mu$$

and

$$dG = dN\mu + Nd\mu = -SdT + Vdp + \mu dN$$

and we get finally the Gibbs Duham relation

$$Nd\mu + SdT - Vdp = 0$$

Many useful relations between thermodynamic variables can be obtained using the fact, that, for example

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$$

Since

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p, N}$$

$$V = \left(\frac{\partial G}{\partial p} \right)_{T, N}$$

we get by the commutativity of second derivatives

$$-\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

This relation is called the Maxwell relation and similar Maxwell relations can be obtained doing the second derivatives of other potential.

The second derivatives of the thermodynamic potentials are usual and often easily measurable physical quantities, so they often get a special name.

For example

$$-T \left(\frac{\partial^2 F}{\partial T^2}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\delta Q}{\partial T}\right)_V = C_V$$

So we get for the specific heat at constant volume

$$C_V = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

Other useful definitions

Expansion coefficient

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

Coefficient of isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

Coefficient of adiabatic compressibility (for constant entropy)

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S$$

In addition to Maxwell relations we also often use the following properties of partial derivatives

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z$$

which is simply the theorem about the derivative of inverse function.

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

This property can be easily derived considering

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

Now we put $dy = 0$ and we get

$$0 = \left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y$$

which is just the required relation if we invert the partial derivative $\left(\frac{\partial y}{\partial x}\right)_z$.

As a demonstration of usage of the Maxwell and other relations we derive the general form of the Mayer relation (the relation between C_p and C_V).

We start with the entropy expressed as a function of (non/natural) variables p, T .

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$TdS = C_p dT + T \left(\frac{\partial S}{\partial p}\right)_T dp$$

Now we use the Maxwell relation

$$\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p$$

and we get

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_p dp$$

Now we use the above general equation for a isochoric process at constant V . We get

$$T \left(\frac{\partial S}{\partial T}\right)_V = C_p + -T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V$$

So we get

$$C_p = C_V + T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V$$

Now we substitute from the general relation

$$\left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T$$

and using the definition of expansion coefficients we get the final formula

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T}$$

We shall now investigate the consequences of the concavity of G , we get so called stability conditions. The concavity conditions are

$$\frac{\partial^2 G}{\partial T^2} \leq 0, \quad \frac{\partial^2 G}{\partial p^2} \leq 0, \quad \left(\frac{\partial^2 G}{\partial p \partial T} \right)^2 - \frac{\partial^2 G}{\partial T^2} \frac{\partial^2 G}{\partial p^2} \leq 0$$

From the first equation we get

$$\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial T} \right)_p = -\frac{1}{T} C_p \leq 0$$

and so we get the stability condition

$$C_p \geq 0$$

From the second concavity condition we get

$$\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial p} \right)_T = V \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -V \kappa_T \leq 0$$

And we get another stability condition

$$\kappa_T \geq 0$$

what means that increasing pressure must decrease the volume.

From the third concavity condition we get

$$\begin{aligned} \left(\frac{\partial^2 G}{\partial p \partial T} \right)^2 - \frac{\partial^2 G}{\partial T^2} \frac{\partial^2 G}{\partial p^2} &\leq 0 \\ \left(\frac{\partial^2 G}{\partial p \partial T} \right)^2 - \left(-\frac{C_p}{T} \right) (-V \kappa_T) &\leq 0 \\ \frac{C_p V \kappa_T}{T} - \left(\left(\frac{\partial V}{\partial T} \right)_p \right)^2 &\geq 0 \\ C_p - \frac{\alpha^2 V T}{\kappa_T} &\geq 0 \end{aligned}$$

So we get another stability condition

$$C_V \geq 0$$

5.3 Applications of thermodynamic relations

5.3.1 Free expansion

We consider isolated system of a gas performing free expansion into vacuum. It is an irreversible process during which the volume is increased $V \mapsto (V + dV)$. Since the system is isolated, its energy remains constant $dU = 0$. Both the initial and the final state are equilibrium states, for which we can write

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

we put $dU = 0$ and get

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V}$$

The l.h.s. is called the Joule coefficient and describes how much the temperature is changed during free expansion.

From molecular consideration it is clear, that for ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

since for fixed temperature the kinetic energies of molecules remain the same while increasing the volume and there is no potential energy in the game. But we can prove this relation on the phenomenological level as well. Starting with the first law of thermodynamics

$$TdS = dU + pdV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{p}{T}$$

Now we use the Maxwell relation (derived from the F potential)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

and get

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{p}{T}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

The trick was that using the Maxwell relation we got rid of the calorical variables and everything on the r.h.s. can be evaluated just from the equation of state. If we use the equation of state for the ideal gas

$$pV = RT$$

we finally get

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

IF we consider the Van der Waals gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

$$p = -\frac{a}{V^2} + \frac{RT}{V - b}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V - b}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 = \frac{TR}{V - b} + \frac{a}{V^2} - \frac{RT}{V - b} = \frac{a}{V^2} > 0$$

to evaluate the Joule coefficient for the Van der Waal gas we still need

$$\left(\frac{\partial U}{\partial T}\right)_V$$

what is the specific heat at constant volume. To get it we first prove, that the specific heat for the Van der Waals gas does not depend on volume at fixed temperature.

We start with the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Differentiating by T

$$\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

$$\left(\frac{\partial}{\partial V}\right)_T T \left(\frac{\partial S}{\partial T}\right)_V = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

Since the Van der Waals equations give

$$p = -\frac{a}{V^2} + \frac{RT}{V-b}$$

we get

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0$$

and

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

So the specific heat at constant volume does not depend on volume, it can be evaluated for large volume where the gas is sufficiently dilute and behaves like ideal gas, so we get

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R$$

For the Joule constant we finally get

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} = -\frac{\frac{a}{V^2}}{\frac{3}{2}R} = -\frac{2a}{3RV^2}$$

5.3.2 Throttling

Joule - Kelvin process (or throttling) is a process where gas is expanding through a porous membrane (or through a valve, the throttle) from a region of high pressure p_1 to the region of low pressure p_2 . The porous membrane has the effect that each of the two gas compartments is by itself in equilibrium state. The process is adiabatically isolated, so no heat is performed on either of the compartment. On the other hand the devices which keep the pressure constant on each side perform mechanical work.

Suppose that initially we have a volume V_1 of gas in the left compartment at pressure p_1 and no gas in the right compartment. At the end we shall have the volume V_2 in the right compartment at pressure p_2 and no gas in the left compartment. The total work performed by the gas during the process will be

$$A = p_2 V_2 - p_1 V_1$$

Since heat is zero the following energy conservation law must hold

$$E_2 - E_1 = -A$$

and we get

$$E_1 + p_1 V_1 = E_2 + p_2 V_2$$

So the process is isenthalpic. For infinitesimal process we get

$$dH = TdS + Vdp$$

Now let us consider entropy being a function of T, p , so that

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$dH = T \left(\frac{\partial S}{\partial T}\right)_p dT + \left(V + T \left(\frac{\partial S}{\partial p}\right)_T\right) dp$$

from the Maxwell relation (for G)

$$\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p$$

$$dH = T \left(\frac{\partial S}{\partial T}\right)_p dT + \left(V - T \left(\frac{\partial V}{\partial T}\right)_p\right) dp$$

$$dH = C_p dT + \left(V - T \left(\frac{\partial V}{\partial T}\right)_p\right) dp$$

putting $dH = 0$ we get for the Joule Kelvin coefficient

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p} \left(T \left(\frac{\partial V}{\partial T}\right)_p - V\right)$$

For the ideal gas we get zero Joule Kelvin coefficient.

5.3.3 Maxwell construction

5.3.4 Osmosis

Chapter 6

Simple statistical systems

6.1 Density of states

First we remind the way we calculated the density of states in the energy space in the Introductory course.

We started with one-particle states in a box, which are sinus waves with zeros at the box boundaries. The states are labeled by three positive integer numbers n_1, n_2, n_3 and their energy is

$$\varepsilon = \frac{\pi^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$$

States correspond to points with integer-valued coordinates in positive octant of the n -space, so the total number of one-particle states with energy less than ε is

$$\varphi(\varepsilon) = \frac{1}{8} \frac{4}{3} \pi \left(\frac{2mL^2}{\pi^2 \hbar^2} \varepsilon \right)^{3/2}$$

And the density of states in the ε -space is

$$\varphi'(\varepsilon) = \frac{2\pi V}{(2\pi \hbar)^3} (2m)^{3/2} \varepsilon^{1/2}$$

An alternative way is to use periodic boundary conditions in the box of size $V = L^3$, so we use $\exp(i \vec{k} \cdot \vec{x})$ waves with wave vectors

$$k_i = \frac{2\pi}{L} n_i \quad \text{where } n_i = 0, \pm 1, \pm 2, \dots$$

So the density of states in the k -space is

$$\frac{V}{(2\pi)^3}$$

and in p -space

$$\frac{V}{(2\pi\hbar)^3}$$

To switch to the ε -space one needs the dispersion relation, which for free particles reads

$$\varepsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

and the substitution in the integrals reads

$$\frac{V}{(2\pi)^3} d^3\vec{k} = \frac{V}{(2\pi)^3} 4\pi k^2 dk = \frac{V}{(2\pi)^3} 4\pi k^2 \frac{d\varepsilon}{\frac{d\varepsilon}{dk}}$$

Substituting from the dispersion relation we get the same density of states in the ε -space as before.

6.2 Ideal Bose gas

We calculate grandcanonical distribution for one one-particle state. The "state of the state j " is given by the occupation number n_j and the relevant grandcanonical sum is

$$\mathcal{Z}_j = \sum_{n_j} \exp\left(\frac{\mu}{kT} n_j - \frac{\varepsilon_j}{kT} n_j\right) = \frac{1}{1 - \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)}$$

We introduce fugacity z by

$$z = \exp\left(\frac{\mu}{kT}\right)$$

So we get

$$\mathcal{Z}_j = \frac{1}{1 - z \exp(-\beta\varepsilon_j)}$$

The one-particle states are independent, so the total grandcanonical sum is given by the product

$$\mathcal{Z} = \prod_j \mathcal{Z}_j$$

$$\ln \mathcal{Z} = - \sum_j \ln(1 - z \exp(-\beta\varepsilon_j))$$

We remind that

$$(Z) = \exp\left(\frac{pV}{kT}\right)$$

and so

$$\frac{pV}{kT} = - \sum_j \ln(1 - z \exp(-\beta\varepsilon_j))$$

We pretend to know the value of μ , but experimentally we rather know the number of particles

$$N = \sum_j \bar{N}_j = \sum_j \frac{1}{\exp\left(\frac{\varepsilon_j - \mu}{kT}\right) - 1} = \sum_j \frac{1}{z^{-1} \exp(\beta\varepsilon_j) - 1}$$

This equation should be inverted: one should calculate μ in terms of N and T , substitute it to the previous equation and get the equation of state.

To perform this program, we need to replace the summations by integration in the energy space, using the known expression of the density of states in the ε -space. We get

$$\begin{aligned} \frac{p}{kT} &= - \frac{2\pi}{(2\pi\hbar)^3} (2m)^{3/2} \int_0^\infty \varepsilon^{1/2} \ln(1 - z \exp(-\beta\varepsilon)) d\varepsilon \\ \frac{N}{V} &= \frac{2\pi}{(2\pi\hbar)^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{z^{-1} \exp(\beta\varepsilon) - 1} d\varepsilon \end{aligned}$$

We switch to dimensionless integration variable

$$\begin{aligned} \frac{p}{kT} &= - \frac{2}{\sqrt{\pi}} \frac{(2\pi mkT)^{3/2}}{(2\pi\hbar)^3} \int_0^\infty x^{1/2} \ln(1 - z \exp(-x)) dx \\ \frac{N}{V} &= \frac{2}{\sqrt{\pi}} \frac{(2\pi mkT)^{3/2}}{(2\pi\hbar)^3} \int_0^\infty \frac{x^{1/2}}{z^{-1} \exp(x) - 1} dx \end{aligned}$$

We introduce the notation (de'Broglie thermal length)

$$\lambda = \frac{2\pi\hbar}{(2\pi mkT)^{1/2}}$$

and using the relation

$$\Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2}$$

we get

$$\frac{p}{kT} = - \frac{1}{\lambda^3} \frac{1}{\Gamma(3/2)} \int_0^\infty x^{1/2} \ln(1 - z \exp(-x)) dx$$

$$\frac{N}{V} = \frac{1}{\lambda^3} \frac{1}{\Gamma(3/2)} \int_0^\infty \frac{x^{1/2}}{z^{-1} \exp(x) - 1} dx$$

Since similar integrals are often met in statistical physics, new special functions are introduced (called Einstein functions) as

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}}{z^{-1} \exp(x) - 1} dx$$

which can be expanded into Taylor series as

$$g_\nu(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^\nu}$$

The expression for N/V is already written in terms of an Einstein function, the expression for $\frac{p}{kT}$ has to be transformed by the per partes method

$$\begin{aligned} \frac{1}{\Gamma(3/2)} \int_0^\infty x^{1/2} \ln(1 - z \exp(-x)) dx &= \frac{1}{\Gamma(3/2)} \int_0^\infty \frac{2}{3} x^{3/2} \frac{-z \exp(-x)}{1 - z \exp(-x)} dx = \\ &= -\frac{2}{3} \frac{1}{\Gamma(3/2)} \int_0^\infty \frac{x^{3/2}}{z^{-1} \exp(-x) - 1} = -\frac{1}{\Gamma(5/2)} \int_0^\infty \frac{x^{3/2}}{z^{-1} \exp(-x) - 1} = -g_{5/2}(z) \end{aligned}$$

So we get

$$\begin{aligned} \frac{p}{kT} &= \frac{1}{\lambda^3} g_{5/2}(z) \\ \frac{N}{V} &= \frac{1}{\lambda^3} g_{3/2}(z) \end{aligned}$$

Now the idea is we should calculate z from the second equation and substitute it to the first one to get the equation of state, formally

$$\frac{pV}{NkT} = \frac{V}{N} \frac{1}{\lambda^3} g_{5/2}(g_{3/2}^{-1}(\lambda^3 \frac{N}{V}))$$

The problem is we do not know how to invert the Einstein function $g_{3/2}(z)$. We know only its Taylor series expansion. What we can do is to find the Taylor series expansion for its inverse function by the method of "series reversion"¹. We get

¹If we have series

$$y = a_1 x + a_2 x^2 + a_3 x^3 + \dots$$

we can look for its inverse in the form

$$x = A_1 y + A_2 y^2 + A_3 y^3 + \dots$$

Plugging the second equation into the first one one gets

$$y = a_1 A_1 y + (a_2 A_1^2 + a_1 A_2) y^2 + \dots$$

Comparing coefficients on both sides one gets

$$A_1 = a_1^{-1}, \quad A_2 = -a_1^{-3} a_2, \quad \dots$$

the equation of states in the form of series

$$\frac{pV}{Nkt} = \sum_{l=1}^{\infty} A_l \left(\frac{\lambda^3}{N/V} \right)^{l-1}$$

where the coefficients A_l have to be found by the series inversion.

In the classical limit we have $z \ll 1$, so to get the first correction we expand to the second order in z

$$\lambda^3 \frac{N}{V} = z + \frac{z^2}{2^{3/2}}$$

We look for z in the form

$$z = \lambda^3 \frac{N}{V} + c \left(\lambda^3 \frac{N}{V} \right)^2$$

We find

$$c = -\frac{1}{2^{3/2}}$$

And we subsequently get

$$\frac{pV}{NkT} = \frac{V/N}{\lambda^3} \left(z + \frac{1}{2^{5/2}} z^2 \right) = \frac{V/N}{\lambda^3} \left(\frac{\lambda^3}{V/N} - \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{V/N} \right)^2 + \frac{1}{2^{5/2}} \left(\frac{\lambda^3}{V/N} \right)^2 \right)$$

$$\frac{pV}{NkT} = 1 - \frac{1}{4\sqrt{2}} \frac{\lambda^3}{V/N}$$

6.3 Van der Waals gas

we consider gas of molecules which interact via pairwise interaction:

$$U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{\text{pairs}} u(\mathbf{r}_i, \mathbf{r}_j)$$

Statistical sum

$$Z = \frac{1}{N!} \int \frac{1}{(2\pi\hbar)^{3N}} \prod_i d^3\mathbf{p}_i d^3\mathbf{r}_i \exp \left(\frac{\sum_j \frac{\mathbf{p}_j^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{kT} \right)$$

$$Z = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} (2\pi mkT)^{3N/2} Z_U$$

where

$$Z_U = \int \prod_i d^3\mathbf{r}_i \exp \left(\frac{-U}{kT} \right)$$

We calculate Z_U using the following trick with the mean potential energy

$$\bar{U} = -\frac{d}{d\beta} \ln Z_U(\beta)$$

and since $Z_U(0) = V^N$ we get

$$\ln Z_U(\beta) = N \ln V - \int_0^\beta \bar{U}(\beta') d\beta'$$

Now we assume that we can neglect correlations between pairs of particles and we get

$$\bar{U} = \frac{1}{2} N(N-1) \bar{u}$$

where

$$\bar{u} = \frac{\int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 u(\mathbf{r}_1, \mathbf{r}_2) \exp\left(-\frac{u(\mathbf{r}_1, \mathbf{r}_2)}{kT}\right)}{\int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \exp\left(-\frac{u(\mathbf{r}_1, \mathbf{r}_2)}{kT}\right)}$$

Using substitution

$$\mathbf{r}_1, \mathbf{r}_2 \mapsto \mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

we get

$$\bar{u} = \frac{\int d^3 \mathbf{R} \int d^3 \mathbf{r} u(\mathbf{r}) \exp\left(-\frac{u(\mathbf{r})}{kT}\right)}{\int d^3 \mathbf{R} \int d^3 \mathbf{r} \exp\left(-\frac{u(\mathbf{r})}{kT}\right)}$$

$$\bar{u} = -\frac{d}{d\beta} \ln \int \exp(-\beta u) d^3 \mathbf{R}$$

$$\int \exp(-\beta u) d^3 \mathbf{r} = \int [1 + (\exp(-\beta u) - 1)] d^3 \mathbf{r} = V + I = V \left(1 + \frac{I}{V}\right)$$

where

$$I(\beta) = \int (\exp(-\beta u) - 1) d^3 \mathbf{r} = \int_0^\infty (\exp(-\beta u) - 1) 4\pi r^2 dr$$

and

$$I(0) = 0$$

$$\bar{u} = -\frac{d}{d\beta} \left[\ln V + \ln \left(1 + \frac{I(\beta)}{V}\right) \right] \approx -\frac{d}{d\beta} \frac{I(\beta)}{V} = -\frac{1}{V} \frac{dI(\beta)}{d\beta}$$

$$\bar{U}(\beta) = -\frac{1}{2} \frac{N^2}{V} \frac{dI(\beta)}{d\beta}$$

$$\ln Z_U(\beta) = N \ln V + \frac{1}{2} \frac{N^2}{V} \int \frac{dI(\beta)}{d\beta} = N \ln V + \frac{1}{2} \frac{N^2}{V} I(\beta)$$

For the equation of state we get

$$\frac{p}{kT} = \frac{\partial \ln Z_U}{\partial V} = \frac{N}{V} - \frac{1}{2} \frac{N^2}{V^2} I(\beta)$$

$$u(r) = \infty \quad \text{for } r < r_0$$

$$u(r) = f(r) \quad \text{for } r > r_0$$

$$I(\beta) = -4\pi \int_0^{r_0} r^2 dr + 4\pi \int_{r_0}^{\infty} (\exp(-\beta f) - 1) r^2 dr = -\frac{4}{3} \pi r_0^3 - \frac{4\pi}{kT} \int_{r_0}^{\infty} f(r) r^2 dr$$

$$I(\beta) = -2b + \frac{2a}{kT}$$

where we have denoted

$$b = \frac{2\pi}{3} r_0^3$$

$$a = -2\pi \int_{r_0}^{\infty} f(r) r^2 dr$$

So for the equation of motion we get

$$\frac{p}{kT} = \frac{N}{V} + \frac{N^2}{V^2} \left(b - \frac{a}{kT} \right)$$

$$\left(p + a \frac{N^2}{V^2} \right) = \frac{N}{V} kT \left(1 + b \frac{N}{V} \right) \approx \frac{\frac{N}{V} kT}{1 - b \frac{N}{V}}$$

$$\left(p + a \frac{N^2}{V^2} \right) (V - bN) = NkT$$

what is Van der Waal equation.

Chapter 7

Critical phenomena

7.1 Spin-spin interaction

See also [ZK] (p. 455), [Noga] (p. 172), or Feynmann (*Statistical Physics*, p. 198).

Our goal is to understand - qualitatively - the phenomenon of ferromagnetism. Our feeling is that the good working hypothesis is that the "elementary magnets" in the solid get aligned and the summary effect of their magnetic field is the strong observed magnetic field of the ferromagnet. The nature of "elementary magnets" in the solid is assumed to be the magnetic moment of a (charged) particle with spin. Spin is the internal angular momentum of the particle and it is natural to expect that it is related to the particle (internal) magnetic moment. The reason is, that for the orbital angular momentum we are aware of such a relation between the angular momentum and the magnetic moment of a charged particle.

Classically the magnetic moment of a current loop is given as $m = IS$ (where I is the current, and S the surface of the loop). One can generalize this to a classical case of a point particle with charge q moving with a velocity v . We get $m = (q/2m)L$, where L is the particle (orbital) angular momentum $L = mrv$. If we expect that a similar relation holds for the internal angular momentum, spin, we get for the electron (having spin $\hbar/2$ the magnetic moment $e\hbar/4m$. Experiment (Einstein, de Haas) however shows that the electron (internal) magnetic moment is $\mu_B = e\hbar/2m$ (this value is called Bohr magneton). This value of the electron magnetic moment (the "mysterious factor 2") is explained by the Dirac equation.

Now back to the question of magnetic moment alignment in a ferromagnet. The first guess might be, that it is the interaction of magnetic moment with each other, which is responsible for the alignment. A quick order-of-magnitude esti-

mate shows, that it is most probably not so.

Here is the brief sketch of the estimate. The magnetic field induced by a (point-like) magnetic moment is

$$\mathbf{B} = \frac{\mu_0}{4\pi} \left(\frac{3\mathbf{r}(\mathbf{m} \cdot \mathbf{r})}{r^5} - \frac{\mathbf{m}}{r^3} \right).$$

So $B \approx \mu_0 m / 4\pi r^3$, therefore the interaction energy of a magnetic moment with its neighbours in a lattice is $W \approx z\mu_0 m^2 / 4\pi r^3$ (z is the number of nearest neighbours (In a cubic lattice $z = 6$). Numerically $\mu_B \doteq 9,27 \cdot 10^{-24} \text{ Am}^2$. So the interaction energy for $r = 2 \cdot 10^{-10} \text{ m}$ is roughly 10^{-4} eV , what in temperature units means roughly 1 K. So we expect that at temperatures above 1 K the spin orientations would be randomized by thermal fluctuations and the ferromagnetism could not be observed at room temperatures. The solution of the puzzle is the effect of an electrostatic interaction combined with the Pauli exclusion principle.

Let us consider two non-interacting electrons in states with quantum numbers a and b , The state Ψ_a has energy E_a , the state Ψ_b energy E_b . The electron coordinates are denoted as \mathbf{x}_1 a \mathbf{x}_2 , spins \mathbf{S}_1 a \mathbf{S}_2 . If we consider two particle states, let us first forget about the fact that the two electrons are identical (indistinguishable). We can construct two states, the first will be $\Psi_{ab}(\mathbf{x}_1, \mathbf{x}_2) = \Psi_a(\mathbf{x}_1)\Psi_b(\mathbf{x}_2) \equiv \Psi_{ab}$ and the second one will be $\Psi_{ba}(\mathbf{x}_1, \mathbf{x}_2) = \Psi_b(\mathbf{x}_1)\Psi_a(\mathbf{x}_2) \equiv \Psi_{ba}$. The energies of these two states (as of any of their linear combinations) are the same $E(\Psi_{ab}) = E(\Psi_{ba}) = E_a + E_b$. For interacting electrons changes the situation considerably. The interaction potential between two electrons must be symmetric $V(\mathbf{x}_1, \mathbf{x}_2) = V(\mathbf{x}_2, \mathbf{x}_1) \neq 0$, the Hamiltonian of the system is $H_1 + H_2 + V$. We can construct two different two-particle states, a symmetric and an antisymmetric one

$$\Psi_S = \frac{1}{\sqrt{2}}(\Psi_{ab} + \Psi_{ba}), \quad \Psi_A = \frac{1}{\sqrt{2}}(\Psi_{ab} - \Psi_{ba}).$$

Their mean energies we calculate as $\langle \Psi | H_1 + H_2 + V | \Psi \rangle$. As a result we get two different energies

$$E_S = E_a + E_b + I - J, \quad E_A = E_a + E_b + I + J,$$

where I and J denote the integrals (J is called the exchange integral)

$$I = \int \Psi_{ab}^* V \Psi_{ab} = \int \Psi_{ba}^* V \Psi_{ba}, \quad J = - \int \Psi_{ab}^* V \Psi_{ba} = - \int \Psi_{ba}^* V \Psi_{ab}.$$

Now let us consider spins and the fact that the electrons are identical particles. The complete state Ψ_χ (χ is a spinor describing the spin part of the state) must be antisymmetric, since electrons are fermions. It is wise first to combine individual electron spin states into the total spin states. From two spins $1/2$ we can make 3 symmetrical total spin states, which correspond to total spin 1 (with different spin

projections $(+1, 0, -1)$ and one antisymmetric state, corresponding to total spin 0.

The total antisymmetry of the state requires that we combine the symmetrical spin function with the antisymmetrical spatial function and the antisymmetrical spin function with the symmetrical space function. So legal two-particle states are $\Psi_S\chi^{(0)}$ and $\Psi_A\chi^{(1)}$. When we denote the total spin as s we get for the corresponding mean energy values

$$\begin{aligned} E_{s=0} &= E_S \\ E_{s=1} &= E_A \end{aligned}$$

We can combine these two expression formally into one

$$E = E_S + (E_A - E_S) \frac{s(s+1)}{2} \implies H = E_S + (E_A - E_S) \frac{\mathbf{S} \cdot \mathbf{S}}{2}.$$

The first expression here is just "artificial" expression which holds for the two possible values of s which are $s = 0$ and $s = 1$. In the second expression we have introduced a ne "effective" energy operator giving the same mean energy values for the two two-particle states considered. The formal Hamiltonian contains the total spin operator $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$. The eigenvalue of the square of this operators is just the required $s(s+1)$. We can further simplify the expression as follows

$$\mathbf{S} \cdot \mathbf{S} = (\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_1 + \mathbf{S}_2) = \underbrace{\mathbf{S}_1 \cdot \mathbf{S}_1}_{\frac{1}{2}(\frac{1}{2}+1)} + \underbrace{\mathbf{S}_2 \cdot \mathbf{S}_2}_{\frac{1}{2}(\frac{1}{2}+1)} + 2\mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{3}{2} + 2\mathbf{S}_1 \cdot \mathbf{S}_2,$$

and so

$$H = E_S + (E_A - E_S) \left(\frac{3}{4} + \mathbf{S}_1 \cdot \mathbf{S}_2 \right) = E_a + E_b + I + \frac{J}{2} + \underbrace{(E_A - E_S)}_{2J} \mathbf{S}_1 \cdot \mathbf{S}_2.$$

So we have found that the splitting of the energies caused by the exchange integral (and the Pauli principle) can be formally rewritten as if caused by some effective spin-spin interaction. Since the size of the effect is given by the value of the exchange integral, the effect is significant only for spatially close electron states, otherwise the overlap of the wave function in the exchange integral is small.

Summarizing: the exchange Coulomb potential combined with the Pauli exclusion principle leads to effective spin-spin interactions which we consider to be responsible for the ferromagnetic effect observed in some materials.

Since we shall investigate this effect in more detail, let us summarize here basic phenomenological facts about magnetic properties of amaterials

1. Diamagnetism is a result of influence of external magnetic field on electron orbitals. This effect is present in all materials, however in many of them it

is overshadowed by stronger paramagnetic or ferromagnetic properties. The magnetic susceptibility of these materials is negative, so these materials are repulsed by the magnetic field. No magnetization is present without external magnetic field. Some examples: water ($\chi = -9 \cdot 10^{-6}$), mercury ($\chi = -29 \cdot 10^{-6}$) a bismuth ($\chi = -166 \cdot 10^{-6}$).

2. Paramagnetism is caused by the interaction of (permanent) magnetic moments of atoms or molecules with the external magnetic field. Paramagnets do not retain any magnetization at zero external field (the magnetic moments of the atoms are oriented randomly) The magnetic susceptibility is positive $\chi > 0$. Some examples aluminium ($\chi = 22 \cdot 10^{-6}$), magnesium ($\chi = 12 \cdot 10^{-6}$).
3. Ferromagnetism is observed for some materials for which $\chi \gg 1$ (the magnetic susceptibility for special alloys can reach the value 10^6). Ferromagnetic materials have permanent magnetic moments of molecules as paramagnets. However their local magnetic moments interact with each other with the tendency to align the moments to be parallel. Ferromagnetic materials retain their magnetization at zero field (at temperatures below Curie point). Their material parameters depend on temperature, and the relation between the magnetic flux density (B) and magnetic field strength (H) is nonlinear, what formally looks like dependence of the magnetic susceptibility on the magnetic field. Some examples: iron, nickel, cobalt.
4. Antiferromagnetism: oppositely to ferromagnetic materials the interaction of local magnetic moments tends to align them to be antiparallel (under the temperature point called Néel temperature) thus canceling each other and the material shows diamagnetic properties. Above the Néel temperature the material behaves like paramagnet.

Exercise

Langevin theory of paramagnetism

Study a "classical spin" (magnetic moment). Its state is given by spatial angles ϑ, φ , its energy in external magnetic field is

$$E = -\boldsymbol{\mu}_B \cdot \mathbf{B} = -\mu_B B \cos \vartheta,$$

where μ_B je the Bohr magneton $e\hbar/2m$. The volume density of spins in the material is denoted as $N/V \equiv n$.

What is the mean magnetization of the material in unit volume $m = N\langle\boldsymbol{\mu}_B\rangle/V$? How the magnetic susceptibility $\chi = \partial m/\partial H$ depends on temperature T ? What are its limit values for small and large temperatures?

- One has to calculate the statistical sum in classical approximation and calculate $\langle\cos \vartheta\rangle$. We get

$$Z_1 = \int_0^{2\pi} d\varphi \int_0^\pi d\vartheta e^{\beta\mu_B B \cos \vartheta} \sin \vartheta$$

and to find that the mean magnetic moment can be calculated by a suitable derivative of it. We get

$$M = n\mu_B L(\beta\mu_B B), \quad L(x) = \coth x - \frac{1}{x}.$$

From there the susceptibility follows directly ($x = \beta\mu_B B$, $n = N/V$)

$$\chi = n\beta\mu_B^2 (x^{-2} - 1/\sinh^2 x).$$

For $T \rightarrow \infty$ we get $\chi \rightarrow n\beta\mu_B^2/6$ (in accordance to Curie law, $\chi \sim 1/T$). For $T \rightarrow 0$ we get $\chi \rightarrow nkT/B^2$. ■

7.2 Ising model

A simple model with interaction between (classical) spins is the Ising model, where the interaction is limited to nearest neighbours. As already said the model is classical, what means, that in the hamiltonian there are no operators, just variables, which, however, can have only discrete values $-1, 1$. Energy of the system is given by the following formula

$$E(\{s\}) = -J \sum_{i \sim j} s_i s_j - \mu_B B \sum_i s_i,$$

where $i \sim j$ means summation over the different pairs of neighbouring spins. The first author who formulated the model was Wilhelm Lenz (1920). Ernest Ising was his student who in his thesis described the first exact solution in the one-dimensional case (1924). The two-dimensional model (for zero external field) was solved by Lars Onsager (1944). For higher dimensions we do not know (up to now) an exact solution, we have just numerical simulations.

Below there are three web pages with useful information on Ising model. The first web page contains many on-line simulations, the second page contains an exe-file with the Metropolis algorithm and the third page contains many demonstrations of thermodynamical calculations with the program Mathematica.

1. <http://stp.clarku.edu/simulations>
2. <http://www.iasbs.ac.ir/faculty/langari/courses/stat-mech-2>
3. <http://www.physics.umd.edu/courses/Phys603/kelly>

Exercise

Calculate the statistical sum for the Ising model on a square 2×2 (four spins) for periodic boundary conditions. What is the mean energy value at zero external

field. What is the value of the magnetic susceptibility for zero field in the limits $T \rightarrow 0, T \rightarrow \infty$?

- Let us denote $\beta J \equiv j, \beta \mu_B B \equiv b$. The statistical sum will be

$$Z = 2e^{8j} \cosh(4b) + 8 \cosh(2b) + 2e^{-8j} + 4.$$

For zero external field $b = 0$ and we get $Z = 12 + 4 \cosh(8j)$. The mean energy is

$$\langle E \rangle = -J \frac{1}{Z} \frac{\partial Z}{\partial j} = -8J \frac{\sinh(8j)}{3 + \cosh(8j)}.$$

Note that $\langle E \rangle \in (-8J, 0)$.

For $b \neq 0$ the mean sum of the spins equals ($Z = \exp[j \sum s_i s_j + b \sum s_i]$)

$$\left\langle \sum s_i \right\rangle = \frac{1}{Z} \frac{\partial Z}{\partial b} = 4 \frac{e^{8j} \sinh(4b) + 2 \sinh(2b)}{e^{8j} \cosh(4b) + 4 \cosh(2b) + e^{-8j} + 2}.$$

The mean spin value is $\langle s \rangle = \langle \sum s_i \rangle / 4$. The susceptibility for zero field is easily calculated, since for $x \rightarrow 0$ $\cosh x \approx 1$ and $\sinh x \approx x$. We get

$$\chi = \frac{\partial(\mu_B \langle s \rangle)}{\partial H} = \mu_B \frac{\langle s \rangle_{b \rightarrow 0}}{B/\mu_0} = 16\beta\mu_0\mu_B^2 \frac{e^{8j} + 1}{e^{8j} + 6 + e^{-8j}}.$$

The required limiting values are $\chi = 16\beta\mu_0\mu_B^2$ for $T \rightarrow 0$, and $\chi = 4\beta\mu_0\mu_B^2$ for $T \rightarrow \infty$. ■

There is no phase transition in the one-dimensional Ising model. The lowest energy state is the state with no excited links. By excited links we mean here a link for which the spins on its two sites are oppositely oriented. In one-dimensional model the state closest to the lowest energy state is a state with exactly one link excited, the energy difference being $2J$. For such a state roughly one half of the spin is oriented "up" and the other half is oriented "down". The magnetization for most of such states is equal to zero. A finite lattice with N sites has (roughly, for large N) N links. One excited link can be therefore chosen in N ways, so there are N states with energy larger from the lowest energy by $2J$. The entropy of the "macrostate" with the energy $E_0 + 2J$ is therefore proportional to $\ln(N)$, so the free energy of such a state is

$$F = E_0 + 2J - T \ln(N)$$

For a non-zero temperature the state with higher energy has lower free energy and so for a non-zero temperature the mean magnetization is zero.

The Ising model in one dimension is explicitly calculable. Let us fix the boundary conditions so that the first spin from left has value $s_1 = 1$. Then the state of every other spin is given if we know about every link whether it is excited or not.

Let us introduce a dual lattice which correspond to the original lattice in such a way that to every link of the original lattice there corresponds a site of the new lattice with a spin having value q with value $q = 1$ if that link is not excited and $q = -1$ if that link is excited. The states of the dual lattices exactly correspond to each other. If we require, that the energies of the corresponding states are equal then the energy of the new lattice should be given as

$$H = \sum_{\text{link}} -Jq_i$$

This, however, describes the model of independent spins, the statistical sum is easily calculated as

$$Z = (\exp(J/kT) + \exp(-J/kT))^{N-1}$$

and we see there is no singularity in the thermodynamic limit and so there is no phase transition.

7.3 Mean field theory

The statistical physics of a classical ideal gas can be expressed in two ways.

- As a canonical distribution for the whole gas
- As a Boltzmann distribution for one selected molecule

In the case of the Boltzmann distribution, the other molecules play the role of a thermal reservoir characterized by the macroscopic parameter temperature. The second way (Boltzmann distribution) is possible because the molecules do not feel each other. the change of state of the selected molecule does not influence (for large total number of molecules) the characteristics of the reservoir.

In the Ising model we have a different situation, the "one-particle approach" can not be realized. It is however possible to try an approximative one-particle solution, introducing an effective Hamiltonian of one spin in the "external space" of the other spins.

$$H_1(s) = \sum_{\text{neighbour}} -Jss_{\text{neighbour}}$$

The formally external (and therefore "given") states of the neighbouring spins are not really given by the macroscopic parameters of the whole system. We can, however look for an approximation, where the states of the neighbouring spins are

given by a suitable macroscopic parameter. The clear candidate is the mean spin value, and the effective Hamiltonian

$$H'_1(s) = \sum_{\text{sused}} -Js\langle s \rangle = -Jn\langle s \rangle s$$

where n is the number of nearest neighbours. Because of the symmetry reasons, the mean values for all the spins are equal. We have got the Hamiltonian of one spin in an external field $B = Jn\langle s \rangle$. This problem is easily solvable, and for the mean spin value we get a self-consistent equation¹

$$\langle s \rangle = \tanh(B/kT) = \tanh(Jn\langle s \rangle/kT)$$

The solution of this selfconsistent equation can be looked for graphically. It is clear that for

$$\frac{Jn}{kT} < 1$$

there exists just one solution $\langle s \rangle = 0$, while for

$$\frac{Jn}{kT} > 1$$

there exist three solutions. The change happens in the critical point

$$\frac{Jn}{kT_c} = 1$$

¹Let us discuss now an alternative argumentation, which, however, is wrong and leads to wrong answer. Let us try to solve the Ising model approximately, so that the real Hamiltonian is replaced by new (approximate) Hamiltonian

$$H' = \sum_{\text{link}} -Js_i\langle s_j \rangle$$

so one of the spins on the considered link is replaced by its mean value. Because of the symmetry reasons all the spins have the same mean value and we get

$$H' = \sum_{\text{link}} -Js_i\langle s \rangle$$

The sum over the links can be replaced by the sum over the spins if we realize that each link has two spins on its ends and so each link can be assigned to one of its spins as "being owned" by that spin. The lattice determines the number of nearest neighbours n . Each spin therefore "owns" $n/2$ links. We get

$$H' = \sum_i -J\frac{n}{2}s_i\langle s \rangle = \sum_i -Bs_i$$

where $B = Jn\langle s \rangle/2$ is the effective mean field felt by each spin. This is an easy problem of independent spins, with the (selfconsistent) solution

$$\langle s \rangle = \tanh(B/kT) = \tanh(Jn\langle s \rangle/(2kT))$$

So we again got a selfconsistent solution, however, different from the correct one, with twice smaller the selfconsistent field.

Note that in the mean field approximation we get the phase transition also for one-dimensional model. In this case the mean field method does not correspond to the true solution even qualitatively.

7.4 Mean field method as a variation problem

In the previous section we used the Ansatz $B = Jn\langle s \rangle$. This Ansatz was guided by our intuition. Had we not the relevant insight into the problem, we could use more blind variation technique. Even more, as it was discussed in the footnote, we could have two different "insights", one of them being wrong. We even did not argue properly which of the two possible approaches was really correct. This section, and the variation method described here, can be seen as such argumentation.

We begin by constructing a trial Hamiltonian

$$H' = \sum_i -Bs_i$$

where B is so far unknown parameter. The free energy for the model with the Hamiltonian H' is

$$F' = -kT \ln Z = -kT \ln((2 \cosh(B/kT))^N) = -NkT \ln(2 \cosh(B/kT))$$

The variation method still needs the mean value of the true Hamiltonian averaged over the canonical ensemble generated by the trial Hamiltonian (we denote this as $\langle H \rangle'$), and we also need the mean value of the trial Hamiltonian averaged over the same canonical ensemble generated by the same trial Hamiltonian (we denote this as $\langle H' \rangle'$). We get

$$\langle H \rangle' = \left\langle \sum_{\text{link}} -Js_i s_j \right\rangle' = \sum_{\text{link}} -J \langle s_i s_j \rangle' = -\frac{n}{2} JN \langle s \rangle'^2$$

because the spins are independent in the trial ensemble and the lattice with N spins has $nN/2$ links.

$$\langle H' \rangle' = \left\langle \sum_i -Bs_i \right\rangle' = -BN \langle s \rangle'$$

Variation function is

$$\langle H \rangle' - \langle H' \rangle' + F' = -\frac{n}{2} JN \langle s \rangle'^2 + BN \langle s \rangle' - NkT \ln(2 \cosh(B/kT))$$

The value of the variation parameter B is found by the minimization of the variation function. Differentiating with respect to B we get

$$-nJN \langle s \rangle' \frac{d\langle s \rangle'}{dB} + N \langle s \rangle' + BN \frac{d\langle s \rangle'}{dB} - N \tanh(B/kT) = 0$$

On the other hand the following relation holds

$$\langle s \rangle' = \tanh(B/kT)$$

and so we get

$$-nJN\langle s \rangle' \frac{d\langle s \rangle'}{dB} + BN \frac{d\langle s \rangle'}{dB} = 0$$

$$B = nJ\langle s \rangle'$$

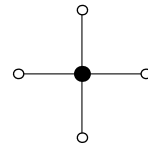
We got the same expression as in the intuitive Boltzmann-like approach².

7.5 Bethe approximation

See also [GuT] (pp. 355-358).

The mean field method assumes, that each spin "feels" just the mean spin values of its neighbours. This rather crude assumption leads to results that are in some cases too far from the exact results.

Bethe approximation represents an improvement of the mean field method which takes into account not individual spins but rather cluster of spins. A simple cluster of spins for the square lattice is presented in the figure.



²So we have solved the question which of the two intuitive approaches in the mean field method was the correct one. However the variation method does really show **why** the Boltzmann-like approach is correct. We therefore add here another, not quite rigorous, but more transparent argument.

Something similar can happen also in classical mechanics. Let us consider a two-body problem with the Hamiltonian

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + U(x_1, x_2)$$

The Hamiltonian is the sum of the two kinetic energies and the potential energy of interaction. The potential energy is there "in one copy only". Let us imagine now that we want to solve the problem by an iteration technique. We start with some approximate solutions, that means with explicit functions $\tilde{x}_1(t)$ and $\tilde{x}_2(t)$ and we want to find an iterative procedure which would improve the solutions step-by-step. The iteration step can be looked for by solving the equations of motion resulting from the Hamiltonian

$$H_{\text{iter}} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + U(x_1, \tilde{x}_2) + U(\tilde{x}_1, x_2)$$

In this Hamiltonian the "previous iterations" play the role of external fields, but now the interaction energy must appear **twice**: as the potential energy of the first particle in the external field of the second particle and also as the potential energy of the second particle in the external field of the first one. (This is the factor two which played the role in our intuitive mean field approach.) And we look for a selfconsistent solution.

We shall, however, for simplicity reasons, consider just a one-dimensional Ising model and the cluster of one spin and its two nearest neighbours $s_{0,1,2}$. During the calculation we shall assume, that the edge spins of the cluster (s_1, s_2) interact with the "mean values" of the spins outside the cluster. Inner spins of the cluster interact with the true values of the spins in the cluster.

It is important to note that we shall not directly use the mean spin values of the spins outside the cluster. The interaction of the edge spins will be with an effective mean field B_{eff} . If we used directly the mean spin values, we would get the result $\langle s_0 \rangle \neq \langle s_{1,2} \rangle$, what is not acceptable because of the translational invariance of the problem. The use of the effective field B_{eff} will provide the necessary freedom required to get $\langle s_0 \rangle = \langle s_{1,2} \rangle$.

The statistical sum for the considered cluster has the form

$$Z_C(T, B) = \sum_{0,1,2} e^{-\beta E_C}, \quad E_C(T, B) = -J \sum_{1,2} s_0 s_i - \mu_B B_{eff} \sum_{1,2} s_i - \mu_B B s_0$$

Here we have added also the external field B what enables us to calculate easily the mean spin value $\langle s_0 \rangle$ by differentiating with respect to B . Let us stress that the interaction of the external field B with the spins s_1 and s_2 is not missing in the formula: the field B is included in the value of the effective field B_{eff}). Let us denote $\mu_B B_{eff} \equiv b_e$. So we have

$$\begin{aligned} Z_C(T, B) &= e^{\beta \mu_B B} \left[e^{2\beta(J+b_e)} + 2 + e^{-2\beta(J+b_e)} \right] + \\ &+ e^{-\beta \mu_B B} \left[e^{2\beta(-J+b_e)} + 2 + e^{-2\beta(J-b_e)} \right] = \\ &= 4 \left[e^{\beta \mu_B B} \cosh^2 \beta(J+b_e) + e^{-\beta \mu_B B} \cosh^2 \beta(J-b_e) \right]. \end{aligned}$$

For the d -dimensional lattice ($d = 2$ for the square lattice etc.) the powers of \cosh^2 will change into \cosh^{2d} and the factor 4 would change into 4^d (the reader can check this). Differentiating with respect to B we get

$$\begin{aligned} \langle s_0(T, B) \rangle &= \frac{\partial \ln Z_C}{\partial(\beta \mu_B B)} \Big|_{B=0} = \frac{4^d}{Z_C} \left[\cosh^{2d} \beta(J+b_e) - \cosh^{2d} \beta(J-b_e) \right], \\ \langle s_1(T, B) \rangle &= \frac{1}{2d} \frac{\partial \ln Z_C}{\partial(\beta b_e)} \Big|_{B=0} = \frac{4^d}{Z_C} \left[\sinh \beta(J+b_e) \cosh^{2d-1} \beta(J+b_e) - \right. \\ &\quad \left. - \sinh \beta(J-b_e) \cosh^{2d-1} \beta(J-b_e) \right]. \end{aligned}$$

The (translational symmetry) requirement $\langle s_0 \rangle = \langle s_1 \rangle$ gives for b_e , the equation

$$\frac{\cosh^{2d-1} \beta(J+b_e)}{\cosh^{2d-1} \beta(J-b_e)} = e^{2\beta b_e}.$$

This is again a selfconsistent equation which cannot be solved explicitly. It is obvious that it always has a trivial solution $b_e = 0$. Let us investigate when the equation has also a non-trivial solution. The right hand side increases with b_e without limitation, the left hand side approaches a constant $\exp[2\beta J(2d - 1)]$ independent of b_e . Therefore if the slope of the left hand side at $b_e = 0$ is greater than the slope of the right hand side the nontrivial solution exists for sure. If the slopes are of the opposite relation, the non-trivial solution does not exist. A critical point is the situation when the slopes are equal. Differentiating with respect to b_e we get for the critical value β_c

$$\coth \beta_c J = 2d - 1.$$

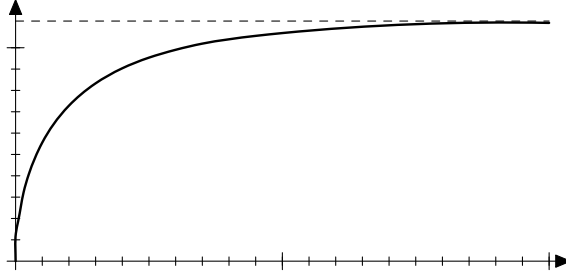
For $d = 1$ we get $\coth \beta_c J = 1$, therefore $\beta_c = \infty$, and so $T_c = 0$. So the Bethe approximation correctly gave (by a happy accident) the exact value of the critical temperature for the one-dimensional Ising model. In the following table³ we see that the Bethe approximation results approach the exact results with increasing dimension.

lattice	1D	2D	3D	4D
exact result	0,0	2,269	4,512	6,682
Bethe approximation	0,0 (0 %)	2,885 (27 %)	4,933 (9 %)	6,952 (4 %)
mean field	2,0 (∞)	4,0 (76 %)	6,0 (33 %)	8,0 (20 %)

The fact that the mean spin is not equal to the mean field acting on the spins of the cluster seems to be surprising. It is difficult to imagine the reasons for it. (it is only the failure of the naive expectation which forces us to consider the case more carefully.) One of the possible reasons might be a sort of "screening" of the mean spin value by the fluctuations. Close to the critical point the spin fluctuations are so important (big and "quick") that the cluster spins do not feel the mean value but something smaller.

This is documented by the following graph showing the dependence of the fraction $\mu_B B_{eff}/J$ on T_c^B/T (here T_c^B denotes the critical temperature as given by the Bethe approximation. If the effective field were given by the mean spin value, this ratio would be equal to the number of neighbours of the spins from the cluster (3 in our case). It is clear that it is not so. For the temperatures much smaller than T_c^B it is approximately so. For temperatures approaching T_c^B the value of B_{eff} decreases, for $T = T_c^B$ we get $B_{eff} = 0$.

³The data in the table are obtained from the web page <http://www.hermetic.ch/compsci/thesis/chap7.htm>.



We shall now describe an alternative formalism to the mean field theory and the the Bethe approximation.

The Ising model takes into account only the interactions with nearest neighbours (their number we denote as z). Now let us denote the number of positively oriented spins as N_+ , the number of negatively oriented spins as N_- . The neighbouring spin pair can happen to be in three different states, let us denote the number of corresponding pairs as N_{++} , N_{--} and N_{+-} . The total energy of the system can be calculated as

$$E(N_+, N_-, N_{++}, N_{--}, N_{+-}) = -J(N_{++} + N_{--} - N_{+-}) - \mu_B B(N_+ - N_-).$$

However the 5 used numbers are not independent of each other. One condition is trivially clear $N_+ + N_- = N$. Now let us consider a particular spin configuration. If to every "+" spin we draw lines connecting it to all its neighbours, we draw zN_+ lines. By that there will be N_{++} double lines and N_{+-} single lines. Therefore $zN_+ = 2N_{++} + N_{+-}$. By similar argument we get the relation $zN_- = 2N_{--} + N_{+-}$. So only two of the 5 N-numbers are independent We usually take them to be N_+ and N_{++} , the system energy will then be

$$E(N_+, N_{++}) = -4JN_{++} + 2(zJ - B\mu_B)N_+ - (zJ/2 - B\mu_B)N.$$

The statistical sum can be written as

$$Z_N(T, B) = e^{\beta N(zJ/2 - \mu_B B)} \sum_{N_+=0}^N e^{-2\beta(zJ - \mu_B B)N_+} \sum_{N_{++}=0}^N g(N_+, N_{++}) e^{4\beta J N_{++}},$$

where $g(N_+, N_{++})$ is the number of different spin state leading to the same given numbers N_+ a N_{++} . This, however, is a complicated function, we shall need a suitable simplification

One possible approximation is

$$\frac{N_{++}}{\frac{1}{2}zN} = \left(\frac{N_+}{N} \right)^2,$$

this approximation is equivalent to the mean field theory. This is understandable: the approximation assumes that the number of positively oriented neighbours (left hand side) is given by random distribution of positively oriented spins in the lattice (right hand side). It reminds the mean field theory where we assumed the influence on the neighbouring spins given only by the mean number of N_+ in the whole system.

This approximation can be characterized so that it totally neglects correlations between neighbouring spins. Said differently: the energy of the system does not depend on that whether the positively oriented spins are close to each other or are randomly distributed. This is nonphysical, but simple enough for the calculation.

Now in the expression for Z_N one should change $g(N_+, N_{++})$ for $g(N_+)$, which is given by the standard combination numbers. It is also useful to change the variable N_+ for $L \equiv (N_+ - N_-)/N$ ($N_+ = N(L + 1)/2$). L is called the order parameter. Then

$$Z_N(T, B) = \sum_{L=-1}^{+1} \frac{N!}{\left[\frac{1}{2}N(1+L)\right]!\left[\frac{1}{2}N(1-L)\right]!} e^{\beta N(zJL^2/2 + \mu_B BL)} \approx$$

$$\approx \sum_{L=-1}^{+1} \frac{e^{\beta N(zJL^2/2 + \mu_B BL)}}{\sqrt{2\pi N} \left(\frac{1-L}{2}\right)^{N(1-L)/2+1/2} \left(\frac{1+L}{2}\right)^{N(1+L)/2+1/2}} \equiv \sum_{L=-1}^{+1} \frac{C(L)}{\sqrt{N}} A_L^N.$$

The corresponding free energy is

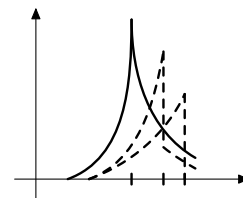
$$F(T, B) = \lim_{N \rightarrow \infty} \left[-\frac{kT}{N} \ln Z_N(T, B) \right].$$

Similarly as we have seen it in the calculation of the transfer matrix, only the largest term (from the terms A_L) in the sum contributes (one can easily check, that the term $C(L)/\sqrt{N}$ does not play a significant role). Let the maximum is reached for L_m (clearly then $L_m = \langle L \rangle$). According to the expression for Z_N the following relation holds for L_m

$$\ln \frac{1 + L_m}{1 - L_m} = 2\beta (\mu_B B + zJL_m) \implies L_m = \tanh (\beta zJL_m + \beta \mu_B B).$$

This is exactly the result of the mean field theory.

In the similar way an approximation corresponding to the Bethe approximation can be formulated. In the figure the graphs for the heat capacity for the 2D Ising model are presented for the exact solution (ξ_0), Bethe approximation (ξ_1) and the mean field theory (ξ_2).



Exercise

Use the Bethe approximation and calculate the critical temperature for the hexagonal lattice. For simplicity use the smallest possible 4-spin cluster

- One can easily find the solution substituting $d = 3/2$ into the already known result for the hypercubic lattice (one should think a while why the trick works). Without the trick one can directly calculate

$$\begin{aligned} Z &= 4 [\cosh(3j) \cosh(3b) + 3 \cosh(j) \cosh(b)], \\ \langle s_0 \rangle &= \frac{1}{Z} [\sinh(3j) \sinh(3b) + 3 \sinh(j) \sinh(b)], \\ \langle s_1 \rangle &= \frac{1}{Z} [\cosh(3j) \sinh(3b) + \cosh(j) \sinh(b)]. \end{aligned}$$

The requirement $\langle s_0 \rangle = \langle s_1 \rangle$ leads to an equation from which, after putting $b = 0$ (do think what is the reason for this) follows $\sinh(3j_c) + \sinh(j_c) = \cosh(3j_c) + \cosh(j_c)/3$, odkial' $\cosh j_c = 2/\sqrt{3}$ (numerically $kT_c \doteq 1.52J$). The result for the triangle lattice and the smallest triangle cluster is $kT_c \doteq 3.43J$ (the exact solution is $kT_c \doteq 3.64J$). For the diamond structure (3D) we get $kT_c \doteq 2.70J$ and for hexagonal lattice and the smallest 4-spin cluster $kT_c \doteq 1.82J$. ■

We can again investigate how large is the effective field generated for different temperatures T_c/T . For the hexagonal lattice and 4-spin cluster the results are presented in the table.

T_c/T	1.0	1.01	1.1	1.2	1.5	2.0	3.0	∞
$\mu_B B_{eff}/J$	0.00	0.33	0.96	1.27	1.66	1.88	1.98	2

7.6 Landau theory of the phase transitions of the second kind

The essence of the Landau phenomenological approach is the idea where the non-analytic behaviour of the thermodynamic potentia can come from. Let us assume that we have an order parameter M like magnetization. In the equilibrium state this order parameter assumes some equilibrium value. One can calculate this value when one first deals with the non-equilibrium thermodynamic potential, which, in addition to its standard variables (p and T for the Gibbs potential) depends also on the (non-equilibrium) value of the order parameter M . Now we look for the minimum of the thermodynamic potential. The value of M for which the minimum is reached is just the equilibrium value of the order parameter.

Landau idea is now the following. He assumes that the non-equilibrium thermodynamic potential is an analytic function of its variables (and of the order parameter as well). Looking for the minimum one has to differentiate with respect to the order parameter and put the derivative equal to zero. Thus one gets the equation for the equilibrium value of the order parameter. All the expressions in the equations

are analytic functions but its solution need not be analytic. The solution when substituted into the thermodynamic potential leads to a non-analytic expression for the potential.

Let us consider a case where the system is symmetric with respect to the change of sign of the order parameter

$$M \rightarrow -M$$

The parameter is chosen so that it assumes the value zero at the critical point. According to the assumption of analyticity we can expand the non-equilibrium potential (per one molecule) into the Taylor series in M in the form

$$G(p, T, M) = G_0(p, T) + G_2(p, T)M^2 + G_4(p, T)M^4$$

The odd powers are missing because of the symmetry, and we assume that the expansion up to the fourth order is enough. In this case the fourth order term should be positive, otherwise there would be no minimum.

The sign of the quadratic terms is not constrained by any general principles, it can be both positive and negative. The behaviour of the function $G(p, T, M)$ around the point $M = 0$ significantly depends, however, on the sign of the quadratic term.

For $G_2 < 0$ the function has two minima symmetrically positioned with respect to $M = 0$ for $G_2 > 0$ the function has just one minimum at $M = 0$. It is clear that $G_2 > 0$ corresponds to the situation above the critical temperature (without magnetization), while $G_2 < 0$ corresponds to situation below the critical point. In this way the critical point happened just when the parameter G_2 changes its sign, therefore in the vicinity of the critical point we can write

$$G_2(p, T) = \frac{a(p)}{T_c}(T - T_c)$$

where we introduced the (constant) critical temperature T_c into the denominator just for aesthetic reasons to get a dimensionless parameter

$$t = \frac{T - T_c}{T_c}$$

Then the order parameter below the critical temperature will assume the value

$$M = \left(\frac{-at}{2G_4}\right)^{1/2}$$

In the presence of an external (magnetic) field the (non-equilibrium) thermodynamic potential will be

$$G(p, T, M) = G_0(p, T) - HM + G_2(p, T)M^2 + G_4(p, T)M^4$$

The critical isotherm (a graph showing dependence of M on H for constant $T = T_c$) will be

$$M \sim H^{1/3}$$

The magnetic susceptibility

$$\left(\frac{\partial M}{\partial H}\right)_{T=T_c} \sim H^{-2/3}$$

diverges at the critical point.

7.7 Transfer matrix

See also [Yeo] (str. 67-75).

The transfer matrix method (Kramers a Wannier, 1941) is a useful tool to solve the Ising model. Its use in the one-dimensional case is easy and illustrative. In more complicated situations we usually arrive at many-dimensional (or infinitely-dimensional) matrices where only numerical analysis is possible.

So let us investigate the one-dimensional Ising model with N spins in external magnetic field. The energy of the system is given as

$$E_N = -J \sum_{i=0}^{N-1} s_i s_{i+1} - \mu_B B \sum_{i=0}^{N-1} s_i,$$

with $s_i = \pm 1$. Let us assume periodic boundary conditions $s_N = s_0$ (topologically the spins are distributed along a circle) We expect that in the thermodynamic limit $N \rightarrow \infty$ this choice will not influence the result.

The trick consists in suitable rewriting of the statistical sum

$$\begin{aligned} Z_N &= \sum_{\{s\}} \exp [\beta J (s_0 s_1 + \dots + s_{N-1} s_N) + \beta \mu_B B (s_0 + s_1 + \dots + s_N)] = \\ &= \sum_{\{s\}} \exp [\beta J s_0 s_1 + \beta \mu_B B \frac{s_0 + s_1}{2}] \cdot \exp [\beta J s_1 s_2 + \beta \mu_B B \frac{s_1 + s_2}{2}] \cdot \dots \\ &\quad \dots \cdot \exp [\beta J s_{N-1} s_0 + \beta \mu_B B (s_{N-1} + s_0)/2] \equiv \sum_{\{s\}} \mathbb{T}_{0,1} \mathbb{T}_{1,2} \dots \mathbb{T}_{N-1,0} \end{aligned}$$

where summing over $\{s\}$ is meant as summing over all possible spin configurations what means a multidimensional sum over s_0, s_1, \dots, s_{N-1} . We have introduced a matrix \mathbb{T} , with matrix elements $\mathbb{T}_{s_i, s_{i+1}} \equiv \mathbb{T}_{i, i+1}$ (so the matrix rows are

numbered by the values of the spin s_i , the columns are numbered by values of the spin s_{i+1} . In our specific case the matrix is

$$\mathbb{T} = \begin{pmatrix} e^{\beta(J+\mu_B B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-\mu_B B)} \end{pmatrix}.$$

The expression for Z_N can be simplified when we notice that summing over the spins effectively means matrix multiplication. What is left is only summation over s_0 :

$$Z_N = \sum_{s_0=\pm 1} (\mathbb{T}^N)_{0,0} = \text{Sp}(\mathbb{T}^N) = \sum_{i=1}^n \lambda_i^N.$$

Here we have used the fact that the matrix trace $\text{Tr} \mathbb{T}^N$ is not dependent on the choice of base and can be evaluated in the base for which the matrix is diagonal. Let us stress that the result is fairly general, the model details influence the form of the transfer matrix (and the specific values of its eigenvalues). The reader can ponder how the transfer matrix looks for more complicated cases (like when each spin can assume more than two values or when the interactions is not only between nearest neighbours).

Now let us assume that the eigenvalues λ_i are ordered in descending order $\lambda_0 > \lambda_1 > \dots > \lambda_{N-1}$ (for the simple case of a 2×2 matrix we, of course, have only two eigenvalues. The statistical sum Z_N gives the free energy $F = -kT \ln Z_N$. The free energy per spin is then $f = F/N$ and for the thermodynamic limit we get

$$f = -kT \cdot \lim_{N \rightarrow \infty} \frac{1}{N} \ln Z_N = -kT \cdot \lim_{N \rightarrow \infty} \frac{1}{N} \ln \left[\lambda_0^N \left(1 + \sum_{i=1}^{N-1} (\lambda_i/\lambda_0)^N \right) \right] = -kT \ln \lambda_0.$$

The usefulness of the expression through the eigenvalues is manifested in the case of large matrices, since only the largest eigenvalues play a significant role in the thermodynamic limit. It is more feasible to find numerically just a few largest eigenvalues than the whole spectrum. Also note that according to Perron-Frobenius theorem we know that each matrix with positive matrix elements has a non-degenerate positive eigenvalue r , for which $\forall i: |\lambda_i| < r$.

Now we shall evaluate the mean value of spin $\langle s_k \rangle$. We could proceed by differentiating the free energy with respect to the external field, but it is illustrative to calculate the mean spin value using the transfer matrix technique directly. We start with the expression

$$\begin{aligned} \langle s_k \rangle &= \frac{1}{Z_N} \sum_{\{s\}} s_k e^{-\beta H_N} = \frac{1}{Z_N} \sum_{\{s\}} \mathbb{T}_{0,1} \dots \mathbb{T}_{k-1,k} s_k \mathbb{T}_{k,k+1} \dots \mathbb{T}_{N-1,0} = \\ &= \frac{1}{Z_N} \sum_{s_0, s_k} (\mathbb{T}^k)_{0,k} s_k (\mathbb{T}^{N-k})_{k,0} = \frac{1}{Z_N} \sum_{s_k} s_k (\mathbb{T}^N)_{k,k}. \end{aligned}$$

Let us denote the eigenvector of the matrix T corresponding to the eigenvalue λ_i as $|\mathbf{u}_i\rangle$. Now we formally introduce the eigenvectors of the "spin operator" s_k denoting them $|\mathbf{s}_k\rangle$. This formal "spin operator" is diagonal, so its eigenvectors are $|\mathbf{s}_k\rangle = (0, \dots, 0, 1, 0, \dots, 0)^T$. What we did is that we have formally written the matrix elements using the formal Dirac notation. Using this notation we can write

$$T = \sum_i |\mathbf{u}_i\rangle \lambda_i \langle \mathbf{u}_i|, \quad T^m = \sum_i |\mathbf{u}_i\rangle \lambda_i^m \langle \mathbf{u}_i|, \quad (T^m)_{0,m} = \langle \mathbf{s}_0| T^m |\mathbf{s}_m\rangle,$$

If we use this notation in the expression for the mean spin value we get (after dividing both the numerator and denominator by λ_0^N)

$$\begin{aligned} \langle s_k \rangle &= \left[1 + \sum_{i=1}^{N-1} (\lambda_i/\lambda_0)^N \right]^{-1} \sum_k s_k \left(|\mathbf{u}_0\rangle \langle \mathbf{u}_0| + \sum_{i=1}^{N-1} \dots \right)_{k,k} = \sum_k s_k (|\mathbf{u}_0\rangle \langle \mathbf{u}_0|)_{k,k} = \\ &= \sum_k s_k \langle \mathbf{s}_k | \mathbf{u}_0 \rangle \langle \mathbf{u}_0 | \mathbf{s}_k \rangle = \langle \mathbf{u}_0 | \left(\sum_k |\mathbf{s}_k\rangle s_k \langle \mathbf{s}_k| \right) | \mathbf{u}_0 \rangle = \langle \mathbf{u}_0 | \hat{s} | \mathbf{u}_0 \rangle. \end{aligned}$$

This is again a very simple expression. For the correlation length we would get $\xi^{-1} = \ln(\lambda_0/\lambda_1)$.

Exercise

Use the obtained results to calculate the free energy per spin $f = F/N$ for one-dimensional Ising model. What is its limit for $T \rightarrow 0$? Is the result plausible?

- The explicit form of T is presented above. The eigenvalues are easily found

$$\lambda_{0,1} = e^{\beta J} \cosh(\beta \mu_B B) \pm \sqrt{e^{2\beta J} \sinh^2(\beta \mu_B B) + e^{-2\beta J}}.$$

and the calculation of the mean energy is then straightforward. In the limit $\beta \rightarrow \infty$, we get $f = -J - \mu_B B$. Since $F = E - TS$, for $T = 0$ only the E term matters. And the energy of the ground state per spin is really a ten je $-J - \mu_B B$.

■

Exercise

Using the obtained results calculate the mean spin value for the one dimensional Ising model. Evaluate

$\lim_{T \rightarrow 0} \lim_{B \rightarrow 0} \langle s \rangle$ and also $\lim_{B \rightarrow 0} \lim_{T \rightarrow 0} \langle s \rangle$? What is the meaning of the obtained results.

- We need now also the eigenvectors of the transfer matrix

$$\langle \mathbf{u}_0 | = (\alpha_+, \alpha_-), \quad \langle \mathbf{u}_1 | = (\alpha_-, -\alpha_+), \quad \alpha_{\pm}^2 = \frac{1}{2} \left(1 \pm e^{\beta J} \sinh(\beta \mu_B B) / \sqrt{\dots} \right).$$

Then

$$\langle s \rangle = \frac{e^{\beta J} \sinh(\beta \mu_B B)}{\sqrt{\dots}}.$$

Noninteracting spins have $J = 0$, then $\langle s \rangle = \tanh(\beta\mu_B B)$ (a typical result for the paramagnet). If $B = 0$, then $\langle s \rangle = 0$ for any temperature and so also in the limit $T = 0$. If we, however, make the limits in different order (first $T \rightarrow 0$, then $B \rightarrow 0^\pm$), we get different result what signalizes the phase transition for $T = 0$, as expected. ■

Exercise

Find the unitary matrix which diagonalizes the symmetric matrix $\begin{pmatrix} a & b \\ b & c \end{pmatrix}$?

- It is enough to find the eigenvectors of the matrix and normalize them. Then form a matrix out of those vectors, just laying one by the other. ■

Exercise

Using the transfer matrix scheme find the free energy F for the one-dimensional Ising model with free boundary condition (that is without the interaction $J s_1 s_N$). Show that in the thermodynamic limit the result is the same as for the case with periodic boundary conditions.

Hint: one does not need to find explicitly the matrix which diagonalizes the transfer matrix T . It is enough to assume that such a matrix U exists.

- The statistical sum Z_N can be written (using notation $b = \beta\mu_B B$, $j = \beta J$) as

$$\begin{aligned} Z_N &= \sum_{\{s\}} \exp[b \frac{s_1}{2}] \cdot \exp[j s_1 s_2 + b \frac{s_1 + s_2}{2}] \cdot \dots \cdot \exp[j s_{N-1} s_N + b \frac{s_{N-1} + s_N}{2}] \\ &\cdot \exp[b s_N / 2] = \sum_{\{s\}} W_{1,1} T_{1,2} T_{2,3} \dots T_{N-1,N} W_{N,N} = \\ &= \sum_{s_1} \sum_{s_N} W_{1,1} (T^{N-1})_{1,N} W_{N,N} = \\ &= \sum_{s_1} \sum_{s_N} (W T^{N-1} W)_{1,N} \end{aligned}$$

In comparison with the case with the periodic boundary conditions we have at the ends the matrix

$$W_{ij} = \delta_{ij} \exp[b s_i]$$

Another difference is that we do not make a trace of the matrix but we rather sum its elements Let the matrix diagonalizing T is denoted as U and $U T U^T \equiv D$, $U W U^T \equiv Z$. Then

$$W T^{N-1} W = U^T (Z D^{N-1} Z) U$$

The above matrix product need not be evaluated explicitly. It is enough to realize, that the resulting sum of the matrix elements will have the form

$$\lambda_0^{N-1} \cdot X + \lambda_1^{N-1} \cdot Y$$

Here the eigenvalues of T were denoted as $\lambda_0 > \lambda_1$ and X, Y are suitable "sums of products" of the matrix elements of U and Z . In the thermodynamic limit we get

$$\begin{aligned} \lim_{N \rightarrow \infty} \frac{F}{N} &= -kT \lim_{N \rightarrow \infty} \frac{1}{N} \ln Z_N = -kT \lim_{N \rightarrow \infty} \frac{1}{N} \ln \lambda_0^{N-1} \left(X + Y (\lambda_1/\lambda_0)^{N-1} \right) = \\ &= -kT \ln \lambda_0. \end{aligned}$$

The result is the same as for the periodic boundary conditions. ■

Exercise

Solvable transfer matrix larger than 2×2

Solve the Potts model with the help of transfer matrix. The Hamiltonian is

$$H = -K \sum_{i=1}^{N-1} \delta_{s_i, s_{i+1}} - K \delta_{s_N, s_1},$$

where $s_i = 0, 1, \dots, q$. What is its heat capacity in the thermodynamic limit? What is the correlation length ξ

Hint: there is no need to solve the equation of the $(q + 1)$ -th order to find the eigenvalues. The eigenvectors can be simply guessed after thinking a while.

- The transfer matrix has the dimension $(q + 1) \times (q + 1)$ with matrix elements $e^{\beta K}$ on the diagonal, everywhere else are ones. It is easy to guess the eigenvector $(1, \dots, 1)^T$, with corresponding eigenvalue $\lambda_0 = e^{\beta K} + q$. The next guess is the eigenvector $(1, -1, 0, \dots, 0)^T$ (it is easy to check), with the eigenvalue $\lambda_1 = e^{\beta K} - 1 < \lambda_0$. This eigenvector is a template to construct other eigenvectors, each of them having the form $(0, \dots, 0, 1, -1, 0, \dots, 0)^T$ with the same eigenvalue λ_1 . Now we have $q + 1$ eigenvectors, a complete set. Therefore $Z = \lambda_0^N + \lambda_1^N$, and in the thermodynamic limit only the term with λ_0 survives. The heat capacity is $C_V = \partial E / \partial T$, where $E = -\partial \ln Z / \partial \beta$. We get

$$C_V = \frac{qkN(\beta K)^2 e^{\beta K}}{(e^{\beta K} + q)^2},$$

There are no singular points in this function ■

Exercise

Let us consider the one dimensional Ising model with interaction between the nearest neighbours (with coupling constant J), but also next to nearest neighbours (with coupling constant j). Find the relevant transfer matrix.

Hint: For the case with the interaction of nearest neighbours it was useful to write the energy as

$$E = E(s_1, s_2) + E(s_2, s_3) + \dots + E(s_N, s_1).$$

Now it will be useful to write

$$E = E(s_1, s_2, s_3) + E(s_2, s_3, s_4) + \dots + E(s_N, s_1, s_2).$$

Do take care that the indexing of the objects $\exp[-\beta E(\dots)]$ in the expression for the statistical sum has to lead to matrix multiplication. A square matrix is obtained when all the possible states of a spin pair are properly numbered. These numbers will then label the rows and columns of the transfer matrix.

- We have

$$E = \dots + E(s_i, s_{i+1}, s_{i+2}) + \dots$$

, where

$$E(s_i, s_{i+1}, s_{i+2}) = -\mu_B B \frac{s_i + s_{i+1} + s_{i+2}}{3} - J \frac{s_i s_{i+1} + s_{i+1} s_{i+2}}{2} - j s_i s_{i+2}.$$

The statistical sum is

$$Z = \sum_{\{s\}} e^{-\beta E(s_1, s_2, s_3)} \cdot e^{-\beta E(s_2, s_3, s_4)} \dots e^{-\beta E(s_N, s_1, s_2)} \equiv \sum_{\{s\}} \mathbb{T}_{12,23} \mathbb{T}_{23,34} \dots \mathbb{T}_{N1,12}.$$

Now we number the spin-pair states as $(1, 1) = 1$, $(1, -1) = 2$, $(-1, 1) = 3$, $(-1, -1) = 4$, the transfer matrix will be

$$\mathbb{T} = \begin{pmatrix} A & B & 0 & 0 \\ 0 & 0 & C & E \\ B & D & 0 & 0 \\ 0 & 0 & E & F \end{pmatrix}, \quad \begin{aligned} \ln A &= \beta \mu_B B + \beta J + \beta j, & \ln D &= -\frac{1}{3} \beta \mu_B B - \beta J + \beta j, \\ \ln B &= \frac{1}{3} \beta \mu_B B - \beta j, & \ln E &= -\frac{1}{3} \beta \mu_B B - \beta j, \\ \ln C &= \frac{1}{3} \beta \mu_B B - \beta J + \beta j, & \ln F &= -\beta \mu_B B + \beta J + \beta j. \end{aligned}$$

The matrix contains some zeros because some combinations of pair states are inconsistent. ■

7.8 Ising model on a square lattice

The statistical sum for the Ising model can be written as

$$Z = \sum_{states} \prod_{links} \exp(J s_i s_j)$$

where the temperature was hidden into (the only) interaction constant J . The expression is not written in a completely rigorous way, but the meaning should be clear. The sum is over all the possible spin states. Each term in the sum is a product of factors for each link of the lattice. In the exponentials for each link are the spins which sit on the two sites belonging to the considered link.

We shall start with the high-temperature expansion that means the expansion valid for small J . Naively we would start with expanding all the exponentials and then combining the powers from the product of factors, a fairly complicated procedure. Fortunately, it can be reasonably simplified, since we do not need the exact

exponential for arbitrary continuous argument, we need just its two values for two specific values of its argument

$$\exp(J), \exp(-J)$$

and these two values can be expressed using a suitable small variable, using the identity

$$\exp(Js_i s_j) = \frac{\exp(J) + \exp(-J)}{2} + s_i s_j \frac{\exp(J) - \exp(-J)}{2}$$

which holds for

$$s_i s_j \in \{1, -1\}$$

We have

$$\exp(Js_i s_j) = \cosh(j)(1 + s_i s_j t)$$

where

$$t = \tanh(J)$$

and the statistical sum will be

$$Z = \cosh^{2N}(J) \sum_{\text{states}} \prod_{\text{links}} (1 + s_i s_j t) = 2^N Z' \cosh^{2N}(J)$$

where

$$Z' = \frac{1}{2^N} \sum_{\text{states}} \prod_{\text{links}} (1 + s_i s_j t)$$

Expanding the product we get

$$Z' = \frac{1}{2^N} \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} \left\{ 1 + t \sum_{\text{links}} s_i s_j + t^2 \sum_{\text{link pairs}} (s_i s_j)(s_m s_n) + \cdots \right\}$$

The structure of the expression in the square brackets is such that the power t^L is multiplied by a sum of all the products of L pairs of the type $s_i s_j$. Those L pairs correspond to L links. The sum at t^L has as many terms as is the number of possibilities how L links can be highlighted on a square lattice.

Now one has to realize that after summing over the spin states all the products where at least one spin is presented odd number of times (as a factor) give zero. If the spin appears in the product even number of times the product is equal to one and the sum over all the spin states gives 2^N .

So we get

$$Z' = \sum_L g(L) t^L$$

where

$$g(L)$$

denotes the number of possibilities how L links can be highlighted on a square lattice in such a way that every site is highlighted even number of times (zero count as even number here). Expressed differently, $g(L)$ is the number of graphs which can be drawn on a square lattice in such a way that each site on the graph is connected with the remaining sites by even number of edges.

Now we proceed from the side of low temperatures, we make a low-temperature expansion. We have the same statistical sum as before, but we have different (low) temperature, what we denote by using a different coupling constant j .

$$Z = \sum_{\text{stavy linky}} \prod \exp(j s_i s_j)$$

At low temperatures the spins prefer to be oriented in parallel if they sit on the same link. So we expect that at low temperatures those links contribute which have "their spins" oriented in parallel (both having value $+1$ or -1).

For a given spin state each link with parallelly oriented spins contributes to the statistical sum by the factor

$$\exp(j)$$

On the other hand each link with antiparallel spins contributes by the factor

$$\exp(-j)$$

The statistical sum can be expressed as

$$Z = \sum_{\text{stavy}} \exp((2N - L)j) \exp(-Lj)$$

$$Z = \sum_{\text{stavy}} \exp(2Nj) (\exp(-2j))^L$$

where $2N$ is the total number of links (for N sites) and the number L depends on the particular spin states and gives the number of links with antiparallel spins on their sites.

Let us imagine that (for a particular spin state) we highlight (colour) all the links with antiparallel spins, so that L links would be highlighted for the particular spin state. To each state there corresponds a graph with exactly L links highlighted. The statistical sum can be then rewritten as

$$Z = \exp(2Nj) \sum_L m(L) (\exp(-2j))^L$$

where $m(L)$ is the number of states to which (after highlighting) correspond a graph with exactly L links highlighted. Rephrased differently $m(L)$ is the number of possibilities how a graph with L edges can be drawn on a lattice in such a way that a certain spin state corresponds to it (having those L links occupied by antiparallel spins. Let us stress that not to any graph correspond a real spin state. For example if we highlight just one link then no state correspond to it. Such a state should have the two spins of that link oriented in parallel. But all the other spins should be parallel with one as well as with the other spin of that pair, since there is no other highlighted link. This is a clear contradiction.

Let us note, that we have got series expansion in powers of the expression

$$\exp(-2j)$$

This is a low value for low temperatures, so it is effectively a low-temperature expansion.

Now let us ponder how looks the graph corresponding to the lowest possible value of $L > 0$. Obviously it will be the state, with all the spins oriented parallelly just one spin being reversed. Four highlighted links come out of that reversed-spin site in the form of a cross. So the lowest non-zero L is equal to 4.

Bigger L values we obtain if we reverse more spins. Those reversed spins will form a sort of islands in the overall sea of other parallel spins. Let us imagine one such island (fig.7.1 with 8 spins oriented oppositely to the sea of other spins. That particular configurations requires to highlight 12 links as it is shown in the figure. Now let us demarcate the island of "reversed spins" by the boundary line going through the centers of the lattice plaquettes. It is clear that the boundary crosses each of the highlighted link and so it is 12 lattice units long. We could draw the boundary in such a way that we orthogonally cross each of the highlighted link by a boundary element connecting the centers of the two plaquettes which have as a common edge the considered highlighted link.

Now we can imagine that into the original lattice we insert a new, dual, lattice such that the centers of the plaquettes of the original lattice are the sites of the new lattice. The new (dual) lattice is again a square lattice. We see, that the "island boundaries" coincide with edges (links) of the new dual lattice. So to each "low temperature" diagram of L highlighted edges on the original lattice there corresponds a graph on the dual lattice. It is important to realize, that the "boundary graph" on the dual lattice Let us notice now, that the graph which originated as the island boundary and sits on the dual lattice is exactly the same as one of the graphs originated at the high temperature expansion on the original lattice. So there is one-to-one correspondence between the graphs originating at the high-temperature and the low-temperature expansions. Therefore the following relation holds

$$m(L) = g(L)$$

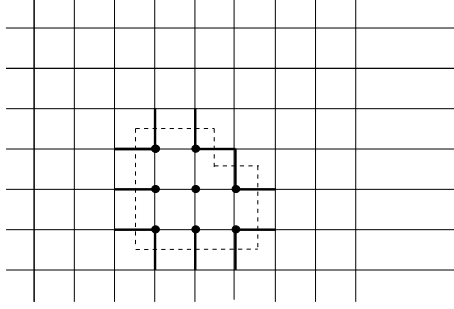


Figure 7.1: Diagram with $L = 12$

So we have got the high-temperature expansion

$$Z(J) = 2^N \cosh^{2N}(J) \sum_L g(L) t^L$$

where

$$t = \tanh(J)$$

and the low-temperature expansion

$$Z(j) = \exp(2Nj) \sum_L g(L) (\exp(-2j))^L$$

Up to now we have two arbitrary independent coupling constants J and j . We assume however that J is large and j is small. Let us now choose j related to J as

$$\exp(-2j) = \tanh(J)$$

Then we get a selfconsistent relation for the statistical sum

$$Z(J) = 2^N \cosh^{2N}(J) \tanh^N(J) Z(j)$$

where

$$j = -\frac{1}{2} \ln(\tanh(J))$$

Let us suppose now that in the thermodynamic limit $N \rightarrow \infty$ the free energy per site (only intensive variable can have thermodynamic limit) has a singularity at some temperature T_c . Let us also suppose that there is just one temperature value for which there is such a singularity. The selfconsistent formula for the statistical sum does not introduce any new singularity. So if there is only one singularity, it must be both at j and at J and the two values must be equal, that is $j = J$ and we get the relation

$$J_c = -\frac{1}{2} \ln(\tanh(J_c))$$

The solution gives for the critical value

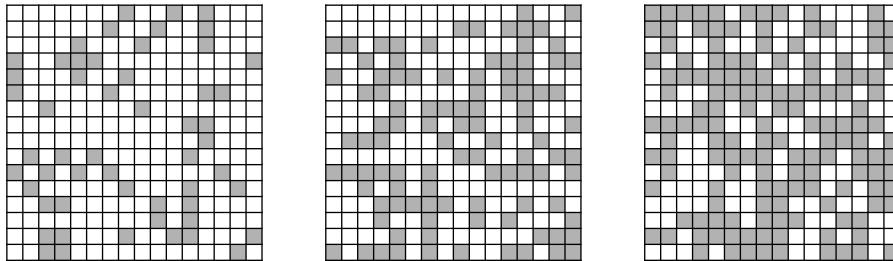
$$J_c = \frac{1}{2} \ln(1 + \sqrt{2})$$

7.9 Renormalization group

See also [GaT] (chapter9), [Yeo] (pp. 8-14, 105-119).

We shall not go much into technical details about the renormalization group technique. we shall just present a few illustrations to get the feeling what this all is about, since renormalization and renormalization group are two very frequent terms in modern physics.

We start with a model which is more geometrical than physical (there is no temperature nor statistical sum involved). It is, however, very useful, since it is very illustrative. We shall investigate the percolation model. The lives on a lattice of square cells. Each cell can be "empty" or "occupied". The probability p of a cell being occupied is independent on the occupation of any other cell. We introduce the notion of cluster: a set of occupied cells which are touching each other by at least one edge. Now we shall investigate a problem whether there exists a spanning cluster: a cluster which reaches from the top side of the lattice continuously to its bottom side. If yes, the lattice is considered to be percolative (imagine that the spanning cluster provides a path for water to percolate from top to bottom). The figure shows examples of possible lattice states for different values of p .



We shall investigate the limit for the size of the lattice going to infinity. We expect that there exists a critical probability p_c above which the lattice is percolative. (The reader can easily make computer experiments for large lattices.) Our goal is to find the critical probability p_c , as well as some relevant critical exponents characterizing some interesting variables like the correlation length ξ ("percolative length").

The main idea is that in the critical point the correlation length goes to infinity. The correlations between cells are present for any distances between them. We expect that the system looks qualitatively the same irrespective what zoom we use to observe it. (So we expect a fractal like behaviour.) The key notion here is "selfsimilarity". The renormalization technique looks for the selfsimilar behaviour by averaging the image at some scale it hopes to find a selfsimilar image.

Let us combine the cells of the original lattice into larger square cells, containing

$b \times b$ original cells. The new squares are cells of a new, renormalized lattice. Now we design a rule to specify which of the new larger cells are considered as occupied. There are many possible rules to be considered (those which have majority of the original cells occupied, those large cells which are percolative horizontally, or vertically, or in both directions ...).

Let us take $b = 2$ and the rule: the renormalized cell is considered to be occupied if at least three of its original cells are occupied. Let the probability that the new renormalized cell is occupied is denoted as p' . Clearly

$$p' = p^4 + 4p^3(1 - p) \equiv R(p).$$

If the original lattice had $p = 0,5$ we get $p' = 0.3125$. By next renormalization we would get $p' \doteq 0.0934$. The fix point of these iterative transformations is $p = 0$ what means an empty lattice. So in this specific case the selfsimilarity is not realized. The selfsimilarity requires to get $p' = p$. A numerical solution of this simple algebraic equation gives $p_* \doteq 0.7676$ (the true value is je $p_c \doteq 0.5927$).

To find the critical exponent for the correlation length ξ , one has to realize that all the corresponding lengths in the renormalized lattice are reduced b -times. Therefore $\xi' = \xi/b$. In the vicinity of the critical point we expect $\xi \sim |p - p_c|^{-\nu}$. Comparing the two expressions we get

$$|p' - p_*|^{-\nu} = \frac{1}{b}|p - p_*|^{-\nu}$$

We have replaced here the true value p_c with our fix point p_* , because for our choice of the renormalization rule the singular behaviour is expected for p_* . Now we have to find the relation between p and p' int the vicinity of the critical point

$$p' - p_* = R(p) - R(p_*) \approx (p - p_*) \left. \frac{dR}{dp} \right|_{p=p_*} \equiv \lambda(p - p_*).$$

Substituting into the previous relation we get

$$\lambda^{-\nu}|p - p_*|^{-\nu} = \frac{1}{b}|p - p_*|^{-\nu} \implies \lambda^{-\nu} = b^{-1} \implies \nu = \frac{\ln b}{\ln \lambda}.$$

In our case $b = 2$ a $\lambda \doteq 1.6432$, so $\nu \doteq 1.40$ (the exact result is $\nu = 4/3$).

Just for reference here are the critical probabilities on hypercubic lattices: for 2D $p_c = 0.592745$ for 3D $p_c = 0.407355$ and for 4D $p_c = 0.168$. For the triangular lattice $p_c = 1/2$.

Now we shall demonstrate the use of renormalization technique for the one-dimensional Ising model.

We consider the periodic boundary condition, so we have the Hamiltonian

$$H = -J \sum_{i=1}^N s_i s_{i+1} - \frac{1}{2} \mu_B B \sum_{i=1}^N (s_i + s_{i+1}).$$

Let us denote $\beta J \equiv j$ and $\beta \mu_B B \equiv b$. We get

$$Z_N = \sum_{\{s\}} \exp \left[\sum_{i=1}^N \left(j s_i s_{i+1} + \frac{1}{2} b (s_i + s_{i+1}) \right) \right],$$

Let us first simplify the model putting $b = 0$. Then we can write

$$\begin{aligned} Z(j, N) &= \sum_{\{s\}} e^{j(s_1 s_2 + s_2 s_3)} e^{j(s_3 s_4 + s_4 s_5)} \dots = \\ &= \sum_{\{s'\}} \underbrace{\left[e^{j(s_1 + s_3)} + e^{-j(s_1 + s_3)} \right]}_{\text{got by summing over } s_2} \cdot \underbrace{\left[e^{j(s_3 + s_5)} + e^{-j(s_3 + s_5)} \right]}_{\text{got by summing over } s_4} \cdot \dots, \end{aligned}$$

where the sum over $\{s'\}$ is the sum over the the spins with even indices So it is the sum over the states of system with $N/2$ spins. we get a selfsimilar expression if this sum can be written as the statistical sum for the Ising model with $N/2$ spins. In order this to be true, the following should hold

$$e^{j(s_1 + s_3)} + e^{-j(s_1 + s_3)} = A(j) e^{j' s_1 s_3},$$

where $A(j)$ je some function independent of the spin states and j' is a suitable constant. The relation should hold just for the possible spin values s_1 a s_3 .

$$\begin{aligned} s_1 = s_3 &\implies A(j) \exp[j'] = \exp[2j] + \exp[-2j], \\ s_1 = -s_3 &\implies A(j) \exp[-j'] = 2. \end{aligned}$$

The solution is

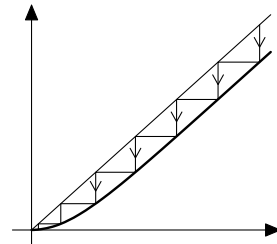
$$j' = \ln \cosh(2j)/2, \quad A(j) = 2 \cosh^{1/2}(2j), \quad Z(j, N) = A(j)^{N/2} Z(j', N/2).$$

In the limit $N \rightarrow \infty$ we expect $\ln Z \sim N$. Let us denote therefore $\ln Z = N f(j)$. Using the above relations we get

$$f(j') = 2f(j) - \ln A(j).$$

The relation $j' = R(j)$ je is reversible. Therefore we can use the last relation and by inverse renormalization to move from the value $j_i = 0$, where we know the exact solution ($T = \infty$, therefore $Z(j) = 2^N$ and $f(j) = -kT \ln Z(j)$), to an arbitrary state at $j_f \neq 0$.

The relations $j' = R(j)$ and $Z' = N(2f(j) - \ln A(j)) \equiv Ng(j)$ are the basic equations of the renormalization

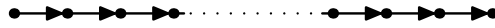


analysis. In the present case this analysis is very simple. The relation $j' = \ln \cosh(2j)/2$ has one stable fix point (see the figure) $j = 0$ (what means $T = \infty$). There is an unstable fix point $T = 0$ ($j = \infty$), any small deviations from it lead to $j = 0$. It all means that for non-zero temperature there is no phase transition.

The relation $j' = R(j)$ is the motivation for the notion *renormalization group*. As we shall see the notion is not a happy one. The group operation here is meant the composition of consecutive scale transformation steps formally R_b (b is the scale size)

$$R_{b_1} \circ R_{b_2} = R_{b_1 b_2}, \quad \text{since the following holds} \quad R_{b_1 b_2}(j) = R_{b_2}[R_{b_1}(j)].$$

The renormalization operation naturally generates a dynamical flow in the space of parameters (where the "constants" like j live / see the figure).



From the mathematical point of view we do not have inverse scale transformation, so the more appropriate notion would be a semigroup.

Exercise

Show, that for the one-dimensional percolation $p_c = 1$ and $\nu = 1$ (the critical exponent related to the correlation length).

- We renormalize at the scale b : b of the neighbouring cells we substitute by just one which we consider to be filled if all the corresponding original cells are filled. Then $p' = R(p) = p^b$. For the fix point p_c we get $p_c = p_c^b$, with the solution $p_c = 1$. For the correlation length we get $\xi' = \xi/b$ and in the vicinity of the critical point $\xi \sim |p - p_c|^{-\nu}$. Combining the two relations we get

$$|p' - p_c|^{-\nu} = \frac{1}{b} |p - p_c|^{-\nu}.$$

It remains to find p' expressed in terms of p in the vicinity of p_c . With the help of the Taylor series we get

$$\left. \frac{dp'}{dp} \right|_{p=p_c} = b \implies p' = p_c + b(p - p_c) \implies |b(p - p_c)|^{-\nu} = \frac{1}{b} |p - p_c|^{-\nu}.$$

From there we get $\nu = 1$.

Let us demonstrate the independence on the details of the renormalization condition. As before b cells are substituted by just one cell, which will be considered as occupied when at most one of the original corresponding cells was empty. So we get $p' = p^b + b(1 - p)p^{b-1}$. The fix point equation cannot be solved exactly, but we expect p_c to be close to 1. So let us try the substitution $p = 1 - x$ (where we

expect small value of x for large b values. The solution is $x = 2/b(b-3)$, so really for large b we get x close to zero. So in the limit of $b \rightarrow \infty$ we get the same result as for the original renormalization scheme. ■

Exercise

Find the critical value for the hexadimensional percolation lattice.

- We shall investigate percolation in the direction NE-SW. The renormalization cell will consist of 4 cells. Out of its 2^4 configurations 6 are percolative. The renormalization equation will be $R(p) = 2p^2(1-p)^2 + 4p^3(1-p) + p^4$. The fixed point solutions of $R(p) = p$ are $p = 0, 1, (\sqrt{5}-1)/2$. The third solution is clearly the critical point we are looking for. ■

Chapter 8

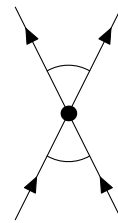
Boltzmann kinetic equation

8.1 Cross sections

See also [LL1] (str. 56-60), [Huang] (str. 59-64).

Scattering experiments are important source of knowledge in particle physics. However the experiment is never done with a single projectile particle and a single target particle. We use a beam of projectile particles which is characterized by the current density j (number of particles per unit of time per unit of area. The projectile particles scattered on target are detected by set of detectors which provide us with the statistics how many particles was scattered into a particular direction. Let us assume that the detector covers certain space angle $d\Omega$ and registers dN particles per unit of time. The scattering process is then characterized by the ratio $dN/j \equiv d\sigma$ (this ratio is independent on the beam current density). It is clear that $d\sigma$ has the dimension of area and is called differential cross section.

The spherical coordinates are introduced so that the angle ϑ is the angle ϑ between the direction of the projectile (scattering angle, polar angle). The angle φ which measures rotation around the beam axis is called azimuthal (axial) angle. Let the detector covers $d\varphi$ around axial angle φ and $d\vartheta$ around polar angle ϑ . Let us assume, that there is a one-to-one relation between the impact parameter b and the scattering angle ϑ . and let the interval $d\vartheta$ corresponds to the interval db in the impact parameter b . Number of particles registered by the detector will be



$$dN = j dS = j b db d\varphi \implies d\sigma = b db d\varphi = b(\vartheta) \left| \frac{db(\vartheta)}{d\vartheta} \right| d\vartheta d\varphi.$$

The absolute value is introduced here because the derivative $db/d\vartheta$ can be (and usually is) negative. The space angle interval can be written as $d\Omega = \sin \vartheta d\vartheta d\varphi$

so we finally can write the above formula as

$$\frac{d\sigma}{d\Omega} = \frac{b(\vartheta)}{\sin \vartheta} \left| \frac{db(\vartheta)}{d\vartheta} \right|.$$

To find the relation between b and ϑ one has to solve the corresponding equation of motion. To simplify the notation, we shall often write just $\sigma(\Omega)$ instead of $d\sigma/d\Omega$. The total cross section (differential cross section integrated over the full solid angle) will be denoted as σ .

The exact shape of $\sigma(\Omega)$ depends on the shape of the interaction potential. However, there are some symmetry relations which are generally valid. We assume that the interactions considered here are of electromagnetic nature, therefore the symmetries of the cross section are those of the electromagnetic interaction. Discussing the symmetries we shall use instead of $\sigma(\Omega)$ the notation¹ $\sigma'(\mathbf{v}, \mathbf{v}_1 \rightarrow \mathbf{v}', \mathbf{v}'_1)$. Ω is the angle between $\mathbf{v}_1 - \mathbf{v}$ and $\mathbf{v}'_1 - \mathbf{v}'$ (see the left figure).

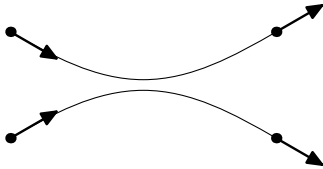
The first obvious property is the invariance with respect to time inversion

$$\sigma'(\mathbf{v}, \mathbf{v}_1 \rightarrow \mathbf{v}', \mathbf{v}'_1) = \sigma'(-\mathbf{v}', -\mathbf{v}'_1 \rightarrow -\mathbf{v}, -\mathbf{v}_1).$$

Next obvious property is the invariance with respect to rotations and reflections.

$$\sigma'(\mathbf{v}, \mathbf{v}_1 \rightarrow \mathbf{v}', \mathbf{v}'_1) = \sigma'(\mathbf{v}^*, \mathbf{v}_1^* \rightarrow \mathbf{v}'^*, \mathbf{v}'_1^*),$$

where \mathbf{v}^* denotes the vector obtained from \mathbf{v} by space rotation or space reflection



Now we introduce a new notion of inverse scattering which we get from the original process by exchanging the initial and final state. We shall prove that for the molecular collisions considered the following invariance holds

$$\sigma'(\mathbf{v}, \mathbf{v}_1 \rightarrow \mathbf{v}', \mathbf{v}'_1) = \sigma'(\mathbf{v}', \mathbf{v}'_1 \rightarrow \mathbf{v}, \mathbf{v}_1).$$

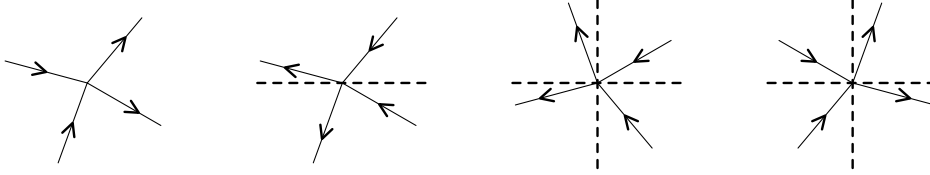
Let us first note that it is not obvious that the relation is true. For example for the collision of the two macroscopic objects in the figure it is not true.

The proof proceeds (for spinless particles) as follows

$$\begin{array}{ccc} \mathbf{v} \ \& \ \mathbf{v}_1 \rightarrow \mathbf{v}' \ \& \ \mathbf{v}'_1 & \xrightarrow{\text{T}} & -\mathbf{v}' \ \& \ -\mathbf{v}'_1 \rightarrow -\mathbf{v} \ \& \ -\mathbf{v}_1 & \xrightarrow{\text{R}(n, 180^\circ)} \\ \mathbf{v}'^* \ \& \ \mathbf{v}'_1^* \rightarrow \mathbf{v}^* \ \& \ \mathbf{v}_1^* & \xrightarrow{\text{Z}(\tau)} & \mathbf{v}'_1 \ \& \ \mathbf{v}' \rightarrow \mathbf{v}_1 \ \& \ \mathbf{v}. \end{array}$$

¹Actually $\sigma(\Omega)$ depends only on two final state variables ϑ and φ and in the notation $\sigma'(\mathbf{v}, \mathbf{v}_1 \rightarrow \mathbf{v}', \mathbf{v}'_1)$ there are 6 final state variables. Not all of them are independent since the conservation laws should be fulfilled. So the function σ' hides several delta functions inside.

Here R is the rotation by 180° around the axis \mathbf{n} perpendicular to the total momentum of the system, Z is the reflection with respect to the plane $\tau \perp \mathbf{n}$ (see the next figure).



Exercise

Calculate $d\sigma/d\Omega$ a σ for the collision of two billiard balls with the same radius R . Assume for simplicity that one of the balls is fixed with respect to the table (has the infinite mass)

- The collision can be understood as a scattering on a fixed "hard core" potential $V(r) = 0$ for $r > R$ and $V(r) = \infty$ for $r < R$. The scattering angle is ϑ . Now $\vartheta = \pi - 2\alpha$, where $\sin \alpha = b/2R$. So

$$b = 2R \sin \alpha = 2R \sin \frac{\pi - \vartheta}{2} = 2R \cos \frac{\vartheta}{2}.$$

Differentiating and substituting to the differential cross section formula we get $d\sigma/d\Omega = R^2$ and $\sigma = \pi(2R)^2$. It is just the cross section of a sphere with the radius $2R$. ■

Exercise

Do the billiard ball calculation for two identical balls (the target ball is at rest initially, but is not fixed to the table)

- Denote the projectile ball velocity as v_0 . Then the centre-of-mass frame moves with respect to the laboratory frame with the velocity $v_0/2$. At the moment of impact, the balls have common tangential plane. We can decompose the ball velocities to components parallel to that plane and perpendicular to it. The kinematics is such that the balls exchange the normal components of the velocities, the parallel components will remain the same as before the collision. In the centre-of-mass frame the velocity of the projectile ball was $(v_0/2, 0)$, its decomposition is

$$v_{\parallel} = (v_0/2) \sin \alpha, \quad v_{\perp} = (v_0/2) \cos \alpha.$$

Here again $\sin \alpha = b/2R$. After the collision the velocity will be v_x, v_y , where

$$\begin{aligned} v_x &= v_{\parallel} \cos(90^\circ - \alpha) - v'_{\perp} \cos \alpha = -(v_0/2) \cos(2\alpha), \\ v_y &= v_{\parallel} \sin(90^\circ - \alpha) + v'_{\perp} \cos \alpha = (v_0/2) \sin(2\alpha). \end{aligned}$$

Now we have to transform back into the laboratory frame, it increases v_x by $v_0/2$. The scattering angle of the projectile particle is therefore $\tan \vartheta_L = v_y/(v_x + v_0/2)$, and from there

$$\tan \vartheta_L = \frac{\sin(2\alpha)}{1 - \cos(2\alpha)} = \cotg \alpha = \sqrt{(2R/b)^2 - 1} \implies b = 2R \sin \vartheta.$$

For the differential cross section we get

$$d\sigma/d\Omega = (2R)^2 \cos \vartheta$$

and by integration $\sigma = \pi(2R)^2$. One just has to be careful not to integrate over the regions where the differential cross section is negative (these are of course unphysical regions). This is more transparent in the relation $\tan \vartheta = \sqrt{\dots}$. From there on can for $b \in \langle 0; 2R \rangle$ never get $\vartheta > 90^\circ$.

We add a note concerning the relation between the differential cross sections in the laboratory and the center-of-mass frames. Since the number of particles registered by the detector is independent of the frame we use for the description the following relation must hold

$$j d\sigma'(\vartheta') \sin \vartheta' |d\vartheta'| = j d\sigma(\vartheta) \sin \vartheta |d\vartheta| \implies \\ \sigma'(\vartheta') = \sigma(\vartheta) \frac{\sin \vartheta}{\sin \vartheta'} \left| \frac{d\vartheta}{d\vartheta'} \right| = \sigma(\vartheta) \frac{d(\cos \vartheta)}{d(\cos \vartheta')}.$$

More detailed discussion (including the case for unequal masses) can be found in [Iro] (pp. 153-157 and 165), and also in [LL 1] (p. 58). ■

Exercise

Show that in the collision of two molecules the following holds

$$d\mathbf{v}_1 d\mathbf{v}_2 = d\mathbf{u} d\mathbf{V},$$

where \mathbf{u} is the relative velocity and \mathbf{V} is the centre of mass velocity.

- The transformation rules between the two sets of variables are

$$\mathbf{v}_1 = \mathbf{V} + \frac{\mu}{m_1} \mathbf{u}, \quad \mathbf{v}_2 = \mathbf{V} - \frac{\mu}{m_2} \mathbf{u}.$$

where μ is the reduced mass $1/\mu = 1/m_1 + 1/m_2$. We have to find the Jacobian. For the x components we get

$$dv_{1x} dv_{2x} = \left| \frac{\partial(v_{1x}, v_{2x})}{\partial(V_x, u_x)} \right| dV_x du_x = \begin{vmatrix} 1 & \frac{\mu}{m_1} \\ 1 & -\frac{\mu}{m_2} \end{vmatrix} dV_x du_x = dV_x du_x,$$

what proves the formula. ■

8.2 Boltzmann equation

Up to now we have investigated only equilibrium statistical systems. Here we start investigating non-equilibrium system. We shall not present any general theory, we limit ourselves to investigating dilute gas not far from equilibrium in classical (non-quantum) approximation.

We consider a classical dilute gas consisting of just one type of molecules. Classically, we know the state of the gas if we know the position and the velocity of each of the molecules. If we consider an ensemble of microstates representing some (in general non-equilibrium) macrostate we should describe it by a probability density which is the function of $6N$ variables. We shall limit ourselves to a drastic approximation: a one-particle description.

So let us look to an infinitesimal region of space around the vector \mathbf{r} and ask what is the mean density of molecules at \mathbf{r} at time t : let us denote it as $n(\mathbf{r}, t)$. Then we ask what is the probability distribution of the velocities of individual molecules in this region. We arrive at the function

$$f(\mathbf{r}, \mathbf{v}, t)$$

whose meaning is the following. $f(\mathbf{r}, \mathbf{v}, t) d^3\mathbf{r} d^3\mathbf{v}$ is the mean number of molecules present at time t in the infinitesimal region around \mathbf{r} and having velocities in the infinitesimal neighbourhood of vector \mathbf{v} . The following (normalization condition) holds

$$n(\mathbf{r}) = \int f(\mathbf{r}, \mathbf{v}, t) d^3\mathbf{v}$$

What we have is in fact a non-equilibrium Boltzmann distribution, however, normalized not to unity but to molecular density. Boltzmann one-particle probability density $\rho(\mathbf{r}, \mathbf{v}, t)$ is the probability density to find a selected particle in the neighbourhood of the phase space point \mathbf{r}, \mathbf{v} . It is a well defined function and does not contain any approximation (if the gas is classical and it is possible to select one specific particle and follow it). The function we consider now, $f(\mathbf{r}, \mathbf{v}, t)$, is related to $\rho(\mathbf{r}, \mathbf{v}, t)$ as

$$f(\mathbf{r}, \mathbf{v}, t) = N\rho(\mathbf{r}, \mathbf{v}, t)$$

where N is the total number of particles in the gas. The relation is intuitively clear but not completely trivial. Some discussion is shifted to the appendix 10.1.

The function $f(\mathbf{r}, \mathbf{v}, t)$ can always be introduced, it has a well defined meaning and by itself it does not mean an approximation. It becomes to be the **one-particle approximation** when we say that it contains **whole statistical information**. By that we mean, that all statistical results (like mean values of all the physical variables) can be obtained just from function $f(\mathbf{r}, \mathbf{v}, t)$. This is, of course not true in general. Only means of one-particle variables can be correctly calculated

from this function. Those are the variables whose values can be obtained experimentally by attaching the measurement apparatus to a single particle. (The mean is then experimentally obtained by repeating measurements on a randomly chosen single particles.) Already the two-particle quantities (like the potential energy between two particles) cannot be exactly statistically evaluated from $f(\mathbf{r}, \mathbf{v}, t)$. To do that we would need two-particle densities $f_2(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, t)$. We can just approximately express the two-particle densities with the help of one particle densities in a so called molecular chaos approximation as

$$f_2(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, t) = f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_2, \mathbf{v}_2, t)$$

Let us note, that here we follow the classical Boltzmann choice of variables \mathbf{r} a \mathbf{v} . It would be more appropriate to use canonical pair of variables the position and momentum. When we consider a classical gas with no magnetic fields it would be just a formal difference.

Let us assume we have an ideal classical gas whose particles do not feel each other. Each molecule moves only under the influence of (possible) external force field. Such a molecule follows in the phase space a (one particle) trajectory which we can find by solving the equation of motion. For example for molecules in a constant force field the phase-space trajectory of the particle which at $t = 0$ was at the phase-space point $\mathbf{r}_0, \mathbf{v}_0$ is given by the relations

$$\mathbf{v}(t) = \mathbf{v}_0 + \frac{\mathbf{F}}{m} t \quad (8.1)$$

$$\mathbf{r}(t) = \mathbf{r}_0 + \mathbf{v}_0 t + \frac{1}{2} \frac{\mathbf{F}}{m} t^2 \quad (8.2)$$

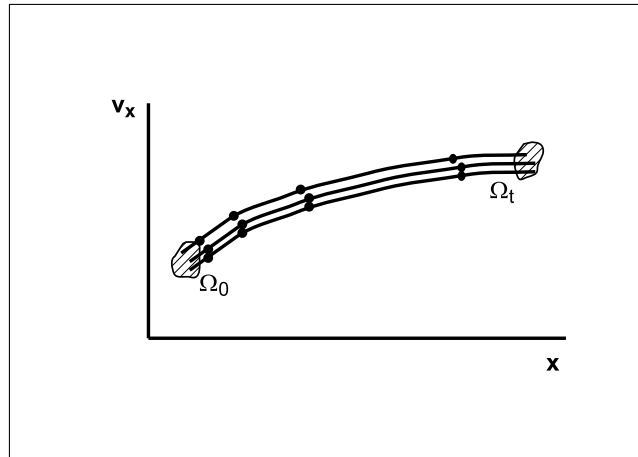


Figure 8.1: Fázové trajektórie

In the figure 8.1 we sketched several such trajectories: the small circles denotes point of equal time intervals. In general the force field need not be constant and we would obtain more complicated formulas then (8.1). But the formal characters

of the equations would be the same. The formulas would contain the initial point parameters $\mathbf{r}_0, \mathbf{v}_0$ and they would express the coordinates $\mathbf{r}(t), \mathbf{v}(t)$ of the phase-space-trajectory point at time t .

Let us imagine now a set of neighbouring points in the phase space, which fill a region Ω_0 . Let these points be the initial states of a set of phase-space trajectories originating in the region Ω_0 at time $t = 0$ and let the end points of those trajectories at time t fill the region Ω_t .

If we imagine, that we are describing an ideal gas, then the particles are not feeling each other, neither scatter on each other. They all move on the phase-space trajectories (8.1). All the particles which at time $t = 0$ were in the phase-space region Ω_0 will at time t be in the region Ω_t . No other particles will be present in the region Ω_t at time t . The reason is the T-invariance of the equations of motion. All the particles, which at time t are in the region Ω_t must have got there somehow so they are the end points of some phase space trajectories. These trajectories we find by back-solving the equations of motion. Because of T-invariance those backward trajectories are the same as the forward trajectories and so at time $t = 0$ the backward trajectories end in the region Ω_0 .

This fact has consequence for the Boltzmann distribution function

$$\int_{\Omega_0} f(\mathbf{r}, \mathbf{v}, t = 0) d^3\mathbf{r} d^3\mathbf{v} = \int_{\Omega_t} f(\mathbf{r}, \mathbf{v}, t) d^3\mathbf{r} d^3\mathbf{v}$$

The integration variables at the right-hand side can be denoted arbitrarily, so let us denote them as $\mathbf{r}_t, \mathbf{v}_t$ and we write

$$\int_{\Omega_0} f(\mathbf{r}, \mathbf{v}, t = 0) d^3\mathbf{r} d^3\mathbf{v} = \int_{\Omega_t} f(\mathbf{r}_t, \mathbf{v}_t, t) d^3\mathbf{r}_t d^3\mathbf{v}_t$$

In the integral at the right-hand side we perform a substitution. The variables $\mathbf{r}_t, \mathbf{v}_t$ will be substituted by variables $\mathbf{r}_0, \mathbf{v}_0$. The substitution relations will be those of (8.1),

$$\begin{aligned} \mathbf{v}_t &= \mathbf{v}_0 + \frac{\mathbf{F}}{m} t \\ \mathbf{r}_t &= \mathbf{r}_0 + \mathbf{v}_0 t + \frac{1}{2} \frac{\mathbf{F}}{m} t^2 \end{aligned}$$

When the "old" variables $\mathbf{r}_t, \mathbf{v}_t$ run through the region Ω_t , the "new" variables $\mathbf{r}_0, \mathbf{v}_0$ run through the region Ω_0 and we get

$$\int_{\Omega_0} f(\mathbf{r}, \mathbf{v}, t = 0) d^3\mathbf{r} d^3\mathbf{v} = \int_{\Omega_0} f(\mathbf{r}_t, \mathbf{v}_t, t) J d^3\mathbf{r}_0 d^3\mathbf{v}_0$$

It is understood that the variables $\mathbf{r}_t, \mathbf{v}_t$ are expressed through the integration variables $\mathbf{r}_0, \mathbf{v}_0$ and J is the Jacobian of the substitution transformation

According to the Liouville theorem

$$J = 1$$

as so we get

$$\int_{\Omega_0} f(\mathbf{r}, \mathbf{v}, t = 0) d^3\mathbf{r} d^3\mathbf{v} = \int_{\Omega_0} f(\mathbf{r}_t, \mathbf{v}_t, t) d^3\mathbf{r}_0 d^3\mathbf{v}_0$$

Now we change the notation of the integration variables on the left-hand side for $\mathbf{r}_0, \mathbf{v}_0$ and we get

$$\int_{\Omega_0} f(\mathbf{r}_0, \mathbf{v}_0, t = 0) d^3\mathbf{r}_0 d^3\mathbf{v}_0 = \int_{\Omega_0} f(\mathbf{r}_t, \mathbf{v}_t, t) d^3\mathbf{r}_0 d^3\mathbf{v}_0$$

This relation holds for an arbitrary region of integration Ω_0 thus the integrands must be equal

$$f(\mathbf{r}_0, \mathbf{v}_0, t = 0) = f(\mathbf{r}_t, \mathbf{v}_t, t)$$

This relation holds for arbitrary t , therefore

$$\frac{d}{dt} f(\mathbf{r}_t, \mathbf{v}_t, t) = 0$$

From there we get the "Boltzmann equation without the right-hand side"

$$\frac{\partial}{\partial t} f + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} f + \frac{\mathbf{F}}{m} \cdot \frac{\partial}{\partial \mathbf{v}} f = 0$$

This equation holds for ideal gas when we neglect collisions between molecules. In a general case the following equation holds

$$\frac{\partial}{\partial t} f + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} f + \frac{\mathbf{F}}{m} \cdot \frac{\partial}{\partial \mathbf{v}} f = D_c f$$

where at the right-hand side one writes so called collision term, which we shall discuss later. The differential operator at the left-hand side is usually denoted as D

$$D = \frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial}{\partial \mathbf{v}}$$

And the Boltzmann equation is then written in a compact form

$$Df = D_C f$$

8.3 Boltzmann equation in the relaxation time approximation

Molecules in gas collide with each other. Let us suppose that the collisions are independent and express the probability that a given particle collides with some other particle in the next infinitesimal time interval dt as

$$\frac{1}{\tau} dt$$

We denote as $\mathcal{P}(t)$ the probability that the given particle does not collide in the time interval t from the present moment. Then

$$\mathcal{P}(t + dt) = \mathcal{P}(t) \left(1 - \frac{1}{\tau} dt\right)$$

This differential equation has the solution

$$\mathcal{P}(t) = \exp(-t/\tau)$$

Now let us denote as $P(t)dt$ the probability that the given particle collides for the first time (from now) at the time interval $(t, t + dt)$. Then

$$P(t)dt = \frac{1}{\tau} \exp(-t/\tau) dt$$

This probability is (of course) correctly normalized as

$$\int dt P(t) = 1$$

The mean time up to the next collision is given as

$$\langle t \rangle = \int dt t P(t) = \tau$$

This time is also called "mean time between two collisions" and one can easily check that the notion is correct. Indeed, due to independence of collisions the "mean time between two collisions" and the "mean time from now to the next collision" is the same. If the collisions are independent, then the two notions "from now" and "from now, when the particle just collided" have the same meaning what concerns future.

Now we shall describe a simple approximate way how to include collisions into the Boltzmann equation. To simplify the explanation, let us assume the gas considered lives in a one-dimensional world without external field. In such a world the molecules between collisions move uniformly (and linearly, but everything is linear in a one-dimensional world).

The expression

$$f(x, v, t) dx dv$$

gives the number of molecules which in the time moment t are in the position interval $(x, x + dx)$ and have velocities from the interval $(v, v + dv)$. Let us ask where these molecules were in past in the time moment $t - t'$, $t' > 0$. If there are no collisions then during the time t' they moved uniformly and so at the time moment $t - t'$ they had velocity $v' = v$ and were positioned in the neighbourhood of the point $x' = x - vt'$. Using the Liouville theorem we get

$$dx dv = dx' dv'$$

and thus the identity

$$f(x, v, t) = f(x - vt', v, t - t')$$

If particles collide, then every particle which at the time t is at the phase-space point (x, v) sa collided somewhere sometimes the last time before the arrival to the point (x, v) . After that last collision the particle moved uniformly. So in that last collision the particle has to obtain just the velocity v and if the last collision happened at the time $t - t'$, then the collision must have happened at the position $x' = x - vt'$. Each particle comes from the point of its last collision, so we can write

$$f(x, v, t) = \int dt' \tilde{f}(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right)$$

Where $\tilde{f}(x, v, t) dx dv dt$ gives the number of particles which at time t are in the interval $(x, x + dx)$, have velocity from $(v, v + dv)$ and in the infinitesimal time interval $(t - dt, t)$ they just collided, so the velocity v was obtained just in that collision. Other molecules which at the time t are present in the interval $(x, x + dx)$ with velocity from $(v, v + dv)$ are those which did not just collide and their number is

$$f(x, v, t) dx dv$$

The normalization is the following

$$dt dx \int dv \tilde{f}(x, v, t) = \frac{dt}{\tau} dx \int dv f(x, v, t)$$

Now the question is how \tilde{f} depends on velocity. Here we make a strong assumption that the distribution \tilde{f} , describing those particles which have just collided is Maxwellian. By that we assume that the particles which just collided are thermalized, so they are a sample from some equilibrium distribution, which is the Maxwell distribution.

We get the expression for the Boltzmann distribution in the form of integral through the trajectory

$$f(x, v, t) = \int dt' \frac{1}{\tau} f_0(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right)$$

where the index 0 denotes, that the function is Maxwellian what means

$$f_0(x, v) = n(x) \left(\frac{m\beta(x)}{2\pi} \right)^{3/2} \exp\left(-\frac{1}{2}\beta(x)v^2\right)$$

If the functions $\beta(x), n(x)$ were known, then the above integral would explicitly define the Boltzmann distribution function. These function, however, are not known a priori. That means that the integral represents a selfconsistent equation, which determines the function f my through $\beta(x)$ a $n(x)$, but these functions are determined through f via the consistency equations

$$\begin{aligned} n(x) &= \int dv f(x, v) \\ \frac{1}{2} \frac{1}{\beta(x)} &= \int dv \frac{1}{2} m v^2 f(x, v) \end{aligned}$$

Now we derive a differential equation satisfied by the Boltzmann function as defined by the integral through the trajectory. We write the expression defining f for two close points in the phase space which are connected by a particle trajectory. We shall assume the external field is zero, to get simple solutions for the trajectory.

$$f(x, v, t) = \int dt' \frac{1}{\tau} f_0(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right)$$

$$f(x + v dt, v, t + dt) = \int dt' \frac{1}{\tau} f_0(x - vt' + v dt, v, t + dt - t') \exp\left(-\frac{t'}{\tau}\right)$$

In the second expression we make the substitution $t'' = t' - dt$ and we get

$$f(x + v dt, v, t + dt) = \int_{-dt}^{\infty} dt'' \frac{1}{\tau} f_0(x - vt'', v, t - t'') \exp\left(-\frac{t'' + dt}{\tau}\right)$$

We expand the exponential up to the first order and write t' instead of t'' . We get

$$\begin{aligned} f(x + v dt, v, t + dt) &= \int_{-dt}^{\infty} dt' \frac{1}{\tau} f_0(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right) + \\ &+ \int_{-dt}^{\infty} dt' \frac{1}{\tau} f_0(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right) \frac{dt}{\tau} \end{aligned}$$

In the second integral the integrand is of the first order in dt so we can shift the lower limit infinitesimally and get

$$\begin{aligned} f(x + v dt, v, t + dt) &= \int_{-dt}^{\infty} dt' \frac{1}{\tau} f_0(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right) + \\ &- \frac{dt}{\tau} \int_0^{\infty} dt' \frac{1}{\tau} f_0(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right) \end{aligned}$$

We subtract the expression for f and get

$$\begin{aligned} f(x + v dt, v, t + dt) - f(x, v, t) &= \int_{-dt}^0 dt' \frac{1}{\tau} f_0(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right) + \\ &\quad - \frac{dt}{\tau} \int_0^\infty dt' \frac{1}{\tau} f_0(x - vt', v, t - t') \exp\left(-\frac{t'}{\tau}\right) \\ &= \frac{dt}{\tau} f_0(x, v, t) - \frac{dt}{\tau} f(x, v, t) \end{aligned}$$

We have got the equation

$$Df = -\frac{f - f_0}{\tau}$$

Boltzmann equation with this choice of the collision term at the right-hand side is called Boltzmann equation in the approximation of relaxation time and is usually just postulated after presenting a few more-or-less plausible arguments. Our approach presented here is taken from Reif.

8.4 Heat conduction in the approximation of relaxation time

As an illustration we present here the problem of energy ("heat") conduction in a pipe filled with gas, which is inserted between two thermal reservoirs, one at temperature T_1 , the other at temperature T_2 . After certain time a stationary regime is established: a constant energy current will flow from the hotter end towards the colder end. Along the pipe a time-constant temperature distribution will be formed, with temperature linearly decreasing from the hotter end towards the colder one.

We shall be looking for the Boltzmann distribution function $f(x, \vec{v})$, which is stationary, that is it does not depend on time explicitly. Non-trivial spatial distribution develops only along the pipe axis, in the direction of the energy flow. We select the x-axis to be in this direction.

We look for the solution of the equation

$$f(x, \vec{v}) = \int \frac{dt'}{\tau} \exp\left(-\frac{t'}{\tau}\right) f_0(x - v_x t', \vec{v})$$

where f_0 has the form of the Maxwell distribution

$$f_0(x, \vec{v}) = n(x) \left(\frac{m\beta(x)}{2\pi} \right)^{3/2} \exp\left(-\frac{1}{2}\beta(x)\vec{v}^2\right)$$

$\beta(x)$ and $n(x)$ are unknown functions which should be found while solving for f . They correspond to the distribution function $f(x, \vec{v})$ as follows

$$\begin{aligned} n(x) &= \int d^3\vec{v} f(x, \vec{v}) \\ \frac{3}{2} \frac{1}{\beta(x)} &= \int d^3\vec{v} \frac{1}{2} m \vec{v}^2 f(x, \vec{v}) \end{aligned}$$

The trick leading to the solution is to do the per-partes transformation

$$f(x, \vec{v}) = f_0(x, \vec{v}) + \int \frac{df_0}{dt'} \exp\left(-\frac{t'}{\tau}\right) dt'$$

Next one has to realize that formally we are integrating through the region $(0, \infty)$, but practically only through the interval of the order $(0, \tau)$. Outside this interval the integrand is exponentially small. Performing the differentiation with respect to t' we get

$$\begin{aligned} f(x, \vec{v}) &= f_0(x, \vec{v}) \\ &+ \int \left(-\frac{dn}{n dx} v_x - \frac{3}{2} \frac{d\beta}{\beta dx} v_x + \frac{1}{2} m \vec{v}^2 \frac{d\beta}{dx} v_x \right) f_0(x, \vec{v}) \exp\left(-\frac{t'}{\tau}\right) dt' \end{aligned}$$

All the terms in the bracket are proportional to the mean free path $v_x \tau$, therefore the variable x in the integrand in functions n, β, f_0 is no more shifted by $-v_x t'$. Such a shift would lead to corrections of higher order in τ .

The integration is therefore trivial and we get

$$f(x, \vec{v}) = f_0(x, \vec{v}) + \tau \left(-\frac{dn}{n dx} v_x - \frac{3}{2} \frac{d\beta}{\beta dx} v_x + \frac{1}{2} m \vec{v}^2 \frac{d\beta}{dx} v_x \right) f_0(x, \vec{v})$$

We are interested only in the stationary situation, when there is no flow of particles along the pipe. So we want a distribution function satisfying the relation

$$\langle v_x \rangle = \frac{1}{n} \int d^3\vec{v} v_x f(x, \vec{v}) = 0$$

The distribution function is expressed through a Maxwell-like distributions, so all the momenta will be expressed through the Maxwellian momenta which are

$$\begin{aligned} \langle v_x \rangle_0 &= 0 \\ \langle v_x^2 \rangle_0 &= \frac{1}{m\beta} \\ \langle v_x^4 \rangle_0 &= \frac{3}{(m\beta)^2} \\ \langle v_x^6 \rangle_0 &= \frac{3 \times 5}{(m\beta)^3} \end{aligned}$$

Using these relations we get

$$\begin{aligned} 0 = \langle v_x \rangle &= \tau \left(-\frac{dn}{ndx} \langle v_x^2 \rangle_0 - \frac{3}{2} \frac{d\beta}{\beta dx} \langle v_x^2 \rangle_0 + \frac{1}{2} m \frac{d\beta}{dx} \langle v_x^4 + v_x^2 v_y^2 + v_x^2 v_z^2 \rangle_0 \right) \\ &= \frac{\tau}{m\beta} \left(-\frac{dn}{ndx} + \frac{d\beta}{\beta dx} \right) \end{aligned}$$

From there

$$\begin{aligned} \frac{dn}{ndx} &= \frac{d\beta}{\beta dx} \\ nkT &= \text{const} \end{aligned}$$

This condition requires constant pressure along the pipe. So we do not have two unknown functions $\beta(x)$ and $n(x)$, but only one. The second one is related to the first one by the condition of constant pressure. By the way, from the external physical insight we also know the function $\beta(x)$, since we know, that the temperature will be a linear function of the coordinate x .

Let us now calculate the density of energy flow, which is given by the relation

$$j_E = \frac{1}{2} nm \langle \vec{v}^2 v_x \rangle$$

$$\begin{aligned} j_E &= \frac{1}{2} nm\tau \left(-\frac{d\beta}{\beta dx} \langle \vec{v}^2 v_x^2 \rangle_0 - \frac{3}{2} \frac{d\beta}{\beta dx} \langle \vec{v}^2 v_x^2 \rangle_0 + \frac{1}{2} m \frac{d\beta}{dx} \langle \vec{v}^2 \vec{v}^2 v_x^2 \rangle_0 \right) \\ &= \frac{1}{2} nm\tau \left(-\frac{25}{2} \frac{1}{(m\beta)^2} \frac{d\beta}{\beta dx} + \frac{1}{2} m \frac{d\beta}{dx} \langle v_x^6 + 2v_x^4 v_y^2 + 2v_x^4 v_z^2 + v_x^2 v_y^4 + v_x^2 v_z^4 + 2v_x^2 v_y^2 v_z^2 \rangle_0 \right) \\ &= \frac{5\tau}{(m\beta)^2} \frac{d\beta}{dx} \\ &= \frac{5}{2} \frac{\tau k^2 T n}{m} \left(-\frac{dT}{dx} \right) \end{aligned}$$

So the coefficient of the heat conduction is

$$\kappa = \frac{5}{2} \frac{\tau k^2 T n}{m}$$

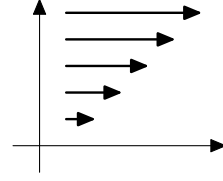
8.5 More examples

See also [Reif] (str. 494-513), [Huang] (str. 96-98, 107).

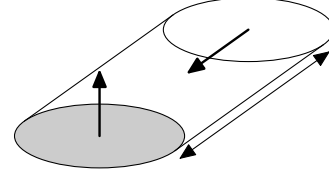
Exercise

Calculate the viscosity coefficient for dilute gas from the Boltzmann equation in the relaxation time approximation.

• Let us denote the chaotic velocities of molecules as v_x, v_y, v_z . Let only the v_x has a non-zero mean (drift) value V_x . Let us denote the velocities from which the drift (mean value) is subtracted as u_x, u_y, u_z . Let us suppose, that the drift velocity is a function of the z coordinate (see figure). Phenomenologically we know, that the tangential tension (force acting tangentially on a unit area) is $F_x = -\eta \partial V_x / \partial z$. The coefficient η is called viscosity.



The viscosity force is generated by molecules which, due to their random motion in perpendicular (to the direction of drift) direction move between the layers of gas having different drift velocities. Molecules from a fast layer come to a slow layer bringing with them their high drift momentum and therefore they accelerate the slow layer. Oppositely, molecules from a slow layer come to a fast layer thus decelerating the fast layer. An effective tangential tension between the slow and the fast layer develops.



According to the Newton law, the tension is given by the transfer (in the direction of z) of the x -coordinate of momentum per unit of time and unit of area.

So we have to calculate how many molecules cross the tangential unit area per unit of time and how much longitudinal momentum they transfer. According to the figure at right the number ddN molecules which cross the area ddS at the point $mbmr$ during the time ddt is given as

$$dN = dS dt \int (\mathbf{n} \cdot \mathbf{v}) f(\mathbf{v}) d\mathbf{v} = n \langle \mathbf{n} \cdot \mathbf{v} \rangle dS dt.$$

Here $n = \int f d\mathbf{v}$. In our case $\mathbf{n} \cdot \mathbf{v} = v_z = u_z$. Each molecule which crosses the area carries its longitudinal momentum with it, so the net longitudinal momentum transfer we get by summing contributions from each individual molecule. One just has to have in mind, that one needs the transfer across the area which is comoving (with the drift velocity $V_x(z)$) with the gas layer. So the momentum Preto je $m(v_x - V_x(z)) = mu_x$ is relevant. In this way we get

$$F'_x = mn \langle u_x u_z \rangle = m \int u_x u_z f d\mathbf{v} \equiv m \int u_x u_z (f^{(0)} + g) d\mathbf{v},$$

where the Boltzmann distribution was written as a sum of the the equilibrium distribution $f^{(0)}$ and a small correction g . The momentum transfer driven by the correction g , the transfer would be zero for equilibrium distribution. The non-equilibrium correction g should be obtained from the Boltzmann equation in the relaxation time approximation. The external forces are zero and we are looking for the stationary situation, therefore there is no explicit time dependence. Therefore the left-hand size of the Boltzmann equation has only one term and we get

$$\mathbf{v} \cdot \nabla f = \frac{f^{(0)} - f}{\tau} \implies \mathbf{v} \cdot \nabla f^{(0)} \doteq -\frac{g}{\tau}.$$

The equilibrium distribution is a Maxwell distribution with velocity drift

$$f^{(0)}(\mathbf{r}, \mathbf{v}, t) = n \left(\frac{m}{2\pi T} \right)^{3/2} \exp \left[-\frac{1}{2} \beta m (\mathbf{v} - \mathbf{V}(z))^2 \right].$$

Differentiating with respect to z we get

$$g = \tau \beta m v_z (v_x - V_x) \frac{\partial V_x}{\partial z} f^{(0)} = \tau \beta m u_z u_x \frac{\partial V_x}{\partial z} f^{(0)}.$$

Here $v_z = u_z$ since $V_z = 0$.

$$F'_x = \frac{\partial V_x}{\partial z} \beta \tau m^2 \int u_x^2 u_z^2 f^{(0)} d\mathbf{v} = \frac{\partial V_x}{\partial z} \beta \tau m^2 \int u_x^2 u_z^2 f^{(0)} d\mathbf{u}.$$

Viscosity η is just the coefficient at the velocity gradient. The integral can be done explicitly. Denoting $f^{(0)} = C \exp[\dots]$ we get

$$\begin{aligned} \eta &= C \beta \tau m^2 \int u_x^2 u_z^2 \exp \left[-m\beta(u_x^2 + u_y^2 + u_z^2)/2 \right] d\mathbf{u} = \\ &= C \beta \tau m^2 \left(\int u_x^2 \exp[-m\beta u_x^2/2] du_x \right)^2 \times \left(\int \exp[-m\beta u_y^2/2] du_y \right) = \\ &= C \beta \tau m^2 \left(\frac{\partial}{\partial a} \sqrt{\pi/a} \right)^2 \sqrt{\pi/a} = n \left(\frac{m\beta}{2\pi} \right)^{3/2} \beta \tau m^2 \frac{1}{4} \pi a^{-3} \sqrt{\pi/a} = \frac{n\tau}{\beta}. \end{aligned}$$

where we used the notation $a \equiv m\beta/2$. ■

Combining the result just obtained with the result for heat conduction $\lambda = 5c_v n\tau/2\beta$ (where $c_v = C_v/M$) we can check the validity of the relaxation time approximation. The point is that the value of τ we can estimate just very roughly, but the ratio $\lambda/\eta c_v = 2,5$ is independent on τ . This ratio is compared with experimental values in the following table ([McQ])

látka	Ne	Ar	Kr	N ₂	CO ₂	CH ₄	C ₂ H ₆
$\lambda/\eta c_v$	2,5	2,5	2,5	1,89	1,67	1,89	1,45

Exercise

In the relaxation time approximation calculate the electric conductivity of gas. Calculate also the electric conductivity of electrons in metal.

- Let us consider the gas of molecules with the mass m charge e in uniform external electric field ϵ in the direction of the z -axis. Since everything is homogeneous and stationary, the distribution function f will be independent of position and time. The force acting on molecules has only the z -component different from zero, so the Boltzmann equation will be

$$\frac{e\epsilon}{m} \frac{\partial f^{(0)}}{\partial v_z} = -\frac{g}{\tau} \implies g = \frac{e\epsilon\tau}{m} \frac{\partial f^{(0)}}{\partial v_z} = -e\epsilon\tau v_z \frac{\partial f^{(0)}}{\partial E}.$$

Here E is the energy of the particle. For Maxwell distribution we get $\partial_E f^{(0)} = -\beta f^{(0)}$.

So we have got the non-equilibrium distribution function; now we need to calculate the corresponding transfer process. Clearly

$$j_z = e \int f v_z d\mathbf{v} = e \int g v_z d\mathbf{v}.$$

Then $\sigma_{\text{el}} = j_z/\epsilon$. The final result is $\sigma_{\text{el}} = ne^2\bar{\tau}/m$.

Now the second part of the exercise, the conduction electrons in a metal. The difference from a dilute classical gas is, that the equilibrium distribution is not the Maxwell distribution but the Fermi Dirac.

$$f^{(0)} \sim (e^{\beta(E-\mu)} + 1)^{-1}.$$

We need the derivative $\partial_E f^{(0)}$. The electron gas is highly degenerate, the Fermi distribution function is practically constant with respect to energy except of the region around the Fermi energy μ . The conduction is therefore caused only by electrons whose energy is close to μ . The relevant relaxation time is therefore that, corresponding to Fermi energy of electrons. The final result therefore is

$$\begin{aligned} \sigma_{\text{el}} &= -e^2\tau_F \iint dv_x dv_y \int_{-\infty}^{\infty} \frac{\partial f^{(0)}}{\partial v_z} \frac{v_z}{m} = \\ &= -\frac{e^2\tau_F}{m} \iint dv_x dv_y \left\{ [f^{(0)}v_z]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f^{(0)} dv_z \right\} = \frac{ne^2}{m}\tau_F. \end{aligned}$$

■

Exercise

Show that the Maxwell-Boltzmann distribution is stationary solution of the Boltzmann equation.

8.6 Collision term

Without collisions the particles move on Newtonian trajectories and Boltzmann equation without the right-hand side holds.

$$\begin{aligned} Df &= 0 \\ D &= \frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial}{\partial \mathbf{v}} \end{aligned}$$

With collisions on the right-hand side there is the collision term

$$Df = D_C f$$

To derive its shape we proceed as follows.

Let us imagine two infinitesimally close regions of the phase space such that they are connected by Newtonian trajectories. If the regions have equal volumes, then each trajectory which begins in the first region ends in the second region and vice versa. When collision take place, the particles do not follow the Newtonian trajectories. Some particles which start in the first region fall out of their trajectory before arriving to the second region and never arrive at the second region. On the other hand, some particles arrive to the second region which never started in the first region. They change the velocity in a collision and get onto a trajectory which leads to the second region somewhere between the two regions. The two regions we are speaking about are infinitesimal regions around the phase space point \mathbf{r}, \mathbf{v} .

Let us first consider a particle which collides in the point \mathbf{r} which before the collision had velocity \mathbf{v} . It collided with a particle which was present in the same space point \mathbf{r} and had before the collision velocity \mathbf{v}_1 .

The definition of the collision cross section says that the number of such collisions within a time interval dt in the volume element $d^3\mathbf{r}$ is

$$D_C^{(-)} f(\mathbf{r}, \mathbf{v}, t) d^3\mathbf{r} d^3\mathbf{v} dt = \mathbf{r} d^3\mathbf{v} dt \int \int \int d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 \\ |\mathbf{v} - \mathbf{v}_1| f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}_1, t) \sigma(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}'_1)$$

We have integrated over the velocities after the collisions and also over the velocity \mathbf{v}_1 , since we are just interested in the fact, that there was a particle with the velocity \mathbf{v} which escaped from the phase space point irrespective what happened to it and its collision partner.

On the other hand, the number of collisions in the considered space volume element such that one of the particles gained the velocity \mathbf{v} after the collision is

$$D_C^{(+)} f(\mathbf{r}, \mathbf{v}, t) d^3\mathbf{r} d^3\mathbf{v} dt = \mathbf{r} d^3\mathbf{v} dt \int \int \int d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 \\ |\mathbf{v}' - \mathbf{v}'_1| f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{v}'_1, t) \sigma(\mathbf{v}', \mathbf{v}'_1; \mathbf{v}, \mathbf{v}_1)$$

The energy momentum conservation gives

$$|\mathbf{v} - \mathbf{v}_1| = |\mathbf{v}' - \mathbf{v}'_1|$$

and P,T invariance of the collision process gives

$$\sigma(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}'_1) = \sigma(\mathbf{v}', \mathbf{v}'_1; \mathbf{v}, \mathbf{v}_1)$$

The total collision term will be

$$D_C = D_C^{(+)} - D_C^{(-)}$$

and so

$$D_C f(\mathbf{r}, \mathbf{v}, t) = \int \int \int d^3 \mathbf{v}_1 d^3 \mathbf{v}' d^3 \mathbf{v}'_1 |\mathbf{v}' - \mathbf{v}'_1| (f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{v}'_1, t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}_1, t)) \sigma(\mathbf{v}', \mathbf{v}'_1; \mathbf{v}, \mathbf{v}_1)$$

The notation is usually make shorter as

$$D_C f(\mathbf{r}, \mathbf{v}, t) = \int \int \int d^3 \mathbf{v}_1 d^3 \mathbf{v}' d^3 \mathbf{v}'_1 |\mathbf{v}' - \mathbf{v}'_1| (f' f'_1 - f f_1) \sigma$$

when we added to the symbol f the index and/or prime sign according to what velocity is to be inserted into the function f as the velocity variable.

8.7 Conservation laws

Let us consider som one-particle physical quantity $\chi(\mathbf{r}, \mathbf{v}, t)$. By that we mean a quantity which has the value χ when a particle is found at the time t in the phase-space point \mathbf{r}, \mathbf{v} . Then the mean value of the quantity χ in the space point \mathbf{r} at time t will be

$$\langle \chi(\mathbf{r}, t) \rangle = \frac{1}{n(\mathbf{r}, t)} \int d^3 \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \chi(\mathbf{r}, \mathbf{v}, t)$$

where

$$n(\mathbf{r}, t) = \int d^3 \mathbf{v} f(\mathbf{r}, \mathbf{v}, t)$$

Let us start from the Boltzmann equation

$$Df = D_C f$$

We get

$$\int d^3 \mathbf{v} \chi Df = \int d^3 \mathbf{v} \chi D_C f$$

At the left-had side we get several term which we rewrite as follows

$$\begin{aligned} \int d^3 \mathbf{v} \chi \frac{\partial f}{\partial t} &= \int d^3 \mathbf{v} \left[\frac{\partial}{\partial t} (f \chi) - f \frac{\partial \chi}{\partial t} \right] = \frac{\partial}{\partial t} (n \langle \chi \rangle) - n \langle \frac{\partial \chi}{\partial t} \rangle \\ \int d^3 \mathbf{v} \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{v}} \chi &= \int d^3 \mathbf{v} v_\alpha \frac{\partial f}{\partial x_\alpha} \chi = \frac{\partial}{\partial x_\alpha} (n \langle v_\alpha \chi \rangle) - n \langle v_\alpha \frac{\partial \chi}{\partial x_\alpha} \rangle \end{aligned}$$

The third term we rewrite assuming that external forces are independent of velocities

$$\int d^3\mathbf{v} \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}} \chi = \int d^3\mathbf{v} \left[\frac{\partial}{\partial v_\alpha} \left(\frac{F_\alpha}{m} f \chi \right) - \frac{F_\alpha}{m} f \frac{\partial \chi}{\partial v_\alpha} \right]$$

Here the first term after the integration gives zero on the integration boundaries and so we get

$$\int d^3\mathbf{v} \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}} \chi = -\frac{F_\alpha}{m} n \left\langle \frac{\partial \chi}{\partial v_\alpha} \right\rangle$$

Now we look at the right-hand side of the Boltzmann equation.

$$\int d^3\mathbf{v} \chi D_C f = \iiint d^3\mathbf{v} d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 (f' f'_1 - f f_1) |\mathbf{v} - \mathbf{v}_1| \sigma(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}'_1) \chi(\mathbf{r}, \mathbf{v}, t)$$

We change the notation for the integration variables $\mathbf{v} \leftrightarrow \mathbf{v}_1$ and $\mathbf{v}' \leftrightarrow \mathbf{v}'_1$. We get

$$\int d^3\mathbf{v} \chi D_C f = \iiint d^3\mathbf{v} d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 (f' f'_1 - f f_1) |\mathbf{v}_1 - \mathbf{v}| \sigma(\mathbf{v}_1, \mathbf{v}; \mathbf{v}'_1, \mathbf{v}') \chi(\mathbf{r}, \mathbf{v}_1, t)$$

This change of notation, however, does not change the values neither of the relative velocity, nor of the cross section, so we get

$$\int d^3\mathbf{v} \chi D_C f = \frac{1}{2} \iiint d^3\mathbf{v} d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 (f' f'_1 - f f_1) |\mathbf{v}_1 - \mathbf{v}| \sigma(\chi + \chi_1)$$

where for the quantity χ we used the same short notation as for f , that is we used indices to denote what velocity should be used as the variable in the function evaluation.

Let us use further symmetry of the above relation: we change variables $\mathbf{v} \leftrightarrow \mathbf{v}'$ and $\mathbf{v}_1 \leftrightarrow \mathbf{v}'_1$. This gives the inverse collision which has the same cross section and we finally get

$$\int d^3\mathbf{v} \chi D_C f = \frac{1}{4} \iiint d^3\mathbf{v} d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 (f' f'_1 - f f_1) |\mathbf{v}_1 - \mathbf{v}| \sigma(\chi' + \chi'_1 - \chi - \chi_1)$$

The result is particularly interesting when the quantity χ is conserved in collisions. Then

$$\chi' + \chi'_1 - \chi - \chi_1 = 0$$

and so

$$\int d^3\mathbf{v} \chi D_C f = 0$$

We get the equation

$$\frac{\partial}{\partial t} \langle n\chi \rangle + \frac{\partial}{\partial x_\alpha} \langle n v_\alpha \chi \rangle = n \langle D\chi \rangle$$

where D is the same differential operator as appears in the left-hand side of the Boltzmann equation.

In general, three conservation laws hold for particle collisions

- conservation of mass $\chi = m$
- conservation of momentum $\chi = mv_\alpha, \quad \alpha = 1, 2, 3$
- conservation of kinetic energy $\chi = \frac{1}{2}mv^2$

The mass conservation gives the equation

$$\frac{\partial}{\partial t} \langle nm \rangle + \frac{\partial}{\partial x_\alpha} \langle nmv_\alpha \rangle = 0$$

The quantity n is independent of velocities, so it can be taken in front of the averaging angle brackets and we get

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_\alpha} \rho \langle v_\alpha \rangle = 0$$

If the mean velocity (drift) is denoted as

$$\mathbf{u} = \langle \mathbf{v} \rangle$$

we get the equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$

The momentum conservation gives the equation

$$\frac{\partial}{\partial t} \langle nmv_\gamma \rangle + \frac{\partial}{\partial x_\alpha} \langle nmv_\alpha v_\gamma \rangle = \langle nm Dv_\gamma \rangle = nm \left\langle \frac{F_\alpha}{m} \frac{\partial v_\gamma}{\partial v_\alpha} \right\rangle$$

If the external force does not depend on velocity we get

$$\frac{\partial}{\partial t} (\rho u_\gamma) + \frac{\partial}{\partial x_\alpha} (\rho \langle v_\alpha v_\gamma \rangle) = \frac{F_\gamma}{m}$$

We separate now the chaotic and the drift velocity

$$\mathbf{v} = \mathbf{u} + \mathbf{U}$$

then

$$\langle v_\alpha v_\gamma \rangle = u_\alpha u_\gamma + \langle U_\alpha U_\gamma \rangle$$

We introduce the tensor of tensions as

$$P_{\alpha\gamma} = \rho \langle U_\alpha U_\gamma \rangle$$

and we get the Euler hydrodynamic equation

$$\frac{\partial}{\partial t} (\rho u_\gamma) + \frac{\partial}{\partial x_\alpha} (\rho u_\alpha u_\gamma) = -\frac{\partial P_{\alpha\gamma}}{\partial x_\alpha} + \frac{F_\gamma}{m}$$

8.8 H-theorem

Let us consider the Boltzmann distribution function satisfying the Boltzmann equation with the collision term on the right-hand side.

$$Df = D_C f$$

where

$$Df = \frac{\partial}{\partial t} f + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} f + \frac{\mathbf{F}}{m} \cdot \frac{\partial}{\partial \mathbf{v}} f$$

and

$$D_C f = \int d^3 \mathbf{v}_1 d^3 \mathbf{v}' d^3 \mathbf{v}'_1 |\mathbf{v} - \mathbf{v}_1| (f' f'_1 - f f_1) \sigma(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}'_1)$$

Let us now investigate the expression

$$H(t) = \int d^3 \mathbf{r} d^3 \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \ln(f(\mathbf{r}, \mathbf{v}, t))$$

Let us study its dependence on time

$$\frac{d}{dt} H(t) = \frac{d}{dt} \int d^3 \mathbf{r} d^3 \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \ln(f(\mathbf{r}, \mathbf{v}, t))$$

Before we apply the differential operator on the integrand we make a simple trick. We change the notation for integration variables

$$H(t) = \int d^3 \mathbf{r}_t d^3 \mathbf{v}_t f(\mathbf{r}_t, \mathbf{v}_t, t) \ln(f(\mathbf{r}_t, \mathbf{v}_t, t))$$

where we introduced a formal index t . Now we make a substitution in the integral so that instead of variables $\mathbf{r}_t, \mathbf{v}_t$ we introduce new variables $\mathbf{r}_0, \mathbf{v}_0$ via the relations

$$\mathbf{r}_t = \mathbf{R}(\mathbf{r}_0, \mathbf{v}_0, t)$$

$$\mathbf{v}_t = \mathbf{V}(\mathbf{r}_0, \mathbf{v}_0, t)$$

where the functions $\mathbf{R}(\mathbf{r}_0, \mathbf{v}_0, t)$ and $\mathbf{V}(\mathbf{r}_0, \mathbf{v}_0, t)$ denote solutions of the Newton equations of motion with initial conditions $\mathbf{r}_0, \mathbf{v}_0$. The Jacobian of this transformation is equal to unity, the integration region is again the whole phase space, so we get

$$H(t) = \int d^3 \mathbf{r}_0 d^3 \mathbf{v}_0 f(\mathbf{R}(\mathbf{r}_0, \mathbf{V}(\mathbf{r}_0, \mathbf{v}_0, t), t), \mathbf{v}_t, t) \ln(f(\mathbf{R}(\mathbf{r}_0, \mathbf{V}(\mathbf{r}_0, \mathbf{v}_0, t), t), \mathbf{v}_t, t))$$

Now we pull in the time differential operator under the integral and we get the Boltzmann operator D

$$\frac{d}{dt} H(t) = \int d^3 \mathbf{r}_0 d^3 \mathbf{v}_0 (Df) \ln(f) + \int d^3 \mathbf{r}_0 d^3 \mathbf{v}_0 Df$$

The second integral is zero, since it represents the time derivative of the total number of particles. In the first integral we use the Boltzmann equation and we get

$$\frac{d}{dt}H(t) = \int d^3\mathbf{r}_0 d^3\mathbf{v}_0 \ln(f) D_C f$$

Now we make the "inverse trick" and we go over to integration variable \mathbf{r}, \mathbf{v} and we get

$$\frac{d}{dt}H(t) = \int d^3\mathbf{r} d^3\mathbf{v} d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 \ln(f) |\mathbf{v} - \mathbf{v}_1| (f' f'_1 - f f_1) \sigma(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}'_1)$$

Now we proceed the same way as we did while deriving the continuity equation we get

$$\frac{d}{dt}H(t) = \frac{1}{4} \int d^3\mathbf{r} d^3\mathbf{v} d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 \ln\left(\frac{f f_1}{f' f'_1}\right) |\mathbf{v} - \mathbf{v}_1| (f' f'_1 - f f_1) \sigma(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}'_1)$$

$$\frac{d}{dt}H(t) = -\frac{1}{4} \int d^3\mathbf{r} d^3\mathbf{v} d^3\mathbf{v}_1 d^3\mathbf{v}' d^3\mathbf{v}'_1 |\mathbf{v} - \mathbf{v}_1| f f_1 \ln\left(\frac{f' f'_1}{f f_1}\right) \left(\frac{f' f'_1}{f f_1} - 1\right) \sigma(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}'_1)$$

The logarithmic function satisfies the inequality (draw the graph of the function)

$$\ln(x)(x - 1) \geq 0$$

and so we get

$$\frac{d}{dt}H(t) \leq 0$$

The function $H(t)$ monotonically decreases with time and when it reaches the minimum it stays constant. This is the statement of so called Boltzmann theorem.

Chapter 9

Kinetic equations

9.1 Langevin equation

The Langevin equation describes movement of a classical particle in the field of a random force.

$$m \frac{d\mathbf{v}}{dt} = \mathbf{F} + \mathbf{f}(t)$$

where \mathbf{F} is deterministic external force and $\mathbf{f}(t)$ is a random force describing for example influence of the collisions of the observed particle with surrounding molecules. The typical correlation time for that force is of the order 10^{-13} s.

We investigate the problem by introducing statistical ensembles. So let us imagine an ensemble where $\bar{\mathbf{v}}$ is the same for all the ensemble members and the ensemble averages of the fluctuating force is $\bar{\mathbf{f}}$. So we have

$$\mathbf{f} = \bar{\mathbf{f}} + \mathbf{f}'$$

If $\mathbf{v} = 0$ then $\bar{\mathbf{f}} = 0$ because there is no preferred direction. Therefore in the lowest approximation the following must hold

$$\bar{\mathbf{f}} = -\alpha \mathbf{v}$$

and we get the Langevin equation

$$m \frac{d\mathbf{v}}{dt} = \mathbf{F} - \alpha \mathbf{v} + \mathbf{f}'$$

To simplify the calculations let us consider one-dimensional case without external deterministic force. We get

$$m \frac{d\dot{x}}{dt} = -\alpha \dot{x} + f'$$

$$m\dot{x} = -\alpha x\dot{x} + x f'$$

$$m\left[\frac{d}{dt}(x\dot{x}) - \dot{x}^2\right] = -\alpha x\dot{x} + x f'$$

Averaging we get (since $\langle f' \rangle = 0$ independently on x and \dot{x})

$$m\left\langle \frac{d}{dt}(x\dot{x}) \right\rangle = \langle m\dot{x}^2 \rangle - \alpha \langle x\dot{x} \rangle$$

$$\frac{d}{dt} \langle x\dot{x} \rangle = \frac{kT}{m} - \frac{\alpha}{m} \langle x\dot{x} \rangle$$

Denoting

$$\varphi(t) = \langle x\dot{x} \rangle - \frac{kT}{\alpha}$$

we get the equation

$$\dot{\varphi}(t) = -\frac{\alpha}{m} \varphi(t)$$

$$\langle x\dot{x} \rangle = C \exp(-\gamma t) + \frac{kT}{\alpha}$$

where

$$\gamma = \frac{\alpha}{m}$$

Let us suppose, that all the particles in the ensemble start at $x = 0$, $\dot{x} = 0$. Then

$$0 = C + \frac{kT}{\alpha}$$

$$\langle x\dot{x} \rangle = \frac{kT}{\alpha} (1 - \exp(-\gamma t))$$

$$\frac{d}{dt} \langle x^2 \rangle = \frac{kT}{\alpha} (1 - \exp(-\gamma t))$$

$$\langle x^2 \rangle = \frac{2kT}{\alpha} \left(t - \frac{1}{\gamma} (1 - \exp(-\gamma t)) \right)$$

This means that for $t < \frac{1}{\gamma}$

$$\langle x^2 \rangle = \frac{kT}{m} t^2$$

and for $t \gg \frac{1}{\gamma}$

$$\langle x^2 \rangle = \frac{2kT}{\alpha} t$$

For strong dumping we can neglect in the Langevin equation the inertial term and we get a Aristotle type of equation

$$0 = -\alpha \dot{x} + f'$$

$$\dot{x} = \frac{1}{\alpha} f'$$

$$x(t) = x(0) + \int_0^t d\tau \frac{f'(\tau)}{\alpha}$$

For the initial condition $x(0) = 0$ we get

$$\langle x^2(t) \rangle = \frac{1}{\alpha^2} \int_0^t d\tau_1 d\tau_2 \langle f'(\tau_1) f'(\tau_2) \rangle$$

Now the correlation depends only on the time difference and we get

$$\langle x^2(t) \rangle = \frac{1}{\alpha^2} \int_0^t d\frac{\tau_1 + \tau_2}{2} d(\tau_1 - \tau_2) \langle f'(0) f'(\tau_1 - \tau_2) \rangle$$

$$\langle x^2(t) \rangle = \frac{t}{\alpha^2} \int_{-\infty}^{\infty} d\tau \langle f'(0) f'(\tau) \rangle$$

where we extended the region of integration formally to $(-\infty, \infty)$ since the correlation function is different from zero only on a very small interval and so the integration region does not play any role.

We, however, know from previous calculation that

$$\langle x^2 \rangle = \frac{2kT}{\alpha} t$$

and comparing the two results we get

$$\alpha = \frac{1}{2kT} \int_{-\infty}^{\infty} d\tau \langle f'(0) f'(\tau) \rangle$$

So the dissipation coefficient α is given by the correlations of the fluctuation force. This is so called fluctuation-dissipation theorem.

Now we return back to the expression

$$x(t) = \int_0^t d\tau \frac{f'(\tau)}{\alpha}$$

The integral is the sum of many random variables, so $x(t)$ must be normally distributed with zero mean and variance

$$\langle x^2 \rangle = \frac{2kT}{\alpha} t$$

so the distribution is

$$\rho(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

where

$$D = \frac{kT}{\alpha}$$

This is called Einstein dissipation theorem. The distribution density satisfies the diffusion equation

$$\frac{\partial \rho}{\partial t} = D \Delta \rho$$

Chapter 10

Appendix

10.1 Mean particle density

Now we shall discuss the fact, that it is quite trivial to speak about the density of particles around some space point \mathbf{r} but there are some quite non-trivial things hidden behind.

Let us consider gas consisting of N particles. We cannot know the microstate of the gas but we can use the technique of statistical ensemble. So let us consider an ensemble of equal systems each system being in some particular microstate. The ensemble we describe statistically, with the help of some N -particle probability density

$$\rho_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$

We shall assume that the particles are identical but distinguishable, so we can index them. We shall not consider the particle velocities (we have integrated over the velocities). The probability density to find particle 1 in the point \mathbf{r} is given by the marginal distribution

$$\rho_1(\mathbf{r}) = \int \rho_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N) d^3\mathbf{r}_2 d^3\mathbf{r}_3 \dots d^3\mathbf{r}_N$$

Since all the particles are identical the probability density for the second particle is given by the same one-particle distribution function $\rho_1(\mathbf{r})$.

Now we argue that the mean particle density around the point \mathbf{r} will be

$$n(\mathbf{r}) = N\rho_1(\mathbf{r})$$

This statement is almost obvious, a formal prove needs some work.

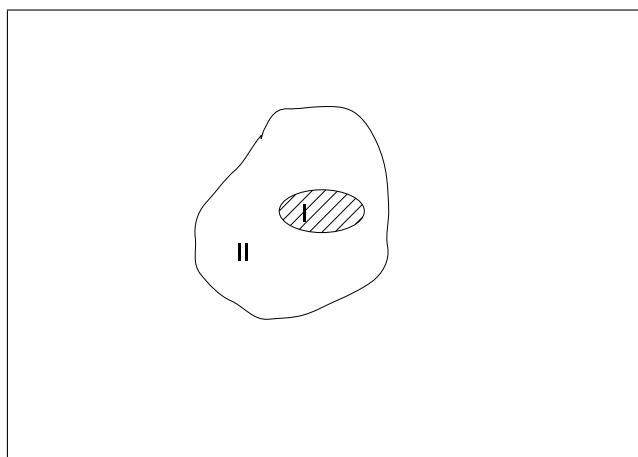


Figure 10.1: Integration regions

Let us divide the whole volume containing the gas to two regions I, and II, as seen in the figure 10.1. Let us ask what is the mean number of particles in the region I. Let us introduce the characteristic function $\chi(\mathbf{r})$. This function is equal to one inside the region I and equal to zero in region II. The characteristic function $\tilde{\chi}(\mathbf{r})$ of region II is then $\tilde{\chi}(\mathbf{r}) = 1 - \chi(\mathbf{r})$

For simplicity let us consider a gas with just three particles. Then the mean number of particles in region I can be expressed as

$$\begin{aligned}
 \bar{N}_I = & \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 [0 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\
 & + 1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\
 & + 1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \chi(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\
 & + 1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\
 & + 2 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \chi(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\
 & + 2 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\
 & + 2 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \chi(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\
 & + 3 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \chi(\mathbf{r}_2) \chi(\mathbf{r}_3)]
 \end{aligned}$$

Let us introduce not an auxiliary variable t and then set it to one. We get

$$\begin{aligned} \bar{N}_I &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 \\ & [0 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + 1t^0 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + 1t^0 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \chi(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + 1t^0 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\ & + 2t^1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \chi(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + 2t^1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\ & + 2t^1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \chi(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\ & + 3t^2 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \chi(\mathbf{r}_2) \chi(\mathbf{r}_3)] \quad \text{for } t = 1 \end{aligned}$$

$$\begin{aligned} \bar{N}_I &= \frac{d}{dt} \left\{ \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 \right. \\ & [t^0 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + t^1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + t^1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \chi(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + t^1 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\ & + t^2 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \chi(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + t^2 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\ & + t^2 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \chi(\mathbf{r}_2) \chi(\mathbf{r}_3) + \\ & \left. + t^3 \times \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi(\mathbf{r}_1) \chi(\mathbf{r}_2) \chi(\mathbf{r}_3) \right\} \quad \text{pre } t = 1 \end{aligned}$$

$$\begin{aligned} \bar{N}_I &= \frac{d}{dt} \left\{ \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 \right. \\ & [\rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) t \chi(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) t \chi(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) t \chi(\mathbf{r}_3) + \\ & + \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) t \chi(\mathbf{r}_1) t \chi(\mathbf{r}_2) \tilde{\chi}(\mathbf{r}_3) + \\ & + \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) t \chi(\mathbf{r}_1) \tilde{\chi}(\mathbf{r}_2) t \chi(\mathbf{r}_3) + \\ & + \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tilde{\chi}(\mathbf{r}_1) t \chi(\mathbf{r}_2) t \chi(\mathbf{r}_3) + \\ & \left. + \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) t \chi(\mathbf{r}_1) t \chi(\mathbf{r}_2) t \chi(\mathbf{r}_3) \right\} \quad \text{for } t = 1 \end{aligned}$$

$$\begin{aligned} \bar{N}_I &= \frac{d}{dt} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) (t\chi(\mathbf{r}_1) + \tilde{\chi}(\mathbf{r}_1)) (t\chi(\mathbf{r}_2) + \tilde{\chi}(\mathbf{r}_2)) (t\chi(\mathbf{r}_3) + \tilde{\chi}(\mathbf{r}_3)) \\ & \quad \text{pre } t=1 \end{aligned}$$

Now explicitly differentiate under the integral and set $t = 1$. We get

$$\bar{n}_I = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) (\chi(\mathbf{r}_1) + \chi(\mathbf{r}_2) + \chi(\mathbf{r}_3))$$

Where we used the equality

$$\chi(\mathbf{r}) + \tilde{\chi}(\mathbf{r})$$

We can integrate over two variables and we get

$$\bar{N}_I = 3 \int d^3\mathbf{r}_1 \rho_1(\mathbf{r}_1) \chi(\mathbf{r}_1)$$

If we are interested in mean density and not in mean number of particles, we have to divide by the volume of the region I and we get

$$\bar{n}_I = 3 \frac{\int d^3\mathbf{r}_1 \rho_1(\mathbf{r}_1) \chi(\mathbf{r}_1)}{\int d^3\mathbf{r}_1 \chi(\mathbf{r}_1)}$$

For infinitesimal region around \mathbf{r} we get

$$\frac{\chi(\mathbf{r}_1)}{\int d^3\mathbf{r}_1 \chi(\mathbf{r}_1)} \rightarrow \delta(\mathbf{r}_1 - \mathbf{r})$$

and so

$$\bar{n}(\mathbf{r}) = 3\rho_1(\mathbf{r})$$

The generalization to arbitrary N is trivial.

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