1

A few well-known basic results

This chapter is just a reminder of some basic results concerning equilibrium statistical mechanics and of a few algebraic techniques used in this book.

1.1 The Boltzmann law

For a system at equilibrium in contact with a heat bath (or thermostat) at temperature $T$, the configurations of the particles and the total energy are random variables. The equilibrium probability distribution for $N$ identical particles confined in a box of volume $V$, whose dynamics are governed by a Hamiltonian $H$, is given by the Boltzmann–Gibbs distribution

$$\rho = \frac{1}{Z} e^{-\beta H},$$

(1.1)

in which $\beta$ is related to the temperature by

$$\beta = \frac{1}{kT}.$$  

(1.2)

1.1.1 The classical canonical ensemble

For classical particles, in three dimensions, $\rho$ is a probability measure in the $6N$-dimensional phase space $(p_a, q_a), a = 1 \ldots 3N$ and the expectation value of an observable $A(p, q)$ is given by

$$\langle A \rangle = \int d\tau A(p, q)\rho(p, q),$$

(1.3)

in which $d\tau$ is the measure $d\tau = \frac{1}{h^{3N}} \frac{1}{N!} \prod_{1}^{3N} dp_a dq_a$. The integrals over the positions $q_a$ are such that every particle is confined in a box of volume $V$.

The factor $1/h^{3N}$, in which $h$ has the dimension of an action (i.e., $ML^2T^{-1}$), makes $d\tau$ dimensionless. Any constant with that dimension would work but the
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classical limit of quantum statistical mechanics provides Planck’s constant, 
\( h = 2\pi \hbar \).

The factor \( 1/N! \) is also of quantum origin: Pauli’s principle allows only for one-
dimensional representations of the permutation group of \( N \) particles, completely
symmetric (bosons) or completely antisymmetric (fermions). This selects only one
state out of the degenerate \( N! \) states obtained by permutations of one of them.

The normalization is fixed by \( \langle 1 \rangle = 1 \), which gives the partition function \( Z \):

\[
Z(\beta, N, V) = \int d\tau e^{-\beta H}. \tag{1.4}
\]

1.1.2 The quantum canonical ensemble

The density matrix \( \rho \), given by (1.1), is an operator in the Hilbert space of symmet-
ric states for integer spin particles, or antisymmetric states for half-integer spins, for
\( N \) particles confined in a box of volume \( V \). The expectation value of an observable 
\( A \) is given by

\[
\langle A \rangle = \text{Tr}(\rho A) = \frac{1}{Z} \text{Tr} A e^{-\beta H} \tag{1.5}
\]

and thus the partition function is given by

\[
Z(\beta, N, V) = \text{Tr} e^{-\beta H}. \tag{1.6}
\]

If the eigenvalues of the \( N \)-body Hamiltonian are labelled as \( E_i \), then

\[
Z = \sum_i e^{-\beta E_i}. \tag{1.7}
\]

If the energy \( E_i \) has a degeneracy \( w_i \) then

\[
Z = \sum' e^{-\beta (E_i - TS_i)}, \tag{1.8}
\]

in which \( S_i = k \log w_i \) and the last sum runs over distinct energies. This expression
shows that the dominant contributions are those that minimize the combination 
\( E - TS \), a competition between energy and entropy to which we shall return in the
next section.

Exercise 1

Quantum effects arise when the typical de Broglie wavelength associated with a
particle becomes comparable to the interparticle distance. Estimate the tempera-
ture below which quantum effects should be taken into account for a gas of nitrogen
of atmospheric density.
1.2 Thermodynamics from statistical physics

1.1.3 The grand canonical ensemble

If the system, in contact with a heat bath, can also exchange particles with a reservoir at temperature $T$ and chemical potential $\mu$, the number of particles is also a random variable. In the simple case in which the Hamiltonian $H_N$ does not change the number of particles, the probability distribution is given by a collection of $\rho_N$ given by

$$\rho_N = \frac{1}{Z_G} e^{\alpha N - \beta H_N}, \quad (1.9)$$

with

$$\mu = \frac{\alpha}{\beta}, \quad (1.10)$$

normalized by

$$Z_G(\alpha, \beta, V) = \sum_N e^{\alpha N} \text{Tr} e^{-\beta H_N},$$

in which $V$ is the volume of the box in which the particles are confined. (If the Hamiltonian does not conserve the number of particles, it is necessary to use the Fock space; this will not be needed within these lectures.)

1.2 Thermodynamics from statistical physics

The canonical free energy is given by

$$F(\beta, N, V) = -\frac{1}{\beta} \log Z. \quad (1.11)$$

Exercise 2

Show that the pressure, the entropy and the chemical potential of the system can all be related to the partition function. Compute the partition function for a classical gas of non-interacting particles.

1.2.1 The thermodynamic limit

The thermodynamic limit is the limit in which $N$ and $V$ go to infinity with a fixed ratio $\nu = N/V$. In this limit one can show that, for particles with short-range interactions, the canonical log $Z$, and thus $F$ are extensive, namely

$$\lim_{N \to \infty, V \to \infty} \left|_{N/V = \nu} \left( \frac{1}{N} \log Z \right) \right|$$

exists and is a function of the two intensive variables $\nu$ and $\beta$. Similarly, for the grand canonical ensemble, $\lim_{V \to \infty} 1/V \log Z_G$ exists and is a function of the intensive variables, temperature and chemical potential.
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Exercise 3
Verify this extensivity for $N$ free classical particles in a box. Reminder: Stirling’s formula $N! = \sqrt{2\pi N} \left( \frac{N}{e} \right)^N (1 + O \left( \frac{1}{N} \right))$.

For charged particles, such as electrons with Coulomb interactions, the thermodynamic limit exists, provided that (a) the system is neutral, i.e., the charge of the ions compensates the charge of the electrons, (b) the system is quantum mechanical, (c) Pauli’s principle is taken into account.¹

Exercise 4
Assume that the potential energy of $N$ interacting classical particles is a homogeneous function $V(\lambda q_1 \cdots \lambda q_{3N}) = |\lambda|^s V(q_1 \cdots q_{3N})$.

Show that the pressure $p(\nu, T)$, where $\nu = N/V$, satisfies the relation $p(\nu, T) = T^{1-3/s} \varphi(\nu T^{3/s})$.

Assume that at low temperature $T_0$ the isotherm in the $(p, V)$ plane presents a phase transition between two phases of different densities. Can there be a critical point for this phase transition, i.e., a temperature at which the transition between the two phases disappears?

1.3 Gaussian integrals and Wick’s theorem

1. One variable
$$
\int_{-\infty}^{+\infty} dx e^{-\frac{1}{2}ax^2} = \sqrt{\frac{2\pi}{a}}. \quad (1.13)
$$

2. $n$ variables
$$
\int_{\mathbb{R}^n} dx_1 \cdots dx_n e^{-\frac{1}{2} \sum x_i A_{ij} x_j} = \frac{(2\pi)^{n/2}}{\sqrt{\det A}}. \quad (1.14)
$$

$A = A^t$ is here a real symmetric matrix with positive eigenvalues. It can thus be diagonalized by an orthogonal transformation $\omega$, i.e., $A = \omega^t D \omega$, in which $D$ is the diagonal matrix of the eigenvalues $(a_1, \ldots, a_n)$ of $A$. The change of variables $\omega x = y$ whose Jacobian $|\det \omega|^{-1}$ is equal to one, leads to the solution.

3. $n$ variables in a source
$$
\int_{\mathbb{R}^n} dx_1 \cdots dx_n e^{-\frac{1}{2} \sum x_i A_{ij} x_j + \sum b_i x_i} = e^{\frac{1}{2} \sum b_i A_{ij}^{-1} b_j}. \quad (1.15)
$$

Translate $x = y + A^{-1} b$.

1.3 Gaussian integrals and Wick’s theorem

4. Wick’s theorem

Apply to (1.15) the operation \( \frac{\partial}{\partial b_{i_1}} \cdots \frac{\partial}{\partial b_{i_n}} \) and then set all the \( b_i = 0 \). The l.h.s. gives

\[
\langle x_{i_1} \cdots x_{i_{2n}} \rangle = \int_{\mathbb{R}^n} dx_1 \cdots dx_n e^{-\frac{1}{2} \sum x_i A_{ij} x_j} x_{i_1} \cdots x_{i_{2n}}.
\]

(1.16)

Applying this to the r.h.s. of (1.15) we can limit ourselves to the term \( \frac{1}{(n!)^2} \times \left( \sum b_i A_{ij}^{-1} b_j \right)^n \); indeed terms of lower degree in the expansion of the exponential will give zero by differentiation; terms of higher degree will give zero because they are left with \( b \) and vanish at \( b = 0 \). Therefore,

\[
\langle x_{i_1} \cdots x_{i_{2n}} \rangle = \frac{\partial}{\partial b_{i_1}} \cdots \frac{\partial}{\partial b_{i_{2n}}} \frac{1}{(n!)^2} \left( \sum b_i A_{ij}^{-1} b_j \right)^n.
\]

(1.17)

Define a complete pairing of the \( \frac{\partial}{\partial b} \) such that each \( \frac{\partial}{\partial b_i} \) has a partner. For this particular pairing, the two paired differentiations go to the same \( \sum \), but there are \( n! \) ways of associating the sums and the chosen pairing. Once this association is made, one has simply to note that

\[
\frac{\partial}{\partial b_k} \frac{\partial}{\partial b_l} \sum b_i A_{ij}^{-1} b_j = 2A_{kl}^{-1}.
\]

Therefore the \( n!2^n \) cancels and we are left with the result, known as Wick’s theorem, for Gaussian integrals.

\[
\langle x_{i_1} \cdots x_{i_{2n}} \rangle = \sum_{\text{pairings}} \prod_{\text{each pair}} A_{i_{id}^{-1}}.
\]

(1.18)

Exercise

Compute the integral

\[
I = \int_{\mathbb{R}^2} dx dy \ y^4 e^{-(x^2+xy+2y^2)}\int_{\mathbb{R}^2} dx dy e^{-(x^2+xy+2y^2)}.
\]

Answer

\[
I = \frac{144}{343},
\]

since

\[
I = 3(\langle xx \rangle)^2 \langle yy \rangle + 12\langle xx \rangle (\langle xy \rangle)^2,
\]

in which

\[
\langle xx \rangle = A_{11}^{-1}, \quad \langle xy \rangle = A_{12}^{-1}, \quad \langle yy \rangle = A_{22}^{-1},
\]

with

\[
A = \begin{pmatrix} 2 & 1 \\ 1 & 4 \end{pmatrix}, \quad A^{-1} = \frac{1}{7} \begin{pmatrix} 4 & -1 \\ -1 & 2 \end{pmatrix}.
\]
1.4 Functional derivatives

A functional \( F\{f\} \) is an application from a space of functions \( f \) to a complex or real number \( F \). For instance the action integral for the motion of a particle, located at the position \( q(t) \) at time \( t \), with potential energy \( V(q) \) is the functional of the trajectory given by

\[
S(q) = \int_{t_1}^{t_2} dt \left[ \frac{m}{2} \dot{q}^2 - V(q) \right].
\]  

(1.19)

Let us work with functions \( f \) of a single real variable \( x \) (the generalization to functions of more variables is immediate). The derivative of the functional with respect to \( f(x) \) at \( x = x_0 \) is defined as follows. Let us consider an increment \( \epsilon \delta \eta(x - x_0) \); the function \( \delta \eta(x) \) is centred at the origin, and it has a width \( \eta \); it is normalized to one, i.e., \( \int_{\mathbb{R}} \delta \eta(x) dx = 1 \). When \( \eta \) goes to zero, this increment approaches the Dirac distribution \( \delta(x) \). (For instance \( \delta \eta(x) = \frac{1}{\sqrt{2\pi \eta}} e^{-x^2/2\eta^2} \).) One computes next the increment of the functional

\[
\Delta F = F\{f + \epsilon \delta \eta(x - x_0)\} - F\{f\}.
\]  

(1.20)

The functional derivative of \( F \) at \( x_0 \) is defined as

\[
\frac{\delta F}{\delta f} \bigg|_{x_0} = \lim_{\eta \to 0} \lim_{\epsilon \to 0} \frac{\Delta F}{\epsilon}.
\]  

(1.21)

The limits have to be taken in the order indicated: if we let \( \epsilon \) go to zero first, we avoid non-linearities in \( \delta \eta \). In the opposite order we would encounter powers of \( \delta \eta \), which do not have a limit when \( \eta \) goes to zero.

Let us apply this to the above action functional:

\[
\lim_{\epsilon \to 0} \frac{1}{\epsilon} \left[ S(q(t) + \epsilon \delta \eta(t - t_0)) - S(q) \right] \quad = \quad \int_{t_1}^{t_2} dt \left[ m \ddot{q} \delta \eta(t - t_0) - V'(q) \delta \eta(t - t_0) \right].
\]  

(1.22)

After an integration by parts of the first term one ends up with

\[
\frac{\delta S}{\delta q}(t_0) = -m \ddot{q}(t_0) - V'(q(t_0))
\]  

(1.23)

and Newton’s law is just given by the vanishing of this functional derivative for any \( t_0 \): the action is stationary (in fact a minimum) for the classical trajectory.

1.5 \( d \)-dimensional integrals

The rules are simple but they may surprise the reader who sees them for the first time. Whenever the dimension \( d \) is an integer, the \( d \)-dimensional integral is the
1.5 \( d \)-dimensional integrals

ordinary integral over the whole space \( \mathbb{R}^d \). But, for arbitrary \( d \), one applies the following rules:

(a) \( \int d^d q f(q + p) = \int d^d q f(q) \),

(b) \( \int d^d q f(\lambda q) = |\lambda|^{-d} \int d^d q f(q) \).

If \( q_1 \) is a \( d_1 \)-dimensional vector and \( q_2 \) is a \( d_2 \)-dimensional vector and \( f(q) = g_1(q_1)g_2(q_2) \) with \( d = d_1 + d_2 \), then

(c) \( \int d^d q f(q) = \int d^{d_1} q_1 g_1(q_1) \int d^{d_2} q_2 g_2(q_2) \).

Consequences:

- From (b) the only finite solution to an integral, such as \( \int d^d q (q^2)^k \) is

\[
\int d^d q (q^2)^k = 0
\]

for any positive or negative real number \( k \), including \( k = 0 \). Note that this integral never exists as an ordinary integral for integer dimensions. The consistency of this rule will be checked below.

- The same would apply to any scale-invariant integral, such as

\[
\int d^d q_1 d^d q_2 (q_1^2)^k [(q_1 + q_2)^2]^l = 0.
\]

- From (c)

\[
\int d^d q e^{-q^2} = \left[ \int_{-\infty}^{+\infty} dx e^{-x^2} \right]^d = \pi^{d/2}.
\]

Let us use these rules to calculate simple integrals:

\[
\int d^d q (q^2 + 1)^{-k} = \frac{1}{\Gamma(k)} \int d^d q \int_0^\infty d\lambda \lambda^{k-1} e^{-\lambda(q^2 + 1)} = \frac{\pi^{d/2} \Gamma(k - d/2)}{\Gamma(k)}.
\]

One can also compute this integral in ‘spherical’ coordinates:

\[
\int d^d q (q^2 + 1)^{-k} = \frac{2\pi^{d/2}}{\Gamma(d/2)} \int_0^\infty dx x^{d-1} \frac{1}{(x^2 + 1)^k} = \frac{2\pi^{d/2}}{\Gamma(d/2)} \frac{1}{2} \int_0^1 dy y^{k-d/2-1} (1 - y)^{d/2-1} = \frac{\pi^{d/2} \Gamma(k - d/2)}{\Gamma(k)}.
\]
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(change $1/(1 + x^2) = y$). It is easy to verify on examples, such as $d = 3$ and $k = 2$, that whenever the integral exists in the ordinary sense it is indeed given by this result.

To check the consistency of rule (b) let us compute

$$J = \int d^d q \frac{1}{q^2(q^2 + 1)}.$$

If we use spherical coordinates,

$$J = \frac{2\pi^{d/2}}{\Gamma(d/2)} \int_0^\infty dx \frac{x^{d-3}}{x^2 + 1} = \frac{2\pi^{d/2}}{\Gamma(d/2)} \frac{1}{2} \int_0^1 dy \frac{y^{1-d/2}(1 - y)^{d/2-2}}{\Gamma(2 - d/2)\Gamma(d/2 - 1)}.$$

It is easy to verify that, for $d = 3$, $J$ exists as an ordinary integral and is indeed given by this result. Alternatively, using the identity $1/q^2(q^2 + 1) = 1/q^2 - 1/q^2 + 1$, we find, from rule (b) and the above $k = 1$ result,

$$J = 0 - \pi^{d/2}\Gamma(1 - d/2),$$

and it is easy to check that this coincides with the above result for $J$.

Additional references


On the existence of the thermodynamic limit:


2
Introduction: order parameters, broken symmetries

2.1 Can statistical mechanics be used to describe phase transitions?

A phenomenological description of a phase transition does not raise any special difficulty a priori. For instance, to describe the solidification of a gas under pressure, one can make a simple theory for the gaseous phase, e.g., an ideal gas corrected by a few terms of the virial expansion. Then, for the solid, one can use the extraction energies of the atoms, and the vibration energies around equilibrium positions. These calculations will provide a thermodynamic potential for each phase. The line of coexistence between the two phases in the pressure–temperature plane will be determined by imposing the equality of the two chemical potentials

$$\mu_I(T, P) = \mu_{II}(T, P).$$

If this method may turn out to be useful in practice, it does not answer any of the questions that one can raise concerning the transition between the two states. Indeed the interactions between the molecules are not statistical in nature: they are independent of the temperature, or of the pressure; the Hamiltonian is a combination of kinetic energy and well-defined interaction potentials between pairs of molecules. How can one see in such a description, following the principles established by Boltzmann, Gibbs and their successors, that at equilibrium the same molecules can form a solid or a fluid, a superconductor, a ferromagnet, etc., without any modification of the interactions? It is so far from obvious that, for a long time, some believed that the principles of statistical mechanics had to be completed to allow for the possibility of a phase transition. It is only after Peierls’ 1936 work (which will be reviewed below)\(^1\) and Onsager’s\(^2\) solution of the two-dimensional Ising model, that it became manifest that the ordinary principles of statistical mechanics contained the possibility of phase transitions and

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Critical points. (A critical point is the endpoint of a line of coexistence between two phases, such as the endpoint of the liquid–vapour line of coexistence in the \((p, T)\) plane. Beyond this point there is only one phase, the fluid phase.)

These same contributions also demonstrated how singularities, such as discontinuities, or divergences of physical quantities at critical points, could arise in statistical mechanics, whereas one could have thought, a priori, that they were not possible. Indeed the thermodynamic properties are determined by the knowledge of the free energy, proportional to \(\log Z\), with

\[
Z = \sum_C e^{-\beta E(C)}. \tag{2.1}
\]

Each term of the sum is analytic in the temperature (except at zero temperature). Assuming that there is a finite number of distinct configurations, as will be the case in many situations that we are going to study, such as the Ising model, then the partition function is analytic in \(T\), as well as the free energy \(F = -kT \log Z\), unless \(Z\) vanishes. But \(Z\) does not vanish for real values of \(T\), and thus \(F\) is non-singular on the real temperature axis. One can thus conclude that singularities cannot exist at any real non-zero temperature: in other words, phase transitions do not exist!

We shall see that the solution to this paradox is that the number \(N\) of constituents is so large that one almost always observes experimentally only the thermodynamic limit and the simplistic argument that I have just used fails in that limit.

2.2 The order–disorder competition

To make the discussion more concrete, I shall introduce immediately the Ising model, whose physical significance will be explained in the next section. We consider a periodic lattice with \(N\) sites in dimension \(d\). To each site \(i\) one attaches a ‘spin’:

\[
\sigma_i = \pm 1 \tag{2.2}
\]

(for a true spin this would be simply the eigenvalues of one component of a spin \(\frac{1}{2}\), up to a factor \(\hbar/2\)). Therefore, there are \(2^N\) configurations \(C\)

\[
C = (\sigma_1, \ldots, \sigma_N). \tag{2.3}
\]

We now have to define the energy of a configuration \(C\). In the simplest model introduced by Ising, a student of Lenz, in 1925,\(^3\) one assumes that only pairs of

\(^3\) Ising solved the model in one dimension, in which there is no phase transition and conjectured (erroneously) on that basis that the model could not describe a phase transition.