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STATISTICAL PHYSICS
EXERCICES

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Gaussian integrals

An integral related to $\Gamma(1/2)$,

$$\boxed{\int_{\mathbb{R}} \mathrm{d}x\, \mathrm{e}^{-\frac{1}{2}ax^2} = \sqrt{\frac{2\pi}{a}}} \tag{0.1}$$

An integral related to $\Gamma(3/2)$,

$$\int_{\mathbb{R}} \mathrm{d}x\, x^2\, \mathrm{e}^{-\frac{1}{2}ax^2} = \frac{1}{a}\sqrt{\frac{2\pi}{a}} \tag{0.2}$$

More generally

$$\int_0^\infty \mathrm{d}x\, x^n\, \mathrm{e}^{-\frac{1}{2}ax^2} = \frac{1}{2}\left(\frac{2}{a}\right)^{\frac{n+1}{2}} \Gamma\left(\frac{n+1}{2}\right) \tag{0.3}$$

where $\Gamma(z)$ is the Gamma function (see below). The Fourier transform of the Gaussian :

$$\int_{\mathbb{R}} \mathrm{d}x\, \mathrm{e}^{-\frac{1}{2}ax^2 + \mathrm{i}kx} = \sqrt{\frac{2\pi}{a}}\, \mathrm{e}^{-\frac{1}{2a}k^2} \tag{0.4}$$

The Euler Gamma function

$$\boxed{\Gamma(z) \stackrel{\text{def}}{=} \int_0^\infty \mathrm{d}t\, t^{z-1}\, \mathrm{e}^{-t} \qquad \text{for } \operatorname{Re} z > 0} \tag{0.5}$$

Remark : All integrals of the type $\int_0^\infty \mathrm{d}x\, x^a\, \mathrm{e}^{-Cx^b}$ can be expressed using the Γ function.

The fonctionnal relation (easy to show) :

$$\boxed{\Gamma(z+1) = z\,\Gamma(z)} \tag{0.6}$$

allows to analytically extend the Γ function to the other half of the complex plane, $\operatorname{Re} z \leqslant 0$.

Particular values : $\boxed{\Gamma(1) = 1 \ \& \ \Gamma(1/2) = \sqrt{\pi}}$ and therefore by iteration

$$\Gamma(n+1) = n! \tag{0.7}$$

$$\Gamma(n + \frac{1}{2}) = \frac{\sqrt{\pi}}{2^n} (2n-1)!! \tag{0.8}$$

where $(2n-1)!! \overset{\text{def}}{=} 1 \times 3 \times 5 \times \cdots \times (2n-1) = \frac{(2n)!}{(2n)!!}$ and $(2n)!! \overset{\text{def}}{=} 2 \times 4 \times \cdots \times (2n) = 2^n n!$.

The Euler Beta function

$$B(\mu, \nu) = \int_0^1 dt\, t^{\mu-1}(1-t)^{\nu-1} = 2\int_0^{\pi/2} d\theta\, \sin^{2\mu-1}\theta \, \cos^{2\nu-1}\theta = \frac{\Gamma(\mu)\Gamma(\nu)}{\Gamma(\mu+\nu)} \tag{0.9}$$

Stirling formula

$$\Gamma(z+1) \simeq \sqrt{2\pi z}\, z^z\, e^{-z} \qquad \text{i.e} \qquad \boxed{\ln\Gamma(z+1) = z\ln z - z + \frac{1}{2}\ln(2\pi z) + \mathcal{O}(1/z)} \tag{0.10}$$

which will be useful to calculate $\ln(n!) \simeq n\ln n - n$ where $\frac{d}{dn}\ln(n!) \simeq \ln n$.

Volume of the hypersphere

$$\mathscr{V}_D = \frac{\pi^{D/2}}{\Gamma(\frac{D}{2}+1)} \tag{0.11}$$

Binomial formula

$$(x+y)^N = \sum_{n=0}^{N} C_N^n\, x^n\, y^{N-n} \qquad \text{où } C_N^n \equiv \binom{N}{n} \overset{\text{def}}{=} \frac{N!}{n!(N-n)!} \tag{0.12}$$

and its extension

$$(x_1 + \cdots + x_M)^N = \sum_{\substack{m_1, \cdots, m_M \\ \text{t.q. } \sum_k m_k = N}} \frac{N!}{m_1! \cdots m_M!} x_1^{m_1} \cdots x_M^{m_M} \tag{0.13}$$

Other useful integrals

$$\int_0^\infty dx\, \frac{x^{\alpha-1}}{e^x - 1} = \Gamma(\alpha)\, \zeta(\alpha) \qquad \text{where } \zeta(\alpha) = \sum_{n=1}^{\infty} n^{-\alpha} \tag{0.14}$$

is the Euler zeta function. We have $\zeta(2) = \frac{\pi^2}{6}$, $\zeta(3) \simeq 1.202$, $\zeta(4) = \frac{\pi^4}{90}$, etc.

$$\int_0^\infty dx\, \frac{x^4}{\text{sh}^2 x} = \frac{\pi^4}{30} \tag{0.15}$$

(we can infer it from the previous relation with $\alpha = 4$).

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TD 1 : Random walks and the central limit theorem

1.1 Binomial law and random walk (*)

We consider a walker who can move on some axis : at each time step he chooses to go either right with probability $p \in [0, 1]$, either left with probability $q = 1 - p$ (see Fig. 1.1). Each step is *independent* of the previous one.
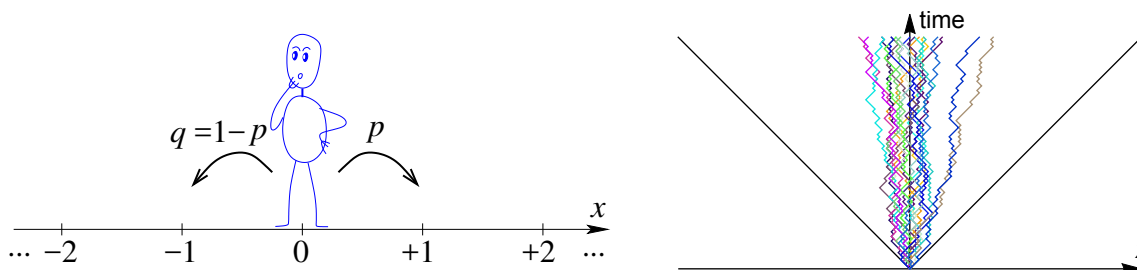
Figure 1.1: *Walker on an axis. Right : We randomly generate* 20 *symmetric walks each containing* 100 *steps.*

A. Binomial law.

1/ Distribution.– After M steps, what is the probability $\Pi_M(n)$ than the walker has made n steps to the right ? Check the normalisation.

2/ Expression of the moments.– Express the kth moment, i.e. $\langle n^k \rangle$, as a summmation (beware that the number of steps n is the random variable while M is just a parameter of the problem). Do you know how to calculate this summation ?

3/ Calculation of the moments : generating function.– We introduce an auxiliary function, called "*generating function*",

$$G_M(s) \overset{\text{def}}{=} \langle s^n \rangle , \tag{1.1}$$

function of the variable s which could be complex.

a) If we assume that the function $G_M(s)$ is known, how can we infer from it the moments ?

b) For the previously determined binomial law $\Pi_M(n)$, calculate explicitly $G_M(s)$; deduce $\langle n \rangle$ and $\langle n^2 \rangle$ and the variance $\text{Var}(n) \overset{\text{def}}{=} \langle n^2 \rangle - \langle n \rangle^2$. Compare the fluctuations to its average value.

c) OPTIONAL : we introduce another definition for the generating function : $W_M(\beta) \overset{\text{def}}{=} \ln G_M(e^{-\beta})$, where β is called "*conjugate variable*" (of the random variable). Check that the expansion $W_M(\beta) = -\beta \langle n \rangle + (\beta^2/2) \text{Var}(n) + \cdots$ (this provides the variance more quickly). We can try to justify more generally this expansion by comparing the definitions of $G_M(s)$ and $W_M(\beta)$.

4/ Limit $M \to \infty$.– In this question we analyze directly the distribution in the limit $M \to \infty$. Using the Stirling formula, expand $\ln \Pi_M(n)$ around its maximum $n = n_*$. Justify that $\Pi_M(n)$ is approximately a gaussian in the limit $M \to \infty$ (give a condition on p). Draw *carefully* the shape of the distribution.

B. Walker.
– We return to the walker's study, whose position on the axis is x. The length of a step is a.

1/ Express x according to the number of steps to the right n. Deduce the first two moments of x (using the results of part **A**).

2/ Drift velocity.– The walker waits for a time τ between two steps. Express the drift velocity

$$V \stackrel{\text{def}}{=} \lim_{t \to \infty} \frac{\langle x \rangle_t}{t} \tag{1.2}$$

as a function of a, τ and the probability p ; $\langle x \rangle_t$ denotes the average at the time $t = M\tau$.

3/Diffusion constant.– In order to characterize the spread of the walker distribution, we introduce the diffusion constant

$$D \stackrel{\text{def}}{=} \lim_{t \to \infty} \frac{\langle x^2 \rangle_t - \langle x \rangle_t^2}{2t} \tag{1.3}$$

Express D as a function of the parameters of the problem.

4/ Continuum limit.– The position is treated as a continuous random variable. Give the expression of the probability density $P_t(x)$ of the walker's position at time t. Check the normalization (in the case $p = 1/2$, we can discuss the precise relationship between $\Pi_M(n)$ and $P_t(x)$).

C. Steps are continuous random variables – Universality.– We consider another model of a random walk : the position of the walker is no longer constrained to be on a latice of points but can take a continuously varying value in $\mathbb{R}$. At each time interval, he makes a step distributed with the law $p(h)$

1/ Justify that the distribution of the position at time t obeys the recursive relation

$$P_{t+\tau}(x) = \int \mathrm{d}h \, p(h) \, P_t(x - h) \,. \tag{1.4}$$

We now choose one of the two methods proposed below to solve this equation.

2/ Method 1 : for the gaussian symmetric walk– We consider a symmetric Gaussian law $p(h) = (\sqrt{2\pi}\,\sigma)^{-1} \exp\left\{-h^2/(2\sigma^2)\right\}$. Using a known result on the convolution of Gaussians, deduce $P_{M\tau}(x)$. Give the expression of the diffusion constant as a function of τ and σ.
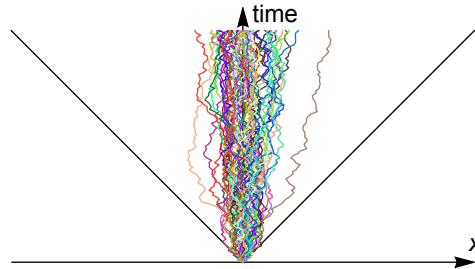
Figure 1.2: 50 *walks generated with* 100 *steps distributed according a Gaussian law.*

3/ Method 2 : for the general case.– We do not specify the explicit form of the law $p(h)$. We make only two fairly weak assumptions: his first two " moments " are finite, $\langle h \rangle < \infty$ and $\langle h^2 \rangle < \infty$. We consider "small " time intervals, $\tau \to 0$, and "small" steps (the width of $p(h)$ goes to zero).

a) Give examples of $p(h)$ (with different types of decay at large h such as exponential, power law, ...).

b) We make the assumption that the distribution $P_t(x)$ is a function that varies "slowly" with t (at the scale of τ) and with x (at the scale h). In the integral equation (1.4), expand $P_{t+\tau}(x)$ to first order in τ and $P_t(x - h)$ and to second order in h.

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c) We suppose that the three parameters $\tau \propto \epsilon$, $\langle h \rangle \propto \epsilon$ et $\langle h^2 \rangle \propto \epsilon$ are proportional to the parameter $\epsilon \to 0^+$ and tend simultaneously to zero. Show that we obtain a partial differential equation for $P_t(x)$, which we write in terms of V and D.

d) Give the solution to the partial differential equation (the simplest method to solve it is to Fourier transform the equation in space).

e) OPTIONAL : *Properties of the random walk.*– We note h_t the step made on time t (given by the distribution law $p(h)$). We assume $\langle h_t \rangle = 0$ to simplify the discussion. We note $x(t)$ the "process". Its evolution is controled by $x(t+\tau) = x(t) + h_t$. In the continuum limit, how $\langle [x(t+\delta t) - x(t)]^2 \rangle$ depends on δt ? Discuss the continuity and differentiability of the random process $x(t)$ in the continuum limit.

4/ Universality.– Explain why the different models of random walks all lead to the same universal distribution law $P_t(x)$, in the limit of a large number of steps (or equivalently in the limit $\epsilon \to 0$).

D. The d-dimensionnal case and application.

1/ We consider a walker in $\mathbb{R}^d$. At every step he is now making a jump $\vec{\delta x} = h_1 \vec{e_1} + \cdots + h_d \vec{e_d}$, where h_i are d *independent* random variables, described by the same symmetric law $p(h)$. Deduce the distribution of the walker's position in $\mathbb{R}^d$ (we will use the result of question **C** for $d = 1$).

2/ Express $\langle \vec{x}^2 \rangle$, as a function of the diffusion constant defined above in the one-dimensional case (it is convenient to consider $\langle x_i x_j \rangle$ for $i = j$ and $i \neq j$).

3/ Joint law *versus* marginal] law.–
   $\vec{x} \in \mathbb{R}^2$ is distributed by the Gaussian law obtained in the limit of a large number of jumps. How to go from the joint distribution $P_t(x, y)$ to the *marginal law* $Q_t(r)$ of $r = \sqrt{x^2 + y^2}$? Compare the calculation of $\langle \vec{x}^2 \rangle$ from $P_t(x, y)$ and $Q_t(r)$. Compute the average value $\langle r \rangle$ and the typical value r_{typ} (for which $Q_t(r)$ is maximum). Plot $Q_t(r)$ with care.

4/ Application : molecule in a gas.–
   Typically, in a gas at room temperature, a molecule has a velocity $v \approx 500$ m/s and has shocks with other molecules every $\tau \approx 2$ ns. Compare the typical distance covered between two shocks with the typical distance to the nearest molecule (for $p = 1$ atm, $T = 300$ K). Compare the diffusive motion of the molecule after one second (number of shocks, typical distance finally traveled), with the ballistic motion.

TD 2 : Phase space and ergodicity

2.1 Evolution in phase space and the Liouville theorem

We discuss various properties of the temporal evolution of the phase space distribution for a conservative system. To simplify, we consider the one-dimensional situation (the extension to the multi-dimensional case and/or to several particles, is straightforward): a particle whose dynamics is described by the Hamilton function $H(q, p)$.

The exercice can be found at http://lptms.u-psud.fr/christophe_texier/
enseignements/enseignement-en-licence/l3-physique-statistique/
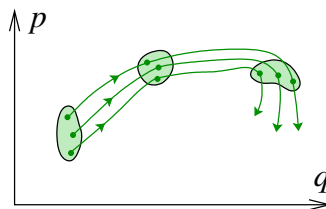
Figure 2.1: *Three trajectories of a small volume in phase space are represented : the temporal evolution keeps the measure* dqdp *invariant.*

2.2 The H theorem

In the previous exercise, we mentioned the existence of various equilibrium measures in phase space. It remains to understand why and how the system relaxes to equilibrate. This is the purpose of this exercise and the next two.

The exercice can be found at http://lptms.u-psud.fr/christophe_texier/
enseignements/enseignement-en-licence/l3-physique-statistique/

2.3 Chaos and ergodicity

In this exercise, we show that the deterministic evolution of an isolated system can lead to ergodicity, assuming certain conditions on the (chaotic) nature of the dynamics.

Exercice available at http://lptms.u-psud.fr/christophe_texier/enseignements/
enseignement-en-licence/l3-physique-statistique/
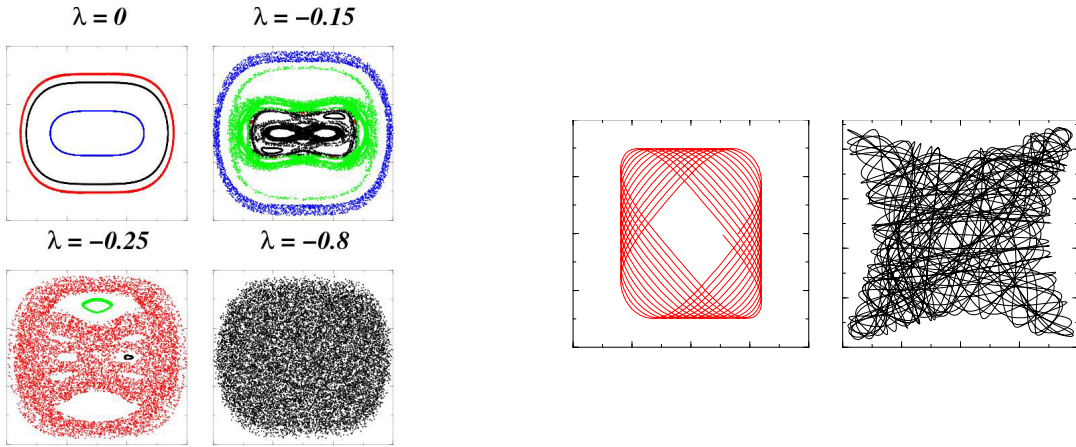
Figure 2.2: Left : *Poincaré sections at $y = 0$ for different values of the parameter λ (in the plane (x, p_x)). Each color correspond to a different trajectory.* Right : *Trajectory in the physical space (x, y) for $\lambda = 0$ and $\lambda = -0.8$.* (Figures by Nicolas Pavloff, LPTMS).

2.4   Ergodicity for a sphere in a fluid

We are going to study the relaxation toward equilibrium for a toy model describing a small sphere subject to an elastic force in a fluid. There are different confining techniques that can be used to achieve. We can, for example, anchor the particle to surface by a polymeric linker (Fig. 2.3) or we can use a laser that, if the particle is made of a dielectric material, acts a confining trap (this setup is known as *optical tweezers*).
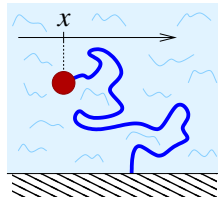
Figure 2.3: *Particle anchored to a surface by a polymeric linker.*

We restrict our-self to the one dimensional case. In this case, the particle follow the evolution as obtained by the Newton equations motion:

$$\dot{x}(t) = v(t) \tag{2.1}$$
$$m\,\dot{v}(t) = -\gamma\,v(t) - k\,x(t) + F(t)\,, \tag{2.2}$$

where k is the elastic constant and γ is the friction coefficient due to the presence of the liquid. $F(t)$ is a random force that models the fluctuations of the fluid (in particular $\langle F(t) \rangle = 0$).

We can identify (at least) two characteristic time scales: the period associated to the elastic force, $T = 2\pi\sqrt{m/k}$, and $\tau_{\text{relax}} = m/\gamma$ that characterizes velocity relaxation. We are going to focus on the *over-damped regime* $\tau_{\text{relax}} \ll T$, i.e. the limit of strong friction γ and small elastic constant k.

A. Velocity relaxation.–

For short times, we can neglect the elastic force, i.e. we can set $k = 0$ in eq. (2.2). We are going to discretize the equation of evolution of velocity by defining: $V_n \equiv v(n\tau)$ where τ is an arbitrary small non-physical time scale such that $\tau \ll \tau_{\text{relax}}$.

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1/ Show that $V_{n+1} = \lambda V_n + \xi_n$ and express λ and ξ_n as a function of the previously introduced quantities.

2/

In which physical conditions is it possible to assume that the forces $F(n\tau)$ at different times are decorrelated, i.e. $\langle F(n\tau) F(m\tau) \rangle \propto \delta_{n,m}$?

We are going to assume that all the forces $F(n\tau)$ are **independent** and **identically** distributed according to a Gaussian distribution of variance $\langle F(n\tau)^2 \rangle = \sigma^2/\tau$.

3/ Show that

$$V_n = \lambda^n V_0 + \sum_{k=0}^{n-1} \lambda^k \xi_{n-k} \tag{2.3}$$

Assuming that V_0 is a random variable (independent also of ξ_n), derive the variance of V_n. Derive, also, the distribution of V_n assuming that V_0 is a Gaussian variable. Consider the case $\tau \ll \tau_{\text{relax}} = m/\gamma$, justify that distribution of the velocity $v(n\tau) \equiv V_n$ becomes independent of the initial conditions in the limit $n = t/\tau \to \infty$ (show that the exact condition is $t \gg \tau_{\text{relax}}$). In this situation $v(t)$ has reached his stationary distribution.

4/ Fluctuation-Dissipation relation (Einstein).– In the course, we will show that average kinetic energy is directly related to the temperature by $\langle E_c \rangle = (1/2)k_B T$ where k_B is the Boltzmann constant. Derive a relation between the friction coefficient γ, the force fluctuation amplitudes σ and the temperature.

5/ Derive the velocity marginal distribution $P_{\text{eq}}(v)$ at equilibrium as a function of T

B. Position relaxation.– In the limit $\tau_{\text{relax}} \ll T$, we can neglect the the acceleration term in the Newton equation :
$$0 \simeq -\gamma \dot{x}(t) - k x(t) + F(t) . \tag{2.4}$$

Without performing any supplementary calculations, discuss the statistical properties of $x(t)$ at "large" times. Show that the equilibrium distribution of the position is given by

$$\widetilde{P}_{\text{eq}}(x) \propto e^{-E_p(x)/(k_B T)} , \tag{2.5}$$

where E_p is the potential energy.

Assuming that position and velocity are independent, derive $\rho_{\text{eq}}(x, p)$, the equilibrium distribution in phase space.

2.5 Trom time average to statistical average – Example of the 1D harmonic oscillator(*)

The Hamiltonian of a classical one-dimensional harmonique oscialltor is given by:

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{2.6}$$

where m is the mass of the particle and ω the angular frequency.

A. Classical mechanics.– We are going to analyze the oscillator in the classical mechanics framework.

1/ Verify that, using Hamilton equations, we obtain the expected equations of motion. Solve these equations for the following initial conditions:

$$x(t = 0) = x_0 \qquad \text{et} \qquad p(t = 0) = 0 \tag{2.7}$$

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2/ Describe the phase space of the system and plot its trajectory. What is the energy E for this trajectory?

3/ Evaluate the fraction of time that the particles spends in a position between x and $x + \mathrm{d}x$. We are going to write down the result as $w(x)\,\mathrm{d}x$ where $w(x)$ is the probability density of the position.

B. Statistical physics.–

We are going to recover the previous result following a completely different route. We assume that the energy of the particle is continuous and can only be known within the interval between E and $E + \mathrm{d}E$.

1/ In phase space, draw the surface where the accessible states of the systems are found.

2/ We make the hypothesis of that all microstates (defined in the previous question) are equi-probable. Evaluate the probability that the particle can be found at a position between x and $x + \mathrm{d}x$.

TD 3 : Density of states

3.1 Two-level systems (*)

A single two-level system is characterised by two eigenstates, denoted $|+\rangle$ and $|-\rangle$, with energies $\varepsilon_\pm = \pm \varepsilon_0$ where ε_0 is a microscopic scale. An example is a spin in magnetic field.

We consider N such two-level systems, *identical* and *independent* (for example N spins $1/2$ at the nodes of a crystal). We denote $\varepsilon_\sigma^{(i)}$ the energy of subsystem i, with $\sigma = +$ or $-$, and $E = \sum_{i=1}^{N} \varepsilon_{\sigma_i}^{(i)}$ the total energy.

1/ Energy spectrum : Describe the microstates of the system. Writing $E = M\varepsilon_0$, how does the integer M vary ?

2/ If the energy is fixed, give the number $N_\pm$ of subsystems in state $|\pm\rangle$. Deduce the degeneracy g_M of level $E_M = M\varepsilon_0$. Relate g_M to the density of states $\rho(E_M)$.

3/ We consider the limit $N \gg 1$. Find an approximation for $\ln g_M$ by using the Stirling formula (assuming $N_\pm \gg 1$). Plot $\ln g_M$ as a function of E_M. Show that the density of states is Gaussian for $E \ll N\varepsilon_0$,
$$\rho(E) \simeq \rho(0)\, e^{-E^2/(2N\varepsilon_0^2)} . \tag{3.1}$$
Compare the width of the function to the width of the full spectrum. What is the total number of states ? Deduce the value of $\rho(0)$.

OPTIONAL : Using $\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N) + \mathcal{O}(N^{-1})$, recover $\rho(0)$ more directly.

3.2 Volume of a hypersphere (*)

A hypersphere of radius R in $\mathbb{R}^d$ is the domain defined by $x_1^2 + x_2^2 + \cdots + x_d^2 \leqslant R^2$. By studying the integral $\int_{\mathbb{R}^d} d\vec{x}\, e^{-\vec{x}^2}$, calculate the surface of the hypersphere $S_d(R)$ and show that the volume is given by
$$V_d(R) = \mathscr{V}_d\, R^d \qquad \text{where} \quad \boxed{\mathscr{V}_d = \frac{\pi^{d/2}}{\Gamma(\frac{d}{2} + 1)}} \tag{3.2}$$
is the volume of the sphere of unit radius (consider the cases $d = 1$, 2, and 3).

Hint: (i) Use separability of integral ; (ii) Use rotational invariance of the function integrated.

3.3 Density of states of free particles (*)

We consider a gas of N free atoms in a cubic box of volume $V = L^3$. The Hamiltonian of the system is
$$H = \sum_{i=1}^{N} \frac{\vec{p_i}^{\,2}}{2m} . \tag{3.3}$$

1/ Distinguishable atoms.– By (incorrectly) considering the atoms as distinguishable, show that the volume $\Phi_{\mathrm{disc}}(E)$ of phase space occupied by states of energy less than E is
$$\Phi(E) = \frac{1}{\Gamma(\frac{3N}{2} + 1)} \left(\frac{E}{\epsilon_0}\right)^{3N/2} \qquad \text{where} \quad \epsilon_0 \stackrel{\text{def}}{=} \frac{2\pi\hbar^2}{mL^2} \tag{3.4}$$

2/ Undistinguishable atoms.– Identical atoms are indistinguishable. Give $\Phi_{\text{indisc}}(E)$ and simplify the result with the help of the Stirling formula. Find the corresponding density of states.

Numerical example: Calculate ϵ_0 (in J and then in eV) for helium atoms in a box of size $L = 1\,\text{m}$.

3.4 Density of state of a free relativistic particle (*)

1/ Non relativistic case.– Recall the density of states for a non relativistic free particle, $\varepsilon_{\vec{k}} = \hbar^2 \vec{k}^2/(2m)$ (see previous exercice).

2/ Ultrarelativist case.– Compute the density of states for an ultrarelativist particle, with $\varepsilon_{\vec{k}} = \hbar \|\vec{k}\| c$.

Indication : Use the representation $\rho(\varepsilon) = \sum_{\vec{k}} \delta(\varepsilon - \varepsilon_{\vec{k}})$.

3/ Relativist case.– (OPTIONAL) Using the semi-classical rule, compute the density of states for a massive relativist particle, $\varepsilon_{\vec{k}} = \sqrt{(\hbar \vec{k} c)^2 + m^2 c^4}$. Recover the two previous limiting behaviours.

3.5 Classical and quantum harmonic oscillators (*)

We consider a system of N independent identical 1D harmonic oscillators. The Hamiltonian of the system is

$$H = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 q_i^2 \right) . \tag{3.5}$$

1/ Semi-classical treatment.– We suppose that the oscillators are classical.

a/ We denote by $\mathcal{V}(E)$ the volume occupied by states of energy $\leqslant E$ in phase space (the dimension of which will be specified). Express $\mathcal{V}(E)$ in terms of the constant $\mathscr{V}_{2N}$, the volume of the hypersphere of unit radius (exercise 3.2).

b/ Using the semi-classical hypothesis that a quantum state occupies a cell of volume h^N in phase space, calculate the number of quantum states of energy less than E (written $\Phi(E)$), and then the density of states $\rho(E)$.

2/ Quantum treatment.– We now suppose that the N oscillators are quantum mechanical. We know that the energy levels of each oscillator are nondegenerate and given by $\varepsilon_n = (n + 1/2)\hbar\omega$ (where n is an integer $\geqslant 0$).

a/ Calculate the number of accessible states of the system when its energy is equal to E.

Indications: We wish to calculate the number of different ways of choosing N nonnegative integers $(n_1, n_2, n_3...n_N)$ such that their sum $\sum_{i=1}^{N} n_i$ equals a given integer M. To do so we use the following method: each choice may be represented by a diagram of n_1 balls, then one bar, then n_2 balls, then one bar, ... The total number of balls is M and the total number of bars is $N - 1$. Permutations of balls and bars each among themselves do not count. Only matter the number of different ways of placing $N - 1$ bars in a linear array of M balls.

c/ Calculate the quantum density of states of the system. Show that, in the limit $E \gg N\hbar\omega$, one recovers the semi-classical result of question (2).

Appendix 2.A: Semi-classical rule for counting states in phase space

When the degrees of freedom can be described in classical terms, the semi-classical rule allows to determine the density of states very efficiently : this is the case for translation degrees of freedom of atomes, but not for a spin $1/2$ which has no classical equivalent.

For a system with D degrees of freedom the phase space of vectors $(q_1, \cdots, q_D, p_1, \cdots, p_D)$ has dimension $2D$. The correspondence between classical and quantum counting of micro-states is ensured by considering that one *quantum state* occupies a volume h^D in *classical phase space*.

Integrated density of states.– Let $H(\{q_i, p_i\})$ be the Hamiltonian governing the dynamics of a system. We denote by $\Phi(E)$ the number of micro-states of energy less than E. In the semi-classical limit, we have

$$\Phi(E) = \frac{1}{h^D} \int_{H(\{q_i,p_i\}) \leqslant E} \prod_{i=1}^{D} \mathrm{d}q_i \mathrm{d}p_i \equiv \frac{1}{h^D} \int \prod_{i=1}^{D} \mathrm{d}q_i \mathrm{d}p_i \; \theta_{\mathrm{H}}\left(E - H(\{q_i, p_i\})\right) \qquad (3.6)$$

where $\theta_{\mathrm{H}}(x)$ is the Heaviside function.

Density of states.– The density of states is given by

$$\rho(E) = \Phi'(E) \qquad (3.7)$$

i.e. $\rho(E)\mathrm{d}E$ represents the number of quantum states of energy in the interval $[E, E + \mathrm{d}E)$.

Indistinguishable particles.– If the system contains N indistinguishable particles (for instance an ideal gas of N particles moving in three-dimensional space, $D = 3N$), we must multiply by an extra factor $1/N!$ to take into account the fact that the particles are indistinguishable (*i.e.* that micro-states differing only by a permutation of particles are equivalent):

$$\Phi_{\mathrm{indist}}(E) = \frac{1}{N!} \Phi_{\mathrm{dist}}(E) \qquad (3.8)$$

Notice, however, that this expression accounts only partially for the symmetrization postulate of quantum mechanics. The full consequences of the latter will be studied in detail in tutorials 8 and 9.

TD 4 : Fundamental postulate and the microcanonical ensemble

4.1 The monoatomic ideal gas and the Sackur-Tetrode formula (*)

We consider a ideal gas of N atoms confined in a box of volume V and we are going to treat it classically.

1/ Remind the definition of the integrated density of states $\Phi(E)$ for the mono-atomic gas (see previous TD) or recalculate it.

2/ Remind the definition of the microcanonical entropy S^*. Explain why we can use the expression

$$S^* \simeq k_B \ln \big[\Phi(E)\big] \tag{4.1}$$

and give its limits. Derive the Sackur-Tetrode formula (1912).

$$S^*(E, V, N) = N k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N} \left[\frac{mE}{3\pi\hbar^2 N} \right]^{3/2} \right) \right] \tag{4.2}$$

3/ Show that S^* can be written as $S^* = 3 N k_B \ln \big(a \Delta x \Delta p / h\big)$, where Δx is a distance and Δp a momentum. Interpret this result.

4/ Calculate the microcanonical temperature T^* and pressure p^*. Derive an expression of the entropy as a function of the number density $n = N/V$ and the de Broglie wavelength $\Lambda_T \stackrel{\text{def}}{=} \sqrt{2\pi\hbar^2/(m k_B T)}$. Discuss the validity of of Eq. 4.2.

Numerical example: Calculate Δx, Δp, and $\Delta x \Delta p / h$ for a helium gas at normal temperature and pressure. Find $S^*/N k_B$.

4.2 Extensivity and Gibbs Paradox (*)

We are going to discuss in details the role of indistinguishability in the entropy calculation of the classical perfect gas.

1/ Extensivity.– Formulate the extensivity property that must be satisfied by the microcanonical entropy $S^*(E, V, N)$ of the gas.

2/ "Distinguishable Atoms".– Toward the end of the 19th century, there was no logical explanation for the factor $1/N!$ related to indistinguishability of the atoms in the calculation of the integrated density of states.

a/ Give the integral $\Phi_{\text{disc}}(E)$ for the density of states of a gas composed of N atoms (you may use exercice 3.3). Calculate the corresponding microcanonical entropy S^*_{dist}.

b/ **Gibbs paradox.**– We consider two identical volumes of the same gas separated by a wall. Calculate the difference between the entropy of this system and the entropy of the system with the wall removed.

$$\Delta S^{\text{mixing}} = S^*_{\text{disc}}(2E, 2V, 2N) - 2 S^*_{\text{disc}}(E, V, N) . \tag{4.3}$$

Why do we say that this result is paradoxal?

c/ **Indistinguishability.**– Compare $S^*_{\text{disc}}(E, V, N)$ to the Sackur-Tetrode formula in Eq. 4.2. Discuss the extensivity in the two cases. Verify that if we calculate the entropy of mixing using $S^*_{\text{indisc}}(E, V, N)$, we have $\Delta S^{\text{mixing}} = 0$.

4.3 Paramagnetic crystal - Negative (absolute) temperatures (*)

We consider a system of N spin 1/2 particles located on the sites of a crystal lattice. Each particle has a magnetic moment $\vec{\mu} = \gamma \vec{S}$, where γ is the *gyro-magnetic factor*. This system is submitted to an uniform magnetic field $\vec{B} = B\vec{u}_z$. We suppose that the interaction between the spins is much smaller than the interaction of the spins with the external magnetic field.

We write $\epsilon_\pm = \mp\epsilon_B$ the energies of the two quantum states of a spin where $\epsilon_B = \gamma\hbar B/2$. In a configuration, we are a going to call N_+ and N_- the spins aligned parallel and anti-parallel to $\vec{B}$.

1/ Give the expression for N_+ and N_- in terms of N, B, ϵ_B, and E (total energy of the system).

2/ Calculate the number of states $\Omega(E, N, B)$ at constant energy. Do we have to take into account indistinguishably?

3/ Derive an expression for the microcanonical entropy S^* of the system when $N_+ \gg 1$ and $N_- \gg 1$. Sketch S as a function of the energy E.

4/ Calculate the microcanonical temperature T^* of the system as a function of the energy, plot it and discuss its sign. Describe the state of the system when $E \to E_{\min}$ and $E \to E_{\max}$ and discuss the sign of T^* in the two cases.
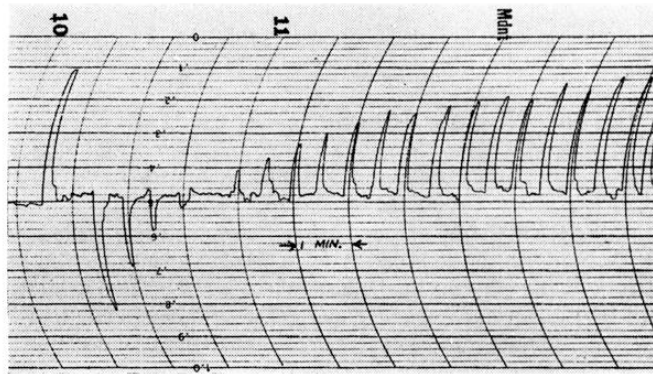
Figure 4.1: *A typical record of nuclear magnetic inversion. The magnetization of the sample is tested every 30s by NMR. Vertical bands on the graph represent 1mn. On the left is sketched a typical signal of normal thermal equilibrium ($T \approx 300$ K) revealing the magnetization of the sample. Subsequently, the magnetic field is reversed during a short time ($T \approx -350K$). The nuclear spins "follow" the field and then relax toward the "normal" thermal equilibrium via a zero magnetization (at this point, the temperature goes from $T = -\infty$ to $T = \infty$). This inversion is observed in lithium fluoride crystals. This behavior is possible because the relaxation time between nuclear spins ($t_1 \sim 10^{-5}$ s) is very short compared to the relaxation time between the spins and the lattice ($t_2 \sim 5$ mn). When the field is rapidly reversed during a time between t_1 and t_2, the system of nuclear spins can reach the thermal equilibrium and exhibit an absolute negative temperature. Reference : E. M. Purcell and R. V. Pound, Phys. Rev. **81**, 279 (1951).*

4.4 The (absolute) negative temperatures are hotter ! (*)

In the previous exercise, we derived the microcanonical temperature for a crystal of nuclear spins. We are going to call this temperature $T^*_{\mathrm{mag}}(E)$ since it is associated to the magnetic energy.

Population inversion corresponding to negative temperatures has been indeed observed in a

crystal of lithium fluoride. In this system, the spin relaxation time, due to spin-spin interactions is very short ($\tau_1 \sim 10^{-5}$s) with respect to the relaxation time due to the interactions between spins and lattice vibrations ($\tau_2 \sim 300$s). As a consequence, the spins can reach some partial equilibrium well before they are ultimately thermalized by the lattice vibrations. In the experiment, the crystal is placed into a magnetic field that is abruptly flipped. As a consequence we are in a state of negative temperature for a time of the order of τ_2.

In this exercise, we are going to model the thermal coupling between the spins and the lattice vibrations. To this end, we are going to describe the lattice vibrations as a collection of $3N$ identical harmonic oscillators (Einstein Model).

$$H_{\mathrm{vib}} = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2 \right) \tag{4.4}$$

We can consider the oscillators as distinguishable as each atom (indistinguishable) is linked to a specific (distinguishable) lattice sites. The vibration are going to be treated classically.

1/ Calculate the number of micro-states accessible for the vibrational energy $\phi_{\mathrm{vib}}(E)$. Derive the associated entropy S^*_{vib} and temperature T^*_{vib}

2/ Discuss the thermal contact between the nuclear spins and the lattice vibrations. In particular, compare the situations in which the initial magnetic temperature $T^*_{\mathrm{mag}}(E)$ is positive and negative. Justify that negative temperatures are hotter than the positive ones.

4.5   Thermal contact between two cubic boxes

Exercice available at `http://lptms.u-psud.fr/christophe_texier/enseignements/` `enseignement-en-licence/l3-physique-statistique/`

4.6   Isothermal and isotropic curves of a perfect gas

Exercice avaialble at `http://lptms.u-psud.fr/christophe_texier/enseignements/` `enseignement-en-licence/l3-physique-statistique/`

REMARK :   See also chapter 5 of : C. Texier & G. Roux, *Physique statistique*, Dunod, 2017.

TD 5 : System in contact with a thermostat – Canonical ensemble

5.1 The crystal of spin $1/2$ (*)

We summarize (quickly) the study of the N identical spin $1/2$ crystal placed at the nodes of a crystal lattice (TD 4). Each spin can be in two quantum states $|\pm\rangle$, of energy $\varepsilon_\pm = \mp\varepsilon_\mathcal{B}$, where $\varepsilon_\mathcal{B} = \gamma\hbar\mathcal{B}/2 \equiv \mathfrak{m}_0\mathcal{B}$. We assume the interactions between the spins to be negligible, which allows to suppose them **independent**. The crystal is in contact with a thermostat that sets its temperature at T.

1/ What are the microstates for a single spin ? And for the crystal ? Justify that the canonical partition function of the crystal is simply connected to that of a spin as : $Z_{\text{cristal}} = (z_{\text{spin}})^N$. What is the probability $p_\pm$ for a *single spin* to be in the quantum state $|\pm\rangle$? Plot these two probabilities as a function of T and give an interpretation.

2/ Calculate explicitly Z_{cristal} then deduce the average magnetic energy of the $\overline{E}^{\text{c}}$ crystal as a function of T. Compare to the microcanonical calculation of T^* based on E (Exercice 4.3).

3/ Give the average magnetization of the crystal $M(T, \mathcal{B})$ (without any further calculations) and plot it as a function of $\mathcal{B}$. Interprete.

4/ Compare with the microcanonical case (TD 4). What is the interest of the canonical formalism?

5.2 Monoatomic ideal gas (*)

We study again the ideal gas (cf. exercice 4.1). We assume that the gas contains N atoms in a fixed volume V but at a fixed temperature T, *i.e.,* we will use the canonical ensemble. We treat the problem **classically**.

1/ Using the semiclassic summation rule in phase space (see appendix), show that the canonical partition function of gas is of the form

$$Z = \frac{1}{N!}(z_{\text{atome}})^N \sim e^N \left(\frac{z_{\text{atome}}}{N}\right)^N \tag{5.1}$$

and express z_{atome} as a function of the **thermal De Broglie length** $\Lambda_T \overset{\text{def}}{=} \sqrt{2\pi\hbar^2/(mk_BT)}$.

A.N. : Calculate Λ_T for Helium atoms at room temperature..

2/ Deduce the free energy of the gas in the thermodynamic limit. Express this result such that it clearly exhibits the extensivity property of the free energy.

3/ Calculate the average energy of the gas as well as its heat capacity. We recall the definition of the heat capacity,

$$C_V \overset{\text{def}}{=} \frac{\partial \overline{E}^{\text{c}}(T, V, N)}{\partial T} \qquad \text{(i.e. } C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} \text{ dans les (horribles) notations de la thermo)} \tag{5.2}$$

Calculate the energy fluctuations of the system, $\text{Var}(E) \overset{\text{def}}{=} \overline{E^2}^{\text{c}} - \left(\overline{E}^{\text{c}}\right)^2$ (recall the relation with C_V). Compare the fluctuations to the average value of the energy.

4/ Calculate the canonical pressure of the system. Provide your comments.

5/ Calculate the canonical entropy of the system. Compare this result to the Sackur-Tetrode formula.

6/ Calculate the chemical potential of the gas μ^c.

7/ Validity of the semiclassical treatment : By analyzing S^c, identify the regime of validity of the semiclassical calculation. Define a scale of density (function of T) over which the present analysis is no longer valid. Equivalently, identify a temperature scale T_* (function of n), below which the classical calculation is not justified. What is the chemical potential at the threshold of validity?

5.3 The diatomic perfect gas (*)

The thermodynamics of a gas of diatomic molecules is studied here. In addition to the obvious physical interest of the exercise, it will allow us to illustrate two important points :

- The factorization of the canonical partition function for **separable** problems.

- The quantum freezing of certain degrees of freedom at low temperature.

Each molecule (two atoms, i.e. 6 degrees of freedom) has three degrees of freedom of translation, two degrees of freedom of rotation and a degree of freedom of vibration. We introduce $\vec{P}$ the total momentum, $\vec{\ell}$ the orbital moment characterizing the rotation of the molecule, and (r, p_r), a couple of canonically conjugated variables describing the vibration of the molecule (relative coordinates). In the vicinity of the equilibrium state for the bond, $r \sim r_*$, the Hamiltonian of a molecule is of the form :

$$H \simeq \frac{\vec{P}^2}{2M} + \frac{\vec{\ell}^2}{2I} + \frac{p_r^2}{2m_r} + \frac{1}{2}m_r\omega^2(r - r_*)^2 - E_{\text{bond}} . \tag{5.3}$$
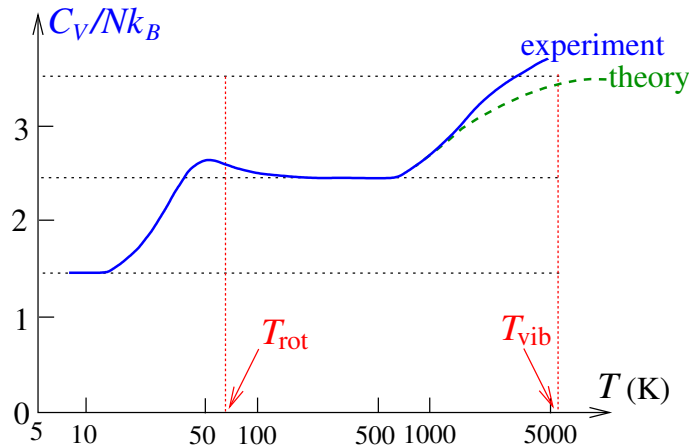
Figure 5.1: *Heat Capacity of a hydrogen gas HD (deuterium-hydrogene).* $T_{\text{rot}} \stackrel{def}{=} \hbar^2/2k_B I$ *et* $T_{\text{vib}} \stackrel{def}{=} \hbar\omega/k_B$. *From : R. Balian, "From microscopic to macroscopic I".*

1/ Give the (quantum) spectra of translation, rotation and vibration energies. Show that the partition function for a molecule can factorize as :

$$z = z_{\text{trans}} \, z_{\text{rot}} \, z_{\text{vib}} \, e^{\beta E_{\text{bond}}} . \tag{5.4}$$

Give the explicit expression of the partition functions (as sums). Recall how the partition function of the gas is expressed in terms of z in the Maxwell-Boltzmann approximation.

2/ The high temperature classical regime.

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a) Calculate the canonical partition function of the gas Z in the semi-classical approximation ($\hbar \to 0$), when all the degrees of freedom are treated classically (either by replacing the sums on the quantum numbers by integrals, or by using directly the semiclassical rule). Discuss the validity of the result (condition(s) on T).

b) Deduce the average energy and then the heat capacity of the gas within this limit. Compare to the experimental data (Fig. 5.1).

3/ Quantum freezing.— At lower temperatures the different degrees of freedom can not always be treated classically.

a) What happens to the average vibration energy in the limit $k_B T \ll \hbar \omega$? Same question for the average energy of rotation when $k_B T \ll \hbar^2/I$.

b) Starting with expressions of partition functions z_{rot} et z_{vib}, give an approximation of the average energies of rotation and vibration for $T \to 0$.

c) Deduce the shape of the heat capacity of the gas as a function of temperature (it will be admitted that $\hbar^2/I \ll \hbar \omega$). Comment the figure 5.1.

5.4   The Langevin paramagnet (*)

We intend to find the equation of state of a paramagnetic material, *i.e.* the relation between the total magnetic moment $\vec{M}$ of the material, the temperature T, and the external magnetic field $\vec{B}$ applied to the material. We consider N independent atoms, fixed at the sites of a crystal lattice. Each atom has a magnetic moment $\vec{\mathfrak{m}}$ of constant modulus, that we treat as a classical vector.

Let us start with a single atom. The spatial orientation of the magnetic moment of each atom is specified by two angles θ and φ. When a magnetic field $\vec{B}$ is applied along the z axis, each atom acquires a potential energy

$$H_{\mathrm{mag}} = -\vec{\mathfrak{m}} \cdot \vec{\mathcal{B}} = -\mathfrak{m}_0 \, \mathcal{B} \cos \theta \, , \tag{5.5}$$

where $\mathfrak{m}_0 = ||\vec{\mathfrak{m}}||$. If each atom has a moment of inertia equal to I, then its dynamics is governed by the Hamiltonian[1]

$$H = \frac{1}{2\,I} \left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2 \theta} \right) + H_{\mathrm{mag}} \, . \tag{5.6}$$

1. Calculate the canonical partition function associated with H. Write the result in the form $z = z_{\mathrm{kin}} z_{\mathrm{mag}}$ où $z_{\mathrm{mag}} = 1$ pour $\mathcal{B} = 0$. Show that $z_{\mathrm{cin}} = \mathrm{Vol}/\widetilde{\Lambda}_T^2$ where $\widetilde{\Lambda}_T$ denotes the thermal length and Vol an accessible volume. Express z_{mag} as a function of $x = \beta \mathfrak{m}_0 \mathcal{B}$.

2. Give the expression for the probability density $w(\theta, \varphi)$ that the magnetic moment points in the direction (θ, φ). Check that the probability density is normalized. Sketch $w(\theta, \varphi)$ *vs.* θ.

3. Calculate the average magnetic moment, $\overline{\mathfrak{m}_z}^{\mathrm{c}}$ per atom. We will refer to $M = N \, \overline{\mathfrak{m}_z}^{\mathrm{c}}$ as the total magnetization of the material.

   [You may use the result given in the appendix and calculate $\partial z/\partial \mathcal{B}$].

4. Discuss the behavior of the magnetization of the paramagnetic material as a function of B and temperature. Show that the high temperature approximation gives **the Curie law** : $M \propto \mathcal{B}/T$

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[1]We recover this result by considering a pendulum of length l and of mass m : in this case $I = ml^2$ and the kinetic energy reads $H_{\mathrm{kin}} = \frac{I}{2}[\dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta]$. Then $p_\theta = \partial H_{\mathrm{cin}}/\partial \dot{\theta} = I\dot{\theta}$ and $p_\varphi = \partial H_{\mathrm{cin}}/\partial \dot{\varphi} = I\dot{\varphi} \sin^2 \theta$.

5.5 Quantum mechanical calculation : Brillouin paramagnetism (*)

We now consider a system of N quamntum mechanical magnetic moments. The Hamiltonian of a particle is given by H_{pot} [Eq. (5.5)]. The magnetic moment $\vec{\mu}$ is now an operator that acts on the quantum states. We call $\vec{J}$ the total angular momentum, which is the sum of the orbital angular momenta and the spins of the electrons for an atom in its ground state. We let J stand for the associated quantum number.
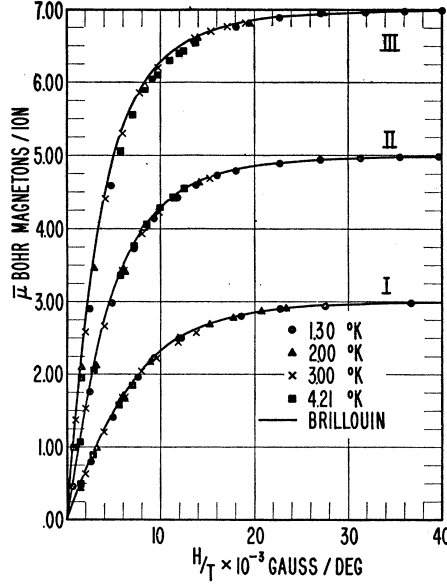

FIG. 3. Plot of average magnetic moment per ion, $\bar{\mu}$ vs H/T for (I) potassium chromium alum ($J=S=3/2$), (II) iron ammonium alum ($J=S=5/2$), and (III) gadolinium sulfate octahydrate ($J=S=7/2$). $g=2$ in all cases, the normalizing point is at the highest value of H/T.

Figure 5.2: *Magnetic moment per ion (in unit of the Bohr magneton) as a function of $\mathcal{B}/T$ for certain paramagnetic ions : (I) Cr^{3+}, (II) Fe^{3+} et (III) Gd^{3+}. In all cases $g = 2$ (because $\ell = 0$). The points are the experimental data and the curves in solid lines correspond to the results obtained using Brillouin functions [from W. E. Henry, Phys. Rev. **88**, 559 (1952)].*

The magnetic moment $\vec{\mathfrak{m}}$ of an atom is related to $\vec{J}$ by :

$$\vec{\mathfrak{m}} = g\mu_B \vec{J}/\hbar , \tag{5.7}$$

where $\mu_B = \frac{q_e \hbar}{2m_e} \simeq -0.927 \times 10^{-23}$ J.T^{-1} is the **Bohr magneton**. The Landé factor g is a dimensionless constant typically of order one [2].

1. What are the eigenvalues and the eigenvectors of the Hamiltonian of an atom (remember that the projection J_z of the angular momentum of an atom may take the values $m\hbar$ avec $m \in \{-J, -J+1, .., J\}$) ?

2. Calculate the partition function Z of an atom as a function of J and $y = \beta g \, |\mu_B| \, JB$. Determine Z for the special case $J = 1/2$.

---

[2] If the angular momentum is due only to the electron spins, we have $g = 2$. If it is due only to the orbital angular momentum, we have $g = 1$, and if it is of mixed origin, then $g = 3/2 + [S(S+1) - L(L+1)]/[2J(J+1)]$, where S and L are the quantum nimbers of the spin and the orbital angular momentum, respectively. J is the quantum number associated with the total angular momentum $\vec{J} = \vec{L} + \vec{S}$. The three numbers obeys at the triangle inequality. See problem 13.1 de C. Texier, *Mécanique quantique*, Dunod, 2015 (2nde éd.).

3. What is the probability for an atom to be in the quantum state of quantum number m ?

4. Calculate $\overline{\mathfrak{m}_x}^{\,c}$ and $\overline{\mathfrak{m}_z}^{\,c}$ for arbitrary J and for $J = 1/2$. Deduce the magnetization M. Find an expression for M in terms of the Brillouin function

$$\mathcal{B}_J(y) \stackrel{\text{def}}{=} \frac{\mathrm{d}}{\mathrm{d}y} \ln \left\{ \sum_{m=-J}^{J} e^{\pm my/J} \right\} = \frac{1 + \frac{1}{2J}}{\text{th}\left[(1 + \frac{1}{2J})y\right]} - \frac{\frac{1}{2J}}{\text{th}(\frac{y}{2J})} . \tag{5.8}$$

Near the origin $\mathcal{B}_J(y) = \frac{J+1}{3J} y + \mathcal{O}(y^3)$. Show that the high temperature approximation gives Curie's law. Show that at low temperature the quantum mechanical result is very different from the classical result obtained in 5.4 (except for large values of J).

5. Determine from the experimental results sketched above the value of J for each ion.

5.6 Ideal, confined, non-ideal, etc... gases.

We consider a gas of N indistinguishable particles without internal degrees of freedom, enclosed by a box of volume V in contact with a thermostat at temperature T

1/ Classical canonical distribution

a) Recall how microstates are described classically. The classical dynamic of the system is given by the Hamiltonian

$$\mathcal{H}(\{\vec{r}_i, \vec{p}_i\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + U(\{\vec{r}_i\}) . \tag{5.9}$$

Give the expression for the canonical distribution, to be denoted by $\rho^c(\{\vec{r}_i, \vec{p}_i\})$.

b) How can we obtain the distribution function f that characterizes the position and momentum of a single particle? We define $f(\vec{r}, \vec{p})\mathrm{d}\vec{r}\mathrm{d}\vec{p}$ as the probability for a particle to have a position in a volume $\mathrm{d}\vec{r}$ at $\vec{r}$ and a momentum in a volume $\mathrm{d}\vec{p}$ at $\vec{p}$.

2/ Monoatomic ideal gas

a) Justify briefly that the partition fonction can be factorized according to

$$Z = \frac{1}{N!} z^N \tag{5.10}$$

where z is the partition function for one particle (we recall that $z = V/\Lambda_T^3$).

b) Calculate the distribution function $f(\vec{r}, \vec{p})$ explicitly. Derive Maxwell's law for the distribution of the particle velocities in the gas.

3/ Other gases.– In this question, we want to test the validity in more general cases of the results obtained for the monoatomic gas. For each of the following situations, answer these two questions:

- Does the factorization (5.10) still hold?

- Is the velocity distribution given by Maxwell's law?

a) Gas confined by an external potential $U_{\text{ext}}(\vec{r})$.
Application: a rubidium gas is trapped in a harmonic potential created by several lasers. Discuss the density profile of the gas.

b) Gas of interacting particules (nonideal gas), *i.e.* $U \neq 0$.

c) Gaz de particules relativistes, *i.e.* $E = \sqrt{\vec{p}^2 c^2 + m^2 c^4}$.

d) Relativistic ideal gas, *i.e.* $E = ||\vec{p}|| c$.

Calculate z explicitly in this case (express z as $z = V/\Lambda_r^3$ where Λ_r is the relativistic thermal wavelength). Derive the energy of the gas and its equation of state.

4/ What is the limit of the classical approximation, *i.e.* of equation (5.10) ? In which cases will quantum effects will dominate (if $T \nearrow$ or $\searrow$? If $n = N/V \nearrow$ or $\searrow$?)

5.7 Partition function of a particule in a box – the role of boundary conditions

The purpose of the exercise is to study the effect of boundary conditions on thermodynamics in the case of a particle in a box (unidimensional to simplify). In other words, we are interested in the effect of the **quantification of the energy spectrum** on the thermodynamic properties.

Exercice available at `http://lptms.u-psud.fr/christophe_texier/enseignements/`
`enseignement-en-licence/l3-physique-statistique/`

To go further : exercice 3.4 of C. Texier & G. Roux, *Physique statistique*, Dunod, 2017.

5.8 Gases of indistinguishable particles in a harmonic well

The purpose of the exercise is to study the effect of indiscernability (i.e., the symmetrization postulate of quantum mechanics) on the thermodynamic properties of the system. We want to analyze in detail the **validity of semiclassical treatment** in the Maxwell-Boltzmann approximation, in particular to identify on which temperature scale this treatment is valid, in a case where the exact calculation of the partition function identical particles is possible.

Exercice available at `http://lptms.u-psud.fr/christophe_texier/enseignements/`
`enseignement-en-licence/l3-physique-statistique/`

To go further : Problem 11.1 of C. Texier & G. Roux, *Physique statistique*, Dunod, 2017.

Appendix 5.A : Semiclassical summation rule the phase space

In the canonical ensemble the summation rule discussed in appendix 3.A takes the following form: for a system with D degrees of freedom and Hamiltonian $H(\{q_i, p_i\})$ the partition function is given by :

$$\boxed{Z_\beta = \frac{1}{h^D} \int \prod_{i=1}^{D} \mathrm{d}q_i \mathrm{d}p_i \, \mathrm{e}^{-\beta H(\{q_i,p_i\})}}$$

(5.11)

If the particles are indistinguishable, the partition function acquires an additional $1/N!$ factor :

$$Z_\beta^{\mathrm{indisc}} = \frac{1}{N!} Z_\beta^{\mathrm{disc}} \qquad \text{(Maxwell-Boltzmann approximation)}.$$

(5.12)

Annexe 5.B : Canonical average of a physical quantity

Let X be a physical quantity with conjugate parameter ϕ, *i.e.,* there is a term $\mathrm{d}E = -X \mathrm{d}\phi$ in the expression of the energy. The canonical average of X is obtained by deriving the thermodynamic potential $F(T, N, \cdots, \phi, \cdots)$ with respect to the "conjugate force" ϕ :

$$\boxed{\overline{X}^{\mathrm{c}} = -\frac{\partial F}{\partial \phi}}$$

(5.13)

Exemple : $X \to M$ is the magnetization, $\phi \to B$ the magnetic field. The mean magnetization is given by $\overline{M}^{\mathrm{c}} = -\frac{\partial F}{\partial B}$.

TD 6 : Kinetic theory

6.1 Maxwell Distribution (*)

We consider a gas in equilibrium at the temperature T in an enclosure of volume V. We place ourselves within the framework of classical mechanics.

1/ Describe the microstates of the system. Give the expression of the canonical distribution in this case.

2/ We introduce $f(\vec{r}, \vec{p})$, the density of states in phase space of *an atom*, which we choose to normalize as $\int \mathrm{d}^3\vec{r}\mathrm{d}^3\vec{p}\, f = N$. Justify that it has the following form $f(\vec{r}, \vec{p}) = n\, w(\vec{p})$ where $n = N/V$ is the average density in the physical space. Give the expression of $w(\vec{p})$ and also give the velocity distribution $p(\vec{v})$.

3/ Calculate the average values $\langle v_x \rangle$, $\langle v_y \rangle$, $\langle v_z \rangle$, $\langle v_x^2 \rangle$, $\langle v_y^2 \rangle$, $\langle v_z^2 \rangle$, $\langle v_x v_y \rangle$, $\langle v_x^2 v_y^2 \rangle$ et $\langle \varepsilon_c \rangle$, où $\varepsilon_c = \frac{1}{2}m\vec{v}^2$.

4/ Marginal law of the modulus $v = ||\vec{v}||$.– Deduce from $p(\vec{v})$ the probability $q(v)\,\mathrm{d}v$ to find the modulus of the velocity between v and $v + \mathrm{d}v$ (use draw the isotropy of p and go to "spherical coordinates"). Check that the probability distribution so obtained is well normalized. Calculate the average value $\langle v \rangle$. Compare to the most likely value of v, the "typical value" v_{typ}. Evaluate the standard deviation of v, $\sigma_v = \sqrt{\langle v^2 \rangle - \langle v \rangle^2}$. Draw carefully $q(v)$ and indicate $\langle v \rangle$, v_{typ} and σ_v on the plot.

6.2 Pressure of a gas (*)

We continue the study of the gas initiated in the exercise 6.1. We start from the microscopic description (kinetic theory) and study the mechanical origin of the pressure exerted on a wall of the whole volume. The atoms are described by the distribution function $f(\vec{r}, \vec{p}) = n\, w(\vec{p})$.

1/ We want to calculate the average force $\vec{F}$ which is exerted on an area element $\mathcal{A}$ of a plane wall located in $x = 0$ (the gas being contained on the negative x side). Justify that if we call $\mathrm{d}\vec{\Pi}^{(+)}$ (resp. $\mathrm{d}\vec{\Pi}^{(-)}$) the momentum which crosses on average the wall in the direction of the increasing x (resp. decreasing) during a time $\mathrm{d}t$ we have :

$$\vec{F} = \frac{1}{\mathrm{d}t}\left(\mathrm{d}\vec{\Pi}^{(+)} - \mathrm{d}\vec{\Pi}^{(-)}\right). \tag{6.1}$$

2/ Show that

$$\mathrm{d}\vec{\Pi}^{(+)} = \frac{n\,\mathcal{A}\,\mathrm{d}t}{m}\int_{p_x>0}\mathrm{d}^3\vec{p}\, p_x\, \vec{p}\, w(\vec{p})\,. \tag{6.2}$$

Calculate also $\mathrm{d}\vec{\Pi}^{(-)}$ and deduce the expression of $\vec{F}$ as an integral in momentumm space.

3/ Show that only the component of $\vec{F}$ normal to the wall is non-zero. Infer that The pressure P is related to the average velocity $\langle \vec{v}^2 \rangle$ and to the kinetic energy $E_c = N\langle \varepsilon_c \rangle$ by :

$$P = \frac{1}{3}\,n\,m\,\langle \vec{v}^2 \rangle \qquad \text{et} \quad PV = \frac{2}{3}\,E_c\,. \tag{6.3}$$

Deduce the equation of state of the gas.

4/ We now consider a gas of it photons. We recall that the photons of momentum $\vec{p}$ have a velocity c and a kinetic energy $\varepsilon_c = c\,||\vec{p}||$. As before, we consider that photons have a uniform density and are characterized by their momentum distribution $w(\vec{p})$. By following for the gas of photons, the same steps than those just followed for the conventional gas, show that we get :

$$PV = \frac{1}{3}\,E_c\,.$$

By calculating $\langle \varepsilon_c \rangle$, deduce the equation of state.

6.3 Effusion

A monoatomic gas is confined to a volume V. A small hole of surface $\mathcal{A}$ is made in the wall. Atoms can escape through this hole. The hole is sufficiently small so that we can assume that the gas is at all times in a state of thermal equilibrium (this hypothesis will be discussed later in the questions 2 and 4). We may then, in particular, introduce a time-dependent temperature and time-dependent pressure.

1/ The gas has temperature T and the atomic velocities are described by the Maxwell distribution. Give the number of atoms $\mathrm{d}N$ exiting the volume during time interval $\mathrm{d}t$. Discuss the dependence of $\mathrm{d}N/\mathrm{d}t$ on N/V and T

2/ Effusion from a volume with fixed temperature. Assume that the volume is in contact with a thermostat which maintains its temperature. Atoms escape from the volume into vacuum.

(a) Discuss the time dependence of the number of atoms N left in the volume.

(b) Consider a gas of helium in a volume $V = 1\,\ell$ at room temperature. The hole has an area $\delta S = 1\,\mu\mathrm{m}^2$. How long does it take for half of the atoms to leave the box?

3/ Effusion from an adiabatic wall. We now analyse the effusion problem in a situation where there is no heat exchange between the box and the external world (adiabatic walls). We will see that then the temperature of the gas in the box will decrease with time.

(a) Calculate the energy loss of the gas in the box during time interval $\mathrm{d}t$. We note $\mathrm{d}E/\mathrm{d}t$ the energy rate lost by the gas per unit time. Calculate the lost energy per atom, $(\mathrm{d}E/\mathrm{d}t)/(\mathrm{d}N/\mathrm{d}t)$? Comment this result.

(b) We set $\lambda = \frac{\mathcal{A}}{V}\sqrt{k_B/(2\pi m)}$. Show that the evolution of the temperature and the number of particles in the box is controlled by the two differential equations :

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\lambda}{3}\,T^{3/2}\,, \quad \frac{\mathrm{d}N}{\mathrm{d}t} = -\lambda\,N\,T^{1/2}\,.$$

(c) Solve this system of coupled nonlinear differential equations. Compare with the solution of question **2**.

4/ Effusion between two thermostated boxes. Two boxes (1 and 2) contain a monatomic gas of same nature. They do not exchange heat and energy transfer may only occur through particle exchange through a little hole connecting the two boxes. The temperature T_1 of box 1 is maintained by a thermostat, and similarly for temperature T_2 of box 2. We denote by P_1 and P_2 the pressures in the two boxes.

(a) Find a relation between temperatures and pressures expressing *stationarity*

(b) We assume a stationnary regime. We note I_N the common value of the particle current from the chamber 1 to the chamber 2 and from the chamber 2 to the chamber 1. Justify that there is then a current of energy I_E from the hot source (let's say the enclosure at the temperature T_2) towards the cold source (the enclosure with temperature T_1). Express I_E as a function of I_N and $T_2 - T_1$.

(c) If the system were in a state of thermodynamic equilibrium, remember what would be the condition of thermodynamic equilibrium. Deduce an equation connecting temperatures and pressures. Why is this condition different from that of question 1 ? (we can use the result of question 4.a).

5/Uranium enrichment. We consider a gas of uranium hexafluoride UF_6 in a box of volume V pierced by a little hole. The two isotopes ^{238}U and ^{235}U are present in nature in proportions 99.3% and 0.7% respectively. We denote by N_1 and N_2 the number of molecules of isotope ^{238}U and ^{235}U, respectively.

(a) Show that the proportion of isotopes ^{238}U and ^{235}U in the gas that has left the box is not the same.

(b) How many times should the effusion process be repeated in order to reach a proportion of 2.5% of ^{235}U ? The molar mass of fluor is 19 g.

TD 7 : Thermodynamics of harmonic oscillators

7.1 Lattice vibrations in a solid (*)

The quantification of the spectrum of energies leads to the possible **freezing** of certain degrees of freedom (at low temperature). We will see that this observation makes it possible to understand the low temperature behavior of the heat capacity of solid bodies.

A. Preliminary: : vibrations of a diatomic molecule– We start by analyzing the spectrum of a **single** one-dimensional harmonic oscillator, which can for example model the vibrations of a diatomic molecule. We recall that the spectrum of the energies of a harmonic oscillator of frequency ω is given by

$$\varepsilon_n = \hbar\omega \left(n + \frac{1}{2} \right) \qquad \text{pour } n \in \mathbb{N} \, . \tag{7.1}$$

1/ Calculate the canonical partition function of an harmonic oscillator.

2/ Deduce the average energy $\bar{\epsilon}^c$ and the average occupation number $\bar{n}^c$. Analyze the classical limit($\hbar \to 0$) of $\bar{\epsilon}^c$. Give a physical interpretation.

3/ Express the specific heat in the form $c_V(T) = k_B \, f(\hbar\omega/k_B T)$, where $f(x)$ is a dimensionless function. Interpret physically the limit behavior for $T \to 0$ and for $T \to \infty$.

B. Einstein model (1907).– We consider a solid of N atoms, each vibrating around its equilibrium position (a site of the crystal lattice). The (quantum and/or thermal) fluctuations induce motions of atoms around their equilibrium position which we assume small. Following a rough model proposed by Einstein, we model the vibration energy of a solid as a set of $3N$ independent and **discernable** [3] one-dimension harmonic oscillators with the same pulsation ω.

1/ Using the results of part **A**, give (without further calculation) the expression for the partition function describing lattice vibrations.

2/ Deduce the total energy of the $3N$ oscillators (the result for $T \to \infty$ may be obtained more easily) and the vibrational contribution $C_V^{(\text{Einst.})}(T)$ to the heat capacity of the solid.

3/ Compare the limiting behavior of the heat capacity $C_V^{(\text{Einst.})}$ in Einstein's model with the experimental results (see Figure 7.1):

- High temperature $(T \to \infty)$: $C_V \to 3Nk_B$ (Dulong & Petit's law).

- Low temperature $(T \to 0)$: $C_V \simeq a \, T + b \, T^3$ with $a \neq 0$ for an electric conductor [4] and $a = 00$ for an insulator.

C. The Debye model(1912).– The weakness of Einstein's model, at the origin of the discrepancy between the theoretical expression $C_V^{(\text{Einst.})}(T \to 0)$ and the experimental observations, lies in the assumption that all oscillators have the same frequency, (*i.e.,* that atoms are independent). A more realistic model should account for the fact that, although the atoms may be described as identical quantum oscillators, they are **coupled** (strongly interacting due to the chemical bonds). Nevertheless, the energy may be written as a quadratic form which may in principle diagonalized, that is, rewritten in the form

$$H = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega_i^2 \, q_i^2 \right) \tag{7.2}$$

---

[3]They are discernable because each one is attached to a specific lattice site (however there are $N!$ different ways to attach the indiscernable atoms to the discernable sites.

[4]The linear contribution $C_V^{(\text{elec})} \simeq a \, T$ is related to the electronic contribution to the energy of the crystal. See for example the chapter 12 of : C. Texier & G. Roux, *Physique statistique*, Dunod, 2017.

where (q_i, p_i) are pairs of conjugate coordinates associated with the *vibrational modes* of the crystal (like the modes of a vibrating string). The crystal is characterized by a full spectrum of distinct eigenfrequencies $\{\omega_i\}$ that form a continuous spectrum. The distribution of the eigenfrequencies is called the spectral density $\rho(\omega) = \sum_i \delta(\omega - \omega_i)$.

1/ Specific heat.– Express the specific heat *formally* as a sum of contributions of vibrational eigenmodes.

2/ Densité spectrale du modèle de Debye.– 2/ A few properties of the spectral density.– The spectral density $\rho(\omega)$ has a finite support $[0, \omega_D]$, where ω_D is the Debye frequency.

a) What is the origin of the upper cutoff and what is the order of magnitude of the wavelength associated with ω_D ?

b) Give a sum rule for $\int_0^{\omega_D} \rho(\omega) d\omega$.

c) In the Debye model we assume that the spectral density has the simple form

$$\rho(\omega) = \frac{3V}{2\pi^2 c_s^3} \omega^2 \qquad \text{for } \omega \in [0, \omega_D] \tag{7.3}$$

Explain the origin of the behavior $\rho(\omega) \propto \omega^2$. Applying the sum rule, find a relation between ω_D, the mean atomic density N/V, and the sound velocity c_s (compare to the result of question *a*).

3/ Limiting behavior of $C_V(T)$.

a) Justify the representation $C_V(T) = k_B \int_0^{\omega_D} d\omega \, \rho(\omega) \, f(\hbar\omega/k_B T)$. Deduce the high temperature behavior and compare to $C_V^{(\text{Einst.})}$.

b) Justify that in the $T \to 0$ limit only the low frequency behavior of $\rho(\omega)$ is important. Deduce the low temperature behavior of $C_V(T)$. Compare to $C_V^{(\text{Einst.})}$ and explain the difference physically. Compare to the experimental data of figure 7.1.
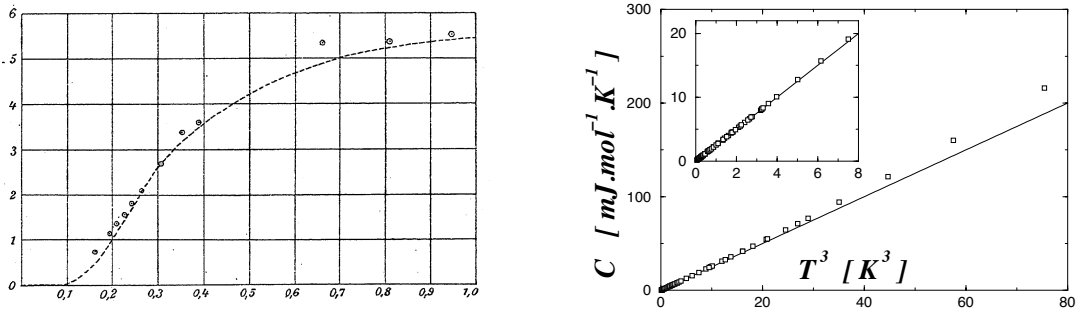

Figure 7.1: Left : *Specific heat of diamond (in cal.mol^{-1}.K^{-1}). Experimental values are compared to the curve resulting from the Einstein model by setting $\theta_E = \hbar\omega/k_B = 1320$ K (from A. Einstein, Ann. Physik **22**, 180 (1907)).* Right : *Specific heat of solid argon as a function of T^3 (from L. Finegold and N.E. Phillips, Phys. Rev. **177**, 1383 (1969)). The straight line is a fit to the experimental data. Insert: zoom onto the low temperature region.*

7.2 Thermodynamics of electromagnetic radiation (*)

We consider a cubic box of volume V containing electromagnetic energy. The system is supposed in thermodynamic equilibrium.

A. General.

1/ Recall how the **eigenmodes** of the electromagnetic field in vacuum are labeled.

2/ Electromagnetic energy.– Using the results of part **A** of Exercice 7.1, express the average electromagnetic energy as a sum over the modes: $\overline{E}^{\mathrm{c}}_{\mathrm{e-m}} = \sum_{\mathrm{modes}} \overline{\epsilon}^{\mathrm{c}}_{\mathrm{mode}}$. Identify the contribution of the vacuum, E_{vacuum} ($= \lim_{T \to 0} \overline{E}^{\mathrm{c}}_{\mathrm{e-m}}$).

3/ Radiation energy.– Radiation corresponds to *excitations* of electromagnetic field: $\overline{E}^{\mathrm{c}}_{\mathrm{radia}} = \overline{E}^{\mathrm{c}}_{\mathrm{e-m}} - E_{\mathrm{vacuum}}$. Identify the contribution of each mode.

4/ Eigenmode density.– Calculate the spectral density $\rho(\omega)$ of eigenfrequencies in the box.

5/ Planck's law.– Writing the energy density (per unit of volume) as an integral over the frequencies, $\frac{1}{V}\overline{E}^{\mathrm{c}}_{\mathrm{radia}} = \int_0^\infty \mathrm{d}\omega\, u(\omega; T)$, recover Planck's law for the spectral energy density $u(\omega; T)$. Plot $u(\omega; T)$ as a function of ω for two temperatures. Interpret physically the expression in terms of the average number of excitations in each mode (*i.e.,* in terms of the number of photons).

6/ The Stefan-Boltzmann law.– Calculate the photon density $n_\gamma(T)$ and the radiation energy density $u_{\mathrm{tot}}(T) = \int_0^\infty \mathrm{d}\omega\, u(\omega; T)$.

B. Cosmic Microwave Background Radiation.– About $380\,000$ years after the big bang atoms formed and matter became eletrically neutral, *i.e.,* light and matter decoupled: the universe became "transparent" for radiation. The period between $380\,000$ year and 100–200 million years, the time of formation of the first stars and galaxies, is referred to as the "**dark ages**" of the universe. After matter-light decoupling, the "Cosmic Microwave Background Radiation" (CMB or CMBR) has maintained its equilibrium distribution while its temperature has decreased due to the expansion of the universe.

1/ Today, at time $t_0 \approx 14 \times 10^9$ years, the CMBR temperature is $T = 2.725$ K. Calculate the corresponding photon density $n_\gamma(T)$ (in mm^{-3}) and the energy density $u_{\mathrm{tot}}(T)$ (in eV.cm^{-3}).

2/ "Dark ages" The expansion of the universe between $t_c \approx 380\,000$ years and today has been mostly dominated by the energy of nonrelativistic matter, which leads to the time dependence of the CMBR temperature according to[5] $T(t) \propto t^{-2/3}$. Deduce $n_\gamma(T)$ (in μm^{-3}) and $u_{\mathrm{tot}}(T)$ (in eV μm^{-3}) at time t_c.

(Compare this to the temperature at the surface of the sun corresponding to the emitted radiation, *i.e.* $T = 5700$ K).

7.3 Equilibrium between matter and light, and spontaneous emission

In a famous article few years before the birth of quantum mechanics,[6] Einstein showed that consistency between quantum mechanics and statistical mechanics implies an imbalance between the absorption and emission probability of light between two atomic (or molecular) levels. The emission probability is larger than the absorption probability due to the phenomenon of **spontaneous emission**, which originates in the quantum nature of the electromagnetic field.

1/ Emission and absorption.– We focus on two quantum levels $|g\rangle$ (ground state) and $|e\rangle$ (excited state) of an atom (or a molecule). The energy gap is $\hbar\omega_0$. Denote by $P_g(t)$ and $P_e(t)$, the probability at time t for the atom to be in state $|g\rangle$ and state $|e\rangle$, respectively.

- In the vacuum, the atom in its excited state falls back to its ground state at a *rate* $A_{e \to g}$ (spontaneous emission).

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[5]Before t_c, the expansion of the universe was more dominated by the radiation energy, which leads to $T(t) \propto t^{-1/2}$.

[6]Albert Einstein, "Zur Quantentheorie der Strahlung", Physikalische Zeitschrift **18**, 121–128 (1917). The article has been reproduced in: A. Einstein, *Œuvres choisies. 1. Quanta*, Seuil (1989), Papers selected and presented by F. Balibar, O. Darrigol & B. Jech.

- When submitted to monochromatic radiation, the atom in its excited state falls back to its ground state with *rate* $A_{e\to g} + B_{e\to g}I(\omega_0)$ (spontaneous and stimulated emission), where $I(\omega_0)$ is the intensity of the radiation field at frequency ω_0.

- The transition rate between the ground state and the excited state is $B_{g\to e}I(\omega_0)$ (absorption).

a) Write down the pair of coupled differential equations for $P_g(t)$ and $P_e(t)$.

b) Derive the *equilibrium* condition.

2/ Thermodynamic equilibrium for matter.– The multiple processes for absorption and emission are responsible of a thermal equilibrium state between light and matter. In this case, the equilibrium probabilities $P_g^{(eq)}$ and $P_e^{(eq)}$ correspond to the canonical distribution. Provide $P_g^{(eq)}/P_e^{(eq)}$.

3/ Thermal equilibrium for radiation.– Assuming thermal equilibrium, recall the expression for the spectral density (Planck's law) $u(\omega;T)$ (*i.e.* Vol $\times\, u(\omega;T)\mathrm{d}\omega$ is the contribution to the energy of radiation of the frequencies $\in [\omega, \omega + \mathrm{d}\omega]$). Henceforth we will assume that the field intensity is given by Planck's law, $I(\omega_0) = u(\omega_0;T)$.

4/ Relation between spontaneous emission and stimulated emission/absorption.–

a) Analyze the high temperature behavior of the equation obtained in 1.b and show that $B_{e\to g} = B_{g\to e}$.

From here on we will simply denote the Einstein coefficients that describe spontaneous and stimulated emission/absorption by $A \equiv A_{e\to g}$ and $B \equiv B_{e\to g} = B_{g\to e}$.

b) Show that $A/B \propto \omega_0^3$.

c) Why is it easier to make a MASER[7] than a LASER ?[8]

This first prediction by Einstein (1917) on the spontaneous emission rate A was confirmed only at the end of the 1920s with the development of quantum electrodynamics; in the framework of this theory Dirac proposed the first microscopic theory for spontaneous emission. [9]

Appendix :

$$\int_0^\infty \mathrm{d}x\,\frac{x^{\alpha-1}}{\mathrm{e}^x - 1} = \Gamma(\alpha)\,\zeta(\alpha) \qquad\qquad \int_0^\infty \mathrm{d}x\,\frac{x^4}{\mathrm{sh}^2 x} = \frac{\pi^4}{30} \tag{7.4}$$

(you may deduce the second integral from the first one for $\alpha = 4$). We have $\zeta(3) \simeq 1.202$ and $\zeta(4) = \frac{\pi^4}{90}$.

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[7] Microwave Amplification by Stimulated Emmission of Radiation

[8] The first ammonia MASER was built in 1953 by Charles H. Townes, who adapted the techniques to light in 1962 and received the Nobel prize in 1964.

[9] P. A. M. Dirac, *The quantum theory of the emission and absorption of radiation*, Proc. Roy. Soc. London A**114**, 243 (1927).

TD 8 : Grand Canonical ensemble
(Systems in contact with a particle reservoir)

8.1 Ideal Gas (*)

We consider an ideal gas at thermodynamic equilibrium in a volume V. We fix the temperature T and chemical potential μ.

1/ Extensivity.– Show that the grand potential may be written as

$$J(T, \mu, V) = V \times j(T, \mu) . \tag{8.1}$$

Discuss the physical interpretation of the "volumetric density of the grand potential" j.

2/ Monatomic classical ideal gas.– We consider a dilute gas of particles, for which we may assume that the Maxwell-Boltzmann approximation is justified. For this question *no supplementary hypothesis* (the number of the degrees of freedom, their relativistic or nonrelativistic nature, their dynamics, etc.) will be needed.
We introduce z, the single particle partition function. Justify that $z \propto V$.
Show that the grand canonical partition function is

$$\Xi = \exp\left[e^{\beta\mu} z\right] . \tag{8.2}$$

3/ Deduce $\overline{N}^{\mathrm{g}}$ and p^{g}. Show that, under this minimal hypothesis, it is possible to derive the equation of state of the ideal gas, $pV = Nk_BT$.

4/ Energy.– We denote $\bar{\varepsilon}^{\mathrm{c}}$ the mean energy per particle. Show that

$$\overline{E}^{\mathrm{g}} = \overline{N}^{\mathrm{g}} \, \bar{\varepsilon}^{\mathrm{c}} . \tag{8.3}$$

Using $\mathrm{Var_g}(E) = \left(-\frac{\partial}{\partial\beta} + \frac{\mu}{\beta}\frac{\partial}{\partial\mu}\right)\overline{E}^{\mathrm{g}}$, show that

$$\mathrm{Var_g}(E) = \overline{N}^{\mathrm{g}} \, \overline{\varepsilon^2}^{\mathrm{c}} \tag{8.4}$$

Compare with the variance of the energy in the canonical ensemble.

5/ Entropy.– Show

$$S^{\mathrm{g}} = \overline{N}^{\mathrm{g}} \, k_B \left(1 - \frac{\partial \ln z}{\partial \ln \beta} - \beta\mu\right) . \tag{8.5}$$

6/ Justify $z \propto V$. Write $z(T, V) = V/\Lambda_T^3$. Express Λ_T (up to a dimensionlesss factor) for non relativistic particles ($\varepsilon = \vec{p}^2/(2m)$) and ultra-relativist particles ($\varepsilon = ||\vec{p}||c$). Recover the expression of $\mu^{\mathrm{c}}(T, n)$ (using **3**). Deduce that the entropy (8.5) coincides with Sackur-Tétrode formula, i.e. recover the "equivalence of ensembles".

8.2 Adsorption of an ideal gas on a solid interface (*)

We consider a container of volume V filled with a monatomic ideal gas of indistinguishable atoms. This gas is in contact with a solid interface that may adsorb (trap) the gas atoms. We model the interface as an ensemble of A adsorption sites. Each site can adsorb only one atom, which then has an energy $-\epsilon_0$
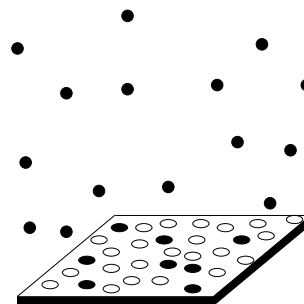
The system is in equilibrium at a temperature T and we model the adsorbed atoms, *i.e.* the adsorbed phase, as a system with a fluctuating number of particles at fixed chemical potential μ and temperature T. The gas acts as a reservoir.

1/ Derive the grand-canonical partition function ξ_{trap} for a single adsorption site. Deduce the grand-canonical partition function $\Xi(T, A, \mu)$ for all atoms adsorbed on the surface.

2/ We will now explore an alternative route. Derive the canonical partition function $Z(T, A, N)$ of a collection of N adsorbed atoms (Note: the number of adsorbed atoms N is much smaller than the number of sites A). Recover the results for $\Xi(T, A, \mu)$ obtained in the previous question.

3/ Calculate the average number of adsorbed atoms $\overline{N}$ as a function of ϵ_0, μ, A, and T. From this, derive the occupation probability $\theta = \overline{N}/A$ of an adsorption site.

4/ The chemical potential μ is fixed by the ideal gas. This may be used to deduce an expression for the site occupation probability θ as a function of the gas pressure P temperature T (note that the number of atoms N is much smaller than the number N_{gas} of gas atoms).
We define a parameter

$$P_0(T) = k_B T \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \exp\left\{ -\frac{\epsilon_0}{k_B T} \right\} \ ,$$

and will express θ as a function of P and $P_0(T)$.

5/ Langmuir isotherm.– How does the curve $\theta(P)$ behave for different temperatures?

6/ (A question for the brave) Calculate the variance σ_N that characterizes the fluctuations of N around its average value. Remember that

$$\sigma_N^2 = \overline{(N - \overline{N})^2} = \overline{N^2} - \overline{N}^2$$

Comment on this result.

8.3 Fluctuations of energy

It has been shown in the main lecture that in the thermodynamic limit, there is equivalence between the thermodynamic properties predicted in the context of the different ensembles. This results in relations between averages in the canonical and grand canonical means, for example.

$$\overline{E}^{\text{g}}(T, V, \mu) = \overline{E}^{\text{c}}\left(T, V, \overline{N}^{\text{g}}(T, V, \mu)\right) \qquad \text{in the thermodynamic limit} \qquad (8.6)$$

We will study what is happening with fluctuations.

A. Probabilistic preliminaries (optional)**.**— Consider a random variable X and its generating function $g(k) \stackrel{\text{def}}{=} \langle e^{kX} \rangle$. By studying the $k \to 0$ limit, show that $\text{Var}(X) = \left. \frac{\partial^2 \ln g(k)}{\partial k^2} \right|_{k=0}$.

B. Canonical ensemble.— We note $\{E_\ell\}$ the energies of the microstates of the system.
   Justify that the canonical variance of energy is given by $\text{Var}_{\text{c}}(E) = \left(-\partial_\beta \right)^2 \ln Z$, where Z is the canonical partition function. Relate $\text{Var}_{\text{c}}(E)$ to $\overline{E}^{\text{c}}$ and deduce the relation

$$\text{Var}_{\text{c}}(E) = k_B T^2 \, C_V \ . \qquad (8.7)$$

C. Grand canonical ensemble .— We now demonstrate a formula relating the variances of energy in the canonical and grand canonical ensembles:

$$\boxed{\text{Var}_{\text{g}}(E) = \text{Var}_{\text{c}}(E) + \left(\frac{\partial \overline{E}^{\text{c}}}{\partial N} \right)^2 \text{Var}_{\text{g}}(N)} \qquad (8.8)$$

1/ Give a heuristic interpretation of this relationship.

2/ We note Ξ the grand partition function.. Justify the relation

$$\mathrm{Var_g}(E) = \left(-\frac{\partial}{\partial\beta} + \frac{\mu}{\beta}\frac{\partial}{\partial\mu} \right)^2 \ln\Xi \tag{8.9}$$

and relate $\mathrm{Var_g}(E)$ to $\overline{E}^{\mathrm{g}}$.

3/ Using (8.6), relate the partial derivatives $\partial\overline{E}^{\mathrm{g}}/\partial T$ and $\partial\overline{E}^{\mathrm{g}}/\partial\mu$ to the partial derivatives of $\overline{E}^{\mathrm{c}}$.

4/ Deduce (8.8) using the thermodynamic identity

$$T\left(\frac{\partial N}{\partial T}\right)_{\mu,V} + \mu\left(\frac{\partial N}{\partial\mu}\right)_{T,V} = \left(\frac{\partial E}{\partial\mu}\right)_{T,V} = \left(\frac{\partial E}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial\mu}\right)_{T,V}. \tag{8.10}$$

Proof of the identity : Start from $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$ and use a Maxwell relation for the partial derivative of S.

D. Application : Monoatomic ideal gas.— Compare the relative fluctuations $\sqrt{\mathrm{Var}(E)}/\overline{E}$ for the three ensembles (microcanonical, canonical and grand-canonical).

8.4 Density fluctuations in a fluid – Compressibility

Let a fluid be thermalized in a box at temperature T. We consider a small volume V inside the total box of volume V_{tot} (figure). The number N of particles in the box fluctuates with time.
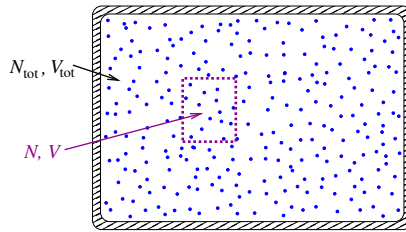

Figure 8.1:   *We consider N particles in the small volume V of a fluid.*

TD 9 : Interacting systems and phase transitions

9.1 Sublimation

In this exercise we study a simple model of sublimation of a solid (transition from the solid phase to the gas phase). We will see that statistical physicst makes it possible to predict *quantitatively* the line describing the equilibrium between the solid and gas phases in the P-T diagram.

The model is based on the following idea : initially, the two phases (gaseous and solid) are described separately, as two thermostated systems. Then we impose an equilibrium condition describing the contact (the exchange of atoms between the "systems").

A. Gas.– The gas has been studied in detail in the exercice 5.2. Justify (briefly) that the partition function of the gas is given by $Z_{\text{gaz}} = \frac{1}{N!}\left(\frac{V}{\Lambda_T^3}\right)^N$ where Λ_T is the DeBroglie thermal length. Deduce the expression of the chemical potential of the gas and its entropy.

B. Model of a solid.– We position ourselves within the framework of the Einstein model: the solid (of N atoms) is equivalent to a set of $3N$ harmonic oscillators of the same pulsation *omega*. To take into account that the crystalline phase is energetically more favorable than the gas phase, the minimum energy for each atom is taken equal to $-\mathcal{E}_0 < 0$:

$$H_{\text{solide}} = \sum_{i=1}^{N}\left(\frac{\vec{p_i}^{\,2}}{2m} + \frac{1}{2}m\omega^2\vec{r_i}^{\,2} - \mathcal{E}_0\right) \tag{9.1}$$

1/ What condition shall satisfy T, ω and $\mathcal{E}_0$ for our model to be applicable ?

2/ Calculate the partition function of the solid Z_{solide} in the semi-classical approximation. Infer its free energy.

3/ Calculate the average energy of the crystal. Express its chemical potential.

4/ Calculate the entropy of a solid.

C. Equilibrium between phases.

1/ Discuss the equilibrium condition between the gaseous and solid phases, assuming the free energies of the two phases are known (i.e. as part of the canonical ensemble).

2/ Deduce the equation describing the equilibrium between the phases in the P–T diagram. Plot carefully $P_s(T)$ (we recall that a condition of validity of the model is $k_B T \ll \mathcal{E}_0$).

3/ Give the expression of the specific heat associated with the sublimation.

D. Experiment.– The sublimation curve of zinc is measured experimentally in the field $500\,\text{K}<T < 600\,\text{K}$. It has been fitted by

$$\ln P_s(T) = 30.3 - 0.5\ln T - \frac{1.6\ 10^4}{T} \quad \text{(SI units)} \tag{9.2}$$

Is this expression in agreement wit our model ?
Compare the values of the fit with the ones given by the studied model. We provide :

- Molar mass of zinc : $M = 65.38\,\text{g.mol}^{-1}$

- $\mathcal{N}_A\mathcal{E}_0 = 1.3\ 10^5\,\text{J.mol}^{-1}$

- $\hbar\omega/k_B = 240\,\text{K}$

9.2 Ising chain and transfer matrix (*)

Introduction : The Ising model has been proposed as a simplified model for describing magnetic materials. It has many other applications. We consider a set of local magnetic moments represented by binary variables $\sigma_i = \pm 1$, attached to the lattice sites of a crystal lattice (here the index i identifies the lattice sites). The model takes into account the competition between the interaction between local magnetic moments (favoring the alignment or the anti-alignment of neighboring spins, depending on the sign of the interaction), the interaction with an external magnetic field (favoring the alignment with the direction of the field) and thermal fluctuations.

We begin by studying the one-dimensional version of the Ising model with nearest neighbor interaction, which is exactly solvable :

$$H(\{\sigma_i\}) = -J \sum_{i=1}^{N} \sigma_i \, \sigma_{i+1} - B \sum_{i=1}^{N} \sigma_i \tag{9.3}$$

where $\sigma_{N+1} = \sigma_1$, which corresponds to the case where N spins are on a ring (figure 9.1).

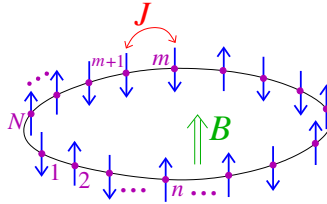

Figure 9.1: *Ising spin chain : the up spin (resp. down) corresponds to $\sigma_n = +1$ (resp. $\sigma_n = -1$).*

We can show that the canonical partition function takes the form of a trace (here for $T = 1$)

$$Z_N = \sum_{\sigma_1} \cdots \sum_{\sigma_N} e^{-H(\{\sigma_i\})} = \text{Tr}\left\{M^N\right\} \qquad \text{with } M \stackrel{\text{def}}{=} \begin{pmatrix} e^{J+B} & e^{-J+B} \\ e^{-J-B} & e^{J-B} \end{pmatrix} \tag{9.4}$$

(you can check it). We will restore the temperature by doing $J \to J/T$ and $B \to B/T$.

1/ Calculate the two eigenvalues of M, denoted $\lambda_\pm$, that you could compare. Infer Z_N. Check the consistency of the result for $J = 0$ by a direct calculation of Z_N.

2/ In the thermodynamical limit, $N \to \infty$, compute the free energy per spin $f = \lim_{N\to\infty} F/N$.

3/ Heat capacity at $B = 0$.– Calculate $f(T, 0)$. Recall the relation between the average energy and βF. Deduce the heat capacity per spin noted $C(T)$. Plot i carefully.

4/ magnetization.– Calculate the magnetization in the general case using $m(T, B) = -\frac{\partial}{\partial B} f(T, B)$ (recall the origin of this expression). Plot $m(T, B)$ as a function of B for different temperatures. Is there a phase transition at finite T as in the mean field treatment of the Ising model ?

5/ Magnetic susceptibility.– The magnetic susceptibility is defined by $\chi(T) \stackrel{\text{def}}{=} \lim_{B\to 0} \frac{\partial m}{\partial B}$. Show that

$$\chi(T) = \frac{1}{T} e^{2J/T} . \tag{9.5}$$

Interpret physically the decrease at high temperature. Explain the origin of the exponential factor for $J > 0$.

9.3 Correlations in the 1D Ising model

In this exercice, we study an important and very general property of the correlation functions, when approaching a phase transition toward an ordered state. We consider the 1D Ising model

for N "spins" interacting **ferromagnetically**, i.e. $J > 0$, between nearest neighbours :

$$H(\{\sigma_i\}) = -J \sum_{i=1}^{N-1} \sigma_i \, \sigma_{i+1} \qquad \text{with } \sigma_i = \pm 1 . \tag{9.6}$$

The model does not have an ordered (ferromagnetic) phase at finite temperature, however its ground state is ferromagnetic. We will therefore study the behavior of the correlation function for $T \to 0$.

1/ Can you describe the microstates of the chain ? How many are there?

2/ Partition function. What is the partition function Z_1 for a single spin ? Show that the canonical partition function of the chain of N spins obeys a recursive equation

$$Z_N = 2 \, \text{ch}(\beta J) \, Z_{N-1} . \tag{9.7}$$

Deduce the expression of Z_N.

3/ Calculate the average canonical energy $\overline{E}^c$ and then the specific heat $C(T)$. Analyze the limiting behaviours of the latter ; what is the physical origin of the low temperature behavior ? Carefully draw the shape of $C(T)$ as a function of T.

4/ Correlation functions.– In this question, we want to calculate the correlation function between two spins $\mathcal{G}(n) \overset{\text{def}}{=} \langle \sigma_i \, \sigma_{i+n} \rangle$. In this respect, we introduce a Hamiltonian with $N-1$ distinct couplings

$$\widetilde{H}(\{\sigma_i\}) = - \sum_{i=1}^{N-1} J_i \, \sigma_i \, \sigma_{i+1} . \tag{9.8}$$

We note $\widetilde{Z}_N$ the associated canonical partition function.

a) Show that $\langle \sigma_i \, \sigma_{i+1} \rangle = \frac{1}{\beta \widetilde{Z}_N} \frac{\partial \widetilde{Z}_N}{\partial J_i} \Big|_{J_i = J}$ (be careful, $\langle \cdots \rangle$ denotes the canonical average associated with H and not $\widetilde{H}$).

b) Show that

$$\mathcal{G}(n) = \frac{1}{\beta^n \widetilde{Z}_N} \frac{\partial^n \widetilde{Z}_N}{\partial J_i \partial J_{i+1} \cdots \partial J_{i+n-1}} \Big|_{J_i = J} . \tag{9.9}$$

c) Calculate explicitly $\widetilde{Z}_N$ inspired by the method of the question **2**.

d) **Correlation function.–** Deduce the expression of the correlation function. We introduce the correlation length $\xi(T)$ by writing $\mathcal{G}(n) = \exp(-n/\xi(T))$. Provide the expression of $\xi(T)$. Analyze its behaviour at low temperature. Give some interpretation.

9.4 Curie-Weiss model: transition Paramagnetic-Ferromagnetic (*)

Another exactly solvable model is when all spins interact in the same way (infinite range interaction). We consider N spins described by the Ising Hamiltonian ($\sigma_i = \pm 1$)

$$H(\{\sigma_i\}) = -\frac{J}{2N} \sum_{1 \leqslant i,\, j \leqslant N} \sigma_i \sigma_j - B \sum_{i=1}^{N} \sigma_i , \tag{9.10}$$

where $J > 0$ is the interaction strength (favoring the alignment of spins) and B the external magnetic field (expressed in unit of energy).

1/ Why was the interaction term divided by N ?

2/ Describe the microstates. What is the total number of microstates Ω_{tot} ? What is the ground state for $B = 0$?

3/ Entropy at fixed magnetization.– We introduce the magnetization per spin :

$$m \stackrel{\text{def}}{=} \frac{1}{N} \sum_{i=1}^{N} \sigma_i \qquad (9.11)$$

a) What are the possible values for m ? What is the number of microstates $\Omega(m)$ for a given m ?

b) Let us introduce the entropy $s(m) = (1/N) \ln \Omega(m)$ (we set $k_B = 1$ to simplify). Show that $s(m) \simeq s_0 - a\, m^2 - b\, m^4$ for $m \to 0$. Gice the three positive constants s_0, a and b.

c) Justify that the sum on the possible value of m can be replaced by an integral $\sum_m \to \frac{N}{2} \int_{-1}^{+1} \mathrm{d}m$. If we neglect the quartic term in the entropy, we have $\Omega(m) \simeq A\,e^{-Nm^2/2}$ for $m \to 0$. Provide the constant A.

3/ Show that the hamiltonian can be written as a function of the magnetization, $H(\{\sigma_i\}) = N\, E(m)$. Provide the expression of the energy per spin $E(m)$. Justify that the canonical partition function can be written in the form

$$Z = \frac{N}{2} \int_{-1}^{+1} \mathrm{d}m\, \Omega(m)\, e^{-\beta N\, E(m)} \qquad (9.12)$$

4/ Let us assume that the expansion of the entropy in question **3** can be justified, $s(m) \simeq s_0 - a\, m^2$, at lowest order.

a) Calculate explicitly Z and deduce the expression of the free energy per spin, $f(T,B) \stackrel{\text{def}}{=} -\frac{1}{N\beta} \ln Z$ in the thermodynamic limit. Find the critical temperature T_c, below which the trunction of $s(m)$ at lowest order is no longer justifed.

b) Let us assume that $T > T_c$. Deduce the entropy of the system $S^c = -N \partial f/\partial T$ and the heat capacity $C_V = T \partial S^c/\partial T$.

c) *Curie-Weiss law.*– Calculate the average magnetization $\overline{m}^c = -\partial f/\partial B$ and then magnetic susceptibility $\chi(T) = \partial \overline{m}^c/\partial B$, as a function of T_c. What happens to the response to the magnetic field when $T \to T_c^+$? Can you guess what this result suggests for the $T < T_c$ properties ?

5/ Regime $T < T_c$. Below T_c, one should consider the expansion $s(m) \simeq s_0 - a\, m^2 - b\, m^4$.

a) Justify that the [artition function can now read

$$Z \sim \int_{-1}^{+1} \mathrm{d}m\, e^{-N\, \phi(m,B)}, \qquad (9.13)$$

and provide the expression of the function $\phi(m, B)$. Plot $\phi(m, 0)$ and $\phi(m, B)$ (for B "small").

b) What do suggest these curves for the behaviour at $T < T_c$? Describe the state of the system if the field is initially positive and decreases until it changes itssign.

6/ Can you physically understand why the mean field model studied here has a phase transition while the 1D model does not have one ?

9.5 Ising model and gas on a lattice

Ising model : The Ising model is of fundamental importance in statistical physics. Introduced as a simplified model to describe magnetism (ferromagnetism, antiferromagnetism, etc.), it also

provides a model for binary alloys, lattice gas, certain socio-economic models (voters, etc.), or even neural networks. We introduce spin variables" $\sigma_i = \pm 1$ associated with the N sites of a network (cubic for example). The Ising model is defined by the Hamiltonian

$$H_{\mathrm{Ising}} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - B \sum_i \sigma_i \tag{9.14}$$

where the first term describes an interaction between neighboring spins (the sum is a sum on the nearest neighbor sites, i.e. on the bonds of the lattice). If $J > 0$ (ferromagnetic interaction), the interaction makes the alignment between spins energetically efficient. The second term describes the effect of an external magnetic field on which the spins try to align with. At finite temperature, three effects therefore compete: thermal agitation, the interaction that aligns the spins between them and the magnetic field that aligns the spins in the direction of B.
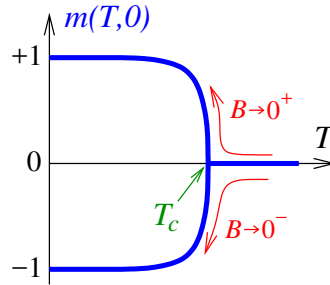

Figure 9.2: *Magnetization $m(T,0) = -\lim_{B \to 0^\pm} \lim_{N \to \infty} \frac{1}{N} \frac{\partial}{\partial B} F_{\mathrm{Ising}}(T, B, N)$ of the Ising model at $B = 0$, as a function of temperature. At high temperature, $T > T_c$, the system is in the paramagnetic phase, characterized by zero magnetization. T_c is the critical temperature below which spontaneous magnetization appears at zero field (ferromagnetic phase). One or the other branch is borrowed according to $B \to 0^+$ or $B \to 0^-$.*

We discuss here the relationship with the lattice gas model.

Model of a gas on a lattice : We consider N sites of a lattice, each site can host one atom at most. We note $n_i \in \{0,1\}$ the number of atoms on site i. By prohibiting more than one atom per site, we model a strong repulsion between atoms, at short distance. Van der Waals forces are responsible for a weak attraction at large distances, which is taken into account by introducing a -4ε energy when two atoms occupy two neighboring sites. The energy of the gas is

$$H_{\mathrm{LG}} = -4\varepsilon \sum_{\langle i,j \rangle} n_i n_j \qquad \text{avec } \mathcal{N} = \sum_i n_i \tag{9.15}$$

the total number of atoms

1/ Justify that the study of lattice gas in the grand canonical ensemble is mapped to the Ising model (in the canonical ensemble). Establish the precise correspondence between the different parameters and variables of the two models. Show that the two thermodynamic potentials are connected as

$$J_{\mathrm{LG}}(T, \mu, N) + \frac{N}{2}(q\,\varepsilon + \mu) = F_{\mathrm{Ising}}(T, B, N)\,, \tag{9.16}$$

where μ denotes the chemical potential of the gas and q the coordinance of the lattice.

Hint : It can be useful to convert the sum on the bonds into a sum on the sites : $\sum_{\langle i,j \rangle} = (1/2) \sum_i \sum_{j \in v(i)}$ where $v(i)$ is the set of q neighbors of the site i. On a regular lattice, the number of bonds is therefore linked to the number of sites $N_{\mathrm{liens}} = Nq/2$ (example : $q = 2d$ on the cuboc lattice of dimension d, therefore $N_{\mathrm{liens}} = Nd$).

2/ Using the mapping between the two models, what information can you deduce for the lattice gas from the magnetization curve of the figure 9.2 ?

9.6 Ferromagnetic and antiferromagnetic Ising model on a hypercubic lattice – mean field analysis (*)

We study the properties of magnetism on a hypercubic lattice of N sites, in the frame of the Ising model. We note q the lattice coordination number ($q = 2d$ for the hypercubic lattice where d is the dimension).

A. Ferromagnetic interaction.– The Ising Hamiltonian reads

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - B \sum_i \sigma_i \tag{9.17}$$

where $\sigma_i = \pm 1$. The interaction $J > 0$ favors a ferromagnetic order at low temperature. The first summation is on nearest neighbors lattice sites, $\langle i, j \rangle$, i.e. on the *links* of the lattice. The second summation is on all lattice *sites*.

B. Antiferromagnetic interaction.– [10] We now consider the Hamiltonian

$$H = +J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - B \sum_i \sigma_i \tag{9.18}$$

where $J > 0$, i.e. an interaction favoring *the opposite alignments of spins*. We admit that the ordered phase at $T = B = 0$ corresponds to the Néel order : namely the Ising spins take alternating values $+1$ and -1.

The exercice can be found at `http://lptms.u-psud.fr/christophe_texier/` `enseignements/enseignement-en-licence/l3-physique-statistique/`

9.7 The variational approach

We want to base the average field approach on a variational principle, i.e. build an approximate free energy, which we will note $f_{\mathrm{var}}(m)$, from a clear minimization criterion.

Exercice available on `http://lptms.u-psud.fr/christophe_texier/enseignements/` `enseignement-en-licence/l3-physique-statistique/`

Pour en savoir plus : Cf. exercice 10.3 de C. Texier & G. Roux, *Physique statistique*, Dunod, 2017.

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[10] A critique of the mean field approach as presented here is at the end of the last exercise.