
Exam — Session 2

Duration: 2h

*Documents, cell phones, computers, tablets, pocket calculators, etc., are not allowed
The text contains 3 pages in total*

1 Ising dimer

Let us consider two Ising spins $s_i = \pm 1$ ($i = 1, 2$) forming a dimer. The two spins are subject to a uniform magnetic field H , and interact through a ferromagnetic exchange interaction J . The dimer is connected to a heat reservoir which maintains its temperature T constant. In what follows, we denote $\beta = 1/k_B T$, with k_B the Boltzmann constant. The Hamiltonian of the system then reads

$$\mathcal{H} = -(s_1 + s_2)H - J s_1 s_2.$$

- What is the sign of J ? Justify your answer.
- At vanishing magnetic field ($H = 0$) and zero temperature ($T = 0$), what are the spin configurations?
- Calculate the exact canonical partition function Z and the free energy F of the system.
- The average magnetization per spin $m = \langle s_i \rangle$ of the system is given by

$$m = -\frac{1}{2} \frac{\partial F}{\partial H}. \quad (1.1)$$

- Justify expression (1.1).
- Show that

$$m = \frac{\sinh(2\beta H)}{\cosh(2\beta H) + \exp(-2\beta J)}. \quad (1.2)$$

- Without interaction between the two spins ($J = 0$), prove that Eq. (1.2) recovers the paramagnetic behavior $m = \tanh(\beta H)$.
 - For a given value of J , plot m as a function of H for various temperatures. What happens in the $T = 0$ limit? Does the system present a phase transition?
- The zero-field magnetic susceptibility is defined as

$$\chi = \left. \frac{\partial m}{\partial H} \right|_{H=0}.$$

Calculate χ and comment on the $T = 0$ limit.

2 Van der Waals equation of state

Let us consider a system of $N \gg 1$ classical particles with mass m occupying a three-dimensional volume V at the temperature T . The particles have no internal degrees of freedom. The Hamiltonian of the system reads

$$\mathcal{H} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

where \mathbf{r}_i and \mathbf{p}_i are the position and momentum of the i^{th} particle, and U is the interaction energy of the system.

2.1 Semiclassical partition function

We recall that the canonical partition function of the system is given, in the dilute limit, by

$$Z = \frac{1}{(2\pi\hbar)^{3N} N!} \int d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N d^3\mathbf{p}_1 \dots d^3\mathbf{p}_N e^{-\beta\mathcal{H}},$$

Using the result

$$\int_{-\infty}^{+\infty} du e^{-u^2} = \sqrt{\pi},$$

show that

$$Z = \frac{1}{N! \Lambda_T^{3N}} \int d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)}, \quad (2.1)$$

where $\Lambda_T = (2\pi\hbar^2/mk_B T)^{1/2}$ is the thermal de Broglie wavelength.

2.2 The ideal gas case

Let us first consider the case of an ideal gas, for which it is assumed that $U(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0$.

- In the noninteracting case, calculate the partition function (2.1) and the free energy F in the thermodynamic limit.¹
- Deduce from the previous question the equation of state of the system.
- In a P - V diagram, sketch the isothermal curves. Does the ideal gas model enable one to describe the liquid-gas phase transition?

2.3 Role of the molecular interactions

Let us now consider the interactions between pairs of molecules only, so that the interaction energy in Eq. (2.1) reads

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N u(r_{ij}),$$

where $u(r_{ij})$ is the potential energy between two pairs of molecules separated by the distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. In what follows, we assume that $u(r)$ is a Lennard–Jones potential that takes the form

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2.2)$$

The Lennard–Jones potential has a minimum at $r = r_0 = 2^{1/6}\sigma$, for which it takes the value $u(r_0) = -\varepsilon$.

- Sketch the Lennard–Jones potential (2.2) as a function of r , and indicate on your graph where are the repulsive and attractive part of the interaction.
- Let us first consider the attractive part $\propto -r^{-6}$ of $u(r)$ and neglect the correlations between the particles. Within a mean-field approximation, assuming that the density of particles is uniform, show that

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) \simeq -\frac{aN^2}{V},$$

with

$$a = -\frac{1}{2} \int d^3\mathbf{r} u(r).$$

¹We recall Stirling's formula $\ln n! \simeq n \ln n - n$ for $n \gg 1$.

(c) Close to a given particle, the approximation above is not valid any longer and one has to take into account the repulsive part $\propto r^{-12}$ of the pair potential (2.2). To this end, we assume that the particles are hard spheres of radius R and that each particle has an excluded volume b . Give an expression of b as a function of R . Justify that when integrating over the particle positions in Eq. (2.1), one has to integrate over $V - Nb$ instead of V , as was done in the ideal gas case.

(d) Considering the approximations of questions (b) and (c) above, show that Eq. (2.1) takes the form

$$Z \simeq \frac{(V - Nb)^N}{N! \Lambda_T^{3N}} e^{\beta a N^2 / V},$$

and calculate F in the thermodynamic limit.

(e) Deduce from the above results the van der Waals equation of state

$$\left(P + a \frac{N^2}{V^2} \right) (V - Nb) = N k_B T. \quad (2.3)$$

2.4 Isothermal curves

(a) Sketch the isothermal curves (2.3) in a P - V diagram. In particular, show that there exists a critical temperature T_c below which the isothermal curves are no longer monotonic functions.

(b) For the critical isothermal curve, there exists an inflection point (P_c, V_c) called the critical point. Give the expressions of P_c , V_c , and T_c as a function of a and b .

(c) Plot the free energy F as a function of V for $T > T_c$ and $T < T_c$.

(d) One can show that a thermodynamical system for which $(\partial P / \partial V)_T > 0$ is unstable. What are the regions in the P - V and F - V diagrams which correspond to thermodynamically unstable states?

(e) Qualitatively explain how to remedy to this incoherence of the van der Waals model, and how to describe the liquid-gas transition.