

Exercise 2.1 Classical Ideal Paramagnet

- a) We define the magnetization $M = nmH$, with $n = n_+ - n_-$ and $N = n_+ + n_-$, such that $n_{\pm} = \frac{N \pm n}{2}$. The (discrete) phase space area is the number of combinations of moments that give the same magnetization, so $\Omega(n) = \frac{N!}{n_+!n_-!}$. We then use the Stirling's approximation $\ln(N!) = N \ln N - N + \mathcal{O}(\ln N)$ and ignore terms of order $\log N$.

$$\begin{aligned} \log \Omega(n) &= \log(N!) - \log(n_+!) - \log(n_-!) \\ &\approx N(\log N - 1) - \frac{N+n}{2} \left(\log \left(\frac{N+n}{2} \right) - 1 \right) - \frac{N-n}{2} \left(\log \left(\frac{N-n}{2} \right) - 1 \right), \end{aligned}$$

where we neglected the term $\frac{1}{2} \log(\pi^2(N^2 - n^2))$. The entropy then reads:

$$S = k_B \log \Omega(n) = Nk_B \log(2) - \frac{Nk_B}{2} \left(\left(1 + \frac{n}{N}\right) \log \left(1 + \frac{n}{N}\right) + \left(1 - \frac{n}{N}\right) \log \left(1 - \frac{n}{N}\right) \right) \quad (1)$$

From the differential $dS = (1/T)dU + (M/T)dH$ we can obtain the temperature as follows. We insert $n = -\frac{E}{Hm}$ to get $S(E, H)$ and differentiate keeping n explicitly:

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S}{\partial E} \right)_H = \left(\frac{\partial n}{\partial E} \right)_H \frac{\partial S}{\partial n} = -\frac{1}{Hm} \frac{\partial S}{\partial n} \\ &= \frac{Nk_B}{2Hm} \left(\frac{1}{N} \log \left(1 + \frac{n}{N}\right) - \frac{1}{N} \log \left(1 - \frac{n}{N}\right) + \frac{1}{N} - \frac{1}{N} \right) = \frac{k_B}{2Hm} \log \left(\frac{N+n}{N-n} \right) \\ &= -\frac{k_B}{2Hm} \log \left(\frac{NHm + E}{NHm - E} \right). \end{aligned}$$

Inverting the above equation yields $E = -NHm \tanh(\beta mH)$, with $\beta = 1/(k_B T)$. In order to obtain the magnetization we first calculate the partial derivative

$$\left(\frac{\partial S}{\partial H} \right)_E = \left(\frac{\partial n}{\partial H} \right)_E \frac{\partial S}{\partial n} = -\frac{E}{H^2 m} \frac{\partial S}{\partial n} = \frac{Ek_B}{2H^2 m} \log \left(\frac{NHm + E}{NHm - E} \right),$$

and then

$$M = T \left(\frac{\partial S}{\partial H} \right)_E = -\frac{E}{H} = Nm \tanh(\beta mH). \quad (2)$$

The susceptibility reads:

$$\chi_H = \left(\frac{\partial M}{\partial H} \right) = \frac{Nm^2 \beta}{\cosh^2(\beta mH)}. \quad (3)$$

It is useful to study the magnetization and the susceptibility in the two regimes $\beta mH \gg 1, \ll 1$ (see Fig. 1). When $\beta mH \ll 1$ (small field and/or large temperature limit) $\tanh x \approx x - \mathcal{O}(x^3)$ and $\cosh x \approx 1 + \mathcal{O}(x^2)$ such that the magnetization grows linearly in the field, i.e., according to the Curie law of independent moments

$$M \approx Nm^2 \beta H = \chi H \quad \text{with} \quad \chi_H \approx Nm^2 \beta = \chi. \quad (4)$$

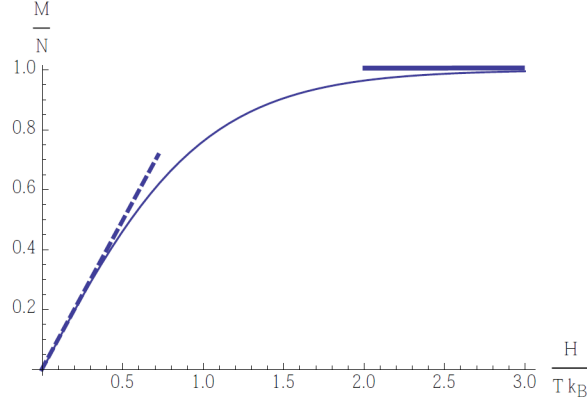


Abbildung 1: Magnetization (2) as a function of magnetic field strength H scaled to $k_B T$. The dashed (solid) line is the asymptote at small (large) field ($m = 1$).

When $\beta m H \gg 1$ (large field and/or small temperature limit) $\tanh x \approx 1 - e^{-2x}$ and the magnetization tends to saturate, i.e.,

$$M \approx mN(1 - 2e^{-2\beta m H}). \quad (5)$$

It is also interesting to consider the heat capacity for constant external field H . From $dU = \left(\frac{\partial U}{\partial T}\right)_H dT + \left(\frac{\partial U}{\partial H}\right)_T dH$ and $dM = \left(\frac{\partial M}{\partial T}\right)_H dT + \left(\frac{\partial M}{\partial H}\right)_T dH$ such that

$$\delta Q = dU - \delta W = dU - H dM = \left[\left(\frac{\partial U}{\partial T}\right)_H - H \left(\frac{\partial M}{\partial T}\right)_H \right] dT + \left[\left(\frac{\partial U}{\partial H}\right)_T - H \left(\frac{\partial M}{\partial H}\right)_T \right] dH. \quad (6)$$

The heat capacity at fixed H is then given by:

$$C_H = \left(\frac{\partial U}{\partial T}\right)_H - H \left(\frac{\partial M}{\partial T}\right)_H = 2 \frac{N k_B (\beta H m)^2}{\cosh^2(\beta m H)}, \quad (7)$$

where we used $\partial_T f(\beta) = -k_B \beta^2 \partial_\beta f(\beta)$. Note that both the susceptibility and the heat capacity are exponentially suppressed at low temperature $\sim T^{-\alpha} e^{-2Hm/k_B T}$ with $\alpha = 1, 2$, which is indicating a freezing of the degrees of freedom.

- b) In order to determine the thermodynamics of the ideal paramagnet in the canonical ensemble, we calculate the partition function:

$$Z = \prod_{i=1}^N \left[\sum_{\sigma=\pm} e^{-\beta H m \sigma} \right] = [2 \cosh(\beta m H)]^N = Z_m^N. \quad (8)$$

We can now easily calculate all the thermodynamic functions, e.g, the free energy:

$$F(T, H, N) = -\frac{1}{\beta} \ln Z = -k_B T N \ln Z_m \quad (9)$$

and the internal energy

$$U(T, H, N) = -\partial_\beta \ln Z = -N m H \tanh(\beta m H). \quad (10)$$

From the free energy (9) we obtain the magnetization and the susceptibility, which are equal to the ones obtained in the micro-canonical case (2), (3).

Exercise 2.2 Classical Ideal Lattice Gas

Micro-canonical case: We need to calculate the number of microscopic realizations that yields the same energy

$$E = N_A E_A + N_B E_B \quad (11)$$

with $N_{A(B)}$ the number of particles on the sites with energy $E_{A(B)}$. Note, that $N_A \leq N_1$, and

$$N_1 = N_A + N_B. \quad (12)$$

At zero temperature, as $N_1 < N_2$ we expect that when $E_A < E_B$, $N_A = N_1$ with zero entropy, as there is only one configuration possible (all atoms sitting on the N_A sites). On the other hand, when $E_A > E_B$, it will be favourable for the system to occupy the B sites, i.e., $N_A = 0$ and since $N_2 > N_1$ the number of allowed configurations will be larger than 1 and the residual entropy non zero. More quantitatively,

$$\Omega = \Omega_A \Omega_B = \frac{N_1!}{(N_1 - N_A)! N_A!} \frac{N_2!}{(N_2 - N_B)! N_B!} = \frac{N_1!}{(N_1 - N_A)! N_A!} \frac{(N - N_1)!}{(N + N_A - 2N_1)! (N_1 - N_A)!}, \quad (13)$$

where we used $N = N_1 + N_2$ and $N_1 = N_A + N_B$. We immediately see that when $N_A = N_1$, $N_B = 0$ and $\Omega = 1$, while when $N_A = 0$ $\Omega = \Omega_B > 1$. The entropy reads $S = k_B \ln \Omega$, with

$$\ln \Omega = [N_1 \ln N_1 + 2N_1 - 2(N_1 - N_A) \ln(N_1 - N_A) - N_A \ln N_A + (N - N_1) \ln(N - N_1) - (N + N_A - 2N_1) \ln(N + N_A - 2N_1)]. \quad (14)$$

In order to obtain the temperature, we write

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial N_A}{\partial E} \frac{\partial S}{\partial N_A} = \frac{1}{E_A - E_B} \frac{\partial S}{\partial N_A}, \quad (15)$$

such that

$$\frac{1}{T} = \frac{k_B}{E_A - E_B} [2 \ln(N_1 - N_A) - \ln(N + N_A - 2N_1) - \ln N_A] \quad (16)$$

which implies

$$\frac{(N_1 - N_A)^2}{N_A(N + N_A - 2N_1)} = e^{-\beta(E_B - E_A)}. \quad (17)$$

At zero T , when $E_A < E_B$ the R. H. S. of the equation above is zero and this can only be satisfied when $N_1 = N_A$. On the other hand, when $E_A > E_B$ the R. H. S. diverges, implying $N_A = 0$, as $N + N_A - 2N_1 = 0$ yields $N_B = N_2$ which is not possible. Therefore, the distribution $N_A(E_A)$ goes from N_1 when $E_A < E_B$ to zero when $E_A > E_B$ in a step-like fashion at zero temperature. For larger T , the step is smeared out over an energy interval $\sim k_B T$.

Grand-canonical case: It is straightforward to write the partition function in the following way:

$$Z = (1 + e^{-\beta(E_A - \mu)})^{N_1} (1 + e^{-\beta(E_B - \mu)})^{N_2} \quad (18)$$

as each one among the $N_{1,2}$ sites can be either occupied or empty. The quantity μ fixes the particle number and results from the shifting of the Hamiltonian $H = H_A + H_B \rightarrow H = H_A + H_B - \mu(N_A + N_B) = \tilde{H}_A + \tilde{H}_B$. Therefore, the internal energy reads:

$$U = -\partial_\beta \ln Z = N_1 \tilde{E}_A \frac{e^{-\beta \tilde{E}_A}}{1 + e^{-\beta \tilde{E}_A}} + N_2 \tilde{E}_B \frac{e^{-\beta \tilde{E}_B}}{1 + e^{-\beta \tilde{E}_B}} \stackrel{!}{=} N_A \tilde{E}_A + N_B \tilde{E}_B, \quad (19)$$

where $\tilde{E}_A = E_A - \mu$ and $\tilde{E}_B = E_B - \mu$ are the shifted energies according to the shifted Hamiltonian. From the last equivalence, we obtain

$$N_A = (N_1 - N_A)e^{-\beta\tilde{E}_A} \quad \text{and} \quad N_B = (N_2 - N_B)e^{-\beta\tilde{E}_B} \quad (20)$$

such that

$$\frac{N_B(N_1 - N_A)}{N_A(N_2 - N_B)} = \frac{(N_1 - N_A)^2}{N_A(N_1 + N_A - 2N_1)} = e^{-\beta(\tilde{E}_B - \tilde{E}_A)} = e^{-\beta(E_B - E_A)}, \quad (21)$$

as in the micro-canonical case discussed above. Alternatively, one could obtain the Boltzmann factors (20) by maximizing the phase space count (13) with respect to N_A with the energy (11) and particle number (12) constraints imposed through Lagrange multipliers. The multiplier β fixing the total energy can be shown to be equal to the inverse temperature via the thermodynamic relation

$$\frac{1}{T} = \frac{dS}{dE} = \frac{\partial S}{\partial N_A} \frac{\partial N_A}{\partial E} + \frac{\partial S}{\partial N_B} \frac{\partial N_B}{\partial E} = k_B \beta. \quad (22)$$

Exercise 2.3 Classical Ideal Gas in a Harmonic Trap

- a) In the micro-canonical ensemble, the connection to thermodynamics is provided through the phase space volume

$$\Phi(E) = \Lambda_N \int_{H(p,q) \leq E} dp dq, \quad (23)$$

with

$$H(p, q) = \sum_{i=1}^N \left[\frac{\vec{p}_i^2}{2m} + a\vec{q}_i^2 \right]. \quad (24)$$

We perform the rescaling, $P_i = p_i/\sqrt{2m}$ and $Q_i = q_i\sqrt{a}$, such that the Hamiltonian is simplified

$$H(P, Q) = \sum_{i=1}^N \left[\vec{P}_i^2 + \vec{Q}_i^2 \right] \quad (25)$$

as well as the phase space integral

$$\Phi(E) = \Lambda_N \left(\frac{2m}{a} \right)^{3N/2} \int_{H(P,Q) \leq E} dP dQ, \quad (26)$$

since $dp = \prod_{i=1}^N d^3 p_i$ and $dq = \prod_{i=1}^N d^3 q_i$. We then need to calculate, as already explained in the lecture, the volume of a sphere in $6N$ dimensional space, i.e.,

$$\Phi(E) = \Lambda_N \left(\frac{2m}{a} \right)^{3N/2} C_{6N} E^{3N}, \quad (27)$$

with

$$C_n = \frac{\pi^{n/2}}{\Gamma(\frac{n}{2} + 1)}. \quad (28)$$

In order to obtain the thermodynamics, we can then refer to the lecture, with the substitutions $2m \rightarrow 2m/a$ and $E^{3N/2} \rightarrow E^{3N}$, i.e., the entropy

$$S(E, N) = Nk_B \ln \left[\frac{1}{N} \left(\sqrt{\frac{2m}{a}} \frac{\pi E}{3Nh} \right)^3 \right] + 4Nk_B. \quad (29)$$

Inverting the above relation we find:

$$U(S, N) = E = \frac{3N^{4/3}h}{\pi} \sqrt{\frac{a}{2m}} \exp \left[\frac{S}{3Nk_B} - 4/3 \right] \quad (30)$$

such that the equation of state can be obtained as follows,

$$T = \left(\frac{\partial U}{\partial S} \right)_N = \frac{U}{3Nk_B} \rightarrow U = 3Nk_B T, \quad (31)$$

which expresses the equipartition law.

b) Within the canonical ensemble, we need again to calculate the partition function. It reads:

$$\begin{aligned} Z &= \Lambda_N \int dp dq e^{-\beta H(p,q)} = \Lambda_N \left[\prod_{i=1}^N \int d^3 p_i e^{-\beta \mathbf{p}_i^2 / 2m} \right] \left[\prod_{i=1}^N \int d^3 q_i e^{-\beta a \mathbf{q}_i^2} \right] = \\ &= \Lambda_N \left[\int dx dy dz e^{-\beta(x^2+y^2+z^2)/2m} \right]^N \left[\int dx dy dz e^{-a\beta(x^2+y^2+z^2)} \right]^N = \\ &= \Lambda_N \left(\frac{2m}{a} \right)^{3N/2} [\pi k_B T]^{3N}. \end{aligned} \quad (32)$$

We can then obtain all thermodynamic functions, as in Ex. 1, e.g., the free energy:

$$F(T, N) = -\frac{1}{\beta} \ln Z = -Nk_B T \ln \left[\frac{1}{N} \left(\sqrt{\frac{2m}{a}} \frac{\pi k_B T}{h} \right)^3 \right] - Nk_B T \quad (33)$$

and the caloric equation of state,

$$U(T, N) = -\partial_\beta \ln Z = 3Nk_B T. \quad (34)$$

c) In the grand-canonical ensemble, the thermodynamics for fixed chemical potential μ and varying particle number N is given through the grand partition function,

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N, \quad (35)$$

with the fugacity $z = \exp(\beta\mu)$, while Z_N is the partition function of the corresponding canonical ensemble (32), i.e., with given N . We then obtain:

$$\begin{aligned} \mathcal{Z} &= \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta\mu N} \left[\sqrt{\frac{2m}{a}} \frac{\pi k_B T}{h} \right]^{3N} = \sum_{N=0}^{\infty} \frac{1}{N!} \left[e^{\beta\mu} \left(\sqrt{\frac{2m}{a}} \frac{\pi k_B T}{h} \right)^3 \right]^N = \\ &= \exp \left[e^{\beta\mu} \left(\sqrt{\frac{2m}{a}} \frac{\pi k_B T}{h} \right)^3 \right]. \end{aligned} \quad (36)$$

We are then able to calculate all thermodynamic functions, i.e., the grand potential

$$\Omega(T, V, \mu) = -pV = -\frac{1}{\beta} \ln \mathcal{Z} = -e^{\beta\mu} \left(\sqrt{\frac{2m}{a}} \frac{\pi}{h} \right)^3 (k_B T)^4. \quad (37)$$

In order to define compressibility, we exploit the Gibbs-Duhem relation

$$G(T, p, N) = \mu N \quad \rightarrow \quad SdT - Vdp + Nd\mu = 0, \quad (38)$$

where G is the Gibbs free energy. We can then write:

$$d\mu = vdp - \frac{S}{N}dT \quad \rightarrow \quad \left(\frac{\partial\mu}{\partial v} \right)_T = v \left(\frac{\partial p}{\partial v} \right)_T, \quad (39)$$

where $v = V/N$. One then obtains

$$\left(\frac{\partial\mu}{\partial v} \right)_T = \left(\frac{\partial N}{\partial v} \frac{\partial\mu}{\partial N} \right)_T = -\frac{N^2}{V} \left(\frac{\partial\mu}{\partial N} \right)_T \quad (40)$$

while for the R.H.S. of (39)

$$\left(\frac{\partial p}{\partial v} \right)_T = \left(\frac{\partial V}{\partial v} \frac{\partial p}{\partial V} \right)_T = N \left(\frac{\partial p}{\partial V} \right)_T \quad (41)$$

such that one can conclude:

$$-\frac{N^2}{V} \left(\frac{\partial\mu}{\partial N} \right)_T = N \left(\frac{\partial p}{\partial V} \right)_T \quad \rightarrow \quad N \left(\frac{\partial\mu}{\partial N} \right)_T = -vV \left(\frac{\partial p}{\partial V} \right)_T. \quad (42)$$

According to the definition of isothermal compressibility,

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T, \quad (43)$$

that quantifies the normalized reduction in volume when changing the pressure at fixed temperature, we obtain:

$$\kappa_T = \frac{v}{N} \left(\frac{\partial N}{\partial\mu} \right)_T. \quad (44)$$

In the grand-canonical ensemble, we replace N with $\langle N \rangle$, which can be calculated as follows:

$$\langle N \rangle = z \partial_z \ln \mathcal{Z} = \ln \mathcal{Z} = -\Omega\beta. \quad (45)$$

Therefore,

$$\kappa_T = \frac{v}{\langle N \rangle} \left(\frac{\partial z}{\partial\mu} \frac{\partial \langle N \rangle}{\partial z} \right)_T = \frac{v}{z} \frac{\partial z}{\partial\mu} = v\beta. \quad (46)$$