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

\[
H = -(s_1 + s_2)H - Js_1s_2.
\]

(a) What is the sign of \( J \)? Justify your answer.

The sign of \( J \) has to be positive, because, when forming a dimer, the two individual spins must reduce their energy, meaning that \(-J\) has to be of negative sign.

(b) At vanishing magnetic field \((H = 0)\) and zero temperature \((T = 0)\), what are the spin configurations?

Without any magnetic field \((H = 0)\), since it’s a ferromagnetic exchange interaction, all the spins are aligned in respect to the others.

(c) Calculate the exact canonical partition function \( Z \) and the free energy \( F \) of the system.

\[
Z = \sum_{s_1=\pm1} \sum_{s_2=\pm1} e^{\beta[(s_1+s_2)H+Js_1s_2]}
= \sum_{s_1=\pm1} \left\{ e^{\beta[(s_1+1)H+Js_1]} + e^{\beta[(s_1-1)H-Js_1]} \right\}
= e^{\beta[(1+1)H+J]} + e^{\beta[(s_1-1)H-J]} e^{\beta[(1+1)H-J]} + e^{\beta[(1-1)H+J]}
= e^{\beta J} \left\{ 2 \cosh(2\beta H) \right\} + 2e^{-\beta J}
\]

\[
F = -k_B T \ln Z
= -k_B T \ln \left\{ e^{\beta J} \left\{ 2 \cosh(2\beta H) \right\} + 2e^{-\beta J} \right\}
= -J - k_B T \ln \left\{ 2 \cosh(2\beta H) + 2e^{-2\beta J} \right\}
\]

(d) The average magnetization per spin \( m = \langle s_i \rangle \) of the system is given by

\[
m = -\frac{1}{2} \frac{\partial F}{\partial H}, \tag{1.1}
\]

(i) Justify expression (1.1).
(ii) Show that

\[ m = \frac{\sinh(2\beta H)}{\cosh(2\beta H) + \exp(-2\beta J)}. \]  

(iii) Without interaction between the two spins \((J = 0)\), prove that Eq. (1.2) recovers the paramagnetic behavior \(m = \tanh(\beta H)\).

\[ m = \frac{\sinh(2\beta H)}{\cosh(2\beta H) + 1} \]

\[ = \frac{\frac{e^{2\beta H} - e^{-2\beta H}}{2}}{\frac{e^{2\beta H} + e^{-2\beta H}}{2} + 1} \]

\[ = \frac{e^{2\beta H} - e^{-2\beta H}}{e^{2\beta H} + e^{-2\beta H} + 2} \]

\[ = \frac{(e^{\beta H} - e^{-\beta H})^2}{(e^{\beta H} + e^{-\beta H})^2} \]

\[ = \tanh(\beta H) \]

(iv) 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?
When $T$ reach $0$, $m$ tend to be the sign function. This sytem has a phase transition for $T = 0$.

(e) The zero-field magnetic susceptibility is defined as

$$
\chi = \frac{\partial m}{\partial H}_{H=0}
$$

Calculate $\chi$ and comment on the $T = 0$ limit.

$$
\chi = \frac{\partial m}{\partial H}_{H=0} = \frac{\partial}{\partial H} \left\{ \frac{\sinh(2\beta H)}{\cosh(2\beta H) + e^{-2\beta J}} \right\}_{H=0} = \frac{2\beta e^{-2\beta J}}{(\cosh(2\beta H) + e^{-2\beta J})^2}_{H=0} = \frac{2\beta e^{-2\beta J}}{(1 + e^{-2\beta J})^2}
$$

Let’s check the limit for $T \to 0$,

$$
\lim_{T \to 0} \chi \approx \frac{2\beta(1 - 2\beta J)}{(2 - 2\beta J)} \approx \beta
$$

$$
\lim_{x \to 0} e^x \approx 1 + x
$$

We know that when the magnetic susceptibility diverges, there is a phase transition. Meaning here, the phase transition occurs at $T = 0$, which is coherent with what we drew for $m(H)$ earlier.
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

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

where $\vec{r}_i$ and $\vec{p}_i$ 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

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

Using the result

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

show that

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

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

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

$$= \frac{1}{(2\pi \hbar)^{3N} N!} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N d^3\vec{p}_1 \cdots d^3\vec{p}_N e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + U(\vec{r}_1, \cdots, \vec{r}_N)}}$$

$$= \frac{1}{(2\pi \hbar)^{3N} N!} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)} \int d^3\vec{p}_1 \cdots d^3\vec{p}_N e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}} \quad \mathcal{P}_i = \sqrt{\frac{\beta}{2m}} p_i$$

$$= \frac{(2mk_B T)^{3N/2}}{(2\pi \hbar)^{3N} N!} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)} \int d^3\vec{P}_1 \cdots d^3\vec{P}_N e^{-\sum_{i=1}^{N} \frac{\vec{P}_i^2}{2m}}$$

$$= \frac{(2mk_B T \pi)^{3N/2}}{(2\pi \hbar)^{3N} N!} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)}$$

$$= \frac{1}{N! \Lambda_T^{3N}} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)}$$
### 2.2 The ideal gas case

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

(a) In the noninteracting case, calculate the partition function (2.1) and the free energy $F$ in the thermodynamic limit.\(^1\)

\[
Z = \frac{1}{(2\pi \hbar)^{3N}} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N d^3\vec{p}_1 \cdots d^3\vec{p}_N e^{-\beta H} \\
= \frac{1}{N! \Lambda_T^{3N}} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)} \\
= \frac{1}{N! \Lambda_T^{3N}} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \\
= \frac{V^N}{N! \Lambda_T^{3N}}
\]

\[
F = -k_B T \ln(Z) \\
= -Nk_B T \ln(V) + k_B T \ln(N!) + Nk_B T \ln(\Lambda_T^3) \\
= -Nk_B T \left\{ \ln\left( \frac{V}{N \Lambda_T^3} \right) + 1 \right\}
\]

(b) Deduce from the previous question the equation of state of the system.

We know the expression of the pressure,

\[
p = -\frac{\partial F}{\partial V} = \frac{Nk_B T}{V}
\]

Meaning the well known equation of state for a perfect gas,

\[pV = Nk_B T\]

(c) In a $P-V$ diagram, sketch the isothermal curves. Does the ideal gas model enable one to describe the liquid-gas phase transition?

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1. We recall Stirling’s formula $\ln n! \approx n \ln n - n$ for $n \gg 1$
There is no phase transition, indeed, we need to have interactions in order to exhibit a 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

\[
U(\vec{r}_1, \cdots, \vec{r}_N) = \frac{1}{2} \sum_{i,j=1, i \neq j}^{N} u(r_{ij})
\]

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

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

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

(a) 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.
(b) 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

$$U(\vec{r}_1, \cdots, \vec{r}_N) \approx -\frac{aN^2}{V},$$

with

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

$$U(\vec{r}_1, \cdots, \vec{r}_N) = \frac{1}{2} \sum_{i,j=1}^{N} u(r_{ij})$$

We can fix $\vec{r}_i$, so we can take $\vec{r}_i = \vec{0}$,

$$\sum_{j=1}^{N} u(r_{ij}) = \sum_{j=1}^{N} u(\vec{r}_j)$$

But, there is a lot’s of particles, so we can replace the summation by an integral,

$$= \sum_{j=1}^{N} u(\vec{r}_j) \approx \int d^3\vec{r} n(\vec{r}) u(r)$$

where $n(\vec{r})$ is the density of particles, we can say that this density is homogeneous, $n(\vec{r}) = N/V$ and so,

$$\sum_{j=1}^{N} u(r_{ij}) \approx \frac{N}{V} \int d^3\vec{r} u(r)$$
This integral doesn’t depend on \( i \), we can call it \(-2a\), so,

\[
U(\vec{r}_1, \ldots, \vec{r}_N) \simeq \frac{1}{2} \left( -\frac{2aN}{V} \right) N
\]

where the right \( N \) comes from the summation over \( i \). Meaning, that, in the end,

\[
U(\vec{r}_1, \ldots, \vec{r}_N) \simeq -\frac{aN^2}{V},
\]

(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.

\[
V_{\text{true volume}} = V_{\text{total}} - (N - 1)b \approx V_{\text{total}} - Nb \quad \quad b = \frac{4}{3}\pi(2R)^3
\]

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

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

and calculate \( F \) in the thermodynamic limit.

\[
Z = \frac{1}{N! \Lambda_T^{3N}} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \ldots, \vec{r}_N)}
\approx \frac{1}{N! \Lambda_T^{3N}} \int_{V-Nb} d^3\vec{r}_1 \cdots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \ldots, \vec{r}_N)}
= \frac{(V - Nb)^N}{N! \Lambda_T^{3N}} e^{\beta aN^2/V}
\]

\[
F = -k_B T \ln Z = \frac{(V - Nb)^N}{N! \Lambda_T^{3N}} e^{\beta aN^2/V} \}
= -Nk_B T \ln \left( \frac{V - Nb}{\Lambda_T^3} \right) - \frac{aN^2}{V} + (-N \ln N + N)(-k_B T)
\]
(e) Deduce from the above results the van der Waals equation of state

\[
\left( P + a \frac{N^2}{V^2} \right) (V - Nb) = Nk_B T
\]  

(2.3)

\[
p = -\frac{\partial F}{\partial V} = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}
\]

We indeed recover van der Waals equation of state,

\[
\left( P + a \frac{N^2}{V^2} \right) (V - Nb) = Nk_B T
\]

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 \( b \).
At $V_c$, the slopes are equal, meaning,

$$\begin{align*}
\frac{\partial}{\partial V} (V - Nb) &= \frac{\partial}{\partial V} \left( \sqrt{\frac{k_BT}{2aN}} V^{3/2} \right) \\
V - Nb &= \sqrt{\frac{k_BT}{2aN}} V^{3/2}
\end{align*}$$

From the first equation we get,

$$1 = \sqrt{\frac{k_BT_c}{2aN}} V_c^{1/2}$$

Meaning,

$$k_BT_c = \frac{8aN}{9V_c}$$

From the second equation,

$$V - Nb = \sqrt{\frac{k_BT}{2aN}} V^{3/2} = \frac{2}{3} V_c$$

Meaning,

$$V_c = 3Nb$$

So now,

$$k_BT_c = \frac{8aN}{9V_c} = \frac{8aN}{9\cdot3Nb} = \frac{8a}{27b}$$
Then, the pressure,

\[ P_c = \frac{N k_B T_c}{V_c - N b} - a \frac{N^2}{V_c^2} \]

\[ = \frac{N}{2} \frac{8 a}{27 b} - \frac{a N^2}{9 N^2 b^2} \]

Meaning,

\[ P_c = \frac{1}{27} \frac{a}{b^2} \]

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

\[ \tau > \tau_c \]

\[ \tau < \tau_c \]

(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?

The region in between \( V_- \) and \( V_+ \) is thermodynamically unstable.

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