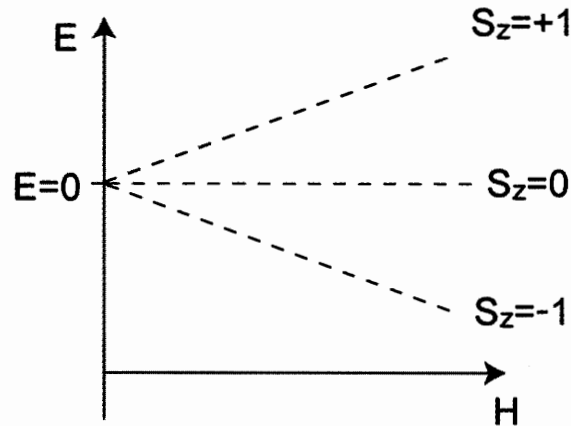


1. Consider a system consisting of N non-interacting particles each with spin $S = 1$ in an external magnetic field, H . For $H = 0$, all of a single particle's spin projections, S_z , are degenerate with energy $E = 0$.
- a) Plot the energies of ALL spin projections, S_z , of a single particle as a function of H .



- b) Calculate the partition function of the system as a function of temperature T and H .

The partition function of a single spin is given by

$$Z_1 = 1 + e^{-\beta g \mu_B H} + e^{\beta g \mu_B H}$$

and hence the partition function of a system of N noninteracting spin is

$$Z_N = Z_1^N = [1 + e^{-\beta g \mu_B H} + e^{\beta g \mu_B H}]^N$$

- c) Compute the average energy, $\langle E \rangle$ of the system. What is the form of $\langle E \rangle$ in the limit $T \rightarrow 0$. Explain your results (1 sentence maximum). What is the form of $\langle E \rangle$ in the limit $\beta g \mu_B H \ll 1$?

Use

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_N = N g \mu_B H \frac{e^{-\beta g \mu_B H} - e^{\beta g \mu_B H}}{1 + e^{-\beta g \mu_B H} + e^{\beta g \mu_B H}} = -N g \mu_B H \frac{e^{\beta g \mu_B H} - e^{-\beta g \mu_B H}}{1 + e^{-\beta g \mu_B H} + e^{\beta g \mu_B H}}$$

For $T \rightarrow 0$ I obtain

$$\langle E \rangle = -N g \mu_B H$$

All spins are in the lowest energy state, which is the $S_z = -1$ state with energy $E_{-1} = -g \mu_B H$.

For $\beta g \mu_B H \ll 1$ one expands the exponential to leading order in $\beta g \mu_B H$ and obtains

$$\langle E \rangle = -N \frac{2(g \mu_B H)^2}{3 k_B T}$$

- d) Compute the specific heat of the system for constant H .

One has

$$\begin{aligned}
C_H &= \frac{\partial \langle E \rangle}{\partial T} = -\beta^2 k_B \frac{\partial \langle E \rangle}{\partial \beta} = \\
&= k_B N (\beta g \mu_B H)^2 \frac{[e^{\beta g \mu_B H} + e^{-\beta g \mu_B H}][1 + e^{-\beta g \mu_B H} + e^{\beta g \mu_B H}] - [e^{\beta g \mu_B H} - e^{-\beta g \mu_B H}]^2}{[1 + e^{-\beta g \mu_B H} + e^{\beta g \mu_B H}]^2} \\
&= k_B N (\beta g \mu_B H)^2 \frac{4 + e^{\beta g \mu_B H} + e^{-\beta g \mu_B H}}{[1 + e^{-\beta g \mu_B H} + e^{\beta g \mu_B H}]^2}
\end{aligned}$$

2. Consider a three-dimensional box with sides of length L . It contains an ideal gas of non-interacting spin-less particles each with kinetic energy

$$\epsilon = \frac{m}{2} \vec{v}^2$$

The temperature of the gas is T , and the particles are uniformly distributed throughout the box.

- a) What is the normalized velocity distribution of the gas?

$$P(\vec{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{m\vec{v}^2}{2k_B T} \right)$$

- b) We now open one side of the box (the one facing the $+x$ -direction) for a given time Δt . Using the result from (a), compute the number of particles that escape from the box in time Δt . To this end, consider these two steps: (i) Divide the box into slices of width dx and compute first the number of particles in a given slice at a distance x from the opening that have escape through the opening in time Δt .

The number of particles contained in this slice is given by

$$\frac{N}{L^3} L^2 dx = \frac{N}{L} dx$$

In order for a particle from this slice to escape in time Δt , its velocity in the $+x$ -direction needs to satisfy $v_x \geq \frac{x}{\Delta t}$. The number of particles contained in the slice with velocity $v_x \geq \frac{x}{\Delta t}$ is given by

$$\begin{aligned}
\frac{N}{L} dx \int_{\frac{x}{\Delta t}}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z P(\vec{v}) &= \frac{N}{L} dx \int_{\frac{x}{\Delta t}}^{\infty} dv_x \left(\frac{m}{2\pi k_B T} \right)^{1/2} \exp\left(-\frac{m\vec{v}^2}{2k_B T} \right) \\
&= \frac{N}{L} dx \left(\frac{m}{2\pi k_B T} \right)^{1/2} \frac{1}{2} \sqrt{\frac{\pi}{\frac{m}{2k_B T}}} \left[1 - \text{Erf}\left(\sqrt{\frac{m}{2k_B T}} \frac{x}{\Delta t} \right) \right] \\
&= \frac{N}{2L} \left[1 - \text{Erf}\left(\sqrt{\frac{m}{2k_B T}} \frac{x}{\Delta t} \right) \right] dx
\end{aligned}$$

- (ii) In order to find the total number of escaped particles, integrate the result you obtained in (i).

$$\begin{aligned}
N_{tot} &= \int_0^L \left[1 - \text{Erf} \left(\sqrt{\frac{m}{2k_B T}} \frac{1}{\Delta t} x \right) \right] dx \\
&= \frac{N}{2L} \frac{1}{\sqrt{\frac{m}{2k_B T}} \frac{1}{\Delta t}} \left\{ \frac{1}{\sqrt{\pi}} \left[1 - \exp \left(-\frac{m}{2k_B T} \left(\frac{L}{\Delta t} \right)^2 \right) \right] + \sqrt{\frac{m}{2k_B T}} \frac{L}{\Delta t} \left[1 - \text{Erf} \left(\sqrt{\frac{m}{2k_B T}} \frac{L}{\Delta t} \right) \right] \right\} \\
&= \frac{N}{2} \frac{1}{z} \left\{ \frac{1}{\sqrt{\pi}} [1 - \exp(-z^2)] + z [1 - \text{Erf}(z)] \right\}
\end{aligned}$$

where I defined

$$z = \sqrt{\frac{m}{2k_B T}} \frac{L}{\Delta t}$$

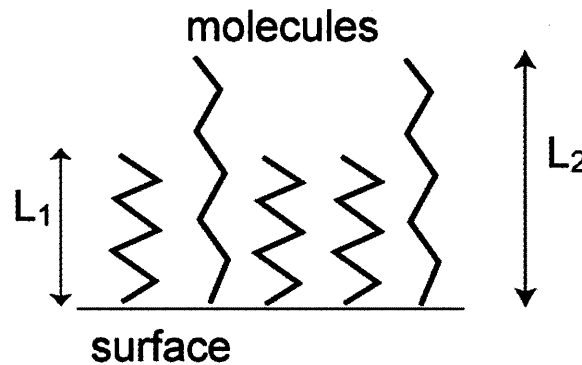
c) How does the total number of escaped particles depend on Δt in the limit $\Delta t \rightarrow 0$?

This limit corresponds to $z \rightarrow \infty$ and I obtain

$$N_{tot} \approx \frac{N}{2} \frac{1}{z} \left\{ \frac{1}{\sqrt{\pi}} [1 - \exp(-z^2)] + z \frac{\exp(-z^2)}{\sqrt{\pi} z} \right\} = \frac{N}{2\sqrt{\pi}} \frac{1}{z} = \frac{N}{2\sqrt{\pi}} \sqrt{\frac{2k_B T}{m}} \frac{\Delta t}{L}$$

Thus, the number of escaped particles is directly proportional to Δt .

3. Consider a two-dimensional surface that is covered by molecules (as shown in the figure below).



The molecules form a quadratic lattice. Each of the molecules can be in one of two states with different length L_1 and L_2 with $L_1 < L_2$. If two neighboring molecules are in the same "length state" their total energy is $-E_0$, if they are in opposite states, their energy is $+E_0$.

a) Using the function

$$f(l_i) = \frac{2l_i - L_1 - L_2}{L_2 - L_1}$$

where l_i is the length of the molecule at site i , write down an expression for the total energy of the system, and for the energy E_i of the molecule at site i .

The total energy of the system is given by

$$E_{tot} = -E_0 \sum_{\langle ij \rangle} f(L_i) f(L_j)$$

where the sum runs over neighboring sites i and j . The energy of the single molecule is

give by

$$E_i = -E_0 \sum_{\langle ij \rangle} f(L_i) f(L_j)$$

where the sum runs over sites j that are neighboring the site i .

b) We next want to compute the average length of a molecule, $\langle L_i \rangle$, which can be obtained via the above equation from the average value $\langle f(L_i) \rangle$. In order to compute $\langle f(L_i) \rangle$ in mean-field theory, we write the energy of the molecule at site i as

$$E_i = -nE_0 f(L_i) \langle f(L_i) \rangle$$

Explain, how this result can be obtained from the result in (a)? What is n ?

One simply replaces $f(L_j)$ by the average value $\langle f(L_i) \rangle$ which is the same for all lattice sites. The factor of $n = 4$ counts the neighboring sites of i on a two-dimensional square lattice.

c) Derive the partition function of the system in terms of $\langle f(L_i) \rangle$.

The partition function for a single molecule is

$$Z_1 = \exp[-n\beta E_0 \langle f(L_i) \rangle] + \exp[n\beta E_0 \langle f(L_i) \rangle] = 2 \cosh[n\beta E_0 \langle f(L_i) \rangle]$$

And the partition function for the entire system is

$$Z_N = Z_1^N = 2^N \cosh^N[n\beta E_0 \langle f(L_i) \rangle]$$

d) Derive a self-consistent equation for $\langle f(L_i) \rangle$. What is the average length of a molecule for $T \rightarrow 0$? Explain your results.

One has

$$\langle f(L_i) \rangle = \frac{\exp[-n\beta E_0 \langle f(L_i) \rangle] - \exp[n\beta E_0 \langle f(L_i) \rangle]}{Z_1} = \frac{2 \sinh[n\beta E_0 \langle f(L_i) \rangle]}{2 \cosh[n\beta E_0 \langle f(L_i) \rangle]} = \tanh[n\beta E_0 \langle f(L_i) \rangle]$$

In the limit $T \rightarrow 0$ one has $\tanh[n\beta E_0 \langle f(L_i) \rangle] \rightarrow \pm 1$, depending on whether $\langle f(L_i) \rangle$ is large or smaller than 0. If $\langle f(L_i) \rangle > 0$, one has

$$\langle f(L_i) \rangle = \tanh[n\beta E_0 \langle f(L_i) \rangle] \rightarrow 1$$

implying that

$$\langle l_i \rangle = L_2$$

On the other hand, if $\langle f(L_i) \rangle < 0$, one has

$$\langle f(L_i) \rangle = \tanh[n\beta E_0 \langle f(L_i) \rangle] \rightarrow -1$$

implying that

$$\langle l_i \rangle = L_1$$

Both solutions are possible and reflect the spontaneously broken symmetry.

4. Consider a system consisting of M molecules at temperature T . Each of these molecules exhibits vibrations with energies

$$E_n = \hbar\omega_0 \left(n + \frac{1}{2} \right) \quad \text{where } n = 0, 1, 2, 3, \dots$$

a) Compute the partition function Z of the system and its free energy F .

Since the molecules do not interact with each other, the partition function of a single molecule is

$$\begin{aligned}
Z_1 &= \sum_{n=0}^{\infty} \exp\left[-\beta\hbar\omega_0\left(n + \frac{1}{2}\right)\right] = \exp\left[-\frac{\beta\hbar\omega_0}{2}\right] \sum_{n=0}^{\infty} (\exp[-\beta\hbar\omega_0])^n \\
&= \exp\left[-\frac{\beta\hbar\omega_0}{2}\right] \frac{1}{1 - \exp[-\beta\hbar\omega_0]} = \frac{1}{\exp\left[\frac{\beta\hbar\omega_0}{2}\right] - \exp\left[-\frac{\beta\hbar\omega_0}{2}\right]} \\
&= \frac{1}{2 \sinh\left[\frac{\beta\hbar\omega_0}{2}\right]}
\end{aligned}$$

The partition function of the entire system is then

$$Z_N = Z_1^N = 2^{-N} \frac{1}{\sinh^N\left[\frac{\beta\hbar\omega_0}{2}\right]}$$

The free energy is given by

$$F = -\frac{1}{\beta} \ln Z_N = \frac{N}{\beta} \left[\ln 2 + \ln \left[\sinh\left(\frac{\beta\hbar\omega_0}{2}\right) \right] \right]$$

b) Compute the average energy $\langle E \rangle$, entropy S and the specific heat C_V of the system.

The average energy is given by

$$\begin{aligned}
\langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z_N = -\frac{N}{Z_1} \frac{\partial}{\partial \beta} \frac{1}{2 \sinh\left[\frac{\beta\hbar\omega_0}{2}\right]} = \frac{N}{2Z_1} \frac{\hbar\omega_0}{2} \frac{\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]}{\sinh^2\left[\frac{\beta\hbar\omega_0}{2}\right]} \\
&= \frac{N}{2} 2 \sinh\left[\frac{\beta\hbar\omega_0}{2}\right] \frac{\hbar\omega_0}{2} \frac{\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]}{\sinh^2\left[\frac{\beta\hbar\omega_0}{2}\right]} = N \frac{\hbar\omega_0}{2} \frac{\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]}{\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]} \\
&= N \frac{\hbar\omega_0}{2} \frac{1}{\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]}
\end{aligned}$$

and the specific heat follows from

$$\begin{aligned}
C_V &= \frac{\partial \langle E \rangle}{\partial T} = -\beta^2 k_B \frac{\partial \langle E \rangle}{\partial \beta} = -\beta^2 k_B N \frac{\hbar\omega_0}{2} \frac{\partial}{\partial \beta} \frac{1}{\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]} \\
&= \beta^2 k_B N \frac{\hbar\omega_0}{2} \frac{1}{\left(\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]\right)^2} \frac{1}{\left(\cosh\left[\frac{\beta\hbar\omega_0}{2}\right]\right)^2} \frac{\hbar\omega_0}{2} \\
&= k_B N \left(\frac{\beta\hbar\omega_0}{2}\right)^2 \frac{1}{\left(\sinh\left[\frac{\beta\hbar\omega_0}{2}\right]\right)^2}
\end{aligned}$$

and the entropy follows from

$$S = \frac{\langle E \rangle - F}{T} = \frac{N}{T} \left\{ \frac{\hbar\omega_0}{2} \frac{1}{\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]} - \frac{1}{\beta} \left[\ln 2 + \ln \left[\sinh\left(\frac{\beta\hbar\omega_0}{2}\right) \right] \right] \right\}$$

5. a) What is the internal energy and the equation of state of an ideal gas?

$$U = \frac{3}{2} N k_B T; \quad pV = N k_B T$$

b) Compute the entropy of an ideal gas as a function of T and V for constant particle

number N starting from

$$dU = TdS - pdV$$

We start from

$$dS = \frac{dU}{T} + \frac{p}{T}dV = \frac{3}{2}Nk_B \frac{dT}{T} + Nk_B \frac{dV}{V}$$

We can now integrate the above expression from a state with entropy S_0 at T_0 and V_0 to obtain

$$S(T, V) - S_0(T_0, V_0) = \frac{3}{2}Nk_B \ln \frac{T}{T_0} + Nk_B \ln \frac{V}{V_0} = Nk_B \ln \left\{ \left(\frac{T}{T_0} \right)^{3/2} \frac{V}{V_0} \right\}$$

c) Compute the chemical potential of the ideal gas (which is a state quantity and thus has a complete differential) as a function of p and T starting from the Gibbs-Duhem relation

$$SdT - Vdp + Nd\mu = 0$$

Thus

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dp$$

Using next

$$\begin{aligned} S(T, V) - S_0(T_0, V_0) &= \frac{3}{2}Nk_B \ln \frac{T}{T_0} + Nk_B \ln \frac{V}{V_0} \\ &= Nk_B \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \frac{V}{V_0} \right\} = Nk_B \ln \left\{ \left(\frac{T}{T_0} \right)^{3/2} \frac{p_0}{p} \right\} \end{aligned}$$

and

$$V = \frac{Nk_B T}{p}$$

I obtain

$$d\mu = -\left[\frac{1}{N}S_0(T_0, V_0) + k_B \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \frac{p_0}{p} \right\} \right] dT + k_B T \frac{dp}{p}$$

and by integrating

$$\begin{aligned} \mu(T, p) - \mu(T_0, p_0) &= -\int_{T_0}^T dT \left[\frac{1}{N}S_0(T_0, V_0) + k_B \frac{5}{2} \ln \left\{ \left(\frac{T}{T_0} \right) \frac{p_0}{p} \right\} \right] + k_B T \int_{p_0}^p \frac{dp}{p} \\ &= -\left[\frac{T-T_0}{N}S_0(T_0, V_0) + \frac{5}{2}k_B [T \ln T - T - (T_0 \ln T_0 - T_0) - (T - T_0) \ln T_0] \right] + k_B T \ln \left(\frac{p}{p_0} \right) \\ &= -\frac{T-T_0}{N}S_0(T_0, V_0) - \frac{5}{2}k_B T \ln \frac{T}{T_0} + \frac{5}{2}k_B (T - T_0) + k_B T \ln \left(\frac{p}{p_0} \right) \end{aligned}$$