

STRUTTURA DELLA MATERIA 1

Problems on statistics of systems with a finite Hilbert space

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The general context is high-temperature gases of objects (e.g. atoms, molecules) carrying internal degrees of freedom.

The relevant degrees of freedom are of two kinds: translational and internal.

These are the fundamental relations valid at high temperature:

$$Z \simeq \frac{(Z_1)^N}{N!}, \quad (1)$$

and

$$Z_1 = Z_{1\text{tr}} Z_{1\text{int}}. \quad (2)$$

They connect the statistics of the entire gas to that of a single “particle”.

We have already dealt with the translational degrees of freedom.

We now focus on internal degrees of freedom characterized by a *finite-dimensional Hilbert state*.

1 Thermodynamics of spin-1/2 atoms

Compute the contribution of the spin degrees of freedom to the thermodynamic functions of a gas of Na atoms (spin-1/2) kept at equilibrium at $T = 500$ K and immersed in a 0.7 T magnetic field.

1.1 Solution

In the sodium gs, $L = 0$, therefore $J = S = 1/2$, and the gyromagnetic factor is $g_J = g_s = 2$.

The spin produces a magnetic moment

$$\boldsymbol{\mu} = -g_J \mu_B \frac{\vec{J}}{\hbar}$$

which couples to the external field as

$$H_{\text{magn}} = -\boldsymbol{\mu} \cdot \vec{B} = -\mu_z B, \quad (3)$$

assuming $\vec{B} = B \hat{\mathbf{z}}$ (as always).

The Hilbert space of relevant quantum states has $(2J + 1)$ dimensions. A basis of this space is labeled by the J_z projection quantum number M_J .

On this basis the coupling Hamiltonian (3) is diagonal with eigenenergies

$$E_{\text{magn}}(M_J) \simeq \langle J, M_J | H_{\text{magn}} | J, M_J \rangle = \langle J, M_J | -\mu_z B | J, M_J \rangle = g_J \mu_B B M_J. \quad (4)$$

For the statistics of this problem, like we did for similar molecular degrees of freedom it is useful to introduce a typical temperature scale

$$\Theta_B = \frac{g_J \mu_B B}{k_B},$$

reflecting the spacing $g_J \mu_B B$ of the magnetic states, and a dimensionless ratio

$$x = \beta g_J \mu_B B = \frac{g_J \mu_B B}{k_B T} = \frac{\Theta_B}{T}.$$

The spin partition function is a finite sum containing $(2J + 1)$ terms, one for each energy level in Eq. (4):

$$Z_{1 \text{ spin}} = \sum_{M_J=-J}^J \exp(-x M_J). \quad (5)$$

The derivation and this final formula are general and valid for any value of J .

In this problem we deal with the simplest case, $J = 1/2$, with 2 terms in the sum, labeled by $M_J = -1/2$ and $M_J = 1/2$:

$$Z_{1 \text{ spin}} = \exp(-x(-1/2)) + \exp(-x(1/2)) = e^{x/2} + e^{-x/2} = 2 \cosh(x/2) \quad (6)$$

Now that we have the partition function, we can obtain the spin-1/2 thermodynamic functions:

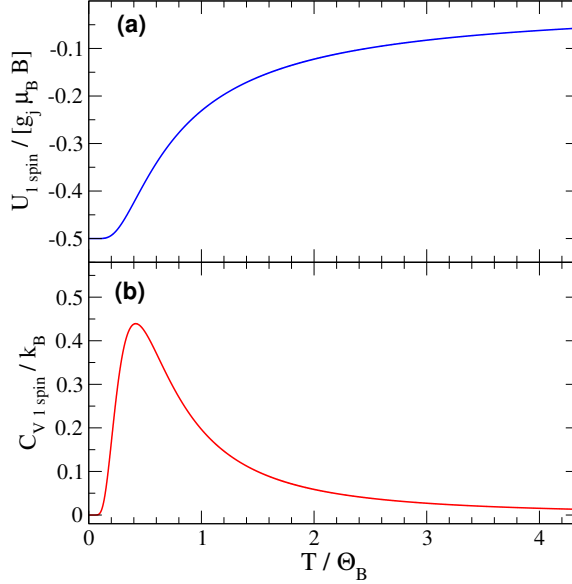
$$F_{1 \text{ spin}} = \frac{F_{\text{spin}}}{N} = -\frac{1}{\beta} \ln Z_{1 \text{ spin}} = -k_B T \ln \left(2 \cosh \frac{x}{2} \right); \quad (7)$$

$$\begin{aligned} U_{1 \text{ spin}} &= \frac{U_{\text{spin}}}{N} = -\frac{\partial}{\partial \beta} \ln Z_{1 \text{ spin}} = -\frac{\partial}{\partial \beta} \ln \left(2 \cosh \frac{x}{2} \right) \quad (8) \\ &= -\frac{\partial}{\partial x} \ln \left(2 \cosh \frac{x}{2} \right) \times \frac{\partial x}{\partial \beta} \\ &= -\frac{1}{2 \cosh \frac{x}{2}} \frac{\partial}{\partial x} \left(2 \cosh \frac{x}{2} \right) \times \frac{\partial (\beta g_J \mu_B B)}{\partial \beta} \\ &= -\frac{1}{2 \cosh \frac{x}{2}} \sinh \frac{x}{2} \times g_J \mu_B B \\ &= -\frac{g_J \mu_B B}{2} \tanh \frac{x}{2} \rightarrow \begin{cases} -\frac{g_J \mu_B B}{2} & \text{for } x \rightarrow \infty, \text{ i.e. } T \rightarrow 0 \\ 0^- & \text{for } x \rightarrow 0, \text{ i.e. } T \rightarrow \infty \end{cases}; \end{aligned}$$

$$\begin{aligned} C_{V 1 \text{ spin}} &= \frac{C_{V \text{ spin}}}{N} = \frac{\partial U_{1 \text{ spin}}}{\partial T} \quad (9) \\ &= \frac{\partial}{\partial T} \left(-\frac{g_J \mu_B B}{2} \tanh \frac{x}{2} \right) = \frac{\partial}{\partial x} \left(-\frac{g_J \mu_B B}{2} \tanh \frac{x}{2} \right) \times \frac{\partial x}{\partial T} \\ &= -\frac{g_J \mu_B B}{2} \frac{\partial}{\partial x} \tanh \frac{x}{2} \times \frac{\partial \Theta_B / T}{\partial T} \\ &= -\Theta_B \frac{g_J \mu_B B}{2} \left(1 - \tanh^2 \frac{x}{2} \right) \times \frac{1}{2} \times \frac{\partial T^{-1}}{\partial T} \\ &= -\Theta_B \frac{g_J \mu_B B}{4} \frac{\cosh^2 \frac{x}{2} - \sinh^2 \frac{x}{2}}{\cosh^2 \frac{x}{2}} \times (-T^{-2}) \\ &= \frac{(g_J \mu_B B)^2}{4 k_B T^2} \frac{1}{\cosh^2 \frac{x}{2}} = \frac{(g_J \mu_B B)^2}{4 k_B T^2} \frac{4}{e^x + 2 + e^{-x}} \\ &= k_B \frac{x^2}{4} \frac{4}{2 \cosh x + 2} = k_B x^2 \frac{1}{2 \cosh x + 2} \\ &= k_B \frac{x^2}{2 \cosh x + 2}; \end{aligned}$$

$$\begin{aligned}
S_{1\text{ spin}} &= \frac{S_{\text{spin}}}{N} = \frac{U_{1\text{ spin}}}{T} + k_B \ln Z_{1\text{ spin}} \\
&= -\frac{gJ\mu_B B}{2T} \tanh \frac{x}{2} + k_B \ln \left(2 \cosh \frac{x}{2} \right) = -\frac{k_B x}{2} \tanh \frac{x}{2} + k_B \ln \left(2 \cosh \frac{x}{2} \right) \\
&= k_B \left[\ln \left(2 \cosh \frac{x}{2} \right) - \frac{x}{2} \tanh \frac{x}{2} \right].
\end{aligned} \tag{10}$$

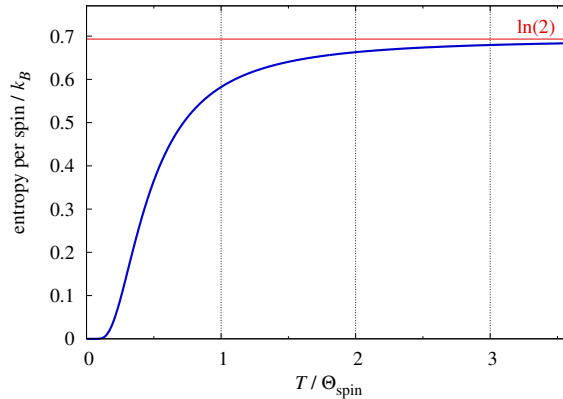
Here we plot the temperature dependence of the internal energy and heat capacity per spin:



As temperature is raised from absolute zero, like molecular rotations and vibrations, the spin degree of freedom “unfreezes”, with an increase in heat capacity. However, when T is raised further, due to the finite spectrum, the internal energy cannot increase indefinitely: $U_{1\text{ spin}}$ flattens out. As a result, the spin heat capacity decays to zero at high temperature $T \gg \Theta_B$.

This behavior is qualitatively different from that of rotational and vibrational excitations in molecules.

We can also plot the entropy:



Note that at low temperature $S_{1\text{ spin}}$ is extremely close to 0, and then it raises toward the high-temperature limit $\ln 2$, expected for a system with 2 equally-accessed states. For the data of the present problem we have:

$$gJ\mu_B B = 1.29836 \times 10^{-23} \text{ J} = 81.0 \text{ } \mu\text{eV};$$

$$\Theta_B = \frac{gJ\mu_B B}{k_B} = 0.940 \text{ K};$$

$$x = \frac{\Theta_B}{T} = 0.001881.$$

Correspondingly, the values of the thermodynamic functions are:

$$\begin{aligned} F_{1\text{ spin}} &= -4.785 \times 10^{-21} \text{ J} = -29.86 \text{ meV}; \\ U_{1\text{ spin}} &= -6.105 \times 10^{-27} \text{ J} = -38.1 \text{ neV}; \\ C_{V1\text{ spin}} &= 8.8435 \times 10^{-7} k_B = 1.2209 \times 10^{-29} \text{ J/K}; \\ S_{1\text{ spin}} &= 0.6931 k_B = 9.570 \times 10^{-24} \text{ J/K}, \end{aligned}$$

extremely close to $\ln(2) k_B$.

2 Magnetic properties of spin- $1/2$ systems

Compute the average spin magnetization and the weak-field magnetic susceptibility of a gas of Na atoms (spin- $1/2$) kept at equilibrium at $T = 500$ K and $P = 10\,000$ Pa, and immersed in a 0.7 T magnetic field.

2.1 Solution

1. The magnetization density of N uniformly distributed magnetic moments in a volume V equals

$$\vec{M} = \frac{N}{V} [\mu_1]. \quad (11)$$

This is a relevant quantity that can be directly measured in the lab.

For an ideal gas \vec{M} is necessarily oriented parallel to the magnetic field, $\vec{M} = M\hat{z}$.

With the same notation as for the previous problem, we have

$$\begin{aligned} [\mu_{1z}] &= \text{Tr}(\hat{\rho}_1 \mu_{1z}) = \sum_{M_J=-J}^J -g_J \mu_B M_J \frac{\exp(-x M_J)}{Z_{1\text{ spin}}} \\ &= -\frac{1}{B} \sum_{M_J=-J}^J \mathcal{E}_{M_J} P_{M_J} = -\frac{U_{1\text{ spin}}}{B}. \end{aligned} \quad (12)$$

The above relation is valid for any J , not just spin- $1/2$.

Now, we compute the magnetization for spin- $1/2$, using the expression (8) derived in the previous problem:

$$M_z = \frac{N}{V} [\mu_{1z}] = -\frac{N}{VB} U_{1\text{ spin}} = \frac{g_J \mu_B N}{2V} \tanh \frac{x}{2}. \quad (13)$$

The average magnetization changes with temperature following the same functional dependence as the internal energy, except for a constant factor $-N/(VB)$, thus we can interpret the $U_{1\text{ spin}}$ plot as magnetization as a function of temperature, as long as we reverse the vertical axis.

We can obtain the atomic number density using the equation of perfect gases $PV = Nk_B T$, which can be safely applied to dilute Na vapor. Using the data of the problem:

$$\frac{N}{V} = \frac{P}{k_B T} = 1.4486 \times 10^{24} \text{ m}^{-3}.$$

Combining this density with the internal energy evaluated in the previous problem, we have:

$$M_z = -\frac{N}{VB} U_{1\text{ spin}} = \frac{g_J \mu_B N}{2V} \tanh \frac{x}{2} \simeq \mu_B \frac{N}{V} \frac{x}{2} \simeq 0.00884 \text{ A m}^{-1}. \quad (14)$$

2. To obtain the linear response of the localized spins to a weak magnetic field B , as we have done above we expand the hyperbolic tangent in the expression for the magnetization (13) to the lowest (=linear) order in x , $\tanh(x/2) \simeq x/2$:

$$M_z \simeq \frac{g_J \mu_B N}{2V} \frac{x}{2} = \frac{g_J \mu_B N}{4V} \frac{g_J \mu_B B}{k_B T} \equiv \chi_B B, \quad (15)$$

with

$$\chi_B = \frac{N}{V} \left(\frac{g_J \mu_B}{2} \right)^2 \frac{1}{k_B T}. \quad (16)$$

χ_B represents the requested paramagnetic susceptibility of the spins to the (weak) total magnetic field \vec{B} . The characteristic inverse- T dependence of the *Curie susceptibility* of the noninteracting spins reflects the disordering effect of temperature.

For the data of our problem,

$$\chi_B = \frac{N}{V} \frac{\mu_B^2}{k_B T} = 0.01805 \text{ F m s}^{-2},$$

or equivalently $\text{A m}^{-1} \text{T}^{-1}$, the same units as $\epsilon_0 c^2$.

In practice it is more common to measure the susceptibility χ_m relative to the *external* applied field $\vec{H} = \epsilon_0 c^2 \vec{B}_{\text{ext}}$. The relation between χ_B and χ_m derives from

$$\vec{M} = \chi_B \vec{B} = \chi_B \left[\vec{B}_{\text{ext}} + \vec{B}_{\text{int}} \right] = \chi_B \left[(\epsilon_0 c^2)^{-1} \vec{H} + (\epsilon_0 c^2)^{-1} \vec{M} \right], \quad (17)$$

where we use the relation $\vec{B}_{\text{int}} = (\epsilon_0 c^2)^{-1} \vec{M}$ for the magnetic field generated by a uniformly magnetized material. We solve Eq. (17) for \vec{M} , obtaining

$$\vec{M} = \frac{(\epsilon_0 c^2)^{-1} \chi_B}{1 - (\epsilon_0 c^2)^{-1} \chi_B} \vec{H}. \quad (18)$$

Noting that the units of \vec{H} and those of \vec{M} are the same, namely A/m , the desired expression for the dimensionless \vec{H} -susceptibility χ_m is

$$\chi_m = \frac{(\epsilon_0 c^2)^{-1} \chi_B}{1 - (\epsilon_0 c^2)^{-1} \chi_B}. \quad (19)$$

In practice the denominator is always very close to unity, so that

$$\chi_m \simeq (\epsilon_0 c^2)^{-1} \chi_B.$$

For the data of our problem,

$$\chi_m = \frac{\chi_B}{\epsilon_0 c^2} = 2.268 \times 10^{-8}.$$

Even at lower temperature, one should not worry about a vanishing denominator in Eq. (19).

Such event would indicate a self-sustained nonzero magnetization for $\vec{H} = \vec{0}$: even at such a low temperature as 1 K, for $g = 2$ the diverging- χ_m condition $(\epsilon_0 c^2)^{-1} \chi_B = 1$ would require a density $N/V \approx 1.3 \times 10^{29} \text{ m}^{-3}$, far too large to describe a dilute gas of spin-carrying atoms.

Actual ferromagnetic states are never associated to a self-sustained magnetization due to a divergence in Eq. (19), but they originate from large exchange interactions similar to those responsible for Hund's rules in open-shell atoms.

3 Occupation distribution of spin-1/2 impurities

An insulating solid contains dilute noninteracting paramagnetic spin-1/2 impurities. It is placed in a magnetic field $B = 3 \text{ T}$, and equilibrated at temperature T . Given that 75% of the spins aligns to the field, determine T and the average magnetic energy per impurity.

3.1 Solution

The probabilities for the 2 levels of this system are:

$$P(M_J) = \frac{1}{Z_{1 \text{ spin}}} \exp(-x M_J)$$

(same notation as in previous problems).

We know that

$$P(-1/2) = \frac{\exp(x/2)}{\exp(x/2) + \exp(-x/2)} = 75\%.$$

We obtain x as follows:

$$\begin{aligned} \frac{1}{1 + \exp(-x)} &= \frac{3}{4}, \\ 1 + \exp(-x) &= \frac{4}{3}, \\ \exp(-x) &= \frac{4}{3} - 1 = \frac{1}{3}, \\ -x &= \ln\left(\frac{1}{3}\right) = -\ln 3, \\ x &= \ln 3. \end{aligned}$$

As $x = \frac{gJ \mu_B B}{k_B T}$, we obtain T as

$$T = \frac{gJ \mu_B B}{k_B x} = \frac{2 \mu_B B}{\ln(3) k_B} = 3.67 \text{ K}.$$

At this temperature, the average magnetic energy per impurity amounts to

$$U_{1 \text{ spin}} = -\frac{gJ \mu_B B}{2} \tanh \frac{x}{2} = -\mu_B B \tanh\left(\frac{\ln 3}{2}\right) = -1.391 \times 10^{-23} \text{ J} = -86.8 \mu\text{eV}.$$

4 Written test 08/02/2002, problem 1 – Spin-1

La molecola di ossigeno (O_2) si trova in uno stato elettronico degenere, caratterizzato da spin $S = 1$. Considerare un gas rarefatto di molecole di ossigeno in equilibrio a temperatura T , immerso in un campo magnetico uniforme $|B| = 25$ T (si trascurino le interazioni dello spin di ciascuna molecola con il moto roto-vibrazionale e con gli spins di differenti molecole). Esprimere la funzione di partizione per lo spin di una singola molecola in termini della variabile adimensionale $x = g\mu_B|B|/(k_B T)$ (dove $g = 2$). Calcolare il momento magnetico medio di una singola molecola. Esprimere in funzione di x il contributo degli spins al calore specifico molare C_B a campo magnetico costante, e valutarlo per $T = 100$ K e $T = 1000$ K.

4.1 Solution

$$Z_{1\text{ spin}} = \sum_{M_J=-1}^1 \exp(-x M_J) = e^x + 1 + e^{-x} = 1 + 2 \cosh x. \quad (20)$$

with, as usual,

$$x = \beta g_J \mu_B B = \frac{\Theta_B}{T},$$

and $g_J = g_s = 2$.

$$\begin{aligned} U_{1\text{ spin}} &= \frac{U_{\text{spin}}}{N} = -\frac{\partial}{\partial \beta} \ln Z_{1\text{ spin}} = -\frac{\partial}{\partial \beta} \ln (1 + 2 \cosh x) \\ &= -\frac{\partial}{\partial x} \ln (1 + 2 \cosh x) \times \frac{\partial x}{\partial \beta} \\ &= -\frac{1}{1 + 2 \cosh x} 2 \sinh x \times \frac{\partial (\beta g_J \mu_B B)}{\partial \beta} \\ &= -g_J \mu_B B \frac{2 \sinh x}{1 + 2 \cosh x} \rightarrow \begin{cases} -g_J \mu_B B & \text{for } x \rightarrow \infty, \text{ i.e. } T \rightarrow 0 \\ 0^- & \text{for } x \rightarrow 0, \text{ i.e. } T \rightarrow \infty \end{cases}. \end{aligned} \quad (21)$$

Like we did for spin-1/2, we have the relation

$$[\mu_{1z}] = \text{Tr}(\hat{\rho}_1 \mu_{1z}) = \sum_{M_J=-J}^J -g_J \mu_B M_J \frac{\exp(-x M_J)}{Z_{1\text{ spin}}} = -\frac{1}{B} \sum_{M_J=-J}^J \mathcal{E}_{M_J} P_{M_J} = -\frac{1}{B} U_{1\text{ spin}}.$$

Inserting the result for $U_{1\text{ spin}}$ we obtain

$$[\mu_{1z}] = -\frac{1}{B} \times \left(-g_J \mu_B B \frac{2 \sinh x}{1 + 2 \cosh x} \right) = g_J \mu_B \frac{2 \sinh x}{1 + 2 \cosh x}.$$

For $B = 25$ T, the characteristic magnetic energy is

$$g_J \mu_B B = 4.637 \times 10^{-22} \text{ J} = 2.894 \text{ meV}.$$

At $T = 100$ K, we obtain $x = 0.335857$, and at $T = 1000$ K, $x = 0.0335857$ (of course!). The average magnetic moment for the given conditions is:

$$\begin{aligned} [\mu_{1z}](T = 100 \text{ K}) &= 4.077 \times 10^{-24} \frac{\text{J}}{\text{T}}; \\ [\mu_{1z}](T = 1000 \text{ K}) &= 4.152 \times 10^{-25} \frac{\text{J}}{\text{T}}. \end{aligned}$$

From $U_{1\text{ spin}}$ we obtain

$$\begin{aligned}
C_{B1\text{ spin}} &= \frac{C_{B\text{ spin}}}{N} = \frac{\partial U_{1\text{ spin}}}{\partial T} & (22) \\
&= \frac{\partial}{\partial T} \left(-g_J \mu_B B \frac{2 \sinh x}{1 + 2 \cosh x} \right) = -g_J \mu_B B \frac{\partial}{\partial x} \left(\frac{2 \sinh x}{1 + 2 \cosh x} \right) \times \frac{\partial x}{\partial T} \\
&= -g_J \mu_B B 2 \frac{\cosh x (1 + 2 \cosh x) - \sinh x (2 \sinh x)}{(1 + 2 \cosh x)^2} \times \frac{\partial \Theta_B / T}{\partial T} \\
&= -\Theta_B 2 g_J \mu_B B \frac{\cosh x + 2 (\cosh^2 x - \sinh^2 x)}{(1 + 2 \cosh x)^2} \times \frac{\partial T^{-1}}{\partial T} \\
&= 2 \frac{\Theta_B g_J \mu_B B}{T^2} \frac{\cosh x + 2}{(1 + 2 \cosh x)^2} \\
&= 2 k_B \frac{\Theta_B^2}{T^2} \frac{2 + \cosh x}{(1 + 2 \cosh x)^2} \\
&= 2 k_B x^2 \frac{2 + \cosh x}{(1 + 2 \cosh x)^2}.
\end{aligned}$$

In the conditions of the problem,

$$C_{B1\text{ spin}}(100 \text{ K}) = 0.07112 k_B = 9.820 \times 10^{-25} \frac{\text{J}}{\text{K}};$$

$$C_{B1\text{ spin}}(1000 \text{ K}) = 0.0007515 k_B = 1.037 \times 10^{-26} \frac{\text{J}}{\text{K}}.$$

The requested molar quantities:

$$C_{B\text{ spin}}^{\text{mol}}(100 \text{ K}) = N_A C_{V1\text{ spin}}(100 \text{ K}) = 0.59137 \frac{\text{J}}{\text{mol K}};$$

$$C_{B\text{ spin}}^{\text{mol}}(1000 \text{ K}) = N_A C_{V1\text{ spin}}(1000 \text{ K}) = 0.0062489 \frac{\text{J}}{\text{mol K}}.$$

5 Written test 18/09/2003, problem 2 – Spin- $3/2$

Si trascuri la probabilità che atomi di bromo gassoso a 500 K occupino stati diversi da $[\text{Ar}]3d^{10}4p^5 \ ^2P_{3/2}$. Accendendo un campo magnetico uniforme la degenerazione delle componenti di questo multipletto è risolta: quale sarebbe l'intensità di tale campo necessaria a stabilire una popolazione d'equilibrio uguale per lo stato fondamentale e per il totale delle componenti eccitate? [Suggerimento: la radice dell'equazione $\cosh(x) = \sinh(3x)$ è $x \simeq 0.304689$]

5.1 Solution

$$E_B(M_J) = g_J \mu_B B M_J$$

$$P_{M_J} = \frac{\exp(-\beta E_B(M_J))}{Z_{1\text{ spin}}} = \frac{\exp(-x M_J)}{Z_{1\text{ spin}}}.$$

with, as usual,

$$x = \beta g_J \mu_B B = \frac{g_J \mu_B B}{k_B T} \equiv \frac{\Theta_B}{T},$$

$$\begin{aligned}
g_J &= \frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} = \frac{3\frac{3}{2}(\frac{3}{2}+1) - 1(1+1) + \frac{1}{2}(\frac{1}{2}+1)}{2\frac{3}{2}(\frac{3}{2}+1)} & (23) \\
&= \frac{3 \times \frac{15}{4} - 2 + \frac{3}{4}}{2 \times \frac{15}{4}} = \frac{\frac{45-8+3}{4}}{2 \times \frac{15}{4}} = \frac{40}{2 \times 15} = \frac{4}{3},
\end{aligned}$$

and

$$\begin{aligned}
Z_{1 \text{ spin}} &= \sum_{M_J=-3/2}^{3/2} \exp(-x M_J) \\
&= e^{\frac{3}{2}x} + e^{\frac{1}{2}x} + e^{-\frac{1}{2}x} + e^{-\frac{3}{2}x} = 2 \cosh\left(\frac{3}{2}x\right) + 2 \cosh\left(\frac{1}{2}x\right).
\end{aligned} \tag{24}$$

The equation we need to solve is

$$P_{-3/2} = P_{-1/2} + P_{1/2} + P_{3/2}.$$

The partition function cancels out (we could omit writing it), and here remains:

$$\begin{aligned}
e^{\frac{3}{2}x} &= e^{\frac{1}{2}x} + e^{-\frac{1}{2}x} + e^{-\frac{3}{2}x}, \\
e^{\frac{3}{2}x} - e^{-\frac{3}{2}x} &= e^{\frac{1}{2}x} + e^{-\frac{1}{2}x}, \\
\sinh\left(\frac{3}{2}x\right) &= \cosh\left(\frac{1}{2}x\right).
\end{aligned}$$

Our x is twice the x in the suggestion: $x = 2 \times 0.304689$.

$$x = \beta g_J \mu_B B = \beta \frac{4}{3} \mu_B B.$$

Whence

$$B = \frac{3}{4} \frac{2 \times 0.304689}{\mu_B \beta} = 0.457034 \frac{k_B T}{\mu_B} = 340.2 \text{ T}.$$

6 Written test 17/04/2012, problem 3

Un solido isolante contiene impurezze diluite, dunque praticamente non interagenti, di concentrazione $8 \times 10^{21} \text{ m}^{-3}$. Ogni impurezza è caratterizzata da uno stato fondamentale tre volte degenere, e da un livello eccitato non degenere, ad energia $E_1 = 2.7 \text{ meV}$ al di sopra dello stato fondamentale. Si valuti il contributo dei livelli delle impurezze al calore specifico (per unità di volume) del materiale, alle temperature di 25 K e 50 K.

6.1 Solution

$$Z_{1 \text{ imp}} = 3e^{-\beta \times 0} + e^{-\beta E_1} = 3 + e^{-\beta E_1}. \tag{25}$$

$$\begin{aligned}
U_{1 \text{ imp}} &= \frac{U_{\text{imp}}}{N} = -\frac{\partial}{\partial \beta} \ln Z_{1 \text{ imp}} = -\frac{1}{Z_{1 \text{ imp}}} \frac{\partial Z_{1 \text{ imp}}}{\partial \beta} \\
&= -\frac{1}{3 + e^{-\beta E_1}} \frac{\partial}{\partial \beta} \left(3 + e^{-\beta E_1} \right) = -\frac{1}{3 + e^{-\beta E_1}} \times e^{-\beta E_1} \times (-E_1) \\
&= E_1 \frac{e^{-\beta E_1}}{3 + e^{-\beta E_1}} = E_1 \frac{1}{3e^{\beta E_1} + 1} \rightarrow \begin{cases} 0 & \text{for } \beta E_1 \rightarrow \infty, \text{ i.e. } T \rightarrow 0 \\ 1/4 E_1 & \text{for } \beta E_1 \rightarrow 0, \text{ i.e. } T \rightarrow \infty \end{cases}.
\end{aligned} \tag{26}$$

$$\begin{aligned}
C_{V1\text{ imp}} &= \frac{\partial}{\partial T} U_{1\text{ imp}} = \frac{\partial}{\partial T} \left(E_1 \frac{1}{3e^{\beta E_1} + 1} \right) \\
&= E_1 \frac{\partial}{\partial \beta} \left(\frac{1}{3e^{\beta E_1} + 1} \right) \times \frac{\partial \beta}{\partial T} = E_1 \frac{-1}{(3e^{\beta E_1} + 1)^2} \times 3e^{\beta E_1} E_1 \times \frac{-1}{k_B T^2} \\
&= \frac{E_1^2}{k_B T^2} \frac{3e^{\beta E_1}}{(3e^{\beta E_1} + 1)^2} = k_B \left(\frac{E_1}{k_B T} \right)^2 \frac{3e^{\beta E_1}}{(3e^{\beta E_1} + 1)^2} \\
&= k_B x^2 \frac{3e^x}{(3e^x + 1)^2} \rightarrow \begin{cases} 0 & \text{for } x = \beta E_1 \rightarrow \infty, \text{ i.e. } T \rightarrow 0 \\ 0 & \text{for } x = \beta E_1 \rightarrow 0, \text{ i.e. } T \rightarrow \infty \end{cases} .
\end{aligned} \tag{27}$$

$$C_{V\text{ vol imp}} = \frac{N}{V} C_{V1\text{ imp}} = \begin{cases} 0.0138 \text{ J K}^{-1} \text{ m}^{-3}, & \text{for } T = 25 \text{ K, i.e. } x = 1.25329 \\ 0.005566 \text{ J K}^{-1} \text{ m}^{-3}, & \text{for } T = 50 \text{ K, i.e. } x = 0.626643 \end{cases} . \tag{28}$$

7 Written test 12/02/2012, problem 1

Un solido isolante contiene impurezze diluite, dunque praticamente non interagenti, di concentrazione $1.2 \times 10^{22} \text{ m}^{-3}$. Ogni impurezza è caratterizzata da uno stato fondamentale non degenero, e da due livelli eccitati, ad energie $E_1 = 2.5$ ed $E_2 = 3.7$ meV rispettivamente al di sopra dello stato fondamentale, entrambi degeneri 2 volte. Si valuti il contributo dei livelli delle impurezze al calore specifico (per unità di volume) del materiale, alle temperature di 20 K e 50 K.

7.1 Solution

$$Z_{1\text{ imp}} = 1 + 2e^{-\beta E_1} + 2e^{-\beta E_2} . \tag{29}$$

$$\begin{aligned}
U_{1\text{ imp}} &= \frac{U_{\text{imp}}}{N} = -\frac{\partial}{\partial \beta} \ln Z_{1\text{ imp}} = -\frac{1}{Z_{1\text{ imp}}} \frac{\partial Z_{1\text{ imp}}}{\partial \beta} \\
&= \frac{2E_1 e^{-\beta E_1} + 2E_2 e^{-\beta E_2}}{1 + 2e^{-\beta E_1} + 2e^{-\beta E_2}} \rightarrow \begin{cases} 0 & \text{for } \beta \rightarrow \infty, \text{ i.e. } T \rightarrow 0 \\ 2/5(E_1 + E_2) & \text{for } \beta \rightarrow 0, \text{ i.e. } T \rightarrow \infty \end{cases} .
\end{aligned} \tag{30}$$

$$\begin{aligned}
C_{V1\text{ imp}} &= \frac{\partial}{\partial T} U_{1\text{ imp}} = \frac{\partial}{\partial \beta} \left(\frac{2E_1 e^{-\beta E_1} + 2E_2 e^{-\beta E_2}}{Z_{1\text{ imp}}} \right) \times \frac{\partial \beta}{\partial T} \\
&= \frac{(-2E_1^2 e^{-\beta E_1} - 2E_2^2 e^{-\beta E_2}) \times Z_{1\text{ imp}} - (2E_1 e^{-\beta E_1} + 2E_2 e^{-\beta E_2})^2 \times (-1)}{Z_{1\text{ imp}}^2} \\
&\quad \times \frac{-1}{k_B T^2} \\
&= k_B \beta^2 \frac{(2E_1^2 e^{-\beta E_1} + 2E_2^2 e^{-\beta E_2}) \times Z_{1\text{ imp}} - (2E_1 e^{-\beta E_1} + 2E_2 e^{-\beta E_2})^2}{Z_{1\text{ imp}}^2} \\
&= k_B \beta^2 \left[\frac{2E_1^2 e^{-\beta E_1} + 2E_2^2 e^{-\beta E_2}}{Z_{1\text{ imp}}} - \left(\frac{2E_1 e^{-\beta E_1} + 2E_2 e^{-\beta E_2}}{Z_{1\text{ imp}}} \right)^2 \right] \\
&= k_B \beta^2 ([H^2] - [H]^2) = k_B \beta^2 ([H^2] - U_{1\text{ imp}}^2) \rightarrow \begin{cases} 0 & \text{for } \beta \rightarrow \infty, \text{ i.e. } T \rightarrow 0 \\ 0 & \text{for } \beta \rightarrow 0, \text{ i.e. } T \rightarrow \infty \end{cases} .
\end{aligned} \tag{31}$$

Numerically

$$C_{V1\text{imp}} = \begin{cases} 1.008 \times 10^{-23} \text{ J K}^{-1}, & \text{for } T = 20 \text{ K} \\ 1.687 \times 10^{-24} \text{ J K}^{-1}, & \text{for } T = 50 \text{ K} \end{cases} . \quad (32)$$

And therefore

$$C_{V\text{vol imp}} = \frac{N}{V} C_{V1\text{imp}} = \begin{cases} 0.1210 \text{ J K}^{-1} \text{ m}^{-3}, & \text{for } T = 20 \text{ K} \\ 0.02024 \text{ J K}^{-1} \text{ m}^{-3}, & \text{for } T = 50 \text{ K} \end{cases} . \quad (33)$$

8 Atomic-level statistics

The following energy levels are given for the $1s^2 2s^2 2p^4$ configuration of atomic oxygen:

Term	degeneracy	Energy $\bar{\nu}$ [cm^{-1}]
$^3\text{P}_2$	5	0.0
$^3\text{P}_1$	3	158.5
$^3\text{P}_0$	1	226.5
$^1\text{D}_2$	5	15 867,7
$^1\text{S}_0$	1	33 792,4

Compute the “electronic” statistical quantities $Z_{1\text{el}}$, $U_{1\text{el}}$, and $C_{V1\text{el}}$ for an O atom in a hypothetical atomic-gas state at equilibrium at $T = 0, 100, 300, 1000,$ and 10000 K.

8.1 Solution

$$Z_{1\text{el}} = 5 + 3 \exp(-\beta E_{3\text{P}_1}) + \exp(-\beta E_{3\text{P}_0}) + 5 \exp(-\beta E_{1\text{D}_2}) + \exp(-\beta E_{1\text{S}_0}) . \quad (34)$$

We need the energy levels in SI units, and it is also instructive to convert them to K:

Term	degeneracy	Energy [J]	Energy/ k_B [K]
$^3\text{P}_2$	5	0.0	0.0
$^3\text{P}_1$	3	3.149×10^{-21}	228.05
$^3\text{P}_0$	1	4.499×10^{-21}	325.89
$^1\text{D}_2$	5	3.152×10^{-19}	22,831
$^1\text{S}_0$	1	6.713×10^{-19}	48,621

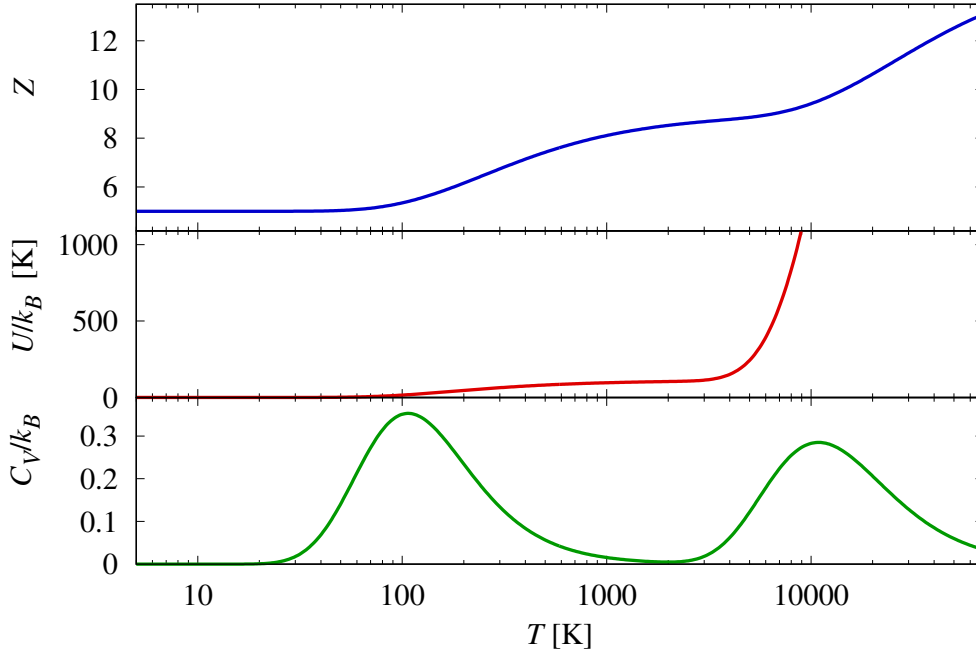
$$\begin{aligned} U_{1\text{el}} &= \frac{U_{\text{el}}}{N} = -\frac{\partial}{\partial \beta} \ln Z_{1\text{el}} = -\frac{1}{Z_{1\text{el}}} \frac{\partial Z_{1\text{el}}}{\partial \beta} \\ &= \frac{3E_{3\text{P}_1} \exp(-\beta E_{3\text{P}_1}) + E_{3\text{P}_0} \exp(-\beta E_{3\text{P}_0}) + 5E_{1\text{D}_2} \exp(-\beta E_{1\text{D}_2}) + E_{1\text{S}_0} \exp(-\beta E_{1\text{S}_0})}{5 + 3 \exp(-\beta E_{3\text{P}_1}) + \exp(-\beta E_{3\text{P}_0}) + 5 \exp(-\beta E_{1\text{D}_2}) + \exp(-\beta E_{1\text{S}_0})} . \end{aligned} \quad (35)$$

$$\begin{aligned} C_{V1\text{el}} &= \frac{\partial}{\partial T} U_{1\text{el}} = \frac{\partial}{\partial \beta} U_{1\text{el}} \times \frac{\partial \beta}{\partial T} \\ &= k_B \beta^2 \left[\frac{3E_{3\text{P}_1}^2 \exp(-\beta E_{3\text{P}_1}) + E_{3\text{P}_0}^2 \exp(-\beta E_{3\text{P}_0}) + \dots}{Z_{1\text{el}}} \right. \\ &\quad \left. - \left(\frac{3E_{3\text{P}_1} \exp(-\beta E_{3\text{P}_1}) + E_{3\text{P}_0} \exp(-\beta E_{3\text{P}_0}) + \dots}{Z_{1\text{el}}} \right)^2 \right] \\ &= k_B \beta^2 ([H^2] - [H]^2) \rightarrow \begin{cases} 0 & \text{for } \beta \rightarrow \infty, \text{ i.e. } T \rightarrow 0 \\ 0 & \text{for } \beta \rightarrow 0, \text{ i.e. } T \rightarrow \infty \end{cases} , \end{aligned} \quad (36)$$

exactly like in the previous problem, just with more terms in the sums.

Then the solution requires a straightforward (rather tedious) exercise in numerical substitution. To avoid very small numbers, we express $U_{1\text{el}}$ in Kelvin units, making use of the figures in the last column in the previous table:

T [K]	$Z_{1\text{el}}$	$U_{1\text{el}}/k_B$ [K]	$C_{V1\text{el}}/k_B$
0	5.0	0.0	0.0
100	5.3451	15.43	0.3510
300	6.7402	64.77	0.1341
1000	8.1101	96.16	0.0155
10000	9.4179	1380.	0.2828



9 Statistics of a continuum model

Evaluate the standard thermodynamic functions for the internal degrees of freedom of a gas of molecules carrying a permanent electric dipole of $p_0 = 1$ Debye, immersed in a uniform electric field $E_z = 3 \times 10^5$ V/m. Treat the angular degrees of freedom of the molecules as if they were classical. Evaluate in particular the average dipole moment component in the direction of the field at $T = 400$ K and the expression for the molecular weak-field polarizability as a function of temperature.

9.1 Solution

What is a Debye?

The Debye is a CGS (non-SI) derived unit of electric dipole. It is defined as the dipole moment resulting from two charges of opposite sign and equal magnitude of 10^{-10} statcoulomb (also called e.s.u.), separated by 1 \AA .

Convert to SI units:

$$\begin{aligned}
 1 \text{ Debye} &= 10^{-10} \text{ statcoulomb} \times 1 \text{ \AA} = 10^{-10} \frac{1}{2997924580} \text{ C} \times 10^{-10} \text{ m} \quad (37) \\
 &= 3.33564 \times 10^{-30} \text{ C m}.
 \end{aligned}$$

To identify the direction where the dipole moment is pointing, 2 angles are sufficient. [In the case of a rigid-body molecule, the third Euler angle is irrelevant: it just provides

an extra degeneracy to all states.] Let us call θ the angle of between the dipole moment and the \hat{z} direction of the field, and φ the azimuthal angle in that the projection of the dipole moment in the xy plane makes with the \hat{x} axis.

The energy of the electric dipole in the field is given by

$$H(\theta, \varphi) = -\vec{p}_0 \cdot \vec{E} = -p_0 E_z \cos \theta = -\varepsilon \cos \theta$$

and is obviously independent of φ . We have introduced the characteristic energy scale of the problem

$$\varepsilon = p_0 E_z = 1.0007 \times 10^{-24} \text{ J} = 6.24583 \text{ } \mu\text{eV}.$$

To tilt the dipole 180° away from perfect alignment with the field, one pays an energy cost 2ε , because $\cos \theta$ changes from 1 to -1 .

The novelty of this problem is that the classical internal degree of freedom has a continuum of states. Therefore

$$\sum_{\alpha} \rightarrow \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \theta d\theta = 2\pi \int_{-1}^1 d \cos \theta$$

The φ variable provides an essentially useless 2π degeneracy, but it is important that the θ integration is carried out as indicated, with the $\sin \theta$ Jacobian, to account for the larger number of directions near the “equator” than near the “poles”.

As usual, we introduce the dimensionless ratio $x = \beta\varepsilon$.

$$\begin{aligned} Z_{1 \text{ dipole}} &= \sum_{\alpha} \exp(-\beta H_{\alpha}) = 2\pi \int_{-1}^1 d \cos \theta \exp(-\beta H(\theta)) & (38) \\ &= 2\pi \int_{-1}^1 d \cos \theta \exp(\beta\varepsilon \cos \theta) = 2\pi \int_{-1}^1 d \cos \theta \exp(x \cos \theta) \\ &= 2\pi \left. \frac{\exp(x \cos \theta)}{x} \right|_{\cos \theta=-1}^{\cos \theta=1} = 2\pi \left[\frac{\exp(x)}{x} - \frac{\exp(-x)}{x} \right] \\ &= 2\pi \left[\frac{\exp(x) - \exp(-x)}{x} \right] = 4\pi \frac{\sinh(x)}{x}. \end{aligned}$$

$$\begin{aligned} U_{1 \text{ dipole}} &= \frac{U_{\text{dipole}}}{N} = -\frac{\partial}{\partial \beta} \ln Z_{1 \text{ dipole}} & (39) \\ &= -\frac{\partial}{\partial \beta} \ln \left(4\pi \frac{\sinh(x)}{x} \right) = -\frac{\partial}{\partial \beta} [\ln 4 + \ln \pi + \ln \sinh(x) - \ln x] \\ &= \frac{\partial}{\partial x} [-\ln \sinh(x) + \ln x] \times \frac{\partial x}{\partial \beta} = \left(-\frac{\cosh x}{\sinh x} + \frac{1}{x} \right) \times \varepsilon \\ &= -\varepsilon \left(\coth x - \frac{1}{x} \right). \end{aligned}$$

We recall the small- x expansion

$$\coth x \simeq \frac{1}{x} + \frac{1}{3}x + \dots$$

This indicates that the small- x singularity of $U_{1 \text{ dipole}}$ is purely apparent. The singularities of the two terms cancel, and in reality the obtained expression for $U_{1 \text{ dipole}}$

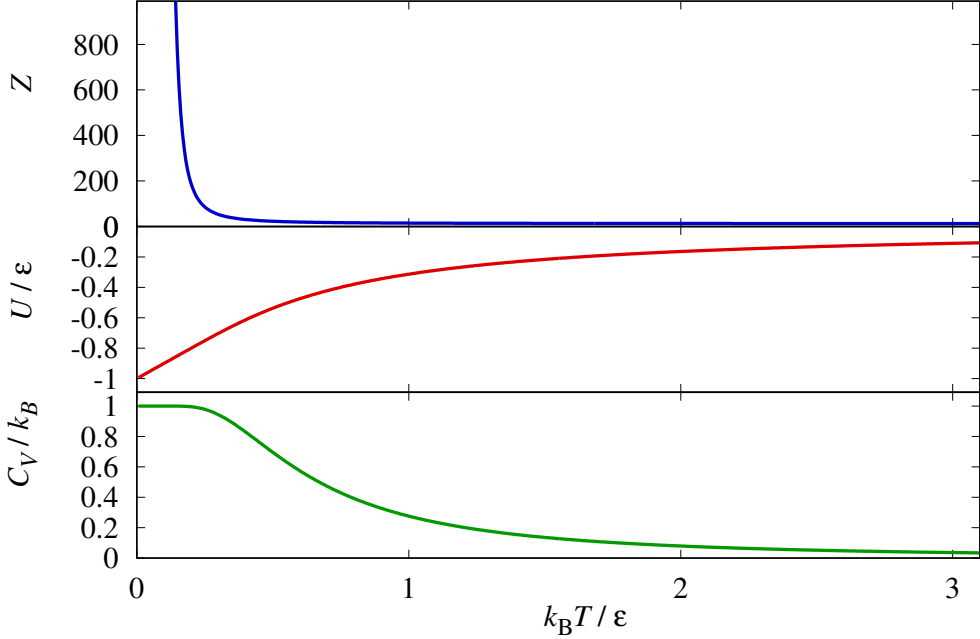
is perfectly smooth and goes to 0 linearly in x , as one expects. The low- and high-temperature limits are indeed:

$$U_{1 \text{ dipole}} = -\varepsilon \left(\coth x - \frac{1}{x} \right) \rightarrow \begin{cases} -\varepsilon & \text{for } x \rightarrow \infty, \text{ i.e. } T \rightarrow 0 \\ 0 & \text{for } x \rightarrow 0, \text{ i.e. } T \rightarrow \infty \end{cases}.$$

The heat capacity:

$$\begin{aligned} C_{V \text{ 1 dipole}} &= \frac{\partial}{\partial T} U_{1 \text{ dipole}} & (40) \\ &= \frac{\partial}{\partial T} \left[-\varepsilon \left(\coth x - \frac{1}{x} \right) \right] = -\varepsilon \frac{\partial}{\partial x} \left(\coth x - \frac{1}{x} \right) \times \frac{\partial x}{\partial T} \\ &= -\varepsilon \left(-\frac{1}{\sinh^2 x} + \frac{1}{x^2} \right) \times \frac{\varepsilon}{k_B} \frac{\partial T^{-1}}{\partial T} = \frac{\varepsilon^2}{k_B T^2} \left(-\frac{1}{\sinh^2 x} + \frac{1}{x^2} \right) \\ &= k_B x^2 \left(\frac{1}{x^2} - \frac{1}{\sinh^2 x} \right) = k_B \left[1 - \left(\frac{x}{\sinh x} \right)^2 \right]. \end{aligned}$$

Although this expression looks benign, it actually exhibits an unphysical behavior for large x , i.e. small temperature: $C_{V \text{ 1 dipole}} \rightarrow k_B$ for $x \rightarrow \infty$!



This low- T behavior contradicts the third law of thermodynamics, which implies that all heat capacities must vanish as $T \rightarrow 0$. This is the result of the unphysical assumption of a rotating molecule pointing classically at some direction. Classical mechanics only approximates the actual quantum motion at high temperature, but fails at low T .

In practice this behavior is more a curiosity than a serious problem because as T is lowered, the ideal gas of molecules turns into a liquid and then a solid far before experiments deviate from Eq. (40).

[Note that the translational contribution $3/2k_B$ to the gas heat capacity is a constant too: it also violates the third law. However, this result only holds for gases at high temperature, while at lower temperature the thermodynamics changes substantially, in a way that certainly produces vanishing low-temperature heat capacities.]

This problem requests the calculation of the average dipole moment component in the

direction of the field:

$$\begin{aligned}
 P_z &= [p_0 \cos \theta] = p_0 [\cos \theta] = \frac{p_0}{-\varepsilon} [-\varepsilon \cos \theta] \\
 &= -\frac{p_0}{\varepsilon} [H(\theta)] = -\frac{p_0}{\varepsilon} U_{1 \text{ dipole}} = -\frac{p_0}{\varepsilon} (-\varepsilon) \left(\coth x - \frac{1}{x} \right) \\
 &= p_0 \left(\coth x - \frac{1}{x} \right) \\
 &= 6.04 \times 10^{-5} \text{ Debye} = 2.015 \times 10^{-34} \text{ C m}.
 \end{aligned} \tag{41}$$

with the data of the problem, implying $x = 0.0001812$.

Note that the function in round parenthesis above is named *Langevin function* after Paul Langevin.

The expression for the weak-field (or equivalently high-temperature) polarizability is

$$\begin{aligned}
 \chi_{\text{el}} &= \left. \frac{\partial P_z}{\partial E_z} \right|_{E_z \rightarrow 0^+} = \left. \frac{\partial}{\partial E_z} p_0 \left(\coth x - \frac{1}{x} \right) \right|_{E_z \rightarrow 0^+} \\
 &= p_0 \left. \frac{\partial}{\partial x} \left(\coth x - \frac{1}{x} \right) \right|_{x \rightarrow 0^+} \times \frac{\partial x}{\partial E_z} \\
 &= p_0 \left. \frac{\partial}{\partial x} \left(\frac{1}{x} + \frac{1}{3}x + \dots - \frac{1}{x} \right) \right|_{x \rightarrow 0^+} \times \frac{p_0}{k_B T} \\
 &= \frac{p_0^2}{k_B T} \left. \frac{\partial}{\partial x} \left(\frac{1}{3}x \right) \right|_{x \rightarrow 0^+} \\
 &= \frac{p_0^2}{3k_B T}.
 \end{aligned}$$

Its value in the problem's conditions is

$$\chi_{\text{el}} = \frac{(1 \text{ Debye})^2}{3k_B \times 400 \text{ K}} = 6.7157 \times 10^{-40} \text{ C}^2 \text{ m}^2 / \text{J} = 6.7157 \times 10^{-40} \text{ F m}^2.$$

Since the electromagnetic vacuum permittivity ε_0 has related units, and numerically $4\pi\varepsilon_0 = 1.11265 \times 10^{-10} \text{ F m}^{-1}$, it is sometimes useful to express the electric polarizability as this factor times a volume:

$$\chi_{\text{el}} = 6.7157 \times 10^{-40} \text{ F m}^2 = 4\pi\varepsilon_0 \times 6.03581 \times 10^{-30} \text{ m}^3.$$

Under typical conditions this volume is characteristically in the $\sim \text{\AA}^3$ region.

10 Statistics of an ideal gas with a finite number of states

For a system of $N = 2$ identical particles which can access 3 states $\alpha = a, b$, and c only, evaluate:

1. the canonical partition function;
2. the approximate canonical partition function adopting the standard high-temperature approximations;
3. the grandcanonical partition function for any number of bosons/fermions, for a given chemical potential μ .

Consider separately the cases of bosons and of fermions.

10.1 Solution

1. Sum-over-particles version:

$$\begin{aligned}
 Z &= \sum_{\alpha_1 \alpha_2 \dots \alpha_N} \frac{n_0! n_1! n_2! \dots}{N!} e^{-\beta \sum_i^N \varepsilon_{\alpha_i}} \\
 &= \sum_{\alpha_1=a,b,c} \sum_{\alpha_2=a,b,c} \frac{n_a! n_b! n_c!}{2!} e^{-\beta(\varepsilon_{\alpha_1} + \varepsilon_{\alpha_2})}
 \end{aligned} \tag{42}$$

Boson case (unconstrained summation):

$$\begin{aligned}
 Z &= \frac{2! 0! 0!}{2!} e^{-\beta(\varepsilon_a + \varepsilon_a)} + \frac{1! 1! 0!}{2!} e^{-\beta(\varepsilon_a + \varepsilon_b)} + \frac{1! 0! 1!}{2!} e^{-\beta(\varepsilon_a + \varepsilon_c)} \\
 &+ \frac{1! 1! 0!}{2!} e^{-\beta(\varepsilon_b + \varepsilon_a)} + \frac{0! 2! 0!}{2!} e^{-\beta(\varepsilon_b + \varepsilon_b)} + \frac{0! 1! 1!}{2!} e^{-\beta(\varepsilon_b + \varepsilon_c)} \\
 &+ \frac{1! 0! 1!}{2!} e^{-\beta(\varepsilon_c + \varepsilon_a)} + \frac{0! 1! 1!}{2!} e^{-\beta(\varepsilon_c + \varepsilon_b)} + \frac{0! 0! 2!}{2!} e^{-\beta(\varepsilon_c + \varepsilon_c)} \\
 &= e^{-\beta \times 2\varepsilon_a} + e^{-\beta \times 2\varepsilon_b} + e^{-\beta \times 2\varepsilon_c} \\
 &+ \frac{1}{2} \left[e^{-\beta(\varepsilon_a + \varepsilon_b)} + e^{-\beta(\varepsilon_b + \varepsilon_a)} \right] \\
 &+ \frac{1}{2} \left[e^{-\beta(\varepsilon_a + \varepsilon_c)} + e^{-\beta(\varepsilon_c + \varepsilon_a)} \right] \\
 &+ \frac{1}{2} \left[e^{-\beta(\varepsilon_b + \varepsilon_c)} + e^{-\beta(\varepsilon_c + \varepsilon_b)} \right] \\
 &= e^{-\beta \times 2\varepsilon_a} + e^{-\beta \times 2\varepsilon_b} + e^{-\beta \times 2\varepsilon_c} \\
 &+ e^{-\beta(\varepsilon_a + \varepsilon_b)} + e^{-\beta(\varepsilon_a + \varepsilon_c)} + e^{-\beta(\varepsilon_b + \varepsilon_c)}
 \end{aligned} \tag{43}$$

Fermion case ($\alpha_1 \neq \alpha_2$):

$$\begin{aligned}
 Z &= \frac{1! 1! 0!}{2!} e^{-\beta(\varepsilon_a + \varepsilon_b)} + \frac{1! 0! 1!}{2!} e^{-\beta(\varepsilon_a + \varepsilon_c)} \\
 &+ \frac{1! 1! 0!}{2!} e^{-\beta(\varepsilon_b + \varepsilon_a)} + \frac{0! 1! 1!}{2!} e^{-\beta(\varepsilon_b + \varepsilon_c)} \\
 &+ \frac{1! 0! 1!}{2!} e^{-\beta(\varepsilon_c + \varepsilon_a)} + \frac{0! 1! 1!}{2!} e^{-\beta(\varepsilon_c + \varepsilon_b)} \\
 &= \frac{1}{2} \left[e^{-\beta(\varepsilon_a + \varepsilon_b)} + e^{-\beta(\varepsilon_b + \varepsilon_a)} \right] \\
 &+ \frac{1}{2} \left[e^{-\beta(\varepsilon_a + \varepsilon_c)} + e^{-\beta(\varepsilon_c + \varepsilon_a)} \right] \\
 &+ \frac{1}{2} \left[e^{-\beta(\varepsilon_b + \varepsilon_c)} + e^{-\beta(\varepsilon_c + \varepsilon_b)} \right] \\
 &= e^{-\beta(\varepsilon_a + \varepsilon_b)} + e^{-\beta(\varepsilon_a + \varepsilon_c)} + e^{-\beta(\varepsilon_b + \varepsilon_c)}
 \end{aligned} \tag{44}$$

Sum-over-state-occupations version:

$$\begin{aligned}
 Z &= \sum_{\substack{\{n_\alpha\} \\ \sum_\alpha n_\alpha = N}} e^{-\beta \sum_\alpha n_\alpha \varepsilon_\alpha} = \sum_{\substack{\{n_\alpha\} \\ \sum_\alpha n_\alpha = N}} \prod_\alpha e^{-\beta \varepsilon_\alpha n_\alpha} \\
 &= \sum_{\substack{n_a \ n_b \ n_c \\ n_a + n_b + n_c = 2}} e^{-\beta \varepsilon_a n_a} \times e^{-\beta \varepsilon_b n_b} \times e^{-\beta \varepsilon_c n_c}.
 \end{aligned} \tag{45}$$

Boson case:

$$\begin{aligned}
Z &= e^{-\beta\mathcal{E}_a2} \times e^{-\beta\mathcal{E}_b0} \times e^{-\beta\mathcal{E}_c0} + e^{-\beta\mathcal{E}_a1} \times e^{-\beta\mathcal{E}_b1} \times e^{-\beta\mathcal{E}_c0} \\
&+ e^{-\beta\mathcal{E}_a1} \times e^{-\beta\mathcal{E}_b0} \times e^{-\beta\mathcal{E}_c1} + e^{-\beta\mathcal{E}_a0} \times e^{-\beta\mathcal{E}_b2} \times e^{-\beta\mathcal{E}_c0} \\
&+ e^{-\beta\mathcal{E}_a0} \times e^{-\beta\mathcal{E}_b1} \times e^{-\beta\mathcal{E}_c1} + e^{-\beta\mathcal{E}_a0} \times e^{-\beta\mathcal{E}_b0} \times e^{-\beta\mathcal{E}_c2} \\
&= e^{-\beta\mathcal{E}_a2} + e^{-\beta\mathcal{E}_b2} + e^{-\beta\mathcal{E}_c2} \\
&+ e^{-\beta\mathcal{E}_a} \times e^{-\beta\mathcal{E}_b} + e^{-\beta\mathcal{E}_a} \times e^{-\beta\mathcal{E}_c} + e^{-\beta\mathcal{E}_b} \times e^{-\beta\mathcal{E}_c} \\
&= e^{-\beta \times 2\mathcal{E}_a} + e^{-\beta \times 2\mathcal{E}_b} + e^{-\beta \times 2\mathcal{E}_c} \\
&+ e^{-\beta(\mathcal{E}_a+\mathcal{E}_b)} + e^{-\beta(\mathcal{E}_a+\mathcal{E}_c)} + e^{-\beta(\mathcal{E}_b+\mathcal{E}_c)}.
\end{aligned} \tag{46}$$

This expression coincides with Eq. (43), as it should.

Fermion case (all $n_\alpha \leq 1$):

$$\begin{aligned}
Z &= e^{-\beta\mathcal{E}_a1} \times e^{-\beta\mathcal{E}_b1} \times e^{-\beta\mathcal{E}_c0} \\
&+ e^{-\beta\mathcal{E}_a1} \times e^{-\beta\mathcal{E}_b0} \times e^{-\beta\mathcal{E}_c1} \\
&+ e^{-\beta\mathcal{E}_a0} \times e^{-\beta\mathcal{E}_b1} \times e^{-\beta\mathcal{E}_c1} \\
&= e^{-\beta\mathcal{E}_a} \times e^{-\beta\mathcal{E}_b} + e^{-\beta\mathcal{E}_a} \times e^{-\beta\mathcal{E}_c} + e^{-\beta\mathcal{E}_b} \times e^{-\beta\mathcal{E}_c} \\
&= e^{-\beta(\mathcal{E}_a+\mathcal{E}_b)} + e^{-\beta(\mathcal{E}_a+\mathcal{E}_c)} + e^{-\beta(\mathcal{E}_b+\mathcal{E}_c)}.
\end{aligned} \tag{47}$$

This expression agrees with Eq. (44), as it should.

2. In the high-temperature limit, one starts from the sum-over-particles version:

$$\begin{aligned}
Z &= \sum_{\alpha_1 \alpha_2 \dots \alpha_N} \frac{n_0! n_1! n_2! \dots}{N!} e^{-\beta \sum_i^N \mathcal{E}_{\alpha_i}} \\
&= \sum_{\alpha_1=a,b,c} \sum_{\alpha_2=a,b,c} \frac{n_a! n_b! n_c!}{2!} e^{-\beta(\mathcal{E}_{\alpha_1}+\mathcal{E}_{\alpha_2})}
\end{aligned}$$

Then approximations are made, replacing the $n_\alpha! \rightarrow 1$ and omitting the Pauli constraint to the Fermion case:

$$\begin{aligned}
Z &\simeq \sum_{\alpha_1 \alpha_2 \dots \alpha_N} \frac{1}{N!} e^{-\beta \sum_i^N \mathcal{E}_{\alpha_i}} \\
&= \sum_{\alpha_1=a,b,c} \sum_{\alpha_2=a,b,c} \frac{1}{2!} e^{-\beta(\mathcal{E}_{\alpha_1}+\mathcal{E}_{\alpha_2})} \\
&= \frac{1}{2} \sum_{\alpha_1=a,b,c} \sum_{\alpha_2=a,b,c} e^{-\beta\mathcal{E}_{\alpha_1}} e^{-\beta\mathcal{E}_{\alpha_2}} \\
&= \frac{1}{2} \sum_{\alpha_1=a,b,c} e^{-\beta\mathcal{E}_{\alpha_1}} \sum_{\alpha_2=a,b,c} e^{-\beta\mathcal{E}_{\alpha_2}} \\
&= \frac{1}{2} (e^{-\beta\mathcal{E}_a} + e^{-\beta\mathcal{E}_b} + e^{-\beta\mathcal{E}_c})(e^{-\beta\mathcal{E}_a} + e^{-\beta\mathcal{E}_b} + e^{-\beta\mathcal{E}_c}) \\
&= \frac{1}{2} (e^{-\beta\mathcal{E}_a} + e^{-\beta\mathcal{E}_b} + e^{-\beta\mathcal{E}_c})^2 \\
&= \frac{1}{2} [e^{-\beta 2\mathcal{E}_a} + e^{-\beta 2\mathcal{E}_b} + e^{-\beta 2\mathcal{E}_c} + 2e^{-\beta(\mathcal{E}_a+\mathcal{E}_b)} + 2e^{-\beta(\mathcal{E}_a+\mathcal{E}_c)} + 2e^{-\beta(\mathcal{E}_b+\mathcal{E}_c)}] \\
&= \frac{1}{2} [e^{-\beta 2\mathcal{E}_a} + e^{-\beta 2\mathcal{E}_b} + e^{-\beta 2\mathcal{E}_c}] + e^{-\beta(\mathcal{E}_a+\mathcal{E}_b)} + e^{-\beta(\mathcal{E}_a+\mathcal{E}_c)} + e^{-\beta(\mathcal{E}_b+\mathcal{E}_c)}
\end{aligned}$$

Compare this approximate result with the exact expressions (46) and (47)!

3. The grandcanonical partition function for any number of bosons/fermions:

$$\begin{aligned}
Q &= \prod_{\alpha} \left(1 - \theta e^{\beta(\mu - \varepsilon_{\alpha})}\right)^{-\theta} \\
&= \left(1 - \theta e^{\beta(\mu - \varepsilon_a)}\right)^{-\theta} \left(1 - \theta e^{\beta(\mu - \varepsilon_b)}\right)^{-\theta} \left(1 - \theta e^{\beta(\mu - \varepsilon_c)}\right)^{-\theta}.
\end{aligned} \tag{48}$$

Boson case:

$$Q = \frac{1}{\left(1 - e^{\beta(\mu - \varepsilon_a)}\right) \left(1 - e^{\beta(\mu - \varepsilon_b)}\right) \left(1 - e^{\beta(\mu - \varepsilon_c)}\right)}. \tag{49}$$

Fermion case:

$$Q = \left(1 + e^{\beta(\mu - \varepsilon_a)}\right) \left(1 + e^{\beta(\mu - \varepsilon_b)}\right) \left(1 + e^{\beta(\mu - \varepsilon_c)}\right). \tag{50}$$

When taking the logarithm of Q in the calculation of the thermodynamic functions, the product turn into a sum of 3 logarithms.