1)   Paramagnet: $dE = TdS - MdB = -BdM - MdB$

   Want to check that $TdS = -BdM \iff \dfrac{dS}{dM} \stackrel{?}{=} -B/T$

(a) $S = k_B \ln \Omega$

   Gaussian approximation: $\Omega \approx \dfrac{2^N}{\sigma_M \sqrt{2\pi}} e^{-M^2/2\sigma_M^2}$

   Here, $M = (N_\uparrow - N_\downarrow)\mu = (2N_\uparrow - N)\mu \implies \sigma_M^2 = N\mu^2$ (variance of binomial distribution).

   $\implies \Omega \approx \dfrac{2^N}{\sqrt{2\pi N}\mu} e^{-M^2/[2N\mu^2]}$

   This approximation is valid provided $N_\uparrow, N_\downarrow \ll N$ but breaks down for $k_B T \ll \mu B$.

   Within the validity of the approximation:

   $S \approx -\dfrac{M^2}{2N\mu^2} \cdot k_B + const \implies \boxed{\dfrac{dS}{dM} = -\dfrac{M k_B}{N\mu^2}}$

(b)
   Now checking $M(T)$ via $M = -E/B$

   $E = -\dfrac{\partial \ln Z}{\partial B}$,   where $Z = \left(e^{-\beta\mu B} + e^{\beta\mu B}\right)^N \implies \ln Z = N \ln\left[e^{-\beta\mu B} + e^{\beta\mu B}\right]$

   $\implies E = -N \cdot \dfrac{\mu B(e^{\beta\mu B} - e^{-\beta\mu B})}{e^{\beta\mu B} + e^{-\beta\mu B}} = -N\mu B \tanh\left(\dfrac{\mu B}{k_B T}\right)$

   For $k_B T > \mu B$, where Gaussian approx. is valid: $\tanh\left(\dfrac{\mu B}{k_B T}\right) \approx \dfrac{\mu B}{k_B T}$
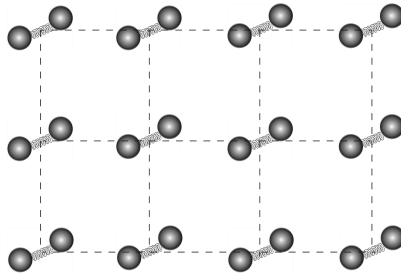
   $\implies E \approx -\dfrac{N(\mu B)^2}{k_B T} \implies M \approx \dfrac{N(\mu B)^2}{k_B T \cdot B} = \dfrac{N\mu^2 B}{k_B T}$

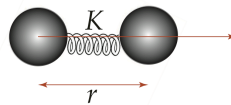 $\implies \boxed{B/T = \dfrac{M k_B}{N\mu^2}}$ so we have verified $\dfrac{dS}{dM} = -B/T$ for $k_B T \gg \mu B$.

   (This is true for all T, but we only explicitly checked it here within the Gaussian approx.)

2) <u>In</u> a molecular crystal, each lattice site is occupied by a molecule. Assume such lattice with N diatomic molecules.

The potential between the two atoms, each of mass m, in a molecule is:

$$U(r) = \epsilon_0 \left[\left(\frac{a}{r} \right)^{12} - 2 \left(\frac{a}{r} \right)^{6} \right] \tag{13}$$

where r is the separation between the two atoms in a molecule. The solid is in contact with a heat reservoir at a temperature T low enough so that $k_B T \ll \epsilon_0$.

a) What is the equilibrium separation of the two atoms in the molecule?.

b) What is the frequency for small vibrations of individual molecule (you may want to first calculate the "spring constant" K).

c) What is the average energy and the specific heat of the solid due to the internal vibrations of the molecules of that solid.

d) What is the condition for a "classical limit" for the vibrations of these molecules?

Hint: Note that the molecules are independent.

Solution:

~~Looking at Problem set #3,~~ we see that the expansion for $U(r)$ around the minimum of $r = a$ is:

$$U(r) = -\epsilon_0 + \frac{1}{2}\frac{72\epsilon_0}{a^2}(r-a)^2 - 252\frac{\epsilon_0}{a^3}(r-a)^3 + \ldots\ldots \tag{14}$$

However, here it is enough to look at the expansion to second order. Comparing the energy to that of a harmonic oscillator:

$$U(r) = -\epsilon_0 + \frac{1}{2}Kr^2 \tag{15}$$

Where the distance is measured in the radial direction between the masses. We identify the spring constant of the oscillator as:

$$K = \frac{72\epsilon_0}{a^2} \tag{16}$$

a) Since we are looking at this oscillator in the center of mass of the molecule, the relevant mass, m is: $m = (M^{-1} + M^{-1})^{-1} = M/2$. The frequency of the oscillator is:

$$\omega = \sqrt{\frac{K}{m}} = \sqrt{\frac{144\epsilon_0}{Ma^2}} \tag{17}$$

b) The rest of the problem becomes very easy as we are dealing with N independent oscillators each oscillating with the same frequency ω, which is basically the Einstein model for the solid. Thus:

$$E = N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) \tag{18}$$

and:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{\frac{\hbar\omega}{k_BT}}}{(e^{\frac{\hbar\omega}{k_BT}} - 1)^2} \tag{19}$$

The condition for classical limit is that we can ignore the difference between the quantum energy levels. At the same time, in this case the temperature is given to be low enough such that $k_BT \ll \epsilon_0$. Thus the condition is:

$$\hbar\sqrt{\frac{144\epsilon_0}{Ma^2}} \ll k_B T \ll \epsilon_0 \qquad (20)$$

3)   a) Show that the work performed by an ideal gas at temperature T as it expands in a piston from volume V_1 to volume V_2 is equal to the decrease ΔF in its free energy.

     b) Is ΔF larger or smaller than the decrease in the internal energy of the gas? What is the origin of the difference?

Solution:

The work performed by a gas in an isothermal (constant temperature) expansion is:

$$W = \int_{V_1}^{V_2} P dV = Nk_B T \int_{V_1}^{V_2} \frac{dV}{V} = Nk_B T (log V_2 - log V_1) \qquad (21)$$

At the same time, the change in free energy is:

$$\Delta F = F_2 - F_1 = -Nk_B T log\left[\frac{V_2}{h^3}(2\pi m k_B T)^{3/2}\right] + Nk_B T log\left[\frac{V_1}{h^3}(2\pi m k_B T)^{3/2}\right] \qquad (22)$$

or;

$$\Delta F = -Nk_B T (log V_2 - log V_1) = -W \qquad (23)$$

From which it follows that $W = -\Delta F$, or the work equals to the *decrease* in free energy.

b) The internal energy of the ideal gas depends only on the temperature, and hence it has not changed during the process: $\Delta E = 0$. The origin of the work is therefore the energy extracted from the heat bath, and converted into mechanical energy by the gas.

4)   An isolated sample consists of N independent electric dipoles. Each dipole has two possible quantum states with energies $\epsilon_\pm = \pm\mu\mathcal{E}$, where $\mathcal{E}$ is the magnitude of the applied electric field. The energy of the system is given as E.

a) Find the electric dipole moment of the sample in an electric field $\mathcal{E}$.

b) Calculate the probability that electric dipole moments 2,4, and 8 will point up

c) Calculate the entropy of the system

d) Without using the formula above, explain physically what the entropy should be in the limits $\mathcal{E} \to \infty$ and $\mathcal{E} \to 0$.

Solution:

To make this problem similar to the paramagnet in a field, let us define σ-variables such that the two possible quantum states with energies $\epsilon_\pm = \mu\mathcal{E}\sigma$ such that $\sigma = \pm 1$.

a) The electric dipole moment of the system is:

$$\langle P \rangle = \sum_{\{\sigma\}} \left(\mu \sum_{i=1}^{N} \sigma_i \right) P(\sigma_1, ...\sigma_N) = \mu \sum_{\sigma_1, \sigma_2, ...} (\sigma_1 + ... + \sigma_N) P(\sigma_1, ...\sigma_N) = N\mu \sum_{\sigma_1} \sigma_1 P(\sigma_1) = N\mu\langle\sigma\rangle$$

$$(24)$$

Again, similar to the paramagnet we write:

$$E = -\mu\mathcal{E}(N_+ - N_-); \quad and \quad N = (N_+ - N_-) \tag{25}$$

Thus:

$$P = \mu N \sum_{i=1}^{N} \sigma_i P(\sigma_i) = N(\mu P(+) + (-\mu)P(-)) = \mu N \left(\frac{N_+}{N} - \frac{N_-}{N} \right) = -\frac{E}{\mathcal{E}} \tag{26}$$

b) We need to calculate $P(+, +, +)$ where the label of the moments does not matter. ~~This was done in homework #1 for the paramagnet and:~~

$$P(+,+,+) = \left(\frac{1}{2} - \frac{E}{2N\mu\mathcal{E}} \right) \left(\frac{N-2}{2(N-1)} - \frac{E}{2(N-1)\mu\mathcal{E}} \right) \left(\frac{N-4}{2(N-2)} - \frac{E}{2(N-2)\mu\mathcal{E}} \right) \tag{27}$$

c) Again, similar to the lecture notes:

$$S(E) = -k_B N (P(+)logP(+) + P(-)logP(-)) \qquad (28)$$

or:

$$S(E) = -k_B N \left(\frac{1}{2} - \frac{E/N}{2\mu\mathcal{E}} \right) log \left(\frac{1}{2} - \frac{E/N}{2\mu\mathcal{E}} \right) - k_B N \left(\frac{1}{2} + \frac{E/N}{2\mu\mathcal{E}} \right) log \left(\frac{1}{2} + \frac{E/N}{2\mu\mathcal{E}} \right) \qquad (29)$$

d) In the limit of zero electric field (no aligning), the probabilities to point up or down should be equal. the number of possibilities is therefore 2^N and the entropy: $S(\mathcal{E} \to 0) \to Nlog2$.

In the limit of very large field we will have full alignment. in that case the system will have only one state and $S(\mathcal{E} \to \infty) \to 0$.