LULEÅ TEKNISKA UNIVERSITET
Avdelningen för materialvetenskap

Exam in: STATISTICAL PHYSICS AND THERMODYNAMICS 2014-08-30 (F7035T)
Suggested solutions

1. The equation of state for an ideal gas is $pV = Nk_BT$ and we have to derive the corresponding equation if the particles interact weakly by a van der Waals interaction.

   From the partition function Z the pressure may be derived according to $P = k_BT \left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{Nk_BT}{V-bN} - \frac{aN^2}{V^2}$ which can be rearranged to $\left(P + \frac{aN^2}{V^2}\right)(V - bN) = Nk_BT$.

   In a similar way the energy can be expressed as a derivative of the logarithm of the partition function with respect to the temperature. The inner energy U is given by $U = k_BT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V = N\left(\frac{3k_BT}{2} - \frac{aN}{V}\right)$

2. From the energy $\epsilon(j) = j(j+1)\epsilon_0$ and degeneration $g(j) = 2j+1$ we arrive at the partition function $Z_R(\tau) = \sum e^{-\epsilon_i/\tau} = \sum_{j=0}^{\infty}(2j+1)e^{-j(j+1)\epsilon_0/\tau}$. The high temperature limit $\tau >> \epsilon_0$ this becomes $Z_R(\tau) \approx \int_0^{\infty}(2j+1)e^{-j(j+1)\epsilon_0/\tau} \, \mathrm{d}j$, a change of variables $(j(j+1) = x^2$ and $\mathrm{d}j(2j+1) = 2x \, \mathrm{d}x)$, $= \int_0^{\infty} 2xe^{-x^2\epsilon_0/\tau} \, \mathrm{d}x = [-\frac{\tau}{\epsilon_0}e^{-x^2\epsilon_0/\tau}]_0^{\infty} = \frac{\tau}{\epsilon_0}$

   The specific heat C_v, (high temperature) The Free energy $F = -\tau \ln Z_R \approx = -\tau \ln \frac{\tau}{\epsilon_0}$, entropy $\sigma = -\frac{\partial F}{\partial \tau} \approx \ln \frac{\tau}{\epsilon_0} + 1$, and $C_v = \tau\frac{\partial\sigma}{\partial\tau} \approx 1$. ie. $C_v = 1k_B$ per molecule in the high temperature limit.

   For low temperatures, $\tau << \epsilon_0$ we get $Z_R(\tau) \approx 1 + 3e^{-2\epsilon_0/\tau}$ and $F = -\tau \ln(1 + 3e^{-2\epsilon_0/\tau})$ and $\sigma = -\frac{\partial F}{\partial \tau} = \ln(1 + 3e^{-2\epsilon_0/\tau}) + \tau\frac{1}{1+3e^{-2\epsilon_0/\tau}} \cdot \frac{6\epsilon_0}{\tau^2}e^{-2\epsilon_0/\tau}$. This leads to $C_v = \tau\frac{\partial\sigma}{\partial\tau} = ... = \frac{18\epsilon_0^2 e^{-2\epsilon_0/\tau}}{\tau^2(1+3e^{-2\epsilon_0/\tau})}\left[1 - \frac{e^{-2\epsilon_0/\tau}}{1+3e^{-2\epsilon_0/\tau}}\right]$ approximate $\frac{1}{1+x} \approx 1-x$ as x is small this gives $C_v \approx \frac{18\epsilon_0^2 e^{-2\epsilon_0/\tau}}{\tau^2}(1 - 3e^{-2\epsilon_0/\tau})(1 - e^{-2\epsilon_0/\tau}(1 - 3e^{-2\epsilon_0/\tau})) \approx \frac{18\epsilon_0^2 e^{-2\epsilon_0/\tau}}{\tau^2}$. Answer $\tau >> \epsilon_0 : C_v = 1$, and $Z_R(\tau) = \frac{\tau}{\epsilon_0}$ and for $\tau << \epsilon_0 : C_v = \frac{18\epsilon_0^2 e^{-2\epsilon_0/\tau}}{\tau^2}$, and $Z_R(\tau) = 1 + 3e^{-2\epsilon_0/\tau}$

3. In a 3D Ising model on a cubic lattice each spin has 6 nearest neighbours, and in a Mean Field assumption these 6 nearest neighbours will have the magnitude $<m>$ and the spin we perform our calculation on will take the following values $s_i = \pm 1$.. This gives $Z = \sum_i e^{-\epsilon_i/\tau} = e^{+6m/\tau} + e^{-6m/\tau}$ and the magnetisation will be $<m> = \frac{+1e^{+6m/\tau} - 1e^{-6m/\tau}}{e^{+6m/\tau} + e^{-6m/\tau}} = \tanh(\frac{6m}{\tau})$. As m s small we may approximate $\tanh x \approx x - x^3/3$. This gives $m = \frac{6m}{\tau} - (\frac{6m}{\tau})^3\frac{1}{3}$ the equation $m^2 = \frac{3\tau^2}{216}(6 - \tau)$ a solution close to $m = 0$ as is $\tau \approx \tau_c$: $m^2 = \frac{3\tau_c^2}{216}(6 - \tau)$ and $m = \frac{\sqrt{3}\tau_c}{\sqrt{216}}\sqrt{(6 - \tau)}$ and we arrive at the exponent $\beta = \frac{1}{2}$.

4. This problem is about comparing Boltzmann factors taking degeneracy into acount.

   a) The energy $2,5\hbar\omega$ implies that one of quantum numbers is one while the other two are zero. The direction of the excitation can be choosen in three different ways, ie the excited state has a threefold degeneracy. We get the following equation for the probabillitys: $e^{-1,5\hbar\omega/k_BT} = 3e^{-2,5\hbar\omega/k_BT}$ leading to $e^{\hbar\omega/k_BT} = 3$ and solving for T gives $T = \frac{\hbar\omega}{k_B \ln 3}$

b) The partition function is given by: $Z = \sum_{n_1=0,n_2=0,n_3=0}^{\infty} e^{-(n_1+n_2+n_3+\frac{3}{2})\,\hbar\omega/k_BT} =$
$\sum_{n=0}^{\infty} g(n)e^{-(n+\frac{3}{2})\,\hbar\omega/k_BT}$, where $g(n)$ is the degeneracy of the energy levels. $g(0) = 1, g(1) = 3, g(2) = 6(=1+2+3), g(3) = 10(=1+2+3+4), g(4) = 15(=1+2+3+4+5)$ and so on. Z may be calculated in different ways. One is by noting that it can be calculated as three separate one dimensional oscillators and then multiplying these three independent results to form the three dimensional result. Another way is to determine $g(n)$ this is done in the following geometrical way, for each n the values for n_x, n_y and n_x form a triangle with sides of equal length $n+1$. Say $n = 4$ the n_x, n_y and n_x will run from 0 to 4 with the constraint $n_x + n_y + n_x = 4$ this is a triangle with side length 5 $(n+1)$. Now $g(n)$ is simply the number of integer coordinate sites on this triangle. On a triangle with n there are $n+1$ rows and the row with the least sites has just 1 site and the one with the most has $n+1$ giving an average of sites per row $(n+2)/2$. Hence we arrive at the desired result $g(n) = (n+1)(n+2)/2$ and is just the average value times the number of terms. The partition sum consists of three geometrical sums. $g(n) = \frac{n^2}{2} + \frac{3n}{2} + 1$. The three sums are given by: $1 + x + x^2 + x^3 + x^4... = \frac{1}{1-x}$ and $x + 2x^2 + 3x^3 + 4x^4.. = \frac{x}{(1-x)^2}$ and $x + 2^2x^2 + 3^2x^3 + 4^2x^4.. = \frac{x(1+x)}{(1-x)^3}$ (you can take the derivative of the first one to arrive at the desired result) and hence:

$$Z = e^{-\frac{3\hbar\omega}{2\tau}}\left(\frac{1}{1-e^{-\frac{\hbar\omega}{\tau}}} + \frac{3}{2}\frac{e^{-\frac{\hbar\omega}{\tau}}}{(1-e^{-\frac{\hbar\omega}{\tau}})^2} + \frac{1}{2}\frac{e^{-\frac{\hbar\omega}{\tau}}(1+e^{-\frac{\hbar\omega}{\tau}})}{(1-e^{-\frac{\hbar\omega}{\tau}})^3}\right)$$

With $\tau = \frac{\hbar\omega}{\ln 3}$ we arrive at:

$$Z = \left(\frac{1}{3}\right)^{\frac{3}{2}}\left(\frac{1}{1-\frac{1}{3}} + \frac{3}{2}\frac{\frac{1}{3}}{(1-\frac{1}{3})^2} + \frac{1}{2}\frac{\frac{1}{3}(1+\frac{1}{3})}{(1-\frac{1}{3})^3}\right) = \left(\frac{1}{3}\right)^{\frac{3}{2}} \cdot 3.375 = 0.649519052$$

The Boltzmann factor of the ground state is $\left(\frac{1}{3}\right)^{\frac{3}{2}}$ and the probabillity for the system to be in the ground state is $1/3.375 = 0.296296...$

5. Funktions formen för trycket är $\ln p = a - \frac{b}{T}$ används längre ner.

Vid trippelpunkten gäller $p_s = p_l$ detta ger temperaturen för trippelpunkten till $T_t = 195.198\text{K} \approx 195.2\text{K}$. **b:** Clausius–Clapeyron $\frac{dp}{dT} = \frac{L}{T\Delta v}$ där $\Delta v = v_g - v_s \approx v_g$ (antagandet att det är gasens volymitet som dominerar) $= \frac{V_g}{N_g}$. Tunn gas antag $pV_g = N_g k_B T$ och därmed $v_g = \frac{k_b T}{p}$. $\frac{dp}{dT} = \frac{L}{T\Delta v} \approx \frac{L}{Tv_g} = \frac{Lp}{k_B T^2}$. vilket ger $\frac{1}{p}\frac{dp}{dT} = \frac{d}{dT}\ln p = \frac{L}{k_B T^2}$ vidare så är $\frac{d}{dT}\ln p = \frac{b}{T^2}$ dvs $L = bk_B$, där b är $\ln p = a - \frac{b}{T}$.

Latent värme för sublimation $b = 3754\text{K}$. $L_s = 3754 \cdot 1.3807\ 10^{-23}\text{J} = 5.183\ 10^{-20}\text{J} = 0.324\text{eV}$.

Latent värme för förångning $b = 3063\text{K}$. $L_s = 3063 \cdot 1.3807\ 10^{-23}\text{J} = 4.229\ 10^{-20}\text{J} = 0.264\text{eV}$.

Skillnaden mellan förångning och sublimation ger smältvärme $(5.183 - 4.229)\ 10^{-20}\text{J} = 9.54\ 10^{-21}\text{J} = 0.060\text{eV}$

(Koll mot fysikalia smältvärme $= 332\ 10^3\text{J/kg}$ för NH_3 vilket blir $9.389\ 10^{-21}$ J per molekyl.)