LULEÅ TEKNISKA UNIVERSITET
Avdelningen för materialvetenskap

Exam in: STATISTICAL PHYSICS AND THERMODYNAMICS 2012-09-01 (F7035T)
Suggested solutions

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1.   a) The partition sum is given by: $Z = \sum_{n_1=0,n_2=0}^{\infty} e^{-(n_1+n_2+1.0)\hbar\omega/k_BT} =$
$\sum_{n=0}^{\infty} g(n)e^{-(n+1.0)\hbar\omega/k_BT}$, where $g(n)$ is the degeneracy of the energy levels and $n = n_1+n_2$.
There are two ways to evaluate this sum. One simple and one more elaborate. Only the
simple solution is presented here. The sum for Z can be done as a product of two separate
independent geometric sums.
$Z = \sum_{n_1=0,n_2=0}^{\infty} e^{-(n_1+n_2+1.0)\hbar\omega/k_BT} = \sum_{n_1=0}^{\infty} e^{-(n_1+0.5)\hbar\omega/k_BT} \cdot \sum_{n_2=0}^{\infty} e^{-(n_2+0.5)\hbar\omega/k_BT} =$
$\left(\sum_{n=0}^{\infty} e^{-(n+0.5)\hbar\omega/k_BT}\right)^2 = e^{-\hbar\omega/k_BT}\left(\sum_{n=0}^{\infty} e^{-n\hbar\omega/k_BT}\right)^2 = e^{-\hbar\omega/k_BT}\left(\frac{1}{1-e^{-\hbar\omega/k_BT}}\right)^2 =$ and we
arrive at the following for the partition function Z:

$$Z = \left(\frac{1}{e^{+\hbar\omega/2k_BT} - e^{-\hbar\omega/2k_BT}}\right)^2 = \text{ or } = e^{-\hbar\omega/k_BT}\left(\frac{1}{1 - e^{-\hbar\omega/k_BT}}\right)^2.$$

   b) There is one state of the lower energy and two states with the next higher energy. The
probability to find the oscillator in a state of energy is proportional to the Boltzmann
factor, we arrive at the following equation. $1e^{-1,0\hbar\omega/k_BT} = 2e^{-2,0\hbar\omega/k_BT}$ and $e^{1\hbar\omega/k_BT} = 2$
which evaluates to $T = \frac{1\hbar\omega}{k_B\ln 2}$ or if you prefer τ, $\tau = \frac{1\hbar\omega}{\ln 2}$, which is equally correct.

   c) The partition sum at this specific temperature is given by: ($k_BT = \tau = \frac{1\hbar\omega}{\ln 2}$) we arrive at
the following

$$Z = \left(\frac{1}{e^{+\frac{\ln 2}{2}} - e^{-\frac{\ln 2}{2}}}\right)^2 = \left(\frac{1}{\sqrt{2} - \frac{1}{\sqrt{2}}}\right)^2$$

We continue with the calculation of the probability: (we may choose any of the two
energies as their probabilities will be equal at the temperature in question: ($1e^{-1,0\hbar\omega/k_BT} =$
$2e^{-2,0\hbar\omega/k_BT}$)

$$P = e^{-\hbar\omega/k_BT}/\left(\frac{1}{\sqrt{2} - \frac{1}{\sqrt{2}}}\right)^2 = 2^{-1}\left(\sqrt{2} - \frac{1}{\sqrt{2}}\right)^2 = \left(\frac{1}{\sqrt{2}}\right)^2\left(\sqrt{2} - \frac{1}{\sqrt{2}}\right)^2 =$$

$$\left(1 - \frac{1}{2}\right)^2 = \frac{1}{4} = 0.25$$

The probability to be in a state of one of these energys is $P = \frac{8}{27} = 0.25$

2. Count the states in a box of size L. After some steps one reaches at (eq 7 page 185 KK)
$\tau_F = (3\pi^2 n)^{2/3}\frac{\hbar^2}{2m}$ this gives $T_F = k_B\tau_F = 5.0K$ which much less than $T = 0.2K$ so the
approximation of the Fermi-Dirac distribution function as a step function will be fairly good.
Calculate U (along lines according to eq 27 page 189 KK) after some steps $C_v = \frac{1}{2}\pi^2 Nk_BT/T_F$
is reached. Evaluating the fermi contribution gives $C_v = 0.196Nk_B = 1.64$ J/mole/K at
$T = 0.2K$.

3. Följande antal tillstånd finns för hemoglogin med 0, 1, 2, 3 eller 4 syremolekyler: 1, 4, 6, 4 och 1. Kemiska aktiviteten för O_2 är $\lambda = e^{\mu/\tau}$, ϵ är energin för en bunden O_2. Stora tillstånds summan är $Z = 1 + 4\lambda e^{-\epsilon/\tau} + 6\lambda^2 e^{-2\epsilon/\tau} + 4\lambda^3 e^{-3\epsilon/\tau} + \lambda^4 e^{-4\epsilon/\tau}$. sannolikheten för 1 syremolekyl $P(1) = \frac{4\lambda e^{-\epsilon/\tau}}{Z}$ och sannolikheten för 4 syremolekyler $P(4) = \frac{\lambda^4 e^{-4\epsilon/\tau}}{Z}$. Figuren över $P(1)$ kommer $P(1)$ att uppvisa ett maximum vid något λ och figuren över $P(4)$ kommer $P(4)$ att gå från 0 mot 1 med ökande λ.

4. The overall strategy is as follows. The specific heat we get from the entropy which we get from the free energy and to reach the free energy we need to calculate the partition function.

   The partition function of the rotor is (approximation for the low temperature limit, in this limit the rotor will spend most of its time in the ground state and litle time in the lowest excited state and negligable time in higher excited states) $Z_{\text{rot}} = \sum_{j=0}^{\infty}(2j+1)e^{-j(j+1)\frac{\hbar^2}{2I\tau}} \approx 1 + 3e^{-\frac{\hbar^2}{I\tau}} = 1 + 3e^{-x}$ where $x = \frac{\hbar^2}{I\tau} >> 1$ in the low temperature limit. For N identical molecules $Z_{\text{rot}}^{(N)} = \frac{1}{N!}Z_{\text{rot}}^N$, and hence the free energy is $F_{\text{rot}} = -N\tau \ln Z_{\text{rot}} + \tau \ln N! = -N\tau \ln(1 + 3e^{-x}) + \tau \ln N! \approx -3N\tau e^{-x} + \tau \ln N! = -3N\tau e^{-\frac{\hbar^2}{I\tau}} + \tau \ln N!$. The entropy is: $\sigma_{\text{rot}} = -(\frac{\partial F}{\partial \tau})_v \approx 3N(1+x)e^{-x} + \ln N! = 3N(1 + \frac{\hbar^2}{I\tau})e^{-\frac{\hbar^2}{I\tau}} + \ln N!$ and the specific heat in the low temperature limit is: $(C_v)_{\text{rot}} = \tau(\frac{\partial \sigma}{\partial \tau})_v \approx 3Nx^2e^{-x} = 3N\left(\frac{\hbar^2}{I\tau}\right)^2 e^{-\frac{\hbar^2}{I\tau}}$.

   An alternative route is as follows. You can also calculate the inner energy $U = -\tau^2(\frac{\partial}{\partial \tau}\frac{F}{\tau})_{v,N} = 3N\left(\frac{\hbar^2}{I\tau}\right)e^{-\frac{\hbar^2}{I\tau}}$. From this you reach the specific heat as well.

5. At the beginning the entropy in part 1 and 2 is given by $\sigma_{1,2} = N_{1,2}\left[\ln\left(\frac{n_Q}{n_{1,2}}\right) + \frac{5}{2}\right]$ and after mixing it is given by (same temperature): $\sigma_e = N_e\left[\ln\left(\frac{n_Q}{n_e}\right) + \frac{5}{2}\right]$.

   The change of entropy is (increase): $\Delta\sigma = \sigma_e - \sigma_1 - \sigma_2 = 2N\left[\ln\left(\frac{n_Q 3V}{2N}\right) + \frac{5}{2}\right] - N\left[\ln\left(\frac{n_Q 2V}{N}\right) + \frac{5}{2}\right] - N\left[\ln\left(\frac{n_Q V}{N}\right) + \frac{5}{2}\right] = 2N\ln\left(\frac{n_Q 3V}{2N}\right) - N\ln\left(\frac{n_Q 2V}{N}\right) - N\ln\left(\frac{n_Q V}{N}\right) = 2N\ln n_Q - N\ln n_Q - N\ln n_Q + 2N\ln 3V - N\ln 2V - N\ln V - 2N\ln 2N + N\ln N + N\ln N = N\left(\ln(9V^2\frac{1}{2V}\frac{1}{V}) - \ln(4N^2N^{-1}N^{-1})\right) = N\ln(3^2 2^{-3}V^0 N^0) = N\ln(\frac{9}{8}) = Nk_B\ln(\frac{9}{8})$