LULEÅ TEKNISKA UNIVERSITET
Avdelningen för materialvetenskap

Exam in: Statistical Physics and Thermodynamics 2014-05-17 (F7035T)
Suggested solutions

---

1. The system is moving along a phase line and we can make use of the Claypeyrons relation which is: $\frac{dp}{dT} = \frac{q}{T\Delta v} = -\frac{3.689 \cdot 10^9}{T}$ ($\Delta v = v_{\text{liquid}} - v_{\text{solid}} = \frac{1}{999.8} - \frac{1}{916.8} = -9.0550 \cdot 10^{-5}$ m^3/kg, $q = 334 \cdot 10^3$ J/kg). This gives for small changes of temperature: $\Delta T = -\frac{T\Delta p}{3.689 \cdot 10^9} = -0.0666 \approx -0.07$K, ie. a small lowering of the freezing temperature by 0.07K.

2. There are several routes to make this calculation, three of them are presented here.

   First route The heat capacity is given by $C = \frac{\partial U_{total}}{\partial \tau}$, where $U_{total} = N \cdot U$. The energy is given by $U = \langle \epsilon \rangle = \tau^2 \frac{\partial \ln Z}{\partial \tau}$. The calculation will follow the line from Z we get U and from U we get C. The energies are given by $0, \epsilon, 2\epsilon, ..., S\epsilon$, where the ground state is not degenerated and the other states all have degeneracy 2. From this information the partition function is constructed. The partition function is:

$$Z = \sum_{states} e^{-\epsilon_{state}/\tau} = 1 + \sum_{n=1}^{S} 2 \cdot e^{-n\epsilon/\tau} = -1 + \sum_{n=0}^{S} 2 \cdot e^{-n\epsilon/\tau} = -1 + 2\frac{1 - e^{-(S+1)\epsilon/\tau}}{1 - e^{-\epsilon/\tau}} \qquad (1)$$

   In the limit $S\epsilon/\tau >> 1$, ($\tau = k_B T$) the last reduces to

$$Z \approx -1 + 2\frac{1}{1 - e^{-\epsilon/\tau}} = \frac{1 + e^{-\epsilon/\tau}}{1 - e^{-\epsilon/\tau}} \qquad (2)$$

   Now we turn to the energy:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = ... = \frac{2\epsilon}{e^{\epsilon/\tau} - e^{-\epsilon/\tau}} \qquad (3)$$

   For the heat capacity we have

$$C = \frac{\partial U_{total}}{\partial \tau} = \frac{\partial}{\partial \tau}\left(\frac{2\epsilon}{e^{\epsilon/\tau} - e^{-\epsilon/\tau}}\right) = 2(\frac{\epsilon}{\tau})^2 \frac{e^{\epsilon/\tau} + e^{-\epsilon/\tau}}{(e^{\epsilon/\tau} - e^{-\epsilon/\tau})^2} \qquad (4)$$

   and hence for the total heat capacity

$$C_{total} = 2N(\frac{\epsilon}{\tau})^2 \frac{e^{\epsilon/\tau} + e^{-\epsilon/\tau}}{(e^{\epsilon/\tau} - e^{-\epsilon/\tau})^2} \qquad (5)$$

   In the limit $S\epsilon/\tau >> 1$ ie $\tau \to 0$

$$C_{total} \to 2N(\frac{\epsilon}{\tau})^2 \frac{e^{\epsilon/\tau}}{(e^{\epsilon/\tau})^2} = 2N(\frac{\epsilon}{\tau})^2 e^{-\epsilon/\tau} \qquad (6)$$

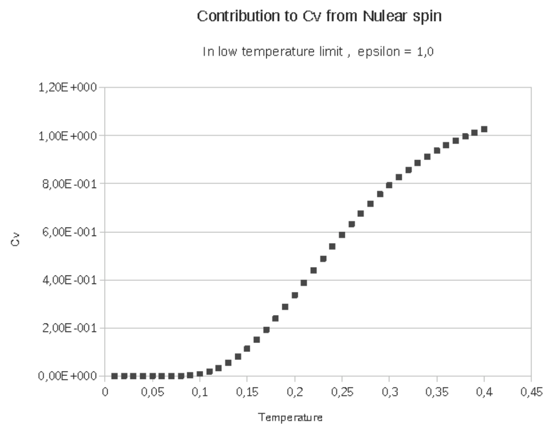

Figure 1: A principal figure showing the heat capacity in the low temperature limit. The choice for the energy $\epsilon = 1.0$ in eq. 7.

The contribution to the heat capacity at low temperatures is

$$C = 2N(\frac{\epsilon}{\tau})^2 e^{-\epsilon/\tau} \tag{7}$$

The pricipal shape of the heat capacity is seen in Figure 1.

Second route The partition function can also be written as:

$$Z = \sum_{states} e^{-\epsilon_{state}/\tau} = 1 + \sum_{n=1}^{S} 2 \cdot e^{-n\epsilon/\tau} \approx 1 + 2 \cdot e^{-\epsilon/\tau} \tag{8}$$

Now we turn to the energy:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = ... = \frac{2\epsilon}{e^{\epsilon/\tau} + 2} \tag{9}$$

For the heat capacity we have

$$C = \frac{\partial U_{total}}{\partial \tau} = \frac{\partial}{\partial \tau}\left(\frac{2\epsilon}{e^{\epsilon/\tau}+2}\right) = 2(\frac{\epsilon}{\tau})^2 \frac{e^{\epsilon/\tau}}{(e^{\epsilon/\tau}+2)^2} \approx 2(\frac{\epsilon}{\tau})^2 e^{-\epsilon/\tau} \tag{10}$$

Third route This problem can also be solved by a route over $F = -\tau \ln(Z)$ and then $\sigma = -(\frac{\partial F}{\partial \tau})_{V,N}$ and at last $C_V = \tau(\frac{\partial \sigma}{\partial \tau})_V$.

The partition function can also be written as:

$$Z = \sum_{states} e^{-\epsilon_{state}/\tau} = 1 + \sum_{n=1}^{S} 2 \cdot e^{-n\epsilon/\tau} \approx 1 + 2 \cdot e^{-\epsilon/\tau} \tag{11}$$

Now we turn to the Free energy and making use of the approximasion $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - ...$ the free energy is

$$F = -\tau \ln(1 + 2 \cdot e^{-\epsilon/\tau}) \approx -2\tau \cdot e^{-\epsilon/\tau} \tag{12}$$

Now we calculate the entropy:

$$\sigma = -(\frac{\partial F}{\partial \tau})_{V,N} = -\frac{\partial}{\partial \tau}(-2\tau \cdot e^{-\epsilon/\tau}) = 2e^{-\epsilon/\tau}(1+\frac{\epsilon}{\tau}) \tag{13}$$

For the heat capacity we have

$$C_V = \tau(\frac{\partial \sigma}{\partial \tau})_V = \tau\frac{\partial}{\partial \tau}\left(2e^{-\epsilon/\tau}(1+\frac{\epsilon}{\tau})\right) = 2\tau e^{-\epsilon/\tau}(\frac{\epsilon}{\tau^2}(1+\frac{\epsilon}{\tau}) - \frac{\epsilon}{\tau^2}) = 2(\frac{\epsilon}{\tau})^2 e^{-\epsilon/\tau} \tag{14}$$

As we can see all three routes, though apparently different, produce the same result for the heat capacity in the limit of small temperatures.

3. As only the difference is of interest we can put the energy of the ground state to zero and the excited state to ϵ. The partition sum becomes: $Z = 1 + 2e^{-\epsilon/\tau}$ and hence the energy will be $U = <\epsilon> = \frac{0+2\epsilon e^{-\epsilon/\tau}}{1+2e^{-\epsilon/\tau}} = \frac{2\epsilon}{2+e^{\epsilon/\tau}} = \frac{2\epsilon}{2+e^{\epsilon/k_BT}}$ an alternative rout is to take the derivative of Z which gives $U = \tau^2\frac{\partial \ln Z}{\partial \tau} = \tau^2\frac{1}{Z}2e^{-\epsilon/\tau}\frac{\epsilon}{\tau^2} = \frac{2\epsilon}{2+e^{\epsilon/\tau}} = \frac{2\epsilon}{2+e^{\epsilon/k_BT}}$. Finally we arrive at C_v by a derivative of U with respect to τ $C_v = \frac{\partial U}{\partial \tau} = \frac{2\epsilon^2 e^{\epsilon/\tau}/\tau^2}{(2+e^{\epsilon/\tau})^2}$. This can be written as $\frac{2x^2e^x}{(2+e^x)^2}$ where $x = \epsilon/\tau$. To find the maximum take the derivative with respect to x. $\frac{(2x+x^2)e^x}{3+e^x)^2} - \frac{2x^2e^{2x}}{(3+e^x)^3} = 0$ which gives the condition $(x-2)(e^x-2) = 8$. This may be solved graphically or by a pocket calculator. The solution is $x \approx 2.655$ ie. $\epsilon = x\ \tau = x\ k_B\ T = 2.655 \cdot 1.3807 \cdot 10^{-23} \cdot 450 = 1.650 \cdot 10^{-20}$J $= 0.103$eV.

4. See also problem 10.5 in Kittel and Kroemer **a:** $F = -N_f\epsilon_0 + N_g\tau\left(\ln\frac{N_g}{Vn_Q} - 1\right)$ **b:** $N_g = Vn_Qe^{-\epsilon_0/\tau}$ **c:** Make a figure of $\ln p$ as a function of $1/T$. The slope of the straight line is $-\frac{\epsilon_0}{k_B}$ which gives an energy $\epsilon_0 = 0.53$eV.

5. 2 particles A and B, 3 states with energy 0, ϵ and 3ϵ **a**) Classical

state	0	ϵ	3ϵ	energy
1	AB	-	-	0
2	-	AB	-	2ϵ
3	-	-	AB	6ϵ
4	A	B	-	ϵ
5	B	A	-	ϵ
6	A	-	B	3ϵ
7	B	-	A	3ϵ
8	-	A	B	4ϵ
9	-	B	A	4ϵ

and $Z = 1 + 2e^{-\epsilon/\tau} + e^{-2\epsilon/\tau} + 2e^{-3\epsilon/\tau} + 2e^{-4\epsilon/\tau} + e^{-6\epsilon/\tau}$

b) Bosons

state	0	ϵ	3ϵ	energy
1	AA	-	-	0
2	-	AA	-	2ϵ
3	-	-	AA	6ϵ
4	A	A	-	ϵ
6	A	-	A	3ϵ
8	-	A	A	4ϵ

and $Z = 1 + e^{-\epsilon/\tau} + e^{-2\epsilon/\tau} + e^{-3\epsilon/\tau} + e^{-4\epsilon/\tau} + e^{-6\epsilon/\tau}$

c) Fermions

state	0	ϵ	3ϵ	energy
4	A	A	-	ϵ
6	A	-	A	3ϵ
8	-	A	A	4ϵ

and $Z = e^{-\epsilon/\tau} + e^{-3\epsilon/\tau} + e^{-4\epsilon/\tau}$