LULEÅ TEKNISKA UNIVERSITET
Avdelningen för materialvetenskap

Exam in: Statistical Physics and Thermodynamics 2017-05-13 (F7035T)
Suggested solutions

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1. For a molecule the heat capacity C_v is given by $C_v = (\frac{\partial U}{\partial T})_V$. The partition function is $Z = 1 + 3e^{-\epsilon/\tau}$. The energy is $U = \frac{3\epsilon e^{-\epsilon/\tau}}{Z}$

$$C_v = (\frac{\partial U}{\partial \tau})_V = \frac{3(\frac{\epsilon}{\tau})^2 e^{\epsilon/\tau}}{(3+e^{\epsilon/\tau})^2} \quad (1)$$

Now let $x = \epsilon/\tau$

$$C_v = \frac{3x^2 e^x}{(3+e^x)^2} \quad (2)$$

Taking the derivative $\frac{\partial C_v}{\partial x}$ we arrive at an equation for the maximum of C_v as $3(2+x)+(2-x)e^x = 0$. The maximum is at about $x \approx 2.845$, which gives $C_v = 1.023$ and using the correct units $C_v = 1.023 k_B$.

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:

$$Z = \sum_{states} e^{-\epsilon_{state}/\tau} = 1 + \sum_{n=1}^{S} 2 \cdot e^{-n\epsilon/\tau} = -1 + \sum_{n=0}^{S} 2 \cdot e^{-n\epsilon/\tau} = -1 + 2\frac{1-e^{-(S+1)\epsilon/\tau}}{1-e^{-\epsilon/\tau}} \quad (3)$$

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

$$Z \approx -1 + 2\frac{1}{1-e^{-\epsilon/\tau}} = \frac{1+e^{-\epsilon/\tau}}{1-e^{-\epsilon/\tau}} \quad (4)$$

Now we turn to the energy:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = ... = \frac{2\epsilon}{e^{\epsilon/\tau} - e^{-\epsilon/\tau}} \quad (5)$$

For the heat capacity we have

$$C = \frac{\partial U_{total}}{\partial \tau} = \frac{\partial}{\partial \tau}\left(\frac{2\epsilon}{e^{\epsilon/\tau} - e^{-\epsilon/\tau}}\right) = 2(\frac{\epsilon}{\tau})^2 \frac{e^{\epsilon/\tau} + e^{-\epsilon/\tau}}{(e^{\epsilon/\tau} - e^{-\epsilon/\tau})^2} \quad (6)$$

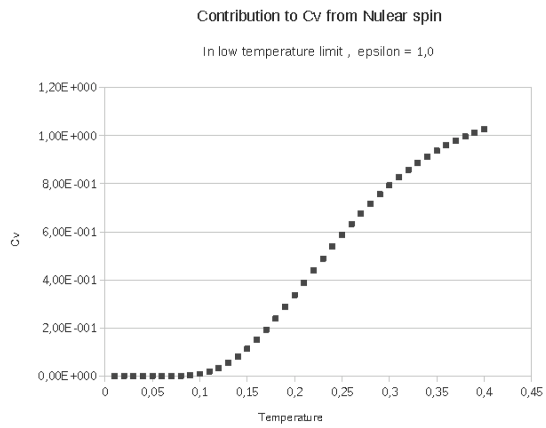

Figure 1: A principal figure showing the heat capacity in the low temperature limit. The choice for the energy $\epsilon = 1.0$ in eq. 9.

and hence for the total heat capacity

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

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

$$C_{total} \to 2N(\frac{\epsilon}{\tau})^2 \frac{e^{\epsilon/\tau}}{(e^{\epsilon/\tau})^2} = 2N(\frac{\epsilon}{\tau})^2 e^{-\epsilon/\tau} \tag{8}$$

The contribution to the heat capacity at low temperatures is

$$C = 2N(\frac{\epsilon}{\tau})^2 e^{-\epsilon/\tau} \tag{9}$$

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

Second route

The partition function can also be written as:

$$Z = \sum_{states} e^{-\epsilon_{state}/\tau} = 1 + \sum_{n=1}^{S} 2 \cdot e^{-n\epsilon/\tau} \approx 1 + 2 \cdot e^{-\epsilon/\tau} \tag{10}$$

Now we turn to the energy:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = ... = \frac{2\epsilon}{e^{\epsilon/\tau} + 2} \tag{11}$$

For the heat capacity we have

$$C = \frac{\partial U_{total}}{\partial \tau} = \frac{\partial}{\partial \tau}\left(\frac{2\epsilon}{e^{\epsilon/\tau} + 2}\right) = 2(\frac{\epsilon}{\tau})^2 \frac{e^{\epsilon/\tau}}{(e^{\epsilon/\tau} + 2)^2} \approx 2(\frac{\epsilon}{\tau})^2 e^{-\epsilon/\tau} \tag{12}$$

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:

$$Z = \sum_{states} e^{-\epsilon_{state}/\tau} = 1 + \sum_{n=1}^{S} 2 \cdot e^{-n\epsilon/\tau} \approx 1 + 2 \cdot e^{-\epsilon/\tau} \tag{13}$$

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

$$F = -\tau \ln(1 + 2 \cdot e^{-\epsilon/\tau}) \approx -2\tau \cdot e^{-\epsilon/\tau} \tag{14}$$

Now we calculate the entropy:

$$\sigma = -(\frac{\partial F}{\partial \tau})_{V,N} = -\frac{\partial}{\partial \tau}(-2\tau \cdot e^{-\epsilon/\tau}) = 2e^{-\epsilon/\tau}(1 + \frac{\epsilon}{\tau}) \tag{15}$$

For the heat capacity we have

$$C_V = \tau(\frac{\partial \sigma}{\partial \tau})_V = \tau\frac{\partial}{\partial \tau}\left(2e^{-\epsilon/\tau}(1 + \frac{\epsilon}{\tau})\right) = 2\tau e^{-\epsilon/\tau}(\frac{\epsilon}{\tau^2}(1 + \frac{\epsilon}{\tau}) - \frac{\epsilon}{\tau^2}) = 2(\frac{\epsilon}{\tau})^2 e^{-\epsilon/\tau} \tag{16}$$

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. Here Clausius–Claypeyrons equation will be used : $\frac{dp}{dT} = \frac{q}{T\Delta v}$ as we follow the phase boundary. $\frac{dp}{dT} = \frac{\Delta p}{\Delta T} = -\frac{3.689 \cdot 10^9}{T}$. ($\Delta v = v_{\text{liquid}} - v_{\text{is}} = \frac{1}{999.8} - \frac{1}{916.8} = -9.0550 \cdot 10^{-5}$ m^3/kg, $q = 334 \cdot 10^3$ J/kg). This gives for small changes of temperature: $\Delta T = -\frac{T\Delta p}{3.689 \cdot 10^9} = -0.143 \approx -0.14$K, ie a lowering of the freezing point by 0.14K.

4. The distribution inside the box is: $P(v) = 4\pi(\frac{M}{2\pi\tau})^{3/2} v^2 e^{-Mv^2/2\tau}$ in the exiting beam from the oven the distribution is $\propto vP(v)$ (sid 395 CK). The most probable velocity is given by the maximum of $\propto vP(v)$. $\frac{\mathrm{d}}{\mathrm{d}v}(v^3 e^{-Mv^2/2\tau} = ... = e^{-Mv^2/2\tau}(3v^2 - v^4 M/\tau) = 0$. Which gives the most probable velocity $v_{ms} = \sqrt{\frac{3\tau}{M}}$. The time for the drum to rotate half a turn is the same as the it takes for a Sodium (Na) with the v_{ms} to travel through the drum the distance d, denote this time as $t_{1/2}$. The equation to solve is $t_{1/2} \cdot v_{ms} = d$. For the angular velocity $\omega = \frac{2\pi}{2t_{1/2}} = \frac{\pi}{d}\sqrt{\frac{3\tau}{M}} = \frac{\pi}{d}\sqrt{\frac{3k_B T}{M}} = \frac{\pi}{0.10}\sqrt{\frac{3 \cdot 1.3807 \cdot 10^{-23} \cdot 573.15}{22.9898 \cdot 1.661 \cdot 10^{-27}}} = 24769.787 \approx 2.48 \cdot 10^4$rad/s (=3942,23 revolutions per second)

5. The partition function is $Z = 1 + e^{\frac{mB}{\tau}} + e^{-\frac{mB}{\tau}} \approx 1 + 1 + \frac{mB}{\tau} + \frac{1}{2}\left(\frac{mB}{\tau}\right)^2 + 1 - \frac{mB}{\tau} + \frac{1}{2}\left(\frac{mB}{\tau}\right)^2 = 3(1 + \frac{1}{3}\left(\frac{mB}{\tau}\right)^2)$. The free energy $F = -\tau \ln Z = -\tau \left[\ln 3 + \ln(1 + \frac{1}{3}\left(\frac{mB}{\tau}\right)^2)\right] \approx -\tau \left[\ln 3 + \frac{1}{3}\left(\frac{mB}{\tau}\right)^2)\right]$. The entropy $\sigma = -\frac{\partial F}{\partial \tau}_V = \ln 3 - \frac{1}{3}\left(\frac{mB}{\tau}\right)^2)$. The decrease in entropy is $\frac{1}{3}\left(\frac{mB}{\tau}\right)^2)$ and $A = \frac{1}{3}(mB)^2$