

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 $C_v = 1.023k_B$.

2. 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): $\Delta\sigma = \sigma_e - \sigma_1 - \sigma_2 = 2N \left[\ln \left(\frac{n_Q 3V}{2N} \right) + \frac{5}{2} \right] - N \left[\ln \left(\frac{n_Q 2V}{N} \right) + \frac{5}{2} \right] - N \left[\ln \left(\frac{n_Q V}{N} \right) + \frac{5}{2} \right] = 2N \ln \left(\frac{n_Q 3V}{2N} \right) - N \ln \left(\frac{n_Q 2V}{N} \right) - N \ln \left(\frac{n_Q V}{N} \right) = 2N \ln n_Q - N \ln n_Q - N \ln n_Q + 2N \ln 3V - N \ln 2V - N \ln V - 2N \ln 2N + N \ln N + N \ln N = N \left(\ln(9V^2 \frac{1}{2V} \frac{1}{V}) - \ln(4N^2 N^{-1} N^{-1}) \right) = N \ln(3^2 2^{-3} V^0 N^0) = N \ln(\frac{9}{8}) = N k_B \ln(\frac{9}{8})$

3. 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 $0, \epsilon, 2\epsilon, \dots, S\epsilon$, 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 $S\epsilon/\tau \gg 1$, ($\tau = k_B T$) the last reduces to

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

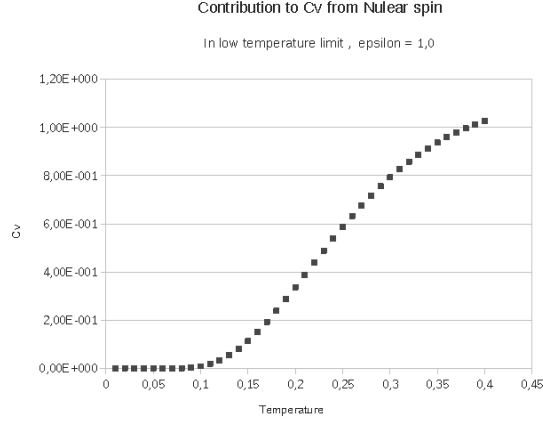


Figure 1: A principal figure showing the heat capacity in the low temperature limit. The choice for the energy $\epsilon = 1.0$ in eq. 9.

Now we turn to the energy:

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

For the heat capacity we have

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

and hence for the total heat capacity

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

In the limit $S\epsilon/\tau \gg 1$ ie $\tau \rightarrow 0$

$$C_{total} \rightarrow 2N \left(\frac{\epsilon}{\tau} \right)^2 \frac{e^{\epsilon/\tau}}{(e^{\epsilon/\tau})^2} = 2N \left(\frac{\epsilon}{\tau} \right)^2 e^{-\epsilon/\tau} \quad (8)$$

The contribution to the heat capacity at low temperatures is

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

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

Second route

The partition function can also be written as:

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

Now we turn to the energy:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = \dots = \frac{2\epsilon}{e^{\epsilon/\tau} + 2} \quad (11)$$

For the heat capacity we have

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

Third route

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

The partition function can also be written as:

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

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

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

Now we calculate the entropy:

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

For the heat capacity we have

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

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

4. As problem 7.1 in Kittel Kroemer. Start to evaluate the Density of States (DOS). As a system use a square of side L . The energy of a particle in a 2 dimensional box is given by

$$\epsilon_n = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 (n_x^2 + n_y^2) = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 n^2 \quad (17)$$

The number of electrons N (Fermions) inside a circle of radius n defined in $n^2 = n_x^2 + n_y^2$ is given by (including spin):

$$N = 2 \cdot \frac{1}{4} \pi n^2 = \frac{\pi 2mL^2}{2\hbar^2 \pi^2} \epsilon \quad \text{for all electrons} = 2 \cdot \frac{1}{4} \pi n_F^2 \quad (18)$$

differentiating to get DOS

$$D(\epsilon) = \frac{dN}{d\epsilon} = \frac{mL^2}{\hbar^2\pi} \quad (\text{a constant}) \quad (19)$$

5. The equation of state for an ideal gas is $pV = Nk_B T$ 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 $P = k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_T = \frac{Nk_B T}{V - bN} - \frac{aN^2}{V^2}$ which can be rearranged to $\left(P + \frac{aN^2}{V^2} \right) (V - bN) = Nk_B T$.

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 $U = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V = N \left(\frac{3k_B T}{2} - \frac{aN}{V} \right)$