Fall 1997 #11

Consider an atom that has a lowest electronic state $^1S_0$ and a first excited state $^3S_1$ with energy ϵ_1 above the ground state. All higher states with energies above the first excited state have energies much greater than kT.

a) For a gas of the atoms at temperature T, find the fraction of excited atoms.

→ This is a two-state system with energies ϵ_0 and $(\epsilon_0+\epsilon_1)$. The partition function is thus

$$Z = e^{-\beta\epsilon_0} + e^{-\beta(\epsilon_0+\epsilon_1)}$$

The fraction of excited atoms is the same as the probability of an atom to be in the excited state:

$$P(\epsilon_0+\epsilon_1) = \frac{e^{-\beta(\epsilon_0+\epsilon_1)}}{e^{-\beta\epsilon_0}+e^{-\beta(\epsilon_0+\epsilon_1)}} = \frac{e^{-\beta\epsilon_0}}{e^{-\beta\epsilon_0}}\left(\frac{e^{-\beta\epsilon_1}}{1+e^{-\beta\epsilon_1}}\right)$$

$$\boxed{\text{Fraction excited atoms} = \frac{e^{-\beta\epsilon_1}}{1+e^{-\beta\epsilon_1}}}$$

b) Give the internal energy of a gas of N atoms as a function of temperature and compute from this the specific heat $c_v(T)$. Make a plot of $c_v(T)$.

the partition function is given by: $Z_{tot} = \frac{1}{N!}(Z_1)^N$

$$Z_{tot} = \frac{1}{N!}\left(e^{-\beta\epsilon_0} + e^{-\beta(\epsilon_0+\epsilon_1)}\right)^N$$

find $\bar{E}(T)$ using $\bar{E} = -\frac{\partial \ln Z}{\partial\beta}$ (Reif eq 6.5.4)

$$\bar{E} = -\frac{\partial}{\partial\beta}\left(-\ln(N!) + N\ln\left(e^{-\beta\epsilon_0}+e^{-\beta(\epsilon_0+\epsilon_1)}\right)\right)$$

$$\bar{E} = -\left(\frac{N}{e^{-\beta\epsilon_0}+e^{-\beta(\epsilon_0+\epsilon_1)}}\right)\left(-\epsilon_0 e^{-\beta\epsilon_0} - (\epsilon_0+\epsilon_1)e^{-\beta(\epsilon_0+\epsilon_1)}\right)$$

$$\bar{E} = \left(\frac{N}{1+e^{-\beta\epsilon_1}}\right)\left(+\epsilon_0 + (\epsilon_0+\epsilon_1)e^{-\beta\epsilon_1}\right)$$

$$\boxed{\vec{E}(T) = \left(\frac{N}{1+e^{-\epsilon_1/kT}}\right)\left(\epsilon_0 + (\epsilon_0+\epsilon_1)e^{-\epsilon_1/kT}\right)}$$

from $\vec{E}(T)$ we see the limiting behavior $E(T\to 0) = N\epsilon_0$ and $E(T\to\infty) = \frac{N}{2}(2\epsilon_0+\epsilon_1)$ as one would expect

$$C_v(T) = \left(\frac{\partial \vec{E}}{\partial T}\right)_v = \left(\frac{\partial E}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right) \qquad \beta = \frac{1}{k}T^{-1} \Rightarrow d\beta = -\frac{1}{kT^2}$$

$$C_v(T) = \frac{\partial}{\partial \beta}\left[N\left(1+e^{-\beta\epsilon_1}\right)^{-1}\left(\epsilon_0+(\epsilon_0+\epsilon_1)e^{-\beta\epsilon_1}\right)\right]\left(\frac{-1}{kT^2}\right)$$

$$C_v(T) = \left[\left(\frac{N(-1)(-\epsilon_1 e^{-\beta\epsilon_1})}{(1+e^{-\beta\epsilon_1})^{-2}}\right)\left(\epsilon_0+(\epsilon_0+\epsilon_1)e^{-\beta\epsilon_1}\right) + \frac{N\left(-\epsilon_1(\epsilon_0+\epsilon_1)e^{-\beta\epsilon_1}\right)}{(1+e^{-\beta\epsilon_1})}\right]\left(\frac{-1}{kT^2}\right)$$

$$C_v(T) = \frac{-N}{kT^2}\left(\frac{\epsilon_0\epsilon_1 e^{-\beta\epsilon_1} + \cancel{\epsilon_1(\epsilon_0+\epsilon_1)e^{-2\beta\epsilon_1}} - \epsilon_1(\epsilon_0+\epsilon_1)(e^{-\beta\epsilon_1} \cancel{+ e^{-2\beta\epsilon_1}})}{(1+e^{-\beta\epsilon_1})^2}\right)$$

$$C_v(T) = \frac{-N}{kT^2}\left(\frac{\cancel{\epsilon_0\epsilon_1 e^{-\beta\epsilon_1}} - \cancel{\epsilon_0\epsilon_1 e^{-\beta\epsilon_1}} - \epsilon_1^2 e^{-\beta\epsilon_1}}{(1+e^{-\beta\epsilon_1})^2}\right)$$

$$\boxed{C_v(T) = \frac{N\epsilon_1^2 e^{-\epsilon_1/kT}}{kT^2\left(1+e^{-\epsilon_1/kT}\right)^2}} \qquad \lim_{T\to 0} C_v(T) = 0 \qquad \lim_{T\to\infty} C_v(T) = 0$$

Plot of $C_v(T)$ vs T yields: