

1. How do you interpret negative temperatures? Show that an object with negative temperature is "hotter" than an object with positive temperature, i.e. heat flows from a negative temperature object to a positive temperature object.

Solution:

Inverse temperature is the rate of change of entropy as a function of Energy. If temperature is negative, this means that entropy decreases as energy increases. Most of the time, this is not realized for physical systems. It happens, for example, if the energy has an upper limit, such as the spin system. In these systems, the maximum energy state is usually unique, and hence the entropy vanishes at maximum energy. Thus as the energy increases, the entropy eventually has to decrease and go to zero as this maximum energy is reached. That is the temperature becomes negative.

Consider two systems, one at the negative temperature  $-T_1$  and the other at some positive temperature  $T_2$ . Let these systems have energies  $E_1$  and  $E_2$  respectively. The total energy  $E = E_1 + E_2$  is conserved. The total entropy of the system is

$$S_T(E, E_1) = S_1(E_1) + S_2(E_2 = E - E_1)$$

. From the law of increase of Entropy, the rate of change of the total entropy  $S_T$  is positive:

$$\frac{d}{dt}S_T(E, E_1) = \frac{d}{dE_1}S_1(E_1)\frac{dE_1}{dt} + \frac{d}{dE_2}S_2(E_2)\frac{dE_2}{dt} > 0 \quad (1)$$

Using the definition of temperature, and  $dE_2/dt = -dE_1/dt$ , one obtains:

$$\frac{1}{-T_1} \frac{dE_1}{dt} - \frac{1}{T_2} \frac{dE_1}{dt} = - \left( \frac{1}{T_1} + \frac{1}{T_2} \right) \frac{dE_1}{dt} > 0 \quad (2)$$

i.e.

$$\frac{dE_1}{dt} < 0,$$

that is the energy of the first system, the system which has negative temperature, is flowing to the system with positive temperature. That is the system with negative temperature is "hotter" than a system with positive temperature.

2. What does "non-interacting" mean? If the particles forming the system do not interact, the system will never reach equilibrium. Hence how is it possible that one can talk about non-interacting systems?

Solution:

"Non-interacting" systems can be considered as zeroth order approximation to interacting systems. By "non-interacting" it is meant that the interaction energy is very small compared to the energy of the system and hence can be neglected. Since there is some (weak) interaction, the system can reach equilibrium at a (long but) finite time. Thus when studying systems which are said to be "non-interacting" it is implied that the interaction energy is small compared to the total energy *and* that we wait for a sufficiently long time so that the system reaches equilibrium.

3. Consider the non-interacting spin system considered during the lecture. The hamiltonian is given by:

$$\hat{H} = \sum_{i=1}^N \frac{\mu B \hbar}{2} \sigma_z^i$$

(a) Consider a subsystem consisting of two spins. What are the possible states that the sub-system can be in? What are the probabilities that the sub-subsystem can be found in these states?

Solution:

Let  $|+\rangle$  and  $|-\rangle$  denote two states such that:

$$\sigma_z |\pm\rangle = \pm |\pm\rangle \quad (3)$$

Then, the possible states of the two spin system are:  $|++\rangle$ ,  $|+-\rangle$ ,  $| - + \rangle$ , and  $|--\rangle$  corresponding to the energies  $2\epsilon$ ,  $0$ ,  $0$  and  $-2\epsilon$  respectively, where  $\epsilon = \frac{\mu B \hbar}{2}$

Since the spins are independent, the probability that the subsystem will be in the state  $|s_1 s_2\rangle$  is:

$$p_2(s_1, s_2) = p_1(s_1)p_1(s_2)$$

where  $p_1(s)$  is the probability that a single spin will be in the state  $|s\rangle$ . This probability was calculated during the lecture and it has been obtained that:

$$p_1(s) = \frac{1}{Z_1} e^{-\beta \epsilon_s}$$

where  $\beta = (kT)^{-1}$ ,  $T$  is the temperature of the system,  $\epsilon_s = \frac{\mu B \hbar}{2} s$  is the energy of the spin, and  $Z_1 = e^{-\beta \epsilon_+} + e^{-\beta \epsilon_-}$  where  $\epsilon_{\pm} = \pm \frac{\mu B \hbar}{2}$ . Thus, the probability for the two spin system is:

$$p_2(s_1, s_2) = \frac{1}{Z_2} e^{-\beta \epsilon_{s_1 + s_2}}$$

where  $\epsilon = \epsilon_{s_1} + \epsilon_{s_2}$  and  $Z_2 = Z_1^2$ . In particular:

$$\begin{aligned} p_2(+, +) &= \frac{1}{Z_2} e^{-2\beta \epsilon} \\ p_2(+, -) = p_2(-, +) &= \frac{1}{Z_2} \\ p_2(-, -) &= \frac{1}{Z_2} e^{2\beta \epsilon} \end{aligned} \quad (4)$$

(b) What is the average energy of the subsystem? The average energy is given by negative of the derivative of  $Z_2$ :

$$\begin{aligned} \langle \epsilon \rangle &= -\frac{\partial}{\partial \beta} \ln Z_2 \\ &= -\frac{\partial}{\partial \beta} \ln \left( e^{-\beta \epsilon_+} + e^{-\beta \epsilon_-} \right)^2 \\ &= 2 \frac{\epsilon_+ e^{-\beta \epsilon_+} + \epsilon_- e^{-\beta \epsilon_-}}{e^{-\beta \epsilon_+} + e^{-\beta \epsilon_-}} \\ &= \mu B \hbar \frac{e^{-\beta \epsilon_+} - e^{-\beta \epsilon_-}}{e^{-\beta \epsilon_+} + e^{-\beta \epsilon_-}} \end{aligned} \quad (5)$$

where  $\epsilon_{\pm} = \pm \frac{\mu B \hbar}{2}$  or using the expression of  $T$  in terms of the total energy:

$$\langle \epsilon \rangle = 2 \frac{E}{N}.$$

(c) What is the relative energy fluctuation of the subsystem? The energy fluctuation is defined as:

$$\langle (\Delta \epsilon)^2 \rangle = \langle \epsilon^2 \rangle - \langle \epsilon \rangle^2$$

. Using the partition function, this can be expressed as:

$$\begin{aligned} \langle (\Delta \epsilon)^2 \rangle &= \frac{1}{Z_2} \frac{\partial^2}{\partial \beta^2} Z_2 - \left( \frac{1}{Z_2} \frac{\partial}{\partial \beta} Z_2 \right)^2 \\ &= \frac{\partial^2}{\partial \beta^2} \ln Z_2 \end{aligned} \quad (6)$$

Substitution the partition function and expressing temperature in terms of Energy of the whole system, one obtain

$$\langle(\Delta\epsilon)^2\rangle = \frac{(\mu B\hbar)^2}{2} \left[ 1 - \left( \frac{2E}{\mu B\hbar N} \right)^2 \right] \quad (7)$$

Thus the relative fluctuation is:

$$\frac{\sqrt{\langle(\Delta\epsilon)^2\rangle}}{\langle\epsilon\rangle} = \frac{\mu B\hbar N}{2\sqrt{2}E} \left[ 1 - \left( \frac{2E}{\mu B\hbar N} \right)^2 \right]^{\frac{1}{2}}$$

Note in particular that for  $E = E_{max} = \frac{\mu B\hbar}{2}N$  and for  $E = E_{min} = -E_{max}$ , the relative fluctuation is zero. This makes sense as for the maximum and minimum energy, the system can be in a unique state only, and hence there can not be any fluctuation.

4. Calculate  $C_v$  and  $C_p$  for the ideal gas.

Solution:

$C_v$  can be obtained directly from

$$C_v = \left( \frac{\partial E}{\partial T} \right)_V$$

. We have shown in the lecture that for the ideal gas  $E = \frac{3}{2}NkT$  and hence, we obtain  $C_v = \frac{3}{2}Nk$

$C_p$  can be obtained from

$$C_p = \left( \frac{\partial W}{\partial T} \right)_P$$

whence  $W = E + PV$  is the heat function. Using the equation of state for the ideal gas (which we have derived in the lecture),  $PV = NkT$ , one obtains

$$W = \frac{5}{2}NkT$$

and hence  $C_p = \frac{5}{2}Nk$ .

5. Calculate  $F$ ,  $W$ , and  $\Phi$  for a gas of  $N$  noninteracting atoms.

Solution:

From the study in the class for  $N$  noninteracting gas of atoms, we know that

$$\begin{aligned} S &= \frac{3}{2}Nk \ln \left[ \frac{me}{3\pi\hbar^2} \left( \frac{eV}{N} \right)^{\frac{2}{3}} \frac{E}{N} \right] \\ E &= \frac{3}{2}NkT \\ PV &= NkT \end{aligned} \tag{8}$$

The heat function,  $W$ , is defined

$$W = E + PV$$

and using Eqs. (8), we get

$$W = \frac{3}{2}NkT + NkT = \frac{5}{2}NkT$$

The Gibbs free energy  $F$  is defined as  $F = E - TS$ . Substituting the expressions for  $E$  and  $S$  from Eqs. (8), one obtains

$$F = \frac{3}{2}NkT \ln \left[ \frac{2\pi\hbar^2}{mkT} \left( \frac{N}{eV} \right)^{\frac{2}{3}} \right] \tag{9}$$

The Helmholtz free energy,  $\Phi$ , can be obtained from  $F$  using  $\Phi = F + PV$  and from Eq. (9) and the equation of state for the ideal gas, we obtain:

$$\Phi = \frac{3}{2}NkT \ln \left[ \frac{2\pi\hbar^2}{mkT} \left( \frac{N}{V} \right)^{\frac{2}{3}} \right] \tag{10}$$