

This discusses some of the issues raised by Ashok during our discussions on the properties of quantum systems and its relation to thermodynamics.

1. Given a density matrix, what is the meaning of temperature of the system?

Temperature has a meaning only under equilibrium conditions and it has the form

$$\hat{\rho} = \frac{\exp(-\beta\hat{H})}{\text{TrTr}(\exp(-\beta\hat{H}))} \quad (1)$$

The same is true for classical systems where we need to have the probability distribution function  $\rho(q, p)$  to be given by

$$\rho(q, p) = \frac{\exp(-\beta H(q, p))}{\int dqdp \exp(-\beta H(q, p))} \quad (2)$$

Thus the system has a temperature only if it (quantum )system satisfies Eq.(??) or (classical) eq.(??).

In general, a density matrix defining a system need not be in thermal equilibrium.

An important question arises is answering the question

What does thermal equilibrium mean ?

Only if they obey eq.(ref1) or (??).

However, if a closed (isolated) system is not in thermal equilibrium, the question arises what happens to it subsequently. The energy of the system is fixed. The law of statistical mechanics states that the system attains an equilibrium state which has the maximum of

$$- \int dqdp \rho \ln(\rho(q, p)) \quad (3)$$

for the classical case and

$$- \text{Tr}(\hat{\rho} \ln(\hat{\rho})) \quad (4)$$

How this comes about is the subject of ergodic theory ( needs sophisticated mathematical analysis, for both the classical and the quantum case). The time scales are important in analysing a process.

Thus in the case of classical adiabatic equation, the time scale of expansion should be larger than the time scale of thermalisation ( relaxation time), so that at every stage, the system has a definite temperature, pressure etc. Here, only states which are in thermal equilibrium is being considered.

On the other hand in the case of quantum adiabatic process, consider a density matrix which is diagonal in the energy basis and is at thermal equilibrium at temperature  $T$ . When this develops quantum adiabatically by changing the Hamiltonian slowly, the probability of a particular state does not change. However energy changes and so the system is out of thermal equilibrium. So in this case, we assume the time scale of thermalization to be larger than the time scale at which the quantum adiabatic theorem is valid.

Finally, all the four postulates of Callen are for thermally equilibrium states only. They are therefore valid for both classical and quantum systems.

Not every state, quantum or classical need satisfy these postulates (non-equilibrium systems) usually referred to as open systems (classical or quantum)