2. Entropy and Temperature

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- The **fundamental assumption** of thermal physics: a closed system is equally likely to be in any of the quantum states accessible to it.
- A **closed system** will hold everything constant, including all external parameters that may influence the system.
- A quantum state is **accessible** if its properties are compatible with the physical specification of the system.
- In a closed system with g accessible quantum states, the probability $P(s)$ for finding the system in the state s is:

$$P(s) = 1/g$$

- Average value:

$$< X >= \sum_s X(s)P(s)$$

- **Ensemble average** (average of a closed system with g equally likely accessible states):

$$< X >= \sum_s X(s)(1/g)$$

- An ensemble of systems is composed of many systems, all constructed alike.
- **thermal contact**: systems brought into contact so that energy can be transferred freely from one to the other.
- The most probable division of the total energy is that for which the combined system has the maximum number of accessible states.
- The energy of the combined system is directly proportional to the total spin excess:

$$U(s) = U_1(s_1) + U_2(s_2) = -2mB(s_1 + s_2) = -2mBs$$

where total number of particles is $N = N_1 + N_2$.

- multiplicity function of the combined system:

$$g(N,s) = \sum_s g_1(N_1,s_1)g_2(N_2,s-s_1)$$

- **thermal equilibrium values**: average values of the most probable configuration, the configuration where the number of accessible states is a maximum, of the combined system.

- entropy σ is defined as:

$$\sigma(N,U) \equiv \log g(N,U)$$

- For an extremum, which governs the properties of the total system in thermal equilibrium, the differential of $g(N,U)$ is zero, so that (derivation shown in KK p.40):

$$\left(\frac{\partial\sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial\sigma_2}{\partial U_2}\right)_{N_2}$$

- **Temperature**:

$$\frac{1}{T} = k_B\left(\frac{\partial\sigma}{\partial U}\right)_N$$

  where k_B is the Boltzmann constant, with value 1.381×10^{-23}joules/kelvin

- **fundamental temperature** τ:

$$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_N$$

  where $\tau = k_B T$

- Because σ is a pure number, τ has the dimensions of energy.

- **Entropy** is defined as the logarithm of the number of states accessible to the system.

- Conventional entropy S:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$

  where

$$S = k_B\sigma$$

- Operations that tend to increase the entropy of a system: add particles, add energy, increase the volume, decompose molecules, etc.

- **Law of increase of entropy**: the entropy of a closed system tends to remain constant or to increase when a constraint internal to the system is removed. It can be expressed as:

$$\sigma_{final} \simeq log(g_1g_2)_{max} \geq \sigma_{initial} = log(g_1g_2)_0$$

- Laws of Thermodynamics

  1. Zeroth law - if two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other.
  2. First law - heat is a form of energy.
  3. Second law (law of increase of entropy) - if a closed system is in a configuration that is not the equilibrium configuration, the most probable consequence will be that the entropy of the system will increase monotonically in successive instants of time.
  4. Third law - the entropy of a system approaches a constant value as the temperature approaches zero.