

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:

$$\langle X \rangle = \sum_s X(s)P(s)$$

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

$$\langle X \rangle = \sum_s X(s)(1/g)$$

- 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:

$$\sigma_{final} \simeq \log(g_1 g_2)_{max} \geq \sigma_{initial} = \log(g_1 g_2)_0$$