- HH0057 -

Temperature

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• equilibrium condition

When two systems are in thermal contact, the most probable configuration corresponds to the maximum of the total multiplicity function $g_1 g_2$,

$$d(g_1 g_2) = 0 \quad \rightarrow \quad \frac{1}{g_1}\left(\frac{\partial g_1}{\partial E_1}\right)_{N_1}\Bigg|_{E_1=U_1} = \frac{1}{g_2}\left(\frac{\partial g_2}{\partial E_2}\right)_{N_2}\Bigg|_{E_2=U_2} \tag{1}$$

where U_1, U_2 are the energies of the most probable configuration and can be viewed as average energies of the subsystems in thermal equilibrium. The above notation is a bit tedious and can be written in the textbook notation as well (though a bit confusing),

$$\frac{1}{g_1}\left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} = \frac{1}{g_2}\left(\frac{\partial g_2}{\partial U_2}\right)_{N_2} \quad \rightarrow \quad \left(\frac{\partial \log g_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \log g_2}{\partial U_2}\right)_{N_2} \tag{2}$$

The equilibrium condition motivates us to define a physical quantity:

$$\boxed{\boxed{\frac{1}{\tau} \equiv \left(\frac{\partial \log g}{\partial U}\right)_N}} \quad \longleftarrow \text{ fundamental temperature} \tag{3}$$

The fundamental temperature τ is related to the usual temperature T by the Bolzmann constant, $\tau = k_B T$.

• temperature as an energy scale

The above definition of temperature is quite far from our common intuition. Can we improve our understanding better?

$$\frac{1}{\tau} \equiv \left(\frac{\partial \log g}{\partial U}\right)_N \quad \longrightarrow \quad \frac{1}{\tau}\Delta U = \Delta \log g, \tag{4}$$

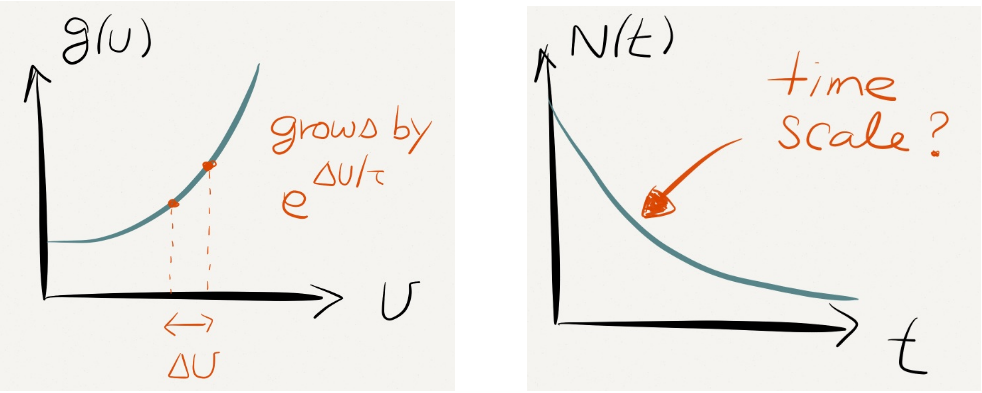

Figure 1: Temperature τ can be viewed as the energy scale for the exponential growth of the multiplicity function $g(U)$. Its role is pretty much as same as the half-life time τ in the decaying process.

where ΔU is small energy derivation from the average energy in equilibrium. Note that $\Delta \log g = \log g(U + \Delta U) - \log g(U) = \log[g(U + \Delta U)/g(U)]$. The above relation can be brought into the form,

$$\frac{1}{\tau}\Delta U = \log[g(U + \Delta U)/g(U)] \quad \longrightarrow \quad g(U + \Delta U) = g(U)\, e^{\Delta U/\tau} \tag{5}$$

The multiplicity $g(U)$ grows by a factor $e^{\Delta U/\tau}$ when U increase to $U + \Delta U$. **That is to say, τ sets the energy scale of the exponential growth of the multiplicity $g(U)$.**

Take decaying process as a comparing example. The surviving quantity evolves as $N(t) = N(0)e^{-t/\tau}$, where τ is the half-life time. To pin down the characteristic time scale of the decaying process, it is unwise to use the decay rate dN/dt because it also depends on the initial condition $N(0)$. A better choice is to use the rate of $\log N$,

$$-\frac{d\log N}{dt} = -\frac{1}{N}\frac{dN}{dt} = \frac{1}{\tau}. \tag{6}$$

The surviving quantity $N(t)$ decays by a factor $e^{-\Delta t/\tau}$ when t increases to $t + \Delta t$. Obviously, the half time τ sets the time scale for the decaying process.

• the concept of reservoir

Going back to the example of two spin systems in thermal equilibrium. One interesting limit is $N_2 \gg N_1$ and the larger system is called “reservoir”. The multiplicity function of the reservoir is

$$g(E_2) = g(0)\exp\left(-\frac{E_2^2}{2N_2m^2B^2}\right) \longrightarrow \log g = \log g(0) - \frac{E_2^2}{2N_2m^2B^2} \tag{7}$$

According to the definition of temperature, $\tau(E)$ of the reservoir at energy close to its equilibrium value $E_2 = U_2 + \Delta U$ is

$$\frac{1}{\tau} \equiv \left(\frac{\partial \log g}{\partial E}\right)_N = -\frac{E_2}{N_2m^2B^2} = -\frac{U_2}{N_2m^2B^2} - \frac{\Delta U}{N_2m^2B^2}. \tag{8}$$

In the limit $N_2 \gg N_1$, the energy exchange between the subsystems $\Delta U \ll U_2$ and the second term can be dropped. We arrive at the very useful approximative relation,

$$\frac{1}{\tau} \approx -\frac{U_2}{N_2m^2B^2} = \frac{1}{\tau_2} \quad \longrightarrow \quad \boxed{\tau_2 = -\left(\frac{N_2}{U_2}\right)m^2B^2 \propto -\frac{1}{u_2}} \tag{9}$$

where $u_2 = U_2/N_2$ is the average energy of each spin in the reservoir. Two strange behaviors need further explanations: (1) If the spin excess is positive (thus corresponds to negative energy), the temperature is positive. However, when spin excess is negative, the temperature is negative as well. It is important to keep in mind that negative temperature is indeed possible for some statistical systems. (2) The temperature of the reservoir is *inversely proportional to* the average energy of each constituent. Therefore, you should abandon the intuition that the temperature is proportional to the average energy of each constituent.

• density of states for ideal gas

Now we try to compute the multiplicity function of an ideal gas. From the multiplicity function, we can then derive the average energy of each molecule, $u = (3/2)\tau$, in thermal equilibrium. Consider a monoatomic ideal gas of N gas molecules. The energy of the system is

$$E = \left(\frac{p_{1x}^2}{2m} + \frac{p_{1y}^2}{2m} + \frac{p_{1z}^2}{2m}\right) + \cdots + \left(\frac{p_{Nx}^2}{2m} + \frac{p_{Ny}^2}{2m} + \frac{p_{Nz}^2}{2m}\right). \tag{10}$$

Adding in the favor of quantum physics: the momentum $p_{1x} = n_{1x}\pi\hbar/L$ is quantized and same for all others. Introduce the $3N$ dimensional vector,

$$\boldsymbol{n} = (n_{1x}, n_{1y}, n_{1z}, \cdots, n_{Nx}, n_{Ny}, n_{Nz}), \tag{11}$$

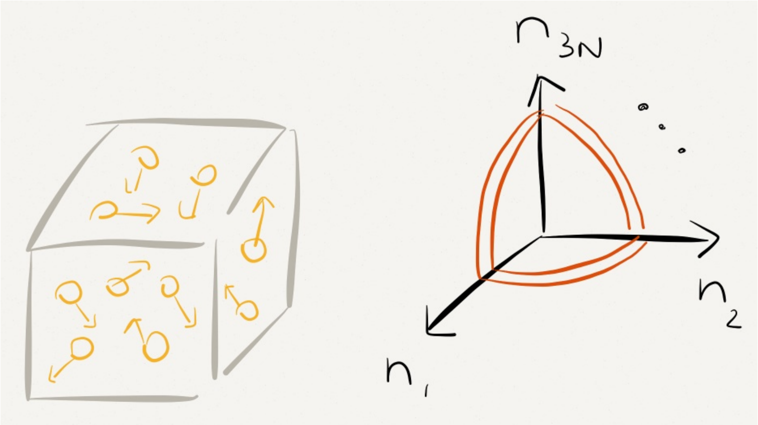

Figure 2: A monoatomic ideal gas of N molecules. All stationary states with quantized momenta can be uniquely labelled by the vector $\boldsymbol{n}$ in the $3N$ dimensional space and its magnitude $n \propto \sqrt{E}$ is proportional to the square root of the total energy E.

the total energy of the system reads

$$U = \frac{\pi^2\hbar^2}{2mL^2}n^2, \tag{12}$$

where $n = |\boldsymbol{n}| = \sqrt{n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + \cdots + n_{Nx}^2 + n_{Ny}^2 + n_{Nz}^2}$. For realistic size of L, the energy levels are extremely close and it is better to view the discrete energy levels as continuous. Instead of computing the multiplicity for each energy level, we compute the total multiplicity for all levels in the energy interval $(E, E+\Delta E)$,

$$\boxed{\boxed{\sum_{E'} g(E') = (\text{number of grid points in the } n\text{−space}) \equiv D(E)\Delta E}} \tag{13}$$

where the summation is over energy E' in the interval $(E, E+\Delta E)$ and $D(E)$ is the density of states. The number of grid points in the thin spherical shell is roughly its volume in the $3N$ space. Therefore, $D(E)\Delta E \approx C \times n^{3N-1}\Delta n$, where C is some constant. Making use of the relation $n = (\sqrt{2m}L/\pi\hbar)E$, the density of states for a monoatomic ideal gas is

$$D(E) \approx C \times n^{3N-1}\frac{dn}{dE} = C' \times E^{(3N-1)/2}\frac{1}{\sqrt{E}} \to \boxed{D(E) \approx C' \times E^{\frac{3}{2}N-1}} \tag{14}$$

In thermal equilibrium, average energy and temperature are related,

$$\frac{1}{\tau} = \frac{\partial \log D}{\partial U} = \frac{1}{D}\frac{\partial D}{\partial U} = \left(\frac{3}{2}N - 1\right)\frac{1}{U} \approx \frac{3}{2}N \times \frac{1}{U}. \tag{15}$$

The average energy of the ideal gas is approximately $U = (3N/2)\tau$ in the thermodynamic limit $N \to \infty$. The average energy of each gas molecule u is

$$\boxed{u = \frac{U}{N} = \frac{3}{2}\tau = f \times \frac{1}{2}\tau} \tag{16}$$

where $f = 3$ is the degrees of freedom, corresponding to the motions in three different spatial directions. The above result can be understood by equipartition of energy for each degree of freedom in the classical limit. However, keep in mind that the theorem of equipartition of energy is only valid in the classical limit and does not hold in general cases.

Happy

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