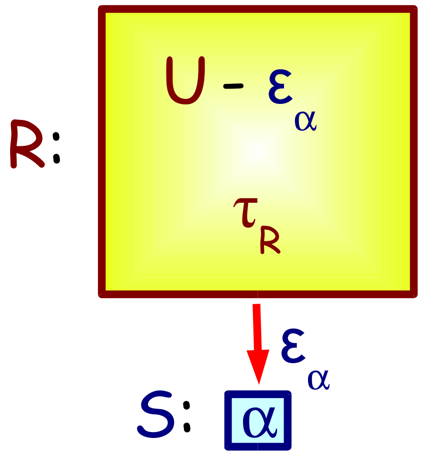
Microstates & Reservoirs



A large heat reservoir R at temperature τ_R initially has a total energy U, but then a tiny bit ε_α of that energy is given to a small system S to put it into one particular fully specified microstate labelled "α" whose energy is ε_α.

The probability P_α of this configuration is proportional to the multiplicity of the combined system (R + S): $\Omega = \Omega_R \cdot \Omega_S$.

But $\Omega_S = 1$. So $P_\alpha \sim \Omega_R = e^{\sigma_R}$ where σ_R (the entropy of R) is now reduced by an amount $-(\partial\sigma_R/\partial U_R)\,\varepsilon_\alpha = -\,\varepsilon_\alpha/\tau_R$ from its original value before ε_α was taken away to form state "α". Thus $P_\alpha \sim \exp(-\varepsilon_\alpha/\tau_R)$.

The Boltzmann Distribution

When a simple system is in thermal equilibrium with a large heat reservoir at temperature τ, the probability P_α of finding it in one particular **fully specified microstate** "α" of energy ε_α is **proportional** to $\exp(-\varepsilon_\alpha/\tau)$:

$$P_\alpha = C \exp(-\varepsilon_\alpha/\tau)$$

Where C is an unknown constant that can be found from the **normalization** condition $\sum_\alpha P_\alpha = 1$. (The sum of all such probabilities over all possible fully specified microstates of that system must be 1.) This is why we try to pick a simple system!

The Isothermal Atmosphere

An example of such a simple system is the height h of one oxygen (O_2) molecule in the Earth's atmosphere. (Not its kinetic energy, nor its spin or vibration, just its height!) Then h is a complete specification of "α" and $\varepsilon_\alpha = \varepsilon(h) = mgh$, where m is the mass of one O_2 molecule and $g = 9.81$ m/s^2. If we pretend that the temperature of the atmosphere is uniform, $\tau = 300\, k_B \approx 4 \cdot 10^{-21}$ J, we conclude $P(h) \sim \exp(-mgh/\tau)$. The partial pressure $p(h)$ of oxygen at altitude h is proportional to the probability of any given O_2 molecule being at that altitude, so we don't need to normalize the Boltzmann distribution to calculate $p(h)$ in terms of $p(0)$:

$$p(h) = p(0)\, e^{-h/h_0} \quad \text{where} \quad h_0 = \tau/mg$$

How Big are Molecules?

Empirical evidence from personal experience: O_2 concentration is markedly reduced (almost a factor of 3?) at 8000 m altitude. Conclusion: $h_0 = \tau/mg \approx 8000$ m where $\tau = 300\, k_B \approx 4 \cdot 10^{-21}$ J and $g = 9.81$ m/s^2. Thus $m \approx 4 \cdot 10^{-21}/(9.81 \cdot 8000) \approx 5 \cdot 10^{-26}$ kg is the mass of one oxygen molecule.

Note that this was estimated using only the Boltzmann distribution and empirical data available to anyone.

Looking it up gives $m(O_2) = 32$ AMU $= 5.3137 \cdot 10^{-26}$ kg.

One mole of O_2 = 32 gm = 0.032 kg = $\mathbf{6.022} \cdot 10^{23}\, m(O_2)$.

↑ Avogadro's number