Thermal forces and diffusion

Boltzmann's law states that in thermal equilibrium, the probability P_i of finding a particle in a state i with energy U_i is

$$P_i = \frac{1}{Z} e^{-\{U_i/kT\}}$$

$$Z = \sum_i e^{-\{U_i/kT\}} \qquad \text{partition function}$$

kT at room temp : $\frac{1}{40}$ eV ≈ 25 meV

2.5 kJ/mol
0.6 kcal/mol

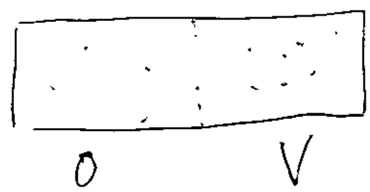
1 calorie = 4.1868 J

Boltzmann's law $\hat{=}$ each configuration of a closed system is equally likely

Comparison of energies

kT	0.6 kcal/mol	1
green 500 nm photon	60 kcal/mol	100
ATP hydrolysis	15 kcal/mol	25
180 mV e^- potential	4.2 kcal/mol	7

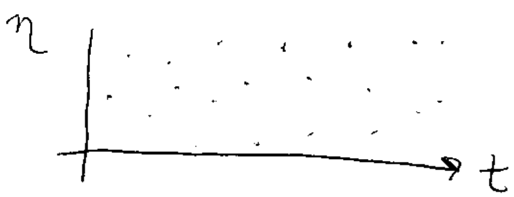
Application — charged particles within two compartments at different potentials



concentration $\quad \dfrac{c_V}{c_0} = \dfrac{P_V}{P_0} = e^{-\frac{U}{kT}} = e^{\frac{-qV}{kT}}$

Nernst equation

Random variables



Function $\eta(t)$ is meaningless for η random variable

Prob $P(\eta, t)$ is useful

Expectation value $\rightarrow$ average over position

$$E\,(f(\eta, x)) = \int_{-\infty}^{+\infty} f(\eta, x)\, P(\eta, x)\, dx$$

Time average

$$\langle f(\eta, t) \rangle_T = \left(\int_0^T f(\eta, t)\, P(\eta, t)\, dt \right)$$

$$= \frac{1}{T} \int_0^T f(\eta, t)\, dt$$

For long times,

time average = expectation value

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