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

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

$$Z = \sum_i e^{-\frac{U_i}{kT}}$$

Partition function

$$kT : \frac{1}{40} \text{ eV} \approx 25 \text{ meV}$$

2.5 kJ/mol

0.6 kcal/mol

1 calorie = 4.1868 J

Boltzmann's law $\equiv$ each configuration of a closed system is equally likely

Comparison of energies

\[ \begin{array}{ccc}
\text{kT} & 0.6 \text{ kcal/mol} & 100 \\
\text{green 500 nm photon} & 60 \text{ kcal/mol} & 25 \\
\text{ATP hydrolysis} & 15 \text{ kcal/mol} & 7 \\
180 \text{ mV e}^- \text{ potential} & 4.2 \text{ kcal/mol} & \\
\end{array} \]
Application: charged particles within two compartments at different potentials

\[ \frac{C_V}{C_0} = \frac{P_V}{P_0} = e^{-\frac{U}{kT}} = e^{-\frac{qV}{kT}} \]

Nernst equation

Random variables

[Diagram of a random variable \( \eta \) with time \( t \)]

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

Prob. \( P(\eta|x) \) is useful

Expectation value

\[ E(\phi(\eta,x)) = \int_{-\infty}^{\infty} \phi(\eta) p(\eta,x) \, dx \]

Time average

\[ \langle f(\eta,t) \rangle_T = \frac{1}{T} \int_0^T f(\eta,t) p(\eta,t) \, dt \]

For long times, time average = expectation value