2 States of a System

Mostly chap 1 of Kittel & Kroemer

2.1 States / Configurations

2.2 Probabilities of States
   • Fundamental assumptions
   • Entropy

2.3 Counting States

2.4 Entropy of an ideal gas
System States, Configurations

Microscopic: each degree of freedom
Classical \( q_i, p_i = \frac{\partial L}{\partial \dot{q}_i} \)
Quantum state # \( \phi_i \)

Statistical Mechanics \( f(q_i, p_i) \)
Moments \( \langle q_i \rangle, \langle p_i \rangle \)

Thermodynamics
Macroscopic Variables

State

State = Quantum State

Configuration = Macroscopic specification of system

In quantum mechanics: a finite system has discrete eigenvalues

Atomic levels
Spins
Spatial states

\[ \Psi(x, y, z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \]

\( n_x, n_y, n_z \) integers \( > 0 \)

\[ \varepsilon_{n_x, n_y, n_z} = \left(\frac{\hbar^2}{2M}\right) \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) \]
Fundamental Postulate

An isolated system in equilibrium is equally likely to be in any of its accessible states.

Related, to the symmetry of transition probabilities:
Probability of transition per unit time state \( r \rightarrow s \) = Prob of transition state \( s \rightarrow r \)
\[
\Gamma_{rs} = \Gamma_{sr}
\]

Can be proved in Quantum mechanics (compatible with statistical mechanics!)

\[\Rightarrow \text{Probability of a configuration} \quad \text{(isolated, in equilibrium)}\]

\[\text{Prob(configuration)} = \frac{\text{Number of states in configuration}}{\text{Total number of states}} = \frac{g}{g_t}\]
Entropy

Definition

\[ \sigma = - \sum_{s} p_s \log p_s = -H \]

For an isolated system in equilibrium:

\[ \sigma = \log (g_t) = \text{Kittel} \]

e.g. for a system of \( N \) spins 1/2 isolated, in equilibrium

\[ \sigma = N \log 2 \]
Counting States

Stirling approximation

$$\log N! \approx N \log N - N + \frac{1}{2} \log(2\pi N) \quad \text{(valid for both integers and half integers)}$$

Independent spins 1/2

N spins, each of them has two states (up, down)

If we define a configuration by the number of spins up, the number of states in the configuration

$$g(n_{\text{up}}, n_{\text{down}}) = \frac{N(N-1)\ldots(N-n_{\text{up}}+1)}{n_{\text{up}}!} = \frac{N!}{n_{\text{up}}!n_{\text{down}}!} \quad \text{with } n_{\text{down}} = N - n_{\text{up}}$$

We do care about order!

Density of spatial states per unit phase space

Phase space element for a single particle in 3 dimensions:

**Theorem:** the density of spatial states (orbitals) per unit phase space for a single particle in 3 dimensions is $1/h^3 = \text{density of quantum states for a spinless particle}$

$$\sin\left(\frac{n\pi x}{L}\right) = \frac{e^{i\frac{n\pi x}{L}} - e^{-i\frac{n\pi x}{L}}}{2i} = \text{superposition of 2 momentum states } \frac{n\pi}{L} \text{ and } -\frac{n\pi}{L} \quad \Delta x \Delta p_x = L \times 2 \frac{\pi\hbar}{L} = h$$
Ideal Gas (optional)

Counting with constraint on \( U \) + undistinguishable

\[
g = \frac{1}{N!} \int \frac{h}{L} \delta \left( \sqrt{\sum_{\text{part } i} \sum_{j=1}^{3} p_{ij}^2} - \sqrt{2MU} \right) \prod_{i} \frac{d^3x_i d^3p_i}{h^3} = \frac{V^{N-1/3} (2MU)^{3N-1}}{N!h^{3N-1}} \Omega_{3N}^3
\]

Sackur Tetrode

Taking into account expression for \( \Omega_{3N}^3 \)

\[
\sigma(U,V,N) = \log g \xrightarrow{N \to \infty} N \log \left[ \left( \frac{2\pi M}{h^2} \right)^{3/2} \right] + N \left( \log \frac{V}{N} + 5/2 \right)
\]

or \[
\sigma(U,V,N) = \frac{S}{k_B} = N \left[ \log \left( \frac{n_Q}{n} \right) + \frac{5}{2} \right] \quad \text{with } n = \frac{N}{V}, n_Q = \left( \frac{2\pi M}{h^2} \frac{2U}{3N} \right)^{3/2}
\]

Conclusion: we can compute the entropy from first principles!

“Micro canonical methods” = Painful!