2 States of a System

Mostly chap 1 of Kittel & Kroemer

2.1 States / Configurations

2.2 Probabilities of States
   • Fundamental postulate
   • Entropy

2.3 Counting States

2.4 Entropy of an ideal gas
System States, Configurations

<table>
<thead>
<tr>
<th>Microscopic: each degree of freedom</th>
<th>Statistical Mechanics $f(q_i, p_i)$</th>
<th>Thermodynamics</th>
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<tbody>
<tr>
<td>Classical $q_i, p_i = \frac{\partial L}{\partial \dot{q}_i}$</td>
<td>Moments $&lt;q_i&gt;, &lt;p_i&gt;$</td>
<td>Macroscopic Variables</td>
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<tr>
<td>Quantum state # $\frac{\partial L}{\partial \dot{q}_i}$</td>
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**State**

**State = Quantum State**

Well defined, unique

**Configuration = Macroscopic specification of system**

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<tr>
<td></td>
<td>$U = \sum_{i=1}^{n} U_i$</td>
<td>$T = \frac{2}{3k_B} \frac{1}{N} \sum_{i=1}^{n} U_i$</td>
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<tr>
<td></td>
<td>Not unique</td>
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Classical $q_i, p_i = \frac{\partial L}{\partial \dot{q}_i}$

Quantum state $\# f(q_i, p_i)$

$U = \sum_{i=1}^{n} U_i$

$T = \frac{2}{3k_B} \frac{1}{N} \sum_{i=1}^{n} U_i$
Quantum Mechanics in 1 transparency

Fundamental postulates
State of one particle is characterized by a wave function

Probability distribution \( \left| \psi(x) \right|^2 \) with \( \langle \psi | \psi \rangle \equiv \int \overline{\psi}(x) \psi(x) \, dx = 1 \)

Physical quantity \( \leftrightarrow \) hermitian operator.

In general, not fixed outcome! Expected value of \( O = \langle \psi | O | \psi \rangle \equiv \int \overline{\psi}(x) O \psi(x) \, dx \)

Eigenstate \( \equiv \) state with a fixed outcome e.g., \( O | \psi \rangle = o | \psi \rangle \) where \( o \) is a number.

\[ i \frac{\partial}{\partial t} = \frac{E}{\hbar} - i \frac{\partial}{\partial x_j} = \frac{p_j}{\hbar} \Leftrightarrow \text{"State" of well defined momentum} \]

\[ \varphi(x,t) = \left( \frac{1}{2\pi\hbar^2} \right)^{3/2} e^{-i \left( \frac{Et - \vec{p} \cdot \vec{x}}{\hbar} \right)} \]

\( E = \frac{p^2}{2M} \Rightarrow -\left( \frac{\hbar^2}{2M} \right) \nabla^2 \Psi = i\hbar \frac{\partial}{\partial t} \Psi \) \( \text{Eigenvalues of energy } \epsilon : -\left( \frac{\hbar^2}{2M} \right) \nabla^2 \Psi = \epsilon \Psi \)

\( \Rightarrow \text{A finite system has discrete eigenvalues} \)
Quantum States

Prototypes:

- Atomic levels

Spin s in general $2s+1$ states (exception photons $s=1$ but 2 states)

- Ideal gas of particles

Single particle in a box: orbital $\psi(x)$ (motion part of the wave function)

Cubic side $L$

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

$n_x, n_y, n_z$ integers $> 0$

$$\epsilon_{n_x, n_y, n_z} = \left(\frac{\hbar^2}{2M}\right)\left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)$$

Ideal ($\approx$ non interacting): orbitals not distorted by presence of $N$ particles.
**Fundamental Postulate**

Probabilistic description of state of a system

Probability of being in state i.

**Equilibrium = No net Flux => Stationary** No evolution of probability distribution with time

**Isolated = closed:**

No energy/particle exchange with outside

**Fundamental Postulate**

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

This fundamental postulate can be demonstrated in Quantum Mechanics

Probability of transition per unit time state \( r \rightarrow s \) = Prob of transition state \( s \rightarrow r \)

\[
\Gamma_{rs} = \Gamma_{sr}
\]
Consequences

Probability of a configuration (isolated, in equilibrium)

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

Entropy

**Definition**

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

For an isolated system in equilibrium: identical to Kittel \( \sigma = \log(g_t) \)
Counting States: Discrete States

Preliminaries

\[ N! = N(N-1)(N-2)\ldots 2.1 = \Gamma(N+1) \]

Stirling approximation

\[ \log N! \approx \frac{N \log N - N + \frac{1}{2} \log(2\pi N)}{N \to \infty} \]

Independent spins 1/2

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

\[ 2s = n_{up} - n_{down} \Rightarrow n_{up} = N/2 + s \quad n_{down} = N/2 - s \]

\[ g(s) = \frac{N!}{\left(\frac{N}{2} + s\right)! \left(\frac{N}{2} - s\right)!} \quad N \to \infty \quad 2^N \frac{1}{\sqrt{2\pi N/4}} \exp\left(-\frac{1}{2} \frac{s^2}{N/4}\right) \]

Particles (very important)

Phase space element for a single particle in 3 dimensions:

\[ d^3x \cdot d^3p \]

Theorem: the density of spatial states (orbitals) per unit phase space for a single particle in 3 dimensions is \( 1/h^3 \)

= density of quantum states for a spinless particle
Ideal Gas

Now consider N particles in weak interactions.

**Calculation of number of states as a function of U**

N particles
Weak interactions => # states =

\[ g = \prod_i \int \frac{d^3 x_i d^3 p_i}{h^3} \]

with the constraint that total energy is \( U \)

\[ \sum_i \sum_j \frac{p_{ij}^2}{2M} = U \]

where \( M \) is the mass.

**Space integral**

\[ \prod_i \int d^3 x_i = V^N \]

**Momentum integral:** we need to conserve energy

\[ \delta \left( \sqrt{\sum_i \sum_j \frac{p_{ij}^2}{2M}} - \sqrt{2MU} \right) \prod_{\text{part}} d^3 p_i \propto U^{3N-1} \]

for large \( N \)

\[ g \propto V^N U^{3N-2} \quad \sigma = \text{Const} + N \log V + 3/2N \log U \]

**Exact factor (Optional):** The surface of a 3N-1 sphere in 3N dimensions is

\[ r^{3N-1} \Omega_{3N} \]

where the solid angle factor is

\[ \Omega_{3N} = \frac{(2\pi)^{\frac{3N-1}{2}}}{2^2 (N-1)!} \left( \frac{m}{2} \right)! \left( \frac{m}{2} - 1 \right) \ldots \left( \frac{1}{2} \right) \]
Sackur Tetrode Formula

We are now in position to compute the entropy

\[ \sigma = \log g = \log \left[ \frac{V^{N-1/3} (2MU)^{3N-1}}{h^{3N-1}} \Omega_{3N}^{3/2} \right] \]

Only problem: violently disagrees with experiment!
Solution: In quantum mechanics, particles are indistinguishable
We have over-counted the number of particles by \( N! \) (Gibbs)

Sackur Tetrode

Dividing by \( N! \) and using the Stirling approximation, we get

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

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