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 # \( \frac{\partial L}{\partial \dot{q}_i} \)

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

Thermodynamics
Macroscopic Variables

State

State = Quantum State
Well defined, unique
Discrete ≠ “classical thermodynamics” where entropy was depending on resolution \( \Delta E \)

Configuration = Macroscopic specification of system

Macroscopic Variables
Extensive: \( U, S, F, H, V, N \)
Intensive: \( T, P, \mu \)

Not unique: depends of level of details needed
Variables+ constraints => not independent
Implicitly assumes at least local equilibrium => intensive variables are well defined

\[
U = \sum_{i=1}^{n} U_i \\
T = \frac{2}{3k_B} \frac{1}{N} \sum_{i=1}^{n} U_i
\]
Fundamental postulates
State of one particle is characterized by a wave function

Probability distribution \( |\psi(x)|^2 \) 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.

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

\( \rightarrow \) A finite system has discrete eigenvalues
Quantum States

Prototypes:

- Atomic levels
  - Have to take into account multiplicity if we consider degenerate states (i.e. have the same energy)

- Spin $s$ in general $2s+1$ states (exception photons $s=1$ but 2 states)
  - Spin $\frac{1}{2}$ $s=\pm\frac{1}{2}$
  - If magnetic field oriented along +/- direction, the energy $= -/+mB$ ($m=$magnetic moment)
  - Note: Idea of an isolated system of spins is somewhat strange <= transition between higher and lower energy states. Isolated = electromagnetic emission reabsorbed or reflected back

- Ideal gas of particles
  - Free particle propagating in space: orbital $\psi(x)$ (motion part of the wave function)
  - Single particle in a box: Cubic side $L$ cf. K&K p.72
    
    $$
    \Psi(x, y, z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)
    $$

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

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

    - Ideal ($\approx$ non interacting): orbitals not distorted by presence of $N$ particles. Wave function = product of single wave functions. Can bounce against each other provided interactions are short!
Fundamental Postulates

**Probabilistic description of state of a system**

Because of microscopic processes, the system experiences slight fluctuations: described by 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

volume constraint OK

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

Notes:

- Kittel does not specify "in equilibrium" does not matter in case where we are close to equilibrium
- "Accessible" e.g. Conservation of energy Some states may not be accessible within time scale of experiment
Remarks

Probabilistic description of state of a system

Two possible definitions:

- Observations of different identical systems at a given time "ensemble" of systems $j$
- Observations at different times, system wanders over its accessible states

**Ergodicity:** under very general conditions, we obtain identical results

$$\langle y \rangle_{\text{ensembles}} = \langle y \rangle_{\text{time}} = \lim_{T \to \infty} \frac{1}{T} \int_0^T y(t) dt$$

The fundamental postulate can be demonstrated in Quantum Mechanics

Related, as Boltzmann already knew, to the symmetry of transition probabilities

Probability of transition per unit time state $r \rightarrow$ state $s = \text{Prob of transition state } s \rightarrow \text{state } r$

$$\Gamma_{rs} = \Gamma_{sr}$$

Celebrated $H$ theorem (demonstration later in course)

valid if no persistence of quantum coherence (generally true)

Quantum mechanics is compatible with statistical mechanics!
**H theorem: an intuitive look**

Based on the fact that probability of transition per unit time from \( r \) to \( s \) is equal to probability of transition per unit time from \( s \) to \( r \)

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

Suppose I have initially \( N_r \) particles in \( r \) and \( N_s << N_r \) in \( r \), the number of particles going from \( r \) to \( s \) in time \( \Delta t \) is much bigger than from \( s \) to \( r \).

\[
N_r \Gamma_{rs} \Delta t >> N_s \Gamma_{sr} \Delta t
\]

Therefore \( N_r \) decreases and \( N_s \) increases, till they are in average equal. The probabilities of \( s \) and \( r \) are then equal!
**Consequences**

**Probability of a configuration** (isolated, in equilibrium)

If we call \( g \) the number of states for a given macroscopic specification of the configuration, and \( g_t \) the total number of states accessible to the system

\[
\text{Prob}(\text{configuration}) = \frac{g}{g_t}
\]

**Entropy**

**Definition**

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

\( H = \text{"Negentropy" = "Information" of Shannon} \)

\( \neq \) Kittel (ours is more general)

\[
\sigma = \log(g_t)
\]

For an isolated system in equilibrium: identical to Kittel

\[
\sum_s p_s = 1 + \text{equi probable } \Rightarrow p_s = \frac{1}{g_t}
\]

where \( g_t \) is the total number of accessible quantum states in the configuration

**Notes:**

- In classical thermodynamics, definition usually used

\[
S = k_B \sigma = \int \frac{dQ}{T} \quad \Leftrightarrow \quad \sigma = \int \frac{dQ}{k_B T} = \int \frac{dQ}{\tau} \quad \text{with } \tau = k_B T \quad k_B = 1.38 \cdot 10^{-23} \text{ J} / \text{K}
\]

where \( k_B \) is the Boltzmann constant

- Entropy requires the use of quantum mechanics: we will see that for an ideal gas

\[
S = \int_0^\tau \frac{dQ}{T} = k_B N \left[ \log \frac{n_Q}{n} + \frac{5}{2} \right] \quad \text{(monoatomic, spinless)}
\]

\[
n_Q = \left( \frac{M k_B T}{2 \pi \hbar^2} \right)^{\frac{3}{2}}
\]
Counting States: Discrete States

Preliminaries

Number of permutations between N objects = factorial

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

Stirling approximation

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

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

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

We could have instead chosen to label the configuration by the difference (proportional to total total spin): suppose N is even

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

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

Gaussian!
Counting States: Particles

Density of orbitals per unit phase space

Phase space element for a single particle in 3 dimensions: \( d^3x \cdot d^3p \)

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

**Proof:** Not in book!

Consider a particle in a box. Its spatial wave function is

\[
\Psi(x,y,z) = A \sin \left( \frac{n_x \pi x}{L} \right) \sin \left( \frac{n_y \pi y}{L} \right) \sin \left( \frac{n_z \pi z}{L} \right) \quad \text{with } n_x, n_y, n_z \text{ integers > 0}
\]

In the \( x \) direction, this corresponds to the superposition of 2 momenta 
\[
\frac{n_x \pi \hbar}{L} \quad \text{and} \quad -\frac{n_x \pi \hbar}{L}
\]

Let us start with \( n_x = 1 \). The \( x \) momentum span is by

\[
\Delta p_x = \frac{\pi \hbar}{L} - \frac{\pi \hbar}{L} = 2 \frac{\pi \hbar}{L}
\]

The \( x \) component of the phase space volume is therefore

\[
\Delta x \Delta p_x = L \times 2 \frac{\pi \hbar}{L} = \hbar
\]

In 3 dimensions the phase space volume occupied by the state \( n_x = 1, n_y = 1, n_z = 1 \) is \( h^3 \)

Increasing \( n_x \) by 1 will add one more state and increase the phase space volume by \( h^3 \) and so on. Therefore the number of states per unit phase space is \( \frac{1}{h^3} \)

This is a totally general and exact result: \( 1/h \) for each of the dimensions!
**Counting States: Particles**

**Proof à la Kittel**

Not explicitly in book but many such types of calculation throughout.

Consider again a particle in a cubic box, and compute number of states between $E$ and $E + dE = \text{number of integers } n_x, n_y, n_z$ such that

$$E \leq \left( \frac{\hbar^2}{2M} \right) \left( \frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) < E + dE$$

In the $n_x, n_y, n_z$ space, each state correspond to a volume of unity.

For $n_x, n_y, n_z$ large enough, the number of states is given by the volume of one quadrant of spherical shell of radius $L \sqrt{\frac{2M}{E}}$ and thickness $dn = \frac{L \sqrt{\frac{2M}{E}}}{2\pi\hbar} dE$.

The number of states is given by

$$\# \text{ of states} = \frac{1}{8} 4\pi n^2 dn = 2\pi \frac{L^3 (2M)^{3/2} \sqrt{E}}{8\pi^3 \hbar^3} dE$$

Continuous approximation

Volume of phase space element such that the energy is between $E$ and $E + dE$ is

$$L^3 4\pi p^2 dp \quad \text{with} \quad E = \frac{p^2}{2M} = \pi \frac{2L^3 (2M)^{3/2}}{8\pi^3 \hbar^3} \sqrt{E} dE$$

$$\Rightarrow \frac{\# \text{ States}}{\text{Phase space volume}} = \frac{1}{8\pi^3 \hbar^3} = \frac{1}{\hbar^3}$$

Calculation done once for all!
**Ideal Gas**

Now consider N particles in weak interactions

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

N particles
Weak interactions ⇒ # states =

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

Space integral

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

Momentum integral: we need to conserve energy

1 particle in 1 dimension: only 1 momentum state with right energy in 2 dimensions circumference of circle

\[
\sqrt{p_1^2 + p_2^2} = \sqrt{2MU} \quad \Rightarrow \quad \int \delta \left( \sqrt{p_1^2 + p_2^2} - \sqrt{2MU} \right) d^2 p_i = 2\pi \sqrt{2MU}
\]

in 3 dimensions area of 2-sphere

\[
\sqrt{p_1^2 + p_2^2 + p_3^2} = \sqrt{2MU} \quad \Rightarrow \quad \int \delta \left( \sqrt{p_1^2 + p_2^2 + p_3^2} - \sqrt{2MU} \right) d^3 p_i = 4\pi \left( \sqrt{2MU} \right)^2
\]

N particles with 3 momentum components area of (3N-1)-sphere \( \leq 3 \times N \) dimensions in total

\[
\delta \left( \sqrt{\sum_{part} \sum_{i=1}^{3} p_{ij}^2} - \sqrt{2MU} \right) \prod_{part} d^3 p_i \propto U^{3N-1}/2
\]

for large N \( g \propto V^N U^{3N/2} \)

\[ \sigma = \text{Const} + N \log V + 3/2N \log U \]
Ideal Gas

2 technical notes (optional)

1) Exact formula: It can be shown that the surface area of sphere of radius \( r \) is:

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

where the solid angle factor is

\[ \Omega_{3N} = \frac{(2\pi)^{3N-1}}{2} \frac{2}{3(N-1)!} \]

with

\[ \left( \frac{m}{2} \right)! = \left( \frac{m}{2} \right)\left( \frac{m}{2} - 1 \right) \ldots \left( \frac{1}{2} \right) \]

2) If you follow carefully the dimensions, we need a factor \( h/L \)

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

⇒ We can compute (painfully) the number of states and then get probabilities: “Microcanonical” methods
Sackur Tetrode Formula

We are now in position to compute the entropy

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

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

We then compute

$$g = \frac{1}{N!} \left( \frac{h}{L} \right) \delta \left( p - \sqrt{2MU} \right) \prod_i \frac{d^3x_i d^3p_i}{h^3} = \frac{V^{N-1/3} \left( 2MU \right)^{3N-1}}{N! h^{3N-1}} \Omega_{3N}$$

For large $N$ we can use the Stirling approximation both for integer and half integer

$$\log \left( \frac{m}{2} \right) \approx \frac{m}{2} \log \left( \frac{m}{2} \right) - \frac{m}{2}$$

and we get

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

Writing $n = \frac{N}{V}, n_Q = \left( \frac{2\pi M 2U}{h^2 3N} \right)^{3/2}$ we get

$$\frac{\sigma}{k_B} = N \left[ \log \left( \frac{n_Q}{n} \right) + \frac{5}{2} \right]$$