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 # \( f(q_i, p_i) \)

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 on level of details needed
Variables + constraints \( \Rightarrow \) not independent

\[
\sum_{i=1}^{n} U_i = \frac{2}{3k_B N} \sum_{i=1}^{n} U_i
\]

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

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

Probability distribution $= \psi(x)^2$ with $\langle \psi | \psi \rangle \equiv \int \bar{\psi}(x)\psi(x)dx = 1$

Physical quantity $\leftrightarrow$ hermitian operator.

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

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

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

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

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

$\Rightarrow$ A finite system has discrete eigenvalues
Quantum States

Prototypes:

- **n=2**
  - Atomic levels
    - Have to take into account multiplicity if we consider degenerate states (i.e. have the same energy)

- **n=1**
  - Spin $s$ in general $2s+1$ states (exception photons $s=1$ but 2 states)
    - Spin 1/2 $s=\pm 1/2$
    - 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 Postulate**

**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

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

\[ <y>_{\text{ensembles}} = <y>_{\text{time}} = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} y(t) dt \]

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 \( r \rightarrow s \) = Prob of transition state \( s \rightarrow r \)

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

Celebrated H theorem (demonstration in slide 8 Optional)
valid if no persistence of quantum coherence (generally true)
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 we have initially \( N_r \) particles in \( r \) and \( N_s \ll N_r \) in \( r \), the number of particles going from \( r \) to \( s \) in time \( \Delta t \) is much bigger than from \( s \) to \( r \).

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

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

**Modern Version:** see Reif A12

Consider an isolated system, and quantum states $s$. The probabilities of occupancy $p_s$ are such that $\sum p_s = 1$

Quantum mechanics: Probabilities per unit time of transition between states $r$ and $s$ are symmetric

$$\Gamma_{rs} = \Gamma_{sr} \propto \langle s | W | r \rangle^2$$

Starting from the detailed balance argument

$$\frac{dp_r}{dt} = \sum_s p_s \Gamma_{sr} - \sum_s p_r \Gamma_{rs} = \sum_s \Gamma_{sr} (p_s - p_r)$$

Consider now

$$H \equiv \sum_s p_s \log(p_s) = -\sigma$$

We have

$$\frac{dH}{dt} = \sum_r \frac{dp_r}{dt} (\log(p_r) + 1) = \sum_r \sum_s \Gamma_{sr} (p_s - p_r) (\log(p_r) + 1)$$

or equally well

$$\frac{dH}{dt} = \sum_s \sum_r \Gamma_{rs} (p_r - p_s) (\log(p_s) + 1) = -\sum_r \sum_s \Gamma_{sr} (p_s - p_r) (\log(p_s) + 1)$$

Add the two quantities

$$\frac{dH}{dt} = -\frac{1}{2} \sum_r \sum_s \Gamma_{sr} (p_s - p_r) (\log(p_s) - \log(p_r))$$

If $p_s > p_r$, $\log(p_r) > \log(p_s)$ and vice versa $\Gamma_{sr} > 0 \implies \frac{dH}{dt} \leq 0$ $\frac{dS}{dt} \geq 0$

Equality holds if $p_s = p_r$ : $\implies$ at equilibrium quantum states have equal probabilities!
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

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

Entropy

Definition

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

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

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

For an isolated system in equilibrium: identical to Kittel

\[
\sum_s p_s = 1 \quad \text{equiprobable} \quad \Rightarrow \quad p_s = \frac{1}{g_t}
\]

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

Notes:

\( \cdot \) In classical thermodynamics, definition usually used

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

where \( k_B \) is the Boltzmann constant

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

\[
S = \int_0^\tau \frac{dQ}{T} = k_B N \left[ \log \frac{n_Q}{n} + \frac{5}{2} \right] \quad (\text{monoatomic, spinless}) \quad n_Q = \left( \frac{M k_B T}{2 \pi \hbar^2} \right)^{\frac{3}{2}}
\]
Counting States: Discrete States

Preliminaries

Number of permutations between N objects = factorial

\[ N! = N(N-1)(N-2)\ldots2.1 = \Gamma(N+1) \]

Stirling approximation

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

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

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

We do not care about order!

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

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

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

Gaussian!
Counting States: Particles

Density of spatial states per unit phase space

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 \( \frac{1}{h^3} \) = density of quantum states for a spinless particle

Proof: Not in book!
Consider a particle in a box. Its spatial wave function is
\[
\Psi(x,y,z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)
\]
with \( n_x, n_y, n_z \) integers > 0

\[
\sin\left(\frac{n_x \pi x}{L}\right) = e^{\frac{n_x \pi x}{L}} - e^{-\frac{n_x \pi x}{L}}
\]

Applying \( \tilde{p} = -i\hbar \nabla \) one sees this is the superposition of 2 momenta

Consider the x direction,
\[
\Delta p_x = \frac{\pi \hbar}{L} - \frac{-\pi \hbar}{L} = 2\frac{\pi \hbar}{L}
\]

Let us start with \( n_x = 1 \). The x momentum span is by
\[
\Delta x \Delta p_x = L \times 2 \frac{\pi \hbar}{L} = h
\]

\( n_x = 1, n_y = 1, n_z = 1 \) is \( h^3 \)

The x component of the phase space volume is therefore

In 3 dimensions the phase space volume occupied by the state
\[
\frac{1}{h^3}
\]
Counting States: Particles

Proof à la Kittel

Not explicitly in book but many such types of calculation through out

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

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

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

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{L \sqrt{2ME}}{\pi \hbar}$$

and thickness $dn = \frac{L \sqrt{2M}}{2\pi \hbar} dE$

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

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

$$L^3 4\pi p^2 \, dp \quad \text{with} \quad E = \frac{p^2}{2M} \quad \text{is} \quad \pi 2L^3 (2M)^{3/2} \sqrt{EdE}$$

$$\Rightarrow \quad \frac{\# \text{ States}}{\text{Phase space volume}} = \frac{1}{8\pi^3 \hbar^3} = \frac{1}{h^3}$$
Now consider N particles in weak interactions

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

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

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

\[ \sum_{\text{part i}} \sum_{j=1}^{3N} \frac{p_{ij}^2}{2M} = U \]

where \( M \) is the mass

**Space integral**

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

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

1 particle in 1 dimension: only 1 momentum state with right energy

in 2 dimensions: circumference of circle

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

in 3 dimensions: area of 2-sphere

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

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

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

for large \( N \)

\[ g \propto V^N U^2 \sigma = k(N) + N \log V + 3 / 2N \log U \]

function of \( N \) (see page 15)
**Ideal Gas**

2 technical notes (optional)

1) Exact formula: It can be shown that the surface area of 3N-1 sphere of radius $r$ is:

$$r^{3N-1} \Omega_{3N}$$

where the solid angle factor is

$$\Omega_{3N} = \frac{2(\pi)^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} = \frac{2(\pi)^{3N/2}}{\left(\frac{3}{2}N - 1\right)!}$$

with

$$\left(\frac{m}{2}\right)! = \left(\frac{m}{2}\right)\left(\frac{m}{2} - 1\right)\ldots\left(\frac{m}{2} - \frac{m}{2}\right)\pi^{1/2} \text{ m odd}$$

$$\left(\frac{m}{2}\right)! = \left(\frac{m}{2}\right)\left(\frac{m}{2} - 1\right)\ldots\left(\frac{1}{2}\right)\pi^{1/2} \text{ m even}$$

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

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

$\delta$ functions have a dimension! \[\int \delta(x) dx = \int \delta[f(x)] \left| \frac{df}{dx} \right| dx = 1\]

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

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

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**

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

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

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

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

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