

Statistical Mechanics

(The Microscopic Theory of Thermodynamics)

VIII. Boltzmann's Formula $S = k \ln W$ of Equilibrium Statistical Mechanics

- $S = k \ln W$ is ALL of Statistical Mechanics
- Conditions that it is valid
- Meaning of the symbols/quantities
- What does it mean about the underlying physics?
- Ensemble theory (theories)
- Applications
- Bases for developing other theories in Stat. Mech.

A. $S = k \ln W$ first encounter

- No proof. It works because it works!
- Statistical Mechanics is the Microscopic Theory of Thermodynamics

Meaning: Starting with
Atoms/Molecules in System

Don't need the
notion of
atoms/molecules

- We do Equilibrium Statistical Mechanics

↑
We wait until system has reached equilibrium
and work out properties from
microscopic physics

described as a few state
variables

(U, V, N) Macrostate ("a" macrostate)

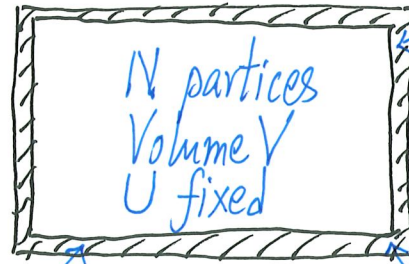
The condition is therefore

Technical Terms:

- No exchange of energy
- No exchange of volume
- No exchange of particles with outside

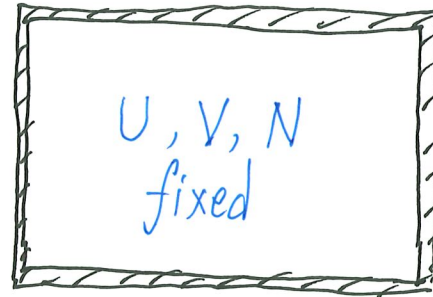
outside the system

Isolated System



walls have
no pores
(no exchange of particles
with outside)

insulating walls
(no heat in/out system)
thus U fixed
rigid walls
(no Work done on/by system)
(thus V fixed)



Thermodynamically, this is ONE equilibrium state
(one point on indicator diagram), or ONE Macrostate

Boltzmann (~1875) says $S = k \ln W$

Its long form is

$$S(U, V, N) = k \ln W(U, V, N) \quad (1)$$

LHS

Remember this! This is ALL of Stat. Mech! Done!

$S(U, V, N)$
 ↑ entropy ↑ internal energy ← number of particles (atoms/molecules)
 Volume of system

LHS is Macroscopic Physics
 Thermodynamics

The thermodynamic equilibrium state is defined by U, V, N for Boltzmann's formula to work

(2)

(U, V, N) is called a Macrostate

$S(U, V, N)$ = Entropy of the macrostate
specified by (U, V, N)

Switch to Stat. Mech. Notations

Use "E" for "U" ($\because$ E is often used in microscopic physics ^{e.g. quantum mechanics}
for energy)

$\therefore (E, V, N)$ specifies a macrostate

$S(E, V, N)$ = Entropy of macrostate (E, V, N)

(3)

Thermodynamics $dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$ (central equation)

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V, N} ; \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E, N} ; \quad \frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E, V}$$

(4)

$$S(E, V, N) = k \ln W(E, V, N) \quad (1)$$

Microscopic physics

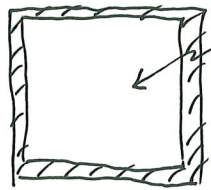
(5) $W(E, V, N) =$ Number of Microstates (microscopic states) that are compatible with the given macrostate specified by (E, V, N)
(also called accessible microstates for a given macrostate)

Key Quantity in Statistical Mechanics

$$k = \text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ J K}^{-1} \quad (6)$$

B. Basic Ideas on what microstates are through a simple example

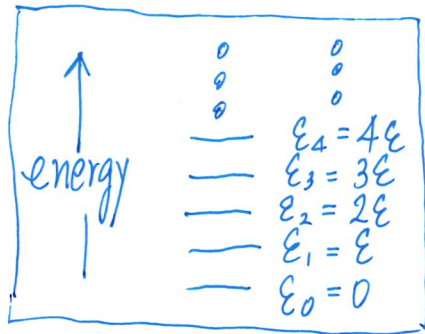
Pay attention: Key ideas here



3 particles (let's say they are distinguishable (A, B, C) for simplicity)

OR (red, green, blue)

For each particle, the allowed single-particle states are found to be (again for simplicity here)



← Meaning: a particle can be in a single-particle state of energy of "0", "1ε", "2ε", "3ε", "4ε", "5ε", and so on (unbounded spectrum)

The system of 3 particles has, say, a total energy of $E = 3ε$.
Macrostate: $E = 3ε, N = 3$

Question: What are the microstates compatible with the given macrostate?

Aside (Can skip and move on to next page)

- Consideration of "single-particle states" here implicitly means that the interaction between the particles in the 3-particle system is weak[†]. [Quantum Mechanically, it means reduction to 1-particle Schrödinger Equation, solving for the single-particle states/energies, and filling particles into the states.]
- Real systems, $N \sim 10^{24}$
- Where is V ? [Think quantum mechanically, V is in the solving of Schrödinger Equation for single-particle states through boundary conditions.]

[†] But $S = k \ln W$ and thus statistical mechanics is applicable to interacting and weakly interacting systems alike.

General Microstates (not necessarily compatible with macrostate)

particle A in which energy level
particle B in which energy level
particle C in which energy level

← Specifying the information
amounts to specifying
one general microstate

e.g.
$$\begin{matrix} A \\ B \\ C \end{matrix} \begin{pmatrix} 8\epsilon \\ 3\epsilon \\ 10\epsilon \end{pmatrix}$$
 is A Microstate with total energy 21ϵ

e.g.
$$\begin{matrix} A \\ B \\ C \end{matrix} \begin{pmatrix} 3\epsilon \\ 0 \\ 0 \end{pmatrix}$$
 is A Microstate with total energy 3ϵ

compatible with $(E=3\epsilon, N=3)$

Microstates Compatible with Given Macrostate

Let's list all the accessible microstates

Particles											
A	ϵ	3ϵ	0	0	2ϵ	2ϵ	ϵ	ϵ	0	0	
B	ϵ	0	3ϵ	0	ϵ	0	2ϵ	0	2ϵ	ϵ	
C	ϵ	0	0	3ϵ	0	ϵ	0	2ϵ	ϵ	2ϵ	
	I	II			III						
	(1)	(3)			(6 microstates)						

There are 10 microstates compatible with $(E=3\epsilon, N=3)$ macrostate
 $\therefore W(E=3\epsilon, N=3) = 10$

Ex: Try $(E=8\epsilon, N=8)$, same E/N , and find W . (Will see W increases rapidly as system is bigger)
 How about $N \sim 10^{23}$? W is a huge number! ($\ln W$ is better behaved)

Aside:

What is the "10" in $W=10$ for $(E=3\epsilon, N=3)$?

- 3 units of energy (each unit is the same as the other units) to be divided into 3 groups (A, B, C)

- $\underbrace{3 \text{ balls} + 2 \text{ sticks}}_{5 \text{ objects}} \Rightarrow 3 \text{ groups}$

e.g. $\underbrace{00}_{A(2\epsilon)} \mid \underbrace{10}_{C(1\epsilon)}$
 $A(2\epsilon) \ B(0) \ C(1\epsilon)$

$$10 = \frac{5!}{3! \ 2!}$$

arranging 5 objects in order

3 units are indistinguishable [3! corrects for overcounting in 5!]
 2 sticks are indistinguishable [2! corrects for overcounting in 5!]

See "Essential Math Skills" for more on counting

Ex: Try also $N=3$, $E=6\epsilon$ (Doubling E/N), find W .

[Will see W increases rapidly with E , for fixed N]

The Points are (i) $W(E, V, N)$ is general a big number for thermodynamic systems (referring to one macrostate)

(ii) $W(E, V, N)$ is very sensitive to increasing E

(iii) $W(E, V, N)$ is a number (no units)

(iv) it is $W(E, V, N)$ that goes into $S(E, V, N) = k \ln W(E, V, N)$

(v) $W(E, V, N)$ is there, doesn't matter whether the N particles are interacting, weakly interacting, or non-interacting. The problem is rather finding $W(E, V, N)$ for different situations.

We need to find $W(E, V, N)$

find $W(E, V, N)$ as a FUNCTION of E, V, N

because we need to take derivatives of $\ln W(E, V, N)$

C. Postulate of equal a priori probabilities for an isolated system in equilibrium

▪ Sounded complicated? No! It is an illustration of the Power of Ignorance.

▪ Context: Isolated System + In Equilibrium

• Thermodynamics $\rightarrow$ macrostate (E, V, N)

• One macrostate $\rightarrow W(E, V, N)$ microstates (huge number)

Question: Will a system bias some microstates? That is to say, if we inspect system (at some time), which microstate will we find?

Ans: Don't know! See no reason for a microstate to appear with a higher chance than other microstates.

A fundamental postulate (no proof[†]) of Statistical Mechanics

For an Isolated System in Equilibrium, all accessible microstates are equally probable (7)

macroscopic (thermodynamics)
[a macrostate]

microscopic
[$W(E, V, N)$ microstates]

postulate

Postulate says

Probability of system being in one of accessible states = $\frac{1}{W}$ (8)

what equally probable means

[†] Its validity is justified by its success (results followed from it). One may use dynamical equation to follow the time evolution of a system of N particles (QM or Classical Mechanics). The postulate is related to the system spending equal amount of time in every accessible microstates in a time window. This is related to the ergodic behavior (遍历) of dynamical systems, for which a proof for a general N -particle system (any Hamiltonian) is extremely hard. We need NOT worry about it in Equilibrium Stat. Mech.

Implications

- Over a (microscopic) time window, the system would have visited all accessible microstates an equal number of times
- Accessible microstates: $\#1, \#2^+, \dots, \#W$ (W of them)
- Some property[†] A (Value): $A_1, A_2, \dots, A_W$

The Postulate is then an Averaging Postulate

- tells us how to do averages
- how to turn time average into Ensemble Average
ensemble theory

[†] For an accessible microstate, it has a particular N -particle wavefunction $\Psi(\vec{r}_1, \dots, \vec{r}_N)$ in QM thinking, or a set of coordinates and momenta $\{\vec{r}_1, \dots, \vec{r}_N; \vec{p}_1, \dots, \vec{p}_N\}$ in classical mechanics. So, a quantity A can be evaluated for the given microstate either QM or CM (ly).

D. Ideas on Time Average and Ensemble Average[†]

Physical Picture behind the "all accessible microstates are equally probable" postulate

Phase space of N-particle system (I^2 -space)

e.g. N particles (interacting) (actually components sum up)

$$H_N = H(\underbrace{\vec{p}_1, \dots, \vec{p}_N}_{3N}, \underbrace{\vec{r}_1, \dots, \vec{r}_N}_{3N}) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} U(\vec{r}_i - \vec{r}_j)$$

Hamiltonian (a classical mechanics concept)

Need a phase space of $6N$ Dimensions (called I^2 -space)

One point in I^2 -space specifies $\{\vec{p}_i, \vec{r}_i\}$ is a microstate, a quantity (e.g. H , or A) can be evaluated.

[†] This section is formal. It needs some degree of maturity in physics. Practically, we don't need the theoretical ideas here for using Stat. Mech. The discussion here is uselessly useful, as it carries over to other ensemble theory.

In an isolated system (our context), an energy E is set (technically a constraint).

$$\therefore \overset{\text{a constant}}{\uparrow} E = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} U(\vec{r}_i - \vec{r}_j)$$

restricting microstates with
 $\{\vec{p}_i, \vec{r}_i\}$'s giving that E

[recall: $U(\vec{r}_i - \vec{r}_j)$ corresponds to conservative forces in system, then conservation of mechanical energy follows]

many of them: $W(E, V, N)$ of them!

Geometrically, once E is set, it defines a $(6N-1)$ -dimensional constant energy "surface", the system can only evolve in time on this $(6N-1)$ -dim surface

(9)

a restricted part of phase space is accessible to system once E is imposed
accessible microstates reside here

$$\therefore W(E, V, N) \propto \text{"Area" of } (6N-1)\text{-dim Constant-energy surface} \\ \text{[off by a constant to make sure } W \text{ is a number]} \quad (10)$$

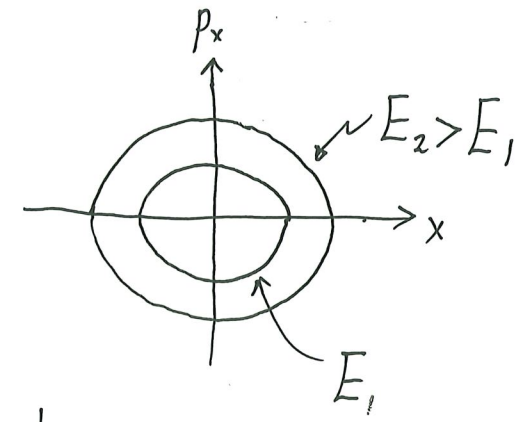
This is a way to visualize what $W(E, V, N)$ is about in an Interacting N -particle system

Aside: 1D harmonic oscillator

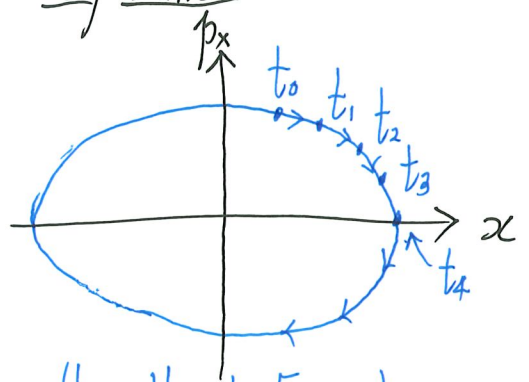
Phase space is 2D (called μ -space for 1 particle)
 (p_x, x)

$$H = \frac{p^2}{2m} + \frac{1}{2}mx^2 \quad \text{[don't know]}$$

Imposing a given E , $E = \frac{p^2}{2m} + \frac{1}{2}mx^2$
 an ellipse



Dynamics



Hamilton's Equations govern how x, p_x evolve

- Constant-energy surface in phase space (2D) is a curve (1D)
- $E_2 > E_1$, constant- E_2 surface > constant- E_1 surface
 more microstates
 $\text{[wavy line]} \leftarrow$ higher energy $\Rightarrow$ bigger range of x and p_x

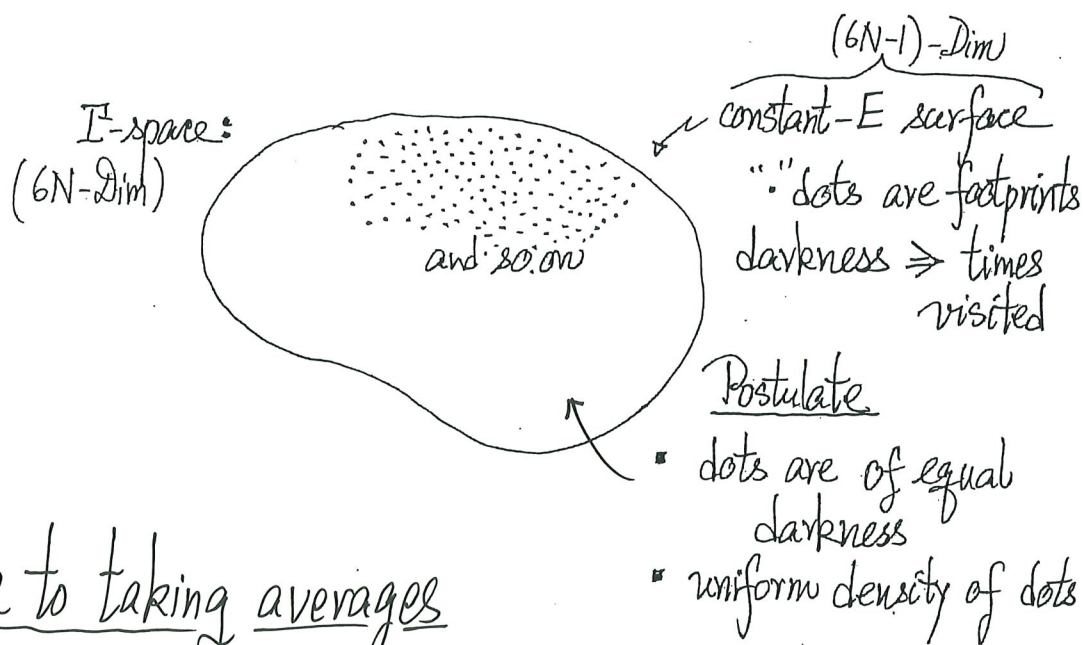
Behind the Postulate of "Equally Probable" is ...



system evolves in time [e.g. Hamilton's Eqs.] and go from one point to another
 a microstate another microstate

If we wait long enough for system to approach equilibrium, system will visit all points on the constant- E surface EVENLY

A picture : System leaves a footprint (stamp) at states on constant- E surface that it visits



Picture behind Postulate

Uniform darkness
Uniform density of stamps
on constant-E surface
at equilibrium

Back to taking averages

- Practically, time of measurement in thermodynamic exp'ts
many collisions[†] during that time [system visits accessible microstates many times]

Time Average: Follow one system in time and take time average

$$\langle A \rangle_{\text{time}} = \frac{1}{T} \int_0^T A(t) dt$$

a time window of duration T

value of property A changes as system spends time at different places (states) on constant-E surface

[†] In metals, $\sim 10^{14}$ collisions per second for an electron

Possible to replace time average by an Ensemble average

Ensemble : A collection (many, infinitely many) of suitably chosen copies of a system so that we can replace a time average following one system in time by an average over the ensemble (copies) of systems (no time now, or at one time) for the conditions under consideration. (11)

General idea of ensemble theories [microcanonical, canonical, grand canonical ensembles]

Key point is to choose the members (copies) of an ensemble suitably according to the macroscopic conditions

↳ (E, V, N) [present context]

(T, V, N) (next ensemble theory, canonical ensemble)

Back to our context : (E, V, N) (isolated system)

all accessible microstates are equally probable

A minimal selection of members is:

1 copy of each of the W microstates (all with (E, V, N))

or a huge number N members with

- $N \cdot \frac{1}{W}$ of them in microstate #1
- $N \cdot \frac{1}{W}$ of them in microstate #2
- $\vdots$
- $N \cdot \frac{1}{W}$ of them in microstate # W

average over members of ensemble gives result same as in time average following one system

This forms a Microcanonical Ensemble that reflects the "equally probable" postulate for thermodynamic system in equilibrium given (E, V, N) [isolated system]

Accessible Microstates: $\#1, \#2, \dots, \#W$

Property A (value) : $A_1, A_2, \dots, A_W$

For the chosen Ensemble, the ensemble average of A is:

$$\langle A \rangle_{\text{ensemble}} = \frac{1}{\mathcal{N}} \sum_{i=1}^W \left(\mathcal{N} \cdot \frac{1}{W} \right) A_i = \sum_{i=1}^W \underbrace{\frac{1}{W}}_{\text{prob. of system in microstate } i} A_i$$

(thus fraction of time spent in microstate i over a time window)
 ↙ equally probable

- This is the idea behind microcanonical ensemble theory (not too useful for this theory)
- Computationally, for (E, V, N) given, should sample the accessible microstates evenly
 - ↳ this is Microcanonical Ensemble
 - [canonical ensemble, need importance sampling]

E. What is $W(E, V, N)$ Quantum Mechanically?

N-interacting particles in Volume V $\nearrow \hat{H}_N = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} U(\vec{r}_i - \vec{r}_j)$

Hamiltonian Operator

Schrödinger Equation⁺

$$\hat{H}_N \underbrace{\Psi(\vec{r}_1, \dots, \vec{r}_N)}_{\text{N-particle state (energy eigenstate of } \hat{H}_N)} = E \underbrace{\Psi(\vec{r}_1, \dots, \vec{r}_N)}_{\text{allowed energy (energy eigenvalue) of N-particle system}} \quad (12)$$

To solve for MANY pairs of $\Psi_i(\vec{r}_1, \dots, \vec{r}_N) \leftrightarrow E_i(N)$

emphasizes it is N-particle system

labelling the eigenstate-eigenvalue pair

⁺ N-particle interacting QM problems are hard to solve. This is what many-body physics is about. We know the governing eq. We assume that some experts can show it for us to do Stat. Mech.

- $W(E, V, N)$ asks for the number of energy eigenstates of the same energy E

∴ $W(E, V, N)$ is the degeneracy at energy E (of the QM problem) (13)

Degeneracy -

$$\begin{array}{ccccccc} \bar{\Psi}_1 & \bar{\Psi}_2 & \dots & \bar{\Psi}_i & \bar{\Psi}_j & \dots & (\text{infinitely many solutions from } \hat{H}_N \bar{\Psi} = E \bar{\Psi}) \\ \updownarrow & \updownarrow & \dots & \updownarrow & \updownarrow & \dots & \\ E_1 & E_2 & \dots & E_i & E_j & \dots \end{array}$$

Sometimes $E_i = E_j = E_k = \dots$ (but $\bar{\Psi}_i \neq \bar{\Psi}_j \neq \bar{\Psi}_k \neq \dots$)

of same energy but different states
is the Degeneracy

Remark

When solving QM $\hat{H}_N \bar{\Psi} = E \bar{\Psi}$, we already need to consider the nature of the N particles (fermions or bosons) because the legal form of $\bar{\Psi}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ will be different as fermions (bosons) require anti-symmetric (symmetric) property w.r.t. interchanging two identical particles. This will affect the degeneracy $W(E, V, N)$ at an energy E .

F. Boltzmann's Formula - A second look

Boltzmann gave a statistical definition of the Entropy

$$S(E, V, N) = k \ln W(E, V, N) \quad (1)$$

↗
bridging microscopic and macroscopic physics

Recipe

- Given E (and V, N), calculate $W(E, V, N)$ (or count, for non-interacting particles)
- Obtain $S(E, V, N)$
- Then obtain $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V, N}$; $\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E, N}$; $\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E, V}$ (4)
- Explore how the state variables are related (equation of state)
- Use thermodynamic relations to get other quantities, $H, F, G, \dots$
- Done! This is the Microcanonical Ensemble Theory of Statistical Mechanics

Boltzmann's Tombstone in Central Cemetery Vienna



Boltzmann killed himself in 1906

The formula $S = k \ln W$ is a breakthrough in science/physics as Newton's law, Einstein's relativity, Maxwell's Equations, and Schrödinger's Equation.