

Chapter 6: Classical Statistical Mechanics

11

6.1 The postulate of classical statistical mechanics

Why start w/ classical statistical mechanics?

Isn't quantum "the law"?

CSM

- CSM is more intuitive
- CSM is, in general, easier
- Many systems can be described by CSM

Statistical mechanics (classical or quantum):
properties of matter in equilibrium

↳ doesn't say how equilibrium is approached

↳ doesn't determine if system can ever be found in equilibrium

Classical system: $N \approx 10^{23}$ (say, molecules)

$$N \rightarrow \infty \quad \& \quad V \rightarrow \infty$$

$$\frac{V}{N} = v \rightarrow \text{given fixed number}$$

$$\frac{N}{V} = \text{density} \rightarrow \text{fixed}$$

We will be considering isolated system
(in the sense that energy is a constant of motion)

↳ note: this is a big idealization
(in most cases)

What do we know from classical mechanics?

System is completely and uniquely defined by
 $3N \cdot 2$ coordinates:

↑
assuming 3
spatial dimensions

$\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N$: canonical coordinates

$\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N$: canonical momenta

Dynamics is governed by Hamiltonian

$$\mathcal{H}(\vec{p}, \vec{q}) \quad \leadsto \quad \vec{p} = (\vec{p}_1, \dots, \vec{p}_N) \ \& \ \vec{q} = (\vec{q}_1, \dots, \vec{q}_N)$$

$$\text{EoM} : \frac{\partial \mathcal{H}(\vec{p}, \vec{q})}{\partial p_i} = \dot{q}_i$$

$$\frac{\partial \mathcal{H}(\vec{p}, \vec{q})}{\partial q_i} = -\dot{p}_i$$

$6N$ -dimensional phase space is denoted by
 $\vec{T} = (\vec{p}, \vec{q})$

book refers to phase
 space as \vec{T} space

Each point in \vec{T} is a state of the system.

Each state of the system is represented by \vec{T} .

The locus of all points in \vec{T} space satisfying
 the condition

$$\mathcal{H}(\vec{p}, \vec{q}) = E$$

defines a surface, called energy surface of energy.

Let the state of the system evolve in time
 \rightarrow path in \vec{T} stays on energy surface
 since the energy is conserved as per
 our ~~assumption~~ assumption.

Keeping track of $6 \cdot 10^{23}$ d-o-f is too much!

Need to do s.th. different...

Let's only require that the system has
 N particles

volume V

energy betw. E and $E + \Delta E$

note: in general, an infinite number of states satisfies these conditions

We consider an isolated system w/ macro-
variables E, V, N

(microcanonical ensemble)

Think of infinite number of copies of systems:
Any one of them can be the one we are
interested in

\leadsto gibbsian ensemble

Represented by a distribution of points in \vec{r} space

density function $\rho(\vec{p}, \vec{q}, t)$

We want:

$\rho(\vec{p}, \vec{q}, t) d^{3N}p d^{3N}q = \#$ of representative points
contained in volume
 $d^{3N}p d^{3N}q$ located at
 (\vec{p}, \vec{q}) in \vec{r} -space at
instant t

According to Liouville's theorem:

$$\frac{d\rho}{dt} = 0 \Rightarrow$$

$$\sum_{i=1}^N \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) + \frac{\partial \rho}{\partial t} = 0$$

$$\text{or } [\rho, \mathcal{H}] + \frac{\partial \rho}{\partial t} = 0$$

↑
this follows by using
Hamilton's eqs. of motion

SISB:

$[,]$: Poisson bracket

Geometrically, the distribution of points in \vec{P} -space moves like an incompressible fluid.

recall: phase space
volume is conserved

~~Geometrically, the distribution of points in \vec{P} -space moves like an incompressible fluid.~~

Let $\frac{\partial \rho}{\partial t} = 0$, i.e., let's assume that we do not have an explicit dependence on time.

→ this is a reasonable thing to do since we are looking at equilibrium situations

If $\frac{\partial \rho}{\partial t} = 0$, then the ensemble described by the density fct. ρ is the same for all times.

Classical statistical mechanics is founded on
"Postulate of equal a priori probability":

When a macroscopic system is in thermodynamic equilibrium, its state is equally likely to be any state satisfying the macroscopic conditions of the system.

In thermodynamic equilibrium, the system under consideration is a member of the microcanonical ensemble w/ density fct.

$$f(\vec{p}, \vec{q}) = \begin{cases} \text{const} & \text{if } E < \mathcal{H}(\vec{p}, \vec{q}) < E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

members have the same N and the same V

Say, we want to measure $f(\vec{p}, \vec{q})$

could be energy, momentum, ...

Observed value should be obtained by averaging f over microcanonical ensemble

Option 1: ensemble average

$$\langle f \rangle = \frac{\int f(\vec{p}, \vec{q}) \rho(\vec{p}, \vec{q}) d^{3N}p d^{3N}q}{\int \rho(\vec{p}, \vec{q}) d^{3N}p d^{3N}q}$$

Option 2: most probable value of $f(\vec{p}, \vec{q})$ is the value of f that is taken by the largest number of systems in the ensemble

ensemble average \approx most probable value if

$$\frac{\langle f^2 \rangle - \langle f \rangle^2}{\langle f \rangle^2} \ll 1$$

mean square fluctuations

If ensemble average \neq most probable value, then there is no unique way to determine how the observed value should be calculated.

Typically: mean square fluctuations $\sim \frac{1}{N} \rightarrow 0$ for $N \rightarrow \infty$

6.2 Microcanonical ensemble

Every system has N molecules

volume V

energy betw. E and $E + \Delta E$



What do we know about thermodynamic entropy?

(a) S is an extensive quantity:

If a system is composed of two sufficiently large subsystems w/ entropies S_A and S_B , then the entropy of the total system is $S_A + S_B$.

(b) S satisfies the properties as required by 2nd law of thermodynamics:

the equilibrium state of the system is the state that maximizes the entropy within the constraints of the system and the conservation

Let's work on establishing the connection:

→ this will be a lot of work... we will be done on page 23

Need to define:

$$T(E) = \int_{E < \mathcal{H} < E + \Delta E} d^{3N} p d^{3N} q$$

def.

volume in phase space / \vec{p} -space
occupied by the microcanonical ensemble

phase space volume is measured consistent w/ our macro-state w/ variables E, N, V

Note: $T(E) = T(\underbrace{E, N, V, \Delta E}_{\text{suppressed dependencies}})$

(ΔE will be going to zero eventually)

$$\Sigma(E) = \int_{\mathcal{H} < E} d^{3N} p d^{3N} q$$

volume in phase space enclosed by the energy surface of energy

Can we express $\Gamma(E)$ in terms of $\Sigma(E)$? ||

Yes:

$$\Gamma(E) = \Sigma(E + \Delta E) - \Sigma(E)$$

Let's assume $\Delta E \ll E$:

In this case, we can Taylor expand

$$\Sigma(E + \Delta E) \approx \Sigma(E) + \frac{\partial \Sigma(E)}{\partial E} \Delta E + \dots$$

define: $\left\{ \frac{\partial \Sigma(E)}{\partial E} \stackrel{\text{def.}}{=} \omega(E) \right\}$

density of states of the system at energy E

$$\Rightarrow \Gamma(E) \approx \omega(E) \Delta E$$

Recall: our goal is to connect "thermodynamics" and "microcanonical ensemble" via "entropy"

We know properties (a) and (b), page 9,

about thermodynamic entropy.

This means that we need to define entropy within microcanonical ensemble.

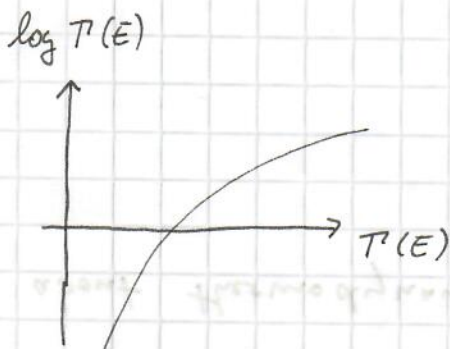
Once we have this, we can show that the entropy within microcanonical ensemble has properties (a) and (b), i.e., that the definition we have chosen makes sense.

So, here's the definition:

$$S(E, V) = k \log T(E)$$

definition

Some universal constant
(will turn out to be
Boltzmann constant)



Interpreting the definition:

the more areas of phase space are consistent w/ macro state, the larger S
 larger choice of microstates \Rightarrow lesser degree of predictability or increased level of disorder

Also: $T = 1 \Rightarrow S = 0$

if we use discrete states, then the integrals turn into sums

Does the definition make sense? It does provided (a) and (b) from p. 9 are fulfilled.

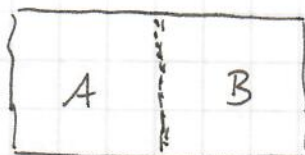
\nearrow
 S extensive

Let's show (a): \leftarrow this will take quite a few pages... we'll be done on p. 19 (I will not show (b) explicitly).

Consider two subsystems A and B

N_A, V_A

N_B, V_B



conducting wall

$$V_A, N_A, V_B, N_B \text{ fixed}$$

Assumptions: • surface-to-volume ratio of each subsystem is negligibly small

• energy associated w/ molecular interaction betw. subsystems is negligible compared to total energy

(this assumes finite-ranged interactions)

↳ not interactions with infinite range

With these assumptions:

$$\mathcal{H}(\vec{p}, \vec{q}) = \mathcal{H}_A(\vec{p}_A, \vec{q}_A) + \mathcal{H}_B(\vec{p}_B, \vec{q}_B)$$

Hamiltonian
of total system

Hamiltonian
of subsystem A

... B

Assume that the two systems are isolated:

Then, we have a microcanonical ensemble for subsystem A and a separate one for subsystem B.

Thus:

Energy of subsystem A lies betw. E_A and $E_A + \Delta E$.

" " " B " " E_B and $E_B + \Delta E$.

$$\begin{aligned} \Rightarrow \text{by def.} \quad & \left\{ \begin{aligned} S_A(E_A, V_A) &= k \log(\Omega_A(E_A)) \\ S_B(E_B, V_B) &= k \log(\Omega_B(E_B)) \end{aligned} \right. \end{aligned}$$

Now: Consider a microcanonical ensemble of the composite system made up of subsystem A and subsystem B w/ energy between E and $E + 2\Delta E$.

$$N = N_A + N_B$$

$$V = V_A + V_B$$

Microcanonical ensemble of composite system contains:

- i) N_A particles w/ (\vec{p}_A, \vec{q}_A) contained in V_A
- ii) N_B " " (\vec{p}_B, \vec{q}_B) " " V_B

$$\text{Also: } E < E_A^* + E_B^* < E + 2\Delta E$$

↑ note: E_A^* and E_B^* can vary (conducting walls)

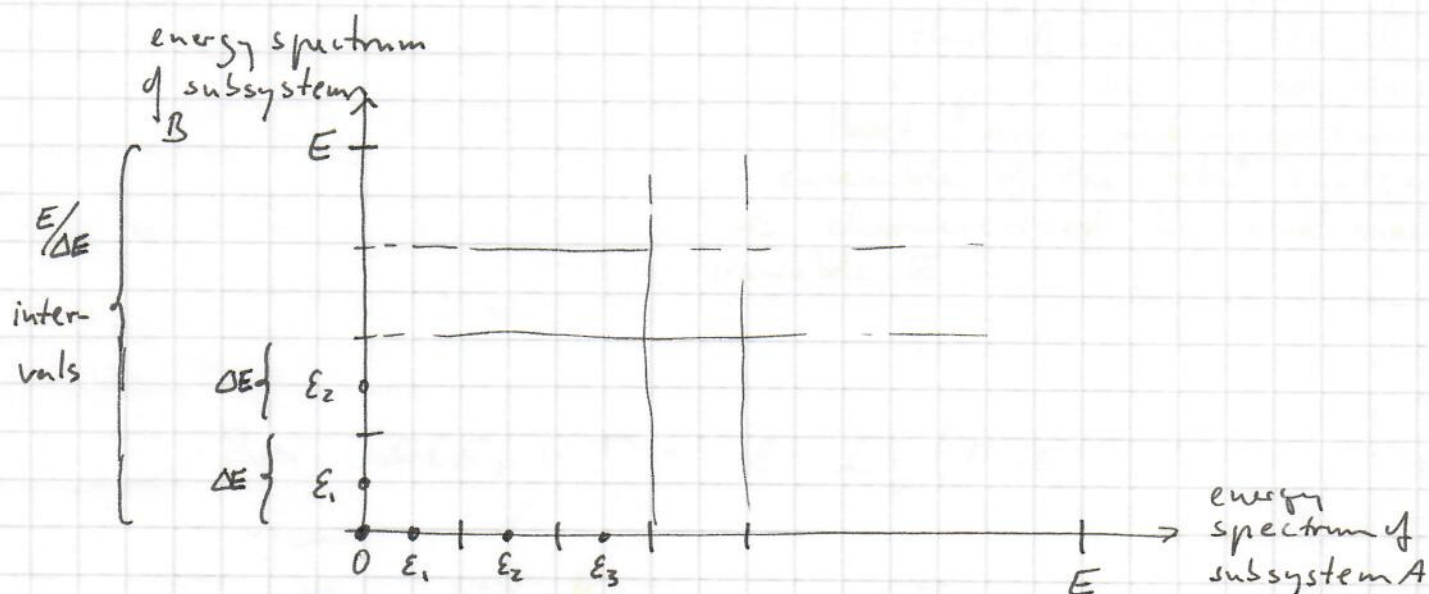
We have a product of two independent integrals:

$$P_A(E_A^*) P_B(E_B^*)$$

}

this fulfills conditions
(i) and (ii) but we
still need to ensure
 $E < E_A + E_B < E + 2\Delta E$

recall: we are
assuming that
interactions betw.
A and B particles
can be neglected



we can always
shift our energy
scale

$E/\Delta E$ intervals

We assume a discretized energy interval (we
can always send ΔE to zero)

each energy spectrum is divided into $E/\Delta E$ energy
intervals

$$\Rightarrow T(E) = \sum_{i=1}^{E/\Delta E} T_A(\varepsilon_i) T_B(E - \varepsilon_i)$$

sum since we discretized
the spectrum

once we pick the
energy of subsystem A,
that of subsystem B
is fixed by the condition
that our microcanonical
ensemble of the total system
is characterized by the macro-
variable E

$$\text{Then: } S(E, V) = k \log(T(E))$$

$$V = V_A + V_B$$

$$\begin{aligned} &= k \log \left(\sum_{i=1}^{E/\Delta E} \underbrace{T_A(\varepsilon_i)}_{\geq 0} \underbrace{T_B(E - \varepsilon_i)}_{\geq 0} \right) \\ &\quad \nearrow \text{inserting from above} \end{aligned}$$

let \bar{E}_A and \bar{E}_B be the values
for which $T_A(\varepsilon_i) T_B(E - \varepsilon_i)$
is maximal (note: there exists
one ε_i that sets \bar{E}_A and \bar{E}_B)

It follows trivially:

$$T_A(\bar{E}_A) T_B(\bar{E}_B) \leq T(E) \leq \underbrace{\frac{E}{\Delta E}}_{\text{\# of intervals}} T_A(\bar{E}_A) T_B(\bar{E}_B)$$

We can use this inequality to "bracket" S :

$$\begin{aligned} k \log(T_A(\bar{E}_A) T_B(\bar{E}_B)) &\leq \underbrace{k \log T(E)}_S \\ &\leq k \log(T_A(\bar{E}_A) T_B(\bar{E}_B)) + k \log\left(\frac{E}{\Delta E}\right) \end{aligned}$$

For $N_A \rightarrow \infty$ and $N_B \rightarrow \infty$, the following scaling is typical:

$$\log T_A \propto N_A$$

$$\log T_B \propto N_B$$

$$E \propto N_A + N_B$$

$$\text{So: } S \leq \underbrace{k \log(T_A(\bar{E}_A))}_{\propto N_A} + \underbrace{k \log(T_B(\bar{E}_B))}_{\propto N_B} + \underbrace{k \log\left(\frac{E}{\Delta E}\right)}_{\propto \log N}$$

$\mathcal{O} \hat{=}$ "of order $\log N$ " [19]

Thus:

large
 N_A, N_B

$$S_A(\bar{E}_A, V_A) + S_B(\bar{E}_B, V_B) + \mathcal{O}(\log N)$$

So: $S(E, V) = k \log(T(E))$ is consistent
w/ extensive property.

(this is what we started off to show on p. 13)

We worked ~~hard~~! Let's get more out of it...

$$S(E, V) = S_A(\bar{E}_A, V_A) + S_B(\bar{E}_B, V_B) + \mathcal{O}(\log N)$$

this means that the
subsystems have the
energies \bar{E}_A and \bar{E}_B , respectively

recall: \bar{E}_A and \bar{E}_B are the values

that maximize $T_A(E_A) T_B(E_B)$

under the constraint $E = E_A + E_B$

Let's maximize $\log(T_A(E_A) T_B(E_B))$ instead of
 $T_A(E_A) T_B(E_B)$ (mathematically identical):

We will treat E_A as our variable and

then use $E_B = E - E_A$ to fix E_B :

$$\Rightarrow \frac{\partial \log(T_A(E_A))}{\partial E_A} + \frac{\partial \log(T_B(E_B))}{\partial E_A} \stackrel{!}{=} 0$$

this is what we want to enforce

$$= - \frac{\partial \log(T_B(E_B))}{\partial E_B}$$

By our construction, the equal sign is fulfilled for $E_A = \bar{E}_A$ and $E_B = \bar{E}_B$:

$$\Rightarrow \left. \frac{\partial \log(T_A(E_A))}{\partial E_A} \right|_{E_A = \bar{E}_A} = \left. \frac{\partial \log(T_B(E_B))}{\partial E_B} \right|_{E_B = \bar{E}_B}$$

This can be rewritten as:

$$\left. \frac{\partial S_A(E_A)}{\partial E_A} \right|_{E_A = \bar{E}_A} = \left. \frac{\partial S_B(E_B)}{\partial E_B} \right|_{E_B = \bar{E}_B}$$

Define : $\left\{ \frac{\partial S(E, V)}{\partial E} \stackrel{\text{def.}}{=} \frac{1}{T} \right\}$ This eq. defines temperature !

So : \bar{E}_A and \bar{E}_B are such that the two sub-systems have the same temperature : $T_A = T_B$!

Let's think about $\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$

the derivative of S with respect to E is taken while keeping V and N constant

a bit more:

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)_{V,N} = \left(\frac{\partial}{\partial E} \left(k \log(\Gamma(E)) \right)\right)_{V,N} \\ &= k \left(\frac{\frac{\partial \Gamma(E)}{\partial E}}{\Gamma(E)} \right)_{V,N} \end{aligned}$$

recall: $\Gamma(E) \hat{=}$ # of states
or phase space volume
consistent w/ macro-state

$\frac{\partial \Gamma}{\partial E} \rightarrow \frac{\Delta \Gamma}{\Delta E}$
"change in Γ per change in E "

think of as $k \frac{\frac{\Delta \Gamma(E)}{\Gamma(E)}}{\frac{1}{\Delta E}}$

fractional change of # of states
change in energy

So: if adding energy greatly ~~changes~~ changes the accessible volume compared to current volume, then $\frac{1}{T}$ large or T low.

if adding energy changes the accessible volume little compared to current volume, then $\frac{1}{T}$ low or T large.

If a system has a finite # of energy states,
then increasing E can reduce the # of accessible
states \rightsquigarrow negative (!) temperature

more on this later (Example that starts on p. 24)

The temperature defined through $\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$

is the absolute temperature of thermodynamics.

We found:

The temperature of an isolated system is the
parameter governing the equilibrium betw. one
part of the system and another.

Recall, we are working on establishing connection
betw. "thermodynamics" and "microcanonical
ensemble". • We showed $S = \log T(E)$ is extensive
(condition (a) on p. 9)

- Still need to show consistency w/ 2nd
law of thermodynamics (condition (b) on p. 9)

Useful reformulation of 2nd law of thermodynamics:

If an isolated system undergoes a change of thermodynamic state such that the initial and final states are equilibrium states, then the entropy of the final state is not smaller than that of the initial state.

It can be shown that our $S = k \log T(E)$ definition is consistent w/ this way of formulating the 2nd law of thermodynamics.

I will not show this \rightarrow See pages 134/135 of text

Note: $S = k \log T(E)$

$S = k \log \omega(E)$

$S = k \log \Sigma(E)$

} these are equivalent definitions up to a constant factor (I will not show this)

constant factor does not matter for thermodynamics