

The Big Idea

Thermal systems = systems with very many components exchanging energy in a disorderly way

Energy distributions stabilize = Equilibrium

Then they possess the properties of ordinary thermodynamics

Hence, the kinetic theory of heat is FALSE
heat \neq motion!

The Big Result

Boltzmann distribution
canonical distribution

Probability that a component or system of components has energy E

$$p(E) = \frac{1}{Z} \exp(-E/kT)$$

Normalizing factor.
IMPORTANT!

Boltzmann's constant

Recover thermodynamic quantities by applying differential operators to Z

Partition function $Z = \int_{\text{all phase space}} \exp(-E/kT) d\Omega$

$\bar{E} = -kT^2 \frac{d}{dT} \ln Z$ $F = \bar{E} - TS = -kT \ln Z$

$S = \bar{E}/T + k \ln Z$ $P = - \left. \frac{\partial F}{\partial V} \right|_T$

Deduce Ideal Gas Law

System consists of n independent ^{sub} systems spread over volume V where the energies are independent of position

$E = \underbrace{E_1 + \dots + E_n}_{\text{NO interaction energy}}$

↑ THE ESSENTIAL CONDITION

$Z = \int \exp(-E/kT) \underbrace{d\Omega}_{\substack{dp dx}} = \int \exp(-E/kT) dp \int dx$

$\underbrace{\prod_{i=1, n} \int \exp(-E_i/kT) dp_i}_{\text{"G}_i(T)\text{"}} V^n$

$P = \left. \frac{\partial}{\partial V} \right|_T kT \ln Z = \left. \frac{\partial}{\partial V} \right|_T \left(\cancel{kT \sum \ln G_i(T)} + kT \ln V^n \right)$

$= n kT / V$

Works for: Rarefied gases, dilute solutes, Brownian particles, Einstein's light quanta

...and the n systems need not be identical!

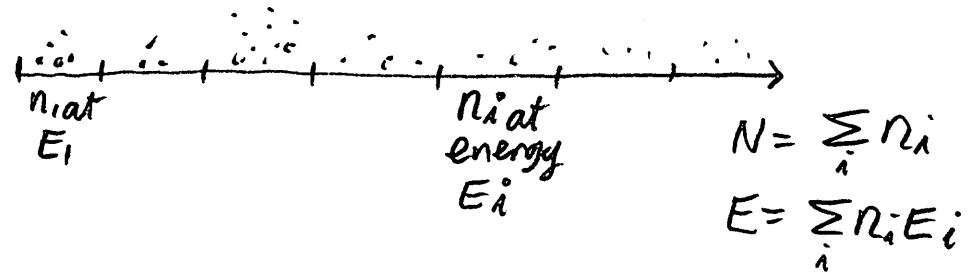
Justifying the Canonical Distribution

O. Inductively. It returns ordinary thermodynamics and more (fluctuations).
Therefore accept it!

I. Assume the system achieves equilibrium
Infer canonical distribution from a property of equilibrium

Boltzmann's
"complexeon"
counting

N components with total energy E distributed over energy cells:



Number of ways of achieving distribution n_1, n_2, \dots

$$W = \frac{N!}{n_1! n_2! \dots}$$

Seek most probable distribution

= Distribution with largest W subject to constraints of

- system number
- total energy E

Convert to unconstrained optimization using Lagrange multipliers:

Optimize $\ln W + \alpha (\sum_i n_i - N) + \beta (\sum_i n_i E_i - E)$

system number

Energy

Variation operator δ varies distribution n_1, n_2, \dots

$0 = \delta (\ln W + \alpha (\sum_i n_i - N) + \beta (\sum_i n_i E_i - E))$

$\ln W \doteq N \ln N - \sum_i n_i \ln n_i$

Energy constraint controls. Without it \rightarrow uniform distribution

$= -\delta \sum_i n_i \ln n_i + \alpha \sum_i \delta n_i + \beta \sum_i E_i \delta n_i$

$= -\sum_i (\ln n_i + 1) \delta n_i$

$= -\sum_i (\ln n_i + (\alpha - 1) + \beta E_i) \delta n_i$

Hence $n_i \propto \exp(\beta E_i)$

\uparrow Elsewhere $\beta = 1/kT$

The entropy gloss:

$\ln W \doteq N \ln N - \sum_i n_i \ln n_i = N (\ln N \sum_i \frac{n_i}{N} - \sum_i \frac{n_i}{N} \ln n_i)$

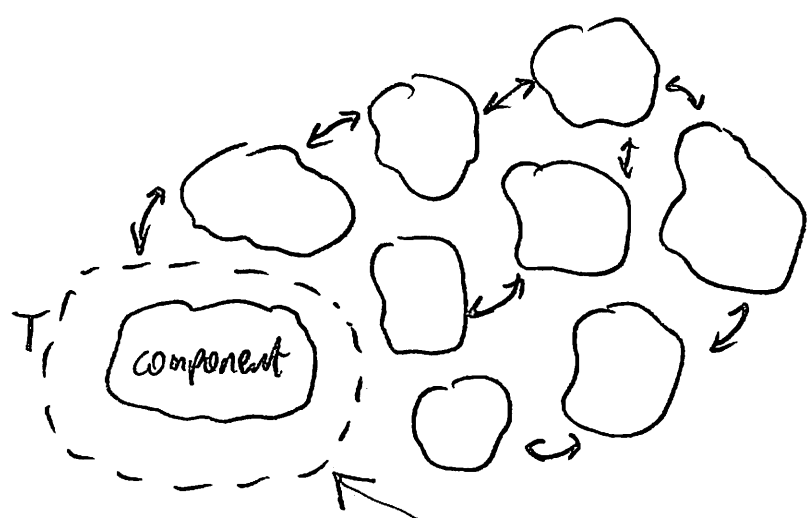
$\doteq N (-\sum_i \frac{n_i}{N} \ln \frac{n_i}{N})$

$p_i = n_i/N$

$(\frac{1}{k}$ Boltzmann entropy)
maximized at equilibrium

Gibbs entropy of one component is $-k \int p \ln p d\Omega$

Inensitivity at equilibrium



Energy distribution
Thermal properties
essentially insensitive
to character of
other components

All that
matters is
"T"

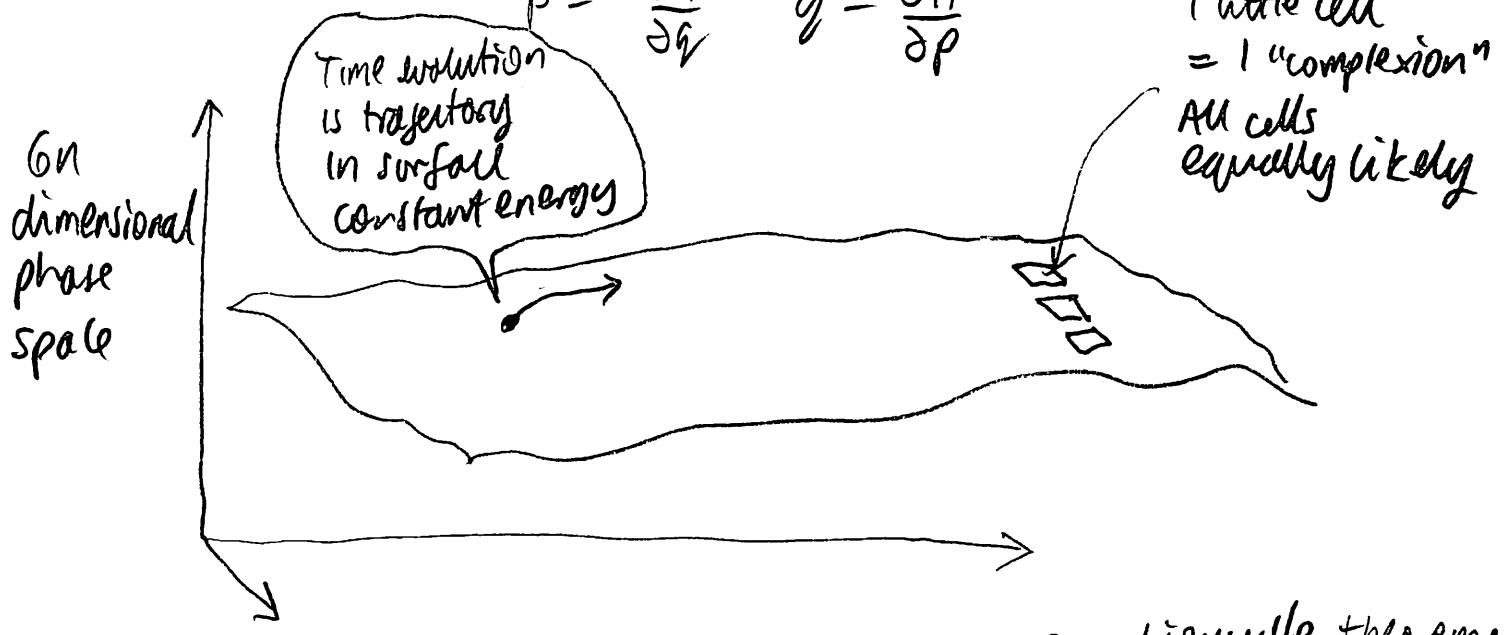
New start a big clean up operation:

- What dynamics underwrites the complexion counting?
- Why is each complexion equally probable?

Gibbs
Einstein
Khinchin
⋮

Mechanics of the total system is Hamiltonian.
Behaviour of n components governed by Hamilton's equations

$$\dot{p} = -\frac{\partial H}{\partial q} \quad \dot{q} = \frac{\partial H}{\partial p}$$



micro-canonical distribution = uniform probability distribution over surface

Liouville theorem: Distribution preserved under time evolution

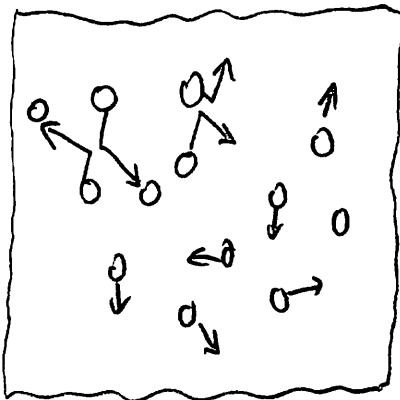
⇓ Fancier version of Boltzmann's complexion counting

Individual systems are canonically distributed

Justify the canonical distribution AND the statistical analysis of irreversible processes by:

II. Tracing the approach to equilibrium

Boltzmann's H-theorem



very many molecules colliding elastically

$f(p, q, t) =$
density particles at point (p, q) in phase space

$$\frac{dH}{dt} \leq 0 \quad \text{where} \quad H = \underbrace{\int f \ln f \, dpdq}_{- \text{Entropy}/k}$$

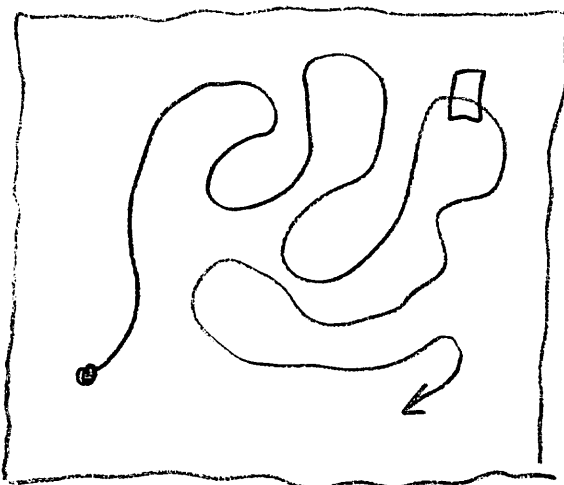
... but needs assumption of "molecular chaos"
else time reversibility of dynamics violated

↑ approaching molecules are uncorrelated

Ergodicity

The hope:

Total phase space of a thermal system



Over time, spends roughly equal time in all cells



Probability of cell \approx relative occupation time is microcanonical.

Further Topics

Boltzmann's principle

$$S = k \log W$$

entropy probability

Generally meaningless since systems do not have probabilities absent specific contexts. If the context is specified, the result can be innocuous

Thermodynamic Entropy and Information

1% interesting results
99% moonbeams