Last time, calculated \( \Omega(E, N, V) \) for ideal gas

\[ \text{# of microstates with total energy } E, \]
\[ \text{number } N, \text{ volume } V \]

- Really \( \# \) of microstates w/ energy close to \( E \) \((\Omega)\)
- or with energy less than \( E \) \((\Sigma)\)
  (all equivalent)

Got \( S = k_B \ln \Omega \)

\[ = N k_B \sum \ln \left[ \frac{U \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \hbar^2}{2} \right] + \frac{3}{2} \sum \]

with \( E = \frac{3}{2} N kT \)

But, we still need to account for fact that particles are indistinguishable

Really should count microstates differently:

Before, used \( (j_{i,1}, j_{i,2}, j_{i,3}) = \) quantum #s
for particle \( i \)

Should instead use \( \Omega(j_{i,1}, j_{i,2}, j_{i,3}) = \# \) of particles

with quantum #s \( (j_{i,1}, j_{i,2}, j_{i,3}) \)

Don't try to say which particle is
in which state
Then microstate defined by $\Xi n_j \Xi^3$ rather than $\Xi j \Xi^3$.

Each $\Xi n_j \Xi^3$ state corresponds to many $\Xi j \Xi^3$ states

$\# = \# \text{ of permutations of } j$'s among different atoms

Number of ways to permute $N$ objects = $N!$

But, exchanging two particles in same state doesn't yield new state, even in $\Xi j \Xi^3$ definition

If $n_j$ particles in state $j$, have $n_j!$ permutations we don't want to count.

So total $\#$ of permutations is

$$P(\Xi n_j \Xi^3) = \frac{N!}{n_1! n_2! \ldots}$$

Dealing with this correctly is a little hard but can be put off to later.

For now, suppose gas is hot & low density
many more states available than particles

Then chance of \( n_j \geq 1 \) is small

Since \( 0! = 1! = 1 \), take \( n_j! \to 1 \)

and \( P(\xi n_j^3) \to N! \)

So we can account for identical particles

by reducing \( S \) (or \( F \) or \( E \)) by \( N! \)

\( \Rightarrow \) reduce \( S \) by \( k_B \ln N! \)

\( \leq k_B \left[ N \ln N - N \right] \)

Finally get

\[
S = N k_B \sum_j \ln \left[ \left( \frac{u_j}{N} \right) \left( \frac{2\pi m k T}{\hbar^2} \right)^{3/2} \right] + \frac{3}{2} \sum_j \xi_j^2
\]

(Still \( E = \frac{3}{2} N k_B T \))

Sackur–Tetrode eqn

Remember as

\[
S = N k \sum_j \xi_j^2 - \ln \rho / \lambda^3 \]

\( \rho = \frac{N}{V} = \text{density} \)

and \( \lambda = \sqrt{\frac{\hbar^2}{2\pi m k T}} \)

"Thermal de Broglie wavelength"
Interpret \( \Lambda \):

Note average energy of particle \( \frac{E}{N} = \frac{3}{2} kT \)

\[ \text{set } E = \frac{1}{2} m v^2 \]

\[ \Rightarrow \quad \langle v \rangle \approx \sqrt{\frac{3kT}{m}} \]

\[ p_{av} = m \langle v \rangle \approx \sqrt{3mkT} \]

De Broglie wavelength

\[ \lambda_{av} = \frac{h}{p_{av}} = \sqrt{\frac{h^2}{3mkT}} \]

So \( \Lambda = \sqrt{\frac{3}{2\pi}} \lambda_{av} \)

\( \approx \) typical wavelength for particle in gas

So \( \rho \Lambda^3 \approx \# \) of particles in volume \( \Lambda^3 \)

\( \approx \# \) of particles per quantum state

Our counting method valid for \( \rho \Lambda^3 \ll 1 \)

"Classical" gas limit: quantum effects not important

Note: \( \rho \rightarrow \infty \) as \( T \rightarrow 0 \)

Violates 3rd law

But classical appx fails as \( T \rightarrow 0 \)

Problem fixed in quantum calc.,
Sackur-Tetrode eqn fixes Gibbs' paradox:

Consider mixing two gases $A$ and $B$

Equal initial densities $\rho_0$

Before mixing:

$$S_{\text{init}} = N_A k \left( \frac{5}{2} - \ln \rho_0 \lambda^3 \right) + N_B k \left( \frac{5}{2} - \ln \rho_0 \lambda^3 \right)$$

$$= (N_A + N_B) k \left( \frac{5}{2} - \ln \rho_0 \lambda^3 \right)$$

After mixing:

$$\rho_A = x_A \rho_0 \quad \rho_B = x_B \rho_0$$

$$S_{\text{final}} = N_A k \left( \frac{5}{2} - \ln x_A \rho_0 \lambda^3 \right)$$

$$+ N_B k \left( \frac{5}{2} - \ln x_B \rho_0 \lambda^3 \right)$$

$$= (N_A + N_B) k \left( \frac{5}{2} - \ln \rho_0 \lambda^3 \right)$$

$$+ N_A k \ln x_A + N_B k \ln x_B$$

$$\Delta S_{\text{mix}}$$

Same as before

But if species identical,

have final $\rho = \rho_0$

$$S_{\text{final}} = (N_A - N_B) k \left( \frac{5}{2} - \ln \rho_0 \lambda^3 \right) = S_{\text{init}}$$

as required
That's Ch 1:
Illustration of basic principle of statist mech

Ch 2:
Develop ideas in a more rigorous way.
in less hand-waving.
Specifically consider true classical system.
Assume particles obey classical mechanics.

First step: describe microstate.
Easy: give coordinates $q_i$ and momenta $p_i$ for each particle.

Could be generalized coords.

General eqn of motion:
\[ \dot{q}_i = \frac{\partial H}{\partial p_i} \]
\[ \dot{p}_i = -\frac{\partial H}{\partial q_i} \]

For Hamiltonian $H = H(q_i, p_i)$

For conservative systems, $H$ is constant in time and
$H = E$ total energy.
Geometrical picture:

phase space

= 6N dimensional space of $\xi q_i, p_i$'s

So one microstate = point in phase space

of points evolve according to Hamilton's eqns.

Simple example of evolution

Set of all microstates consistent with

given macrostate

= surface in phase space

E = const

for $H = \frac{p^2}{2m}$

To firm up idea "all microstates equally likely,"

introduce ensemble

Ensemble = set of (mental) copies of

a system, all prepared in

same way.
Normally don't/don't prepare particular microstate
So each system in ensemble
- distinct point in phase space

Rather than tracking points, define

phase space density \( \rho (q, p; t) \):

\[
\rho (q, p; t) \ d^3q \ d^3p = \# \text{ of points in ensemble contained in volume } \ d^3q \ d^3p \text{ at time } t
\]

Define \( d\omega = \ d^3q \ d^3p \)

Rather than thinking about our system being
in many possible states,
think about measuring average of thermo quantities over states in ensemble

ie, if we're interested in some function
\( f(q, p) \)

then \( \langle f \rangle = \text{average over many similarly prepared copies of system} \)
Then \( \langle f \rangle \) is well-defined:

\[
\langle f \rangle = \frac{\int f(p,q) \rho(p,q,t) \, dq \, dp}{\int \rho(p,q,t) \, dq \, dp}
\]

Say that an ensemble is stationary if

\[
\frac{\partial \rho}{\partial t} = 0
\]

Individual points move in phase space, but distribution of ensemble doesn't change.

From Hamilton's eqn, can derive eqn of motion for \( \rho \):

\[
\frac{\partial \rho}{\partial t} + \left( \frac{\partial \rho}{\partial p} \right)_{q,\rho} + \{\rho, H\} = 0
\]

Since \( q \) and \( p \) vary in time,

\[
\{\rho, H\} = \text{Poisson bracket}
\]

So for stationary ensemble, need \( \{\rho, H\} = 0 \)

General way to achieve this is to require \( \rho(p,q) = \rho(H(p,q)) = \rho(E) \)
In other words, for an ensemble to be stationary, the distribution of microstates in it should depend only on the energy of the microstate.

We'll see various choices for what energy dependence is... defines different ensembles.