

Lecture 11

Last time, calculated $\Omega(E, N, V)$ for ideal gas
= # of microstates with total energy E ,
number N , volume V

- Really # of microstates w/ energy close to E (Ω)
or with energy less than E (Σ)
(all equivalent)

$$\begin{aligned} \text{Got } S &\approx k_B \ln \Sigma \\ &= N k_B \left\{ \ln \left[V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] + \frac{3}{2} \right\} \\ &\quad \text{with } E = \frac{3}{2} N k_B T \end{aligned}$$

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

Really should count microstates differently:

Before, used $(j_{ix}, j_{iy}, j_{iz}) =$ quantum #'s
for particle i

Should instead use $n_{j_x j_y j_z} =$ # of particles
with quantum #'s
 (j_x, j_y, j_z)

Don't try to say which particle is
in which state

Then microstate defined by $\{n_j\}$

11.2

rather than $\{j_r\}$

Each $\{n_j\}$ state corresponds to many $\{j_r\}$ states

= # 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 $\{j_r\}$ definition

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

So total # of permutations is

$$P(\{n_j\}) = \frac{N!}{n_1! n_2! \dots}$$

Dealing with this correctly is a little hard
Put off to later.

For now, suppose gas is hot & low density

⇒ many more states available than particles

Then chance of $n_j > 1$ is small

Since $0! = 1! = 1$, take $n_j! \rightarrow 1$

and $P(\{n_j\}) \rightarrow N!$

So we can account for identical particles by reducing Ω (or Γ or Σ) by $N!$

$$\Rightarrow \text{reduce } S \text{ by } k_B \ln N!$$

$$= k_B [N \ln N - N]$$

Finally get

$$S = N k_B \left\{ \ln \left[\left(\frac{V}{N} \right) \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

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

Sackur-Tetrode eqn

Remember as

$$S = N k \left\{ \frac{5}{2} - \ln \rho \Lambda^3 \right\}$$

$\rho = \frac{N}{V} = \text{density}$

$$\text{and } \Lambda = \sqrt{\frac{h^2}{2\pi m k T}}$$

"Thermal de Broglie wavelength"

Interpret Λ :

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

$$\text{set } = \frac{1}{2} m v^2$$

$$\Rightarrow v_{\text{avg}} \approx \sqrt{\frac{3kT}{m}}$$

$$p_{\text{avg}} = m v_{\text{avg}} = \sqrt{3mkT}$$

De Broglie wavelength

$$\lambda_{\text{avg}} = \frac{h}{p_{\text{avg}}} = \sqrt{\frac{h^2}{3mkT}}$$

$$\text{So } \Lambda = \sqrt{\frac{3}{2\pi}} \lambda_{\text{avg}}$$

\approx typical wavelength for particle
in gas

So $\rho \Lambda^3 = \#$ of particles in volume Λ^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: $S \rightarrow -\infty$ 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 & B

Equal initial densities ρ_0

Before mixing:

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

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

After mixing:

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

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

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

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

$$+ \underbrace{N_A k \ln x_A + N_B k \ln x_B}_{\Delta S_{mix}}$$

same as before

But if species identical,
have final $\rho = \rho_0$

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

as required

That's Ch 1:

Illustration of basic principle of stat mech

Ch 2:

Develop ideas in more rigorous way
... less handwaving

Specifically consider true classical system

Assume particles obey classical mechanics

First step: describe microstate

Easy: give coordinates q_i
& 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

$$H = E \quad \text{total energy}$$

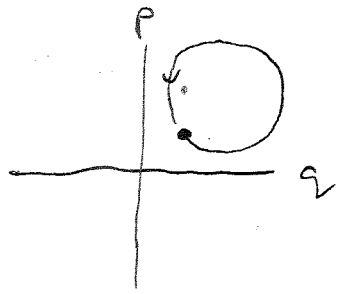
Geometrical picture:

phase space

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

So one microstate = point in phase space

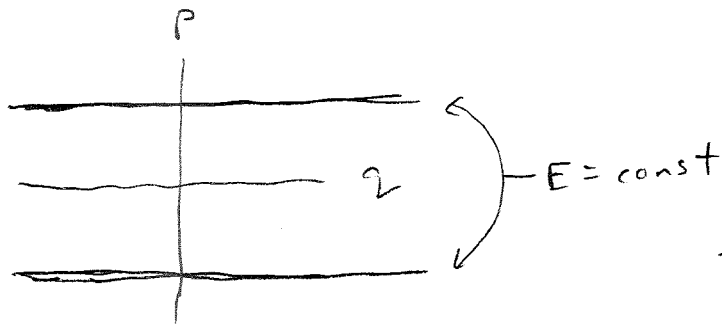
* points evolve according to Hamilton's eqns.



Simple example of evolution

Set of all microstates consistent with given macrostate

= surface in phase space



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/can't prepare particular microstate

So each system in ensemble

= distinct point in phase space

Rather than tracking points, define

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

$$\rho(q, p; t) d^{3N} q d^{3N} p = \# \text{ of points in ensemble}$$

contained in volume

$$d^{3N} q d^{3N} p \text{ at time } t$$

$$\text{Define } dw = d^{3N} q d^{3N} p$$

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 $\langle f \rangle =$ average over many similarly prepared copies of system

Then $\langle f \rangle$ is well-defined:

$$\langle f \rangle = \frac{\int f(p, q) \rho(p, q; t) \, d\omega}{\int \rho(p, q; t) \, d\omega}$$

Say that an ensemble is stationary

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

* Interesting
since relates
to equilibrium

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

From Hamilton's eqn, can derive eqn of
motion for ρ :

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

$$\frac{d\rho}{dt} \neq \left(\frac{\partial \rho}{\partial t} \right)_{q,p} \quad \text{since } q \text{ + } p \text{ vary in time}$$

$[\rho, H] =$ Poisson bracket

So for stationary ensemble, need $[\rho, H] = 0$

General way to achieve this is to

$$\begin{aligned} \text{require } \rho(p, q) &= \rho(H(p, q)) \\ &= \rho(E) \end{aligned}$$

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.