Class 2. Statistical Mechanics

Phase Space (Chapter 5 on → Goldner & Chapter 1 Pathria)

Classical System → it is sufficient to know at a time \( t \)
the generalized coordinates \( q_i(t) \) and momenta \( p_i(t) \)
to know the state of motion of the system.

For a system the set \( (q_i, p_i), \; i = 1, \ldots, 3N \) is the microstate of the system.
→ The set \( (q_i, p_i) \) is a point in a \( 6N \)-dimensional space called PHASE SPACE.

- A point in the phase space exactly corresponds to one microscopic state
  of motion of the system.

Analogously we can relate to each particle a \( 6 \)-dimensional phase space (one-particle phase space). The state of motion of the system is described then by \( N \) points in this one-particle phase space.

- The general case is the phase space of the whole system.

Phase -space Trajectory → A curve \( q_i(t), p_i(t) \) in phase space

describing the temporal evolution of the system.

It is determined by the Hamilton equations of motion

\[
\dot{q}_i = \frac{\partial H}{\partial p_i} ; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}
\]

The Hamiltonian \( H(q_i(t), p_i(t)) \) corresponds to total energy of the system
(That can be time dependent) → depends on \( q_i, p_i \) and time.
In a closed system, Hamiltonian does not depend explicitly on time and the energy

\[ E = H(q, \dot{q}, p, \dot{p}) \]

is conserved.

In general, the time dependence of a quantity \( A(q, \dot{q}, p, \dot{p}) \) is

\[
\frac{dA}{dt} = \frac{\partial A}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right)
\]

\[
= \frac{\partial A}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial A}{\partial q_i} \frac{\partial H}{\partial \dot{q}_i} + \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial \dot{p}_i} \right)
\]

\[
= \frac{\partial A}{\partial t} + \{ A, H \}
\]

↑ This is called 'Poisson Bracket'.

\[ \{ H, H \} = 0 \quad \text{and} \quad \frac{\partial H}{\partial t} = 0 \quad \rightarrow \text{conservation of energy} \]

\[
\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{ A, H \}
\]
describes \( GN-1 \) dimensional hypersurface in phase space.

Example: Harmonic Oscillator

Hamiltonian of harmonic oscillator in 1D

\[
H(q, p) = \frac{p^2}{2m} + \frac{1}{2} Kq^2
\]

Phase Space?
Since $H$ doesn't explicitly depend on time, $E$ is a conserved quantity.

$$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}Kq^2 = \text{cte. is an ellipse} \quad a = \sqrt{2mE}, \quad b = \sqrt{2E/K}$$

with frequency $\omega = \sqrt{K/m}$

In its temporal evolution, the phase space point $q(t), p(t)$ of the system can only move on this ellipse.
If $I$ has a oscillator with $E + \Delta E$

We can subdivide the phase space into volumes elements $d^3q d^3p$ for 2D phase space:

The phase space element $d^3q d^3p$ is called phase-space cell

Phase space volumes abbreviated as $\omega$, so $d\omega = d^3q d^3p$ (don't confuse with frequency).
For example, the phase-space volume between the ellipses of $E$ and $E+\Delta E$

\[ \Delta w = \int dq \int dp \quad \text{for} \quad E \leq H(q, p) < E + \Delta E \]

\[ \Delta w = \int dq \int dp \quad \text{for} \quad E \leq H(q, p) < E + \Delta E \]

We can call Energy Hypersurface

\[ \mathcal{S}(E) = \int_{E-H(q, p)}^{E+\Delta E} ds \quad \text{surface element} \]

\[ \Delta S \int ds \quad \text{for} \quad E \leq E < E + \Delta E \]

Consider a closed system characterized by variables of state $E, V, N$

Now we restrict the possible coordinates of the particles because total energy is given, only phase-space points on the energy surface are allowed.

$\mathcal{R}$ is the number of microstates compatible with a given macrostate $(q_1, p_1)$

So we assume that

\[ \mathcal{R}(E, V, N) = \mathcal{S}(E, V, N) \quad \text{with} \quad \mathcal{S}(E, V, N) = \int_{E-H(q, p)}^{E-H(q, p)} ds \]

(In reality, the Thermodynamic properties do not depend on $\mathcal{R}$ because they will depend on ratios $N_1/N_2$)

In general, integration on a surface in high-dimensional space is complicated.

Calculation of volumes is easier.
Let $w(E, V, N)$ total phase-space volume; boundary is given by the energy hypersurface $E = H(q, p)$.

We have

$$w(E, V, N) = \int d^3q \int d^3p \quad H(q, p) \leq E$$

The volume between two energy surfaces with energies $E$ and $E + \Delta E$ is

$$\Delta w = w(E + \Delta E) - w(E) = \frac{\partial w}{\partial E} \Delta E$$

From Carnot's Theorem, the volume between two neighboring surfaces with area $\sigma(E)$ is given by:

$$\Delta w = \sigma(E) \Delta E$$

$$\Rightarrow \sigma(E) = \frac{\partial w}{\partial E}$$

Example of a sphere in 3D:

Volume up to the radius $R$ is

$$w(R) = \frac{4\pi}{3} R^3$$

Surface area $\sigma(R) = \frac{\partial w}{\partial R} = 4\pi R^2$

So:

$$\mathcal{L}(E, V, N) = \sigma(E, V, N) = \frac{4\pi}{3} \frac{\partial w}{\partial E}$$
**Statistical Definition of Entropy**

In thermodynamic equilibrium, the most probable macroscopic state is the one which corresponds to the largest number of microstates. (Here we assume that all microstates with the same \( E \) appear with the same probability.)

Let us consider a system with two subsystems:

\[
\begin{array}{|c|c|}
\hline
\text{Energy} & \text{Volume} & \text{Particles} \\
\hline
E_1 & V_1 & N_1 \\
E_2 & V_2 & N_2 \\
\hline
\end{array}
\]

and \( E = E_1 + E_2 = c k \),

so \( dE_1 = -dE_2 \).

\[ V = V_1 + V_2 = c k \quad \text{and} \quad dV_1 = -dV_2 \]

\[ N = N_1 + N_2 = c k \quad \text{and} \quad dN_1 = -dN_2 \]

The total number of all microstates \( \mathcal{P}(E, V, N) \) is:

\[ \mathcal{P}(E, V, N) = \mathcal{P}_1(E_1, V_1, N_1) \mathcal{P}_2(E_2, V_2, N_2) \]

The most probable state, i.e., the equilibrium state, is the one with

\[ \mathcal{P} = \mathcal{P}_{\text{max}} \quad \text{and} \quad d\mathcal{P} = 0 \]

or

\[ d\mathcal{P} = \mathcal{P}_2 dE_1 + \mathcal{P}_1 dE_2 \]

\[ \Rightarrow \quad \frac{d\mathcal{P}}{\mathcal{P}} = \frac{dE_1}{E_1} + \frac{dE_2}{E_2} \]

\[ d\ln \mathcal{P} = d\ln \mathcal{P}_1 + d\ln \mathcal{P}_2 \]

In equilibrium \( d\ln \mathcal{P} = 0 \) and \( \ln \mathcal{P} = \ln \mathcal{P}_{\text{max}} \).
In quantum mechanics, however, each microscopic operator leads to a volume \( \Delta Q \geq \hbar \). The cells have finite volume.

So we use arbitrary unit such as does not make much sense. In microscopic, or arbitrary, there

So allow the current to microscopic absolutely. in classical considers

\[
\text{Remember: } R(E,V,N) = \langle E,V,N \rangle
\]

This is why so has no product

\[
\frac{1}{2} = \frac{2}{5}
\]

Through \( S(E,V,N) \) gives us the equation of state

Using the Hamiltonian \( H(p_r,q_r) \) this allows to calculate all the equilibrium properties of a many-body system

\[
\text{Dimension of entropy}
\]

\[
\phi = \sqrt{\frac{S(E,V,N)}{K_B\langle E,V,N \rangle}} + \text{constant}
\]

\[
\text{Reveal the analogy between } S \text{ and } \log
\]

\[
\text{In equilibrium enpropy is maximal: } dS = 0 \quad S_{\text{max}}
\]

\[
dS = dS_1 + dS_2
\]

\[
S(E,V,N) = S_1(E,V,N) + S_2(E,V,N)
\]

\[
\text{when the internal energy } U \text{ of a closed system is: } U = E
\]
In this case, the entropy $S = 0$ corresponds to a system with one exactly microstate $\Omega = 1$. Such systems are, for example, ideal crystals at temperature $T = 0$. Such systems at $T = 0$ have enthalpy $S = 0$ - 'the third law of thermodynamics'.

**Example:** *Statistical Calculation of the Entropy of the Ideal Gas*

Hamiltonian of the ideal gas:

$$H(q, p) = \sum_{\nu=1}^{N} \frac{p_{\nu}^2}{2m} = \sum_{\nu=1}^{3N} \frac{p_{\nu}^2}{2m}$$

So

$$w(E, V, N) = \int_{H(p, q) = E} d^{3n}q \int_{H(p, q) = E} d^{3n}p$$

Hamiltonian doesn't depend on $q$, volume of a

The condition $H(p) \leq E$

$$\sum_{\nu=1}^{3N} p_{\nu}^2 \leq \left( \sqrt{2mE} \right)^2$$

This condition is met by all points of momentum space which lie in the interior of a sphere with radius $\sqrt{2mE}$

$$V_n(R) = \int d^nx_1 \ldots d^nx_n = R^n \int d^nx_1 \ldots d^nx_n$$

$$\sum_{i=1}^{N} x_i^2 \leq R^2$$

\[ \sum_{i=1}^{N} y_i^2 \leq 1 \text{ (w. h. y. ) with } y_i = x_i/R \]
So, \( C_N = \frac{n^{N/2}}{N \Gamma \left( \frac{N}{2} \right)} \)

Remembering that \( \Gamma \left( \frac{3}{2} N \right) = 2E(2) \)

If \( N = 3 \), \( \Gamma \left( \frac{3}{2} \right) = \frac{\sqrt{\pi}}{2} \)

\( \Gamma \left( \frac{3}{2} \right) = \frac{4 \sqrt{\pi}}{3} \)

\( V_3(R) = \frac{3^{3/2}}{2 \sqrt{\pi}} \frac{R^3}{2} = \frac{4 \pi R^3}{3} \) volume of a 3D sphere

The volume of an \( N = 0 \) sphere is then

\[ V_N(R) = \frac{\pi^{N/2}}{\Gamma \left( \frac{N}{2} \right)} \frac{R^N}{N \Gamma \left( \frac{N}{2} \right)} \]

and

\[ \omega(E,V,N) = \frac{3^{N/2}}{2} \left( \frac{2mE}{\Gamma \left( \frac{3N}{2} \right)} \right) \frac{V^N}{N \Gamma \left( \frac{N}{2} \right)} \]

\[ \sigma(E,V,N) = \frac{4}{3} \frac{\partial \omega}{\partial E} = \frac{4}{3} \frac{V^N}{N \Gamma \left( \frac{N}{2} \right)} \frac{3^{N/2} \Gamma \left( \frac{3N}{2} \right) E^{N/2 - 1}}{\Gamma \left( \frac{3N}{2} \right)} \]

The entropy of the ideal gas is:

\[ S(E,V,N) = k \ln \left\{ \frac{4}{3} \frac{V^N}{N \Gamma \left( \frac{N}{2} \right)} \left( \frac{2m}{\Gamma \left( \frac{3N}{2} \right)} \right) \frac{E^{N/2}}{E} \right\} \]

\[ \text{needs to be dimensionless} \]
\[ W(r) = R^n C_n \quad C_n = \sum_{i=1}^{3N} \int \frac{d^N y_i}{\sum y_i^2 + 1} \]

\( C_n \) is the volume of \( N \) dimensional unit sphere.

Now the integrand of \( W(E, V, N) \) depends only on \( R = (x_1^2 + \ldots + x_N^2)^{1/2} \)
so the volume element \( dx_1 \ldots dx_N \) can be expressed by spherical shells:

\[ dx_1 \ldots dx_N \mid_{\text{shell}} = dV_n(R) \mid_{R=1} = N R^{N-1} C_n dR \]

So \( W = V^n \sum_{E \leq \text{V}} \frac{1}{V_n R \left( \text{such that} \frac{1}{2mE} \right)} \)

\[ \frac{1}{V_n R \left( \text{such that} \frac{1}{2mE} \right)} \]

\[ = N C_n \int_0^\infty R^{N-1} dR \exp \left( -\frac{1}{2mE} \right) \]

Now \[ \int_0^\infty dx \exp(-x^2) = \sqrt{\pi} \]

and \[ \int_{-\infty}^{\infty} dx_1 \ldots \int_{-\infty}^{\infty} dx_N \exp \left[ -\left( x_1^2 + \ldots + x_N^2 \right) \right] = \pi^{N/2} \]

So \[ N C_n \int_0^\infty R^{N-1} dR \exp \left( -\frac{1}{2mE} \right) = \pi^{N/2} \]

with \( x = R^2 \)

\[ \frac{1}{2} N C_n \int_0^\infty dx x^{N/2-1} e^{-x} = \frac{\pi^{N/2}}{2}, \quad \Gamma(\frac{N}{2}) = \int_0^\infty x^{\frac{N}{2}-1} e^{-x} \]

\( \Gamma(\frac{N}{2}) \) function.
so \( \frac{1}{60} \left( \frac{\pi}{2} \right)^{3/2} \frac{1}{E} \) = dimension of \( \frac{3N}{E} \)

But the dimension of \( \frac{3N}{E} \) is of \( \psi^3 \), so dimension of \( \frac{3N}{E} \) should be:

If \( N \gg 1 \), \( E^{3N/2 - 1} \sim E^{3N/2} \) and

\[
\ln N(n) \approx (n - 1) \ln(n - 1) - n - 1 \quad \text{Stirling's approximation}
\]

and \( S(E, V, N) \) for an ideal gas then is

\[
S(E, V, N) = N k \left[ \frac{3}{2} + \ln \left( \frac{V (4 \pi m E)^{3/2}}{3 N} \right) \right] \quad \text{with} \quad \delta = \frac{3}{N}
\]

The equations of state:

\[
\frac{1}{T} \frac{\partial S}{\partial E} \bigg|_{V,N} = \frac{3 N k}{2} \frac{1}{E} \quad \text{or} \quad E = \frac{3 N k T}{2}
\]

\[
\frac{P}{T} = \frac{\partial S}{\partial V} \bigg|_{E,N} = \frac{N k}{V} \quad \text{or} \quad PV = N k T
\]

and \( k \): Boltzmann constant

Gibbs Paradox

Substitute equation \( \Box \) in equation \( \bigcirc \) the entropy of an ideal gas becomes:

\[
S(T, V, N) = N k \left[ \frac{3}{2} + \ln \left( \frac{V (2 \pi m k T)^{3/2}}{8} \right) \right]
\]
Now let us consider a closed system consisting of two containers both with ideal gases, both have same $T$; same pressure.

<table>
<thead>
<tr>
<th>gas A</th>
<th>gas B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$, $p$</td>
<td>$T$, $p$</td>
</tr>
<tr>
<td>$N_A$, $V_A$</td>
<td>$N_B$, $V_B$</td>
</tr>
</tbody>
</table>

Let suppose the internal wall is removed, both gases will spread over the whole container until a new equilibrium is reached.

Since internal energy only depends on $T$ and not on volume ($E = \frac{3}{2} N k T$) and since the internal energy remains constant $T$; $p$ do not change, but the entropy will increase.

Before the removal of the separating wall

$$S_{\text{total}}^{(0)} = S_A^{(0)}(T, V_A, N_A) + S_B^{(0)}(T, V_B, N_B)$$

After:

$$S_{\text{total}}^{(0)} = S_A^{(0)}(T, V_A + V_B, N_A) + S_B^{(0)}(T, V_A + V_B, N_B)$$

This is called "entropy of mixing".

If we use Eq. (a) the entropy difference is:

$$\Delta S = S_{\text{total}}^{(0)} - S_{\text{total}}^{(0)} = N_A k \ln \left( \frac{V_A + V_B}{V_A} \right) + N_B k \ln \left( \frac{V_A + V_B}{V_B} \right)$$

So $\Delta S > 0$ as it should be for an irreversible process.

However, let consider two identical gases that will be mixed

So $S_{\text{total}}^{(0)}$ still will be the same, but

$$S_{\text{total}}^{(0)} = S(T, V_A + V_B, N_A + N_B)$$
Classical statistical mechanics predicts that collisions with interior walls of an enclosure lead to randomization of microscopic, classical trajectories.

First, let us consider a particle of mass \( m \) and initial velocity \( \mathbf{v} \) inside a rectangular box of side lengths \( L_x, L_y, L_z \) with reflecting walls.

The Hamiltonian for the particle in the box is:

\[
H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m},
\]

where \( p_x, p_y, p_z \) are the momenta in the directions parallel to the walls of the box.

If the box is large enough, the classical trajectory of the particle is ergodic, meaning that it fills the phase space uniformly.

Here is a scenario:

If the box is large enough, the particle will follow a chaotic trajectory, bouncing off the walls in a seemingly random fashion.

In this case, the particle's path is not predictable, and it fills the entire phase space over long periods of time.

For example, consider a particle of mass \( m \) and initial velocity \( \mathbf{v} \) in a box with side lengths \( L_x, L_y, L_z \). The particle's path will be chaotic, and it will eventually fill the entire box.

In classical mechanics, the paths are distinguishable, but in quantum mechanics, they are indistinguishable.

So in classical mechanics, the paths are distinguishable, but can sentimental.

And we get the same as (A) is 0.
So now let's use \( N! \) and \( \sqrt{S} \) then is reduced by \( -k \ln N! \)
so instead of Eq. (A) we have

\[
S(E, V, N) = Nk \left[ \frac{3}{2} + \ln \left\{ \frac{V}{N \sigma} \left( \frac{4 \pi m E}{3N} \right)^{3/2} \right\} \right] - k \ln N!
\]

For \( N \gg 1 \) (\( \ln N! \approx N \ln N - N \)) we get:

\[
S(E, V, N) = Nk \left[ \frac{3}{2} + \ln \left\{ \frac{V}{N \sigma} \left( \frac{4 \pi m E}{3N} \right)^{3/2} \right\} \right]
\]

\[
V_{\text{mag}} \frac{E}{2} = 3 NkT
\]

\[
S(T, V, N) = Nk \left[ \frac{3}{2} + \ln \left\{ \frac{V}{N \sigma} \left( \frac{2 \pi m kT}{N} \right)^{3/2} \right\} \right]
\]

Now for different gases \( S_{\text{total}} = S_{a}^{(0)} + S_{b}^{(0)} \); \( S_{\text{total}}^{(a)} = S_{a}^{(a)} + S_{b}^{(a)} \)

\[
\Delta S = N_{a}k \ln \left\{ \frac{V_{a} + V_{b}}{V_{a}} \right\} + N_{b}k \ln \left\{ \frac{V_{a} + V_{b}}{V_{b}} \right\}
\]

same as before

But for identical gases \( S_{\text{total}}^{(0)} = S(T, V_{a} + V_{b}, N_{a} + N_{b}) \)

\[
\Delta S = (N_{a} + N_{b}) k \left[ \frac{3}{2} + \ln \left\{ \frac{V_{a} + V_{b}}{(N_{a} + N_{b}) \sigma} \left( \frac{2 \pi m kT}{N_{a} + N_{b}} \right)^{3/2} \right\} \right]
\]

\[
- N_{a}k \left[ \frac{3}{2} + \ln \left\{ \frac{V_{a}}{N_{a} \sigma} \left( \frac{2 \pi m kT}{N_{a}} \right)^{3/2} \right\} \right]
- N_{b}k \left[ \frac{3}{2} + \ln \left\{ \frac{V_{b}}{N_{b} \sigma} \left( \frac{2 \pi m kT}{N_{b}} \right)^{3/2} \right\} \right]
\]

The pressure and temperature do not change during the mixing process so

\[
\frac{V_{a}}{N_{a}} = \frac{V_{b}}{N_{b}} = \frac{V_{a} + V_{b}}{N_{a} + N_{b}}
\]

and \( \Delta S = 0 \) as it should be; so the Gibbs factors \( \sqrt{N!} \) is indeed

the correct recipe for avoiding the Gibbs paradox.
We can see that as the increase with energy or with the radius of the sphere. The number of microstates \( \Omega \) of a given \( E \) is just the number of states.

\[
\Omega = \frac{E^3}{h^3}
\]

The total energy is given by

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

Single-particle states for \( q \) on this sphere are possible with angular m.m. quantum numbers \( \ell = \pm \ell \).}

Particle states of a particle is fixed by \( N \times \int \frac{d^3 \mathbf{p}}{p^3} \). (instead of \( \ell = 0 \) and \( p \)).

\[
E_{\text{min}} = \frac{h^2}{8m} \left( \frac{1}{\ell^2} + \frac{1}{\ell^2} \right) = \frac{1}{2} m \left( \frac{1}{\ell^2} + \frac{1}{\ell^2} \right)
\]

With the corresponding energy

\[
\ell/\ell = 1, 2, 3, ...
\]

Consider a particle in a cubic box of length \( L \). The one-particle states have the wavefunction

\[
\psi_n(x,y,z) = A \sin \pi x / L \sin \pi y / L \sin \pi z / L
\]
Example 3 particles \((N = 3)\) \(\rightarrow\) we have 9 quantum numbers \((n_1, \ldots, n_9)\).

If \(n_i = 1\) lowest state

\(\mathcal{N}_1\) occurs 9 times

\[
E^* = 8\pi^2 m L^2 \frac{E}{h^2} \quad E^* = 9 = 9 \times 1^2, \quad \ell = 1; \text{ configuration } (1)^9
\]

new variable \(\alpha = (n_1^2 + n_2^2 + n_3^2)\)

"dimensionless energy"

The next higher state is reached if one quantum number has the value of 2 while the others remain at value 1.

\[
E^* = 8 \times 1^2 + 1 \times 2^2 = 12; \quad \ell = 9 \quad \text{since each of the 9 quantum numbers can assume the value 2.}
\]

Higher states of \(E^*\):

\[
E^* = 15 = 7 \times 1^2 + 2 \times 2^2 \quad \ell = 3; \quad \text{configuration } (1)^7 (2)^2
\]

\[
E^* = 17 = 8 \times 1^2 + 1 \times 3^2 \quad \ell = 9 \quad (1)^8 (2)^1 (3)^1
\]

\[
E^* = 18 = 6 \times 1^2 + 3 \times 2^2 \quad \ell = 84 \quad (1)^6 (2)^3
\]

We see that \(\ell\) is a very irregular function of \(E^*\) (sometimes there is 36 states, sometimes 9 states).

But in general \(\ell\) increases with energy.
In reality, however, it is impossible to fix the total energy of a closed system
so we want to average over \( \Delta E \).

Number of all microstates in the interior of the energy sphere:

\[
\sum (E, V, N) = \sum \mathcal{N}(E', V, N) \]

\( \Sigma \) is a step function.
We denote \( \bar{\Sigma} \) as a mean of \( \Sigma \).

The mean number of states per energy interval:

\[
g(E, V, N) = \frac{\partial}{\partial E} \bar{\Sigma}(E, V, N) \quad \text{(this is an analogy with classical calculation)}
\]

What is \( \bar{\Sigma} \)? \( \bar{\Sigma} \), a volume of octant, 

\[
\bar{\Sigma}(E, V, N) = \frac{\text{Volume}}{\text{Unit cube}} = 1
\]

\[
g(E, V, N) = \frac{\partial \bar{\Sigma}}{\partial E} = \left( \frac{V}{\hbar} \right)^N \frac{(2\pi \hbar)^{3N/2}}{\Gamma(3N/2)} E^{3N/2-1}
\]

\( g \) : mean number of states per energy interval \( \Delta E \)

The mean number of states of energy \( E \), \( \bar{\mathcal{N}}(E) \) is

\[
\bar{\mathcal{N}}(E) = g(E) \Delta E
\]
Using $E^* = 8mE_L^2/h^2$

$$\bar{J}_c(E^*) = \left( \frac{V}{h^3} \right)^N \frac{(2\pi m E)^{3/2}}{\Gamma(3N/2)} \left( \frac{\hbar^2}{V^{3/3} 8m E^*} \right)^{3N/2} \Delta E^*$$

$$= \frac{\pi^{3/2}}{\Gamma(3N/2)} \frac{1}{2^{3N}} \frac{E^{3N/2}}{E^*} \Delta E^*$$

Considering $\Delta E^* \ll 1$ and $N \gg$

$$\bar{J}_c(E^*) \propto \frac{\pi^{3/2}}{\Gamma(3N/2)} \frac{1}{2^{3N}} E^{3N/2}$$

or

$$\bar{J}_c(E) \propto \left( \frac{V}{h^3} \right)^N \frac{(2\pi m E)^{3N/2}}{\Gamma(3N/2)}$$

We need to include the factor $1/N!$ the Gibbs correction factor because we counted the particles as distinguishable.

$$S = k \ln N$$

with the Stirling formula $\ln \Gamma(n) \propto (n-1) \ln(n-1) - (n-1) + n \ln n - n$

we get for the absolute entropy of an ideal gas:

$$S(E, V, N) = Nk \left[ \frac{S}{2} + \ln \left( \frac{V}{N^3 h^3} \right) \left( \frac{2\pi m E}{3N} \right)^{3/2} \right]$$ (I)

So $S = \frac{h^3}{N}$

Eq. (I) is called the Sackur-Tetrode equation.
So now the prescription for the calculation of the absolute entropy of a classical system, including the Gibbs correction, is:

\[ S(E, V, N) = k \ln \Omega(E, V, N) \]

\[ \Omega = \omega(E, V, N) E \quad ; \quad \omega(E) = \frac{\partial \Sigma(E)}{\partial E} \]

\[ \Sigma(E) = \frac{1}{N! \hbar^3} \int_{H < E} d^3 p \int \frac{d^3 q}{\mathcal{V}(E)} \]

we obtain the the number of quantum states

**Exercise:** Equations of State of the Ideal Gas

Use Eq. (1) and re-arrange it such that

\[ E(S, V, N) = \frac{3}{2} k T \frac{N^{5/3}}{4 \pi m v^{2/3}} \exp \left\{ \frac{2 S - 5}{3 Nk} \right\} \]

\[ dE = TdS - pdV + \mu dN \]

\[ T = \frac{\partial E}{\partial S} \bigg|_{N,V} \]

\[ -p = \frac{\partial E}{\partial V} \bigg|_{N} \]

\[ \mu = \frac{\partial E}{\partial N} \bigg|_{S,V} \]
Free energy: \[ F = E - TS \]

\[ C_v = \frac{\partial E}{\partial T} \bigg|_V \]

\[ C_p = \frac{\partial H}{\partial T} = \frac{\partial}{\partial T} (E + pV) \bigg|_V, \quad \alpha = \frac{\lambda}{V} \frac{\partial V}{\partial T} \bigg|_p \]

Show that: \[ C_p = C_v + TV\alpha^2 \frac{k}{k} \]

\[ k = -\frac{1}{V} \frac{\partial V}{\partial p} \bigg|_T \]