4. Classical phase space

4.1. Phase space and probability density

We consider a system of N particles in a d-dimensional space. Canonical coordinates and momenta

$$
\begin{aligned}
q &= (q_1, \ldots, q_{dN}) \\
p &= (p_1, \ldots, p_{dN})
\end{aligned}
$$

determine exactly the microscopic state of the system. The *phase space* is the $2dN$-dimensional space $\{(p, q)\}$, whose every point $P = (p, q)$ corresponds to a possible state of the system.

A *trajectory* is such a curve in the phase space along which the point $P(t)$ as a function of time moves. Trajectories are determined by the classical equations of motion

$$
\begin{aligned}
\frac{dq_i}{dt} &= \frac{\partial H}{\partial p_i} \\
\frac{dp_i}{dt} &= -\frac{\partial H}{\partial q_i},
\end{aligned}
$$

where

$$
\begin{aligned}
H &= H(q_1, \ldots, q_{dN}, p_1, \ldots, p_{dN}, t) \\
&= H(q, p, t) = H(P, t)
\end{aligned}
$$

is the Hamiltonian function of the system.

The trajectory is *stationary*, if H does not depend on time: trajectories starting from the same initial point P are identical.

Trajectories cannot cross: if trajectories meet at a point, they must be identical!

Let $F = F(q, p, t)$ be a property of the system. Now

$$
\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F, H\},
$$

where $\{F, G\}$ stands for Poisson brackets

$$
\{F, G\} \equiv \sum_i \left(\frac{\partial F}{\partial q_i} \frac{\partial G}{\partial p_i} - \frac{\partial G}{\partial q_i} \frac{\partial F}{\partial p_i} \right).
$$

We define the *volume measure of the phase space*

$$
d\Gamma = \prod_{i=1}^{dN} \frac{dq_i dp_i}{h} = h^{-dN} dq_1 \cdots dq_{dN} dp_1 \cdots dp_{dN}.
$$

Here $h = 6.62608 \cdot 10^{-34}$Js is the Planck constant. (Often $d\Gamma$ has $1/N!$ in front to remove degeneracy caused by identical particles.)

Note: $[dq\, dp] =$ Js, so $d\Gamma$ is dimensionless.

Note: In classical dynamics the normalization is irrelevant. In quantum mechanics, it is natural to choose $h =$ Planck constant.

Note: $\Delta_0\Gamma = 1$ corresponds to the smallest possible volume element of the phase space where a point representing the system can be localized in accordance with the QM uncertainty principle. The volume $\Delta\Gamma = \int d\Gamma$ is then roughly equal to the number of quantum states in the part of the space under consideration.

The *ensemble* or *statistical set* consists, at a given moment, of all those phase space points which correspond to a given macroscopic system.

Corresponding to a *macro(scopic) state* of the system there are thus a set of *micro(scopic) states* which belong to the ensemble with the probability $\rho(P)\, d\Gamma$. $\rho(P)$ is the *probability density* which is normalized to unity:

$$
\int d\Gamma\, \rho(P) = 1,
$$

and it gives the local density of points in (q, p)-space at time t.

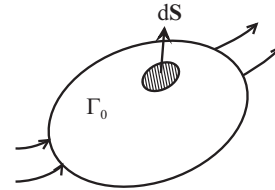The statistical average, or the ensemble expectation value, of a measurable quantity $f = f(P)$ is

$$
\langle f \rangle = \int d\Gamma\, f(P)\rho(P).
$$

We associate every phase space point with the velocity field

$$
\boldsymbol{V} = (\dot{q}, \dot{p}) = \left(\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q} \right).
$$

The probability current is then $\boldsymbol{V}\rho$. The probability weight of an element Γ_0 evolves then like

$$
\frac{\partial}{\partial t} \int_{\Gamma_0} \rho\, d\Gamma = -\int_{\partial\Gamma_0} \boldsymbol{V}\rho \cdot d\boldsymbol{S}.
$$

Because

$$
\int_{\partial\Gamma_0} \boldsymbol{V}\rho \cdot d\boldsymbol{S} = \int_{\Gamma_0} \nabla \cdot (\boldsymbol{V}\rho)\, d\Gamma,
$$

we get in the limit $\Gamma_0 \to 0$ the **continuity equation**

$$
\frac{\partial}{\partial t} \rho + \nabla \cdot (\boldsymbol{V}\rho) = 0.
$$

According to the equations of motion

$$
\begin{aligned}
\dot{q}_i &= \frac{\partial H}{\partial p_i} \\
\dot{p}_i &= -\frac{\partial H}{\partial q_i}
\end{aligned}
$$

we have

$$
\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0,
$$

so we end up with the **incompressibility condition** (sourceless)

$$
\nabla \cdot \boldsymbol{V} = \sum_i \left[\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right] = 0.
$$

From the continuity equation we get then

$$
\begin{aligned}
0 &= \frac{\partial \rho}{\partial t} + \nabla \cdot (\boldsymbol{V}\rho) \\
&= \frac{\partial \rho}{\partial t} + \rho \nabla \cdot \boldsymbol{V} + \boldsymbol{V} \cdot \nabla \rho \\
&= \frac{\partial \rho}{\partial t} + \boldsymbol{V} \cdot \nabla \rho.
\end{aligned}
$$

When we employ the **convective time derivative**

$$
\begin{aligned}
\frac{d}{dt} &= \frac{\partial}{\partial t} + \boldsymbol{V} \cdot \nabla \\
&= \frac{\partial}{\partial t} + \sum_i \left(\dot{q}_i \frac{\partial}{\partial q_i} + \dot{p}_i \frac{\partial}{\partial p_i} \right),
\end{aligned}
$$

the continuity equation can be written in the form known as the *Liouville theorem*

$$
\boxed{\frac{d}{dt}\,\rho(P(t),t) = 0.}
$$

Thus, the points in the phase space move like an incompressible fluid, and the local probability density ρ remains constant during evolution. Different points naturally can have different ρ.

4.2. Flow in phase space

The *(constant) energy surface* Γ_E is the manifold determined by the equation

$$
H(q,p) = E.
$$

If the energy is a constant of motion, every phase point $P^i(t)$ moves on a certain energy surface Γ_{Ei}, of dim. $(2Nd-1)$.
The expectation value of the energy of the system

$$
E = \langle H \rangle = \int d\Gamma \, H\rho
$$

is also a constant of motion.
The volume of the energy surface is

$$
\Sigma_E = \int d\Gamma_E = \int d\Gamma \, \delta(H(P) - E).
$$

The volume of the phase space is

$$
\int d\Gamma = \int_{-\infty}^{\infty} dE \, \Sigma_E.
$$

Let us consider the time evolution of a surface element $\Delta\Gamma_E$ of an energy surface.

Non-ergodic flow: In the course of time the element $\Delta\Gamma_E$ traverses only a part of the whole energy surface Γ_E.

Examples: periodic motion; presence of other constants of motion.

Ergodic flow: Almost all points of the surface Γ_E are sometimes arbitrarily close to any point in $\Delta\Gamma_E$.

$\Leftrightarrow$

The flow is ergodic if $\forall f(P)$, $f(P)$ "smooth enough",

$$
\bar{f} = \langle f \rangle_E
$$

holds. Here $\bar{f}$ is the time average

$$
\bar{f} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt \, f(P(t))
$$

and $\langle f \rangle_E$ the energy surface expectation value

$$
\langle f \rangle_E = \frac{1}{\Sigma_E} \int d\Gamma_E \, f(P).
$$

We define the *microcanonical ensemble* so that its density distribution is

$$
\boxed{\rho_E(P) = \frac{1}{\Sigma_E} \delta(H(P) - E).}
$$

Every point of the energy surface belongs with the same probability to the microcanonical ensemble.
The microcanonical ensemble is stationary, i.e. $\frac{\partial \rho_E}{\partial t} = 0$ and the expectation values over it temporal constants.
The **mixing flow** is such an ergodic flow where the points of an energy surface element $d\Gamma_E$ disperse in the course of time all over the energy surface. If $\hat{\rho}_E(P,t)$ is an arbitrary non stationary density distribution at the moment $t = t_0$, then

$$
\lim_{t \to \infty} \hat{\rho}_E(P,t) = \frac{1}{\Sigma_E} \delta(H(P) - E) = \rho_E(P)
$$

and

$$
\begin{aligned}
\lim_{t \to \infty} \langle f \rangle &= \lim_{t \to \infty} \int d\Gamma \, \hat{\rho}_E(P,t) f(P) \\
&= \int d\Gamma \, f(P) \rho_E(P) \\
&= \langle f \rangle_E
\end{aligned}
$$

i.e. the density describing an arbitrary (non equilibrium) state evolves towards a microcanonical ensemble under mixing flow.
Liouville theorem (volume element(s) are conserved) + mixing: a phase space infinitesimal volume element becomes infinitely stretched and folded and is distributed over the full energy surface.

4.3. Microcanonical ensemble and entropy

If the total energy of a macroscopic system is known exactly and it remains fixed, the equilibrium state can be described by a microcanonical ensemble. The corresponding probability density is

$$
\rho_E(P) = \frac{1}{\Sigma_E} \delta(H(P) - E).
$$

For a convenience we allow the energy to have some "tolerance" and define

$$\rho_{E,\Delta E}(P) = \frac{1}{Z_{E,\Delta E}} \theta(E + \Delta E - H(P))\theta(H(P) - E).$$

Here the normalization constant

$$Z_{E,\Delta E} = \int d\Gamma\, \theta(E + \Delta E - H(P))\theta(H(P) - E)$$

is the *microcanonical state sum* or *partition function*. $Z_{E,\Delta E}$ is the number of states contained in the energy slice $E < H < E + \Delta E$ (see the volume measure of the phase space). In the microcanonical ensemble the probability is distributed evenly in every allowed part of the phase space.

Entropy

We define *statistical entropy* as the quantity (depending on ρ) which is a) maximized for a physical ensemble and b) is an extensive quantity, in order to connect to the laws of thermodynamics. The maximization of the entropy determines the physical distribution ρ. The *Gibbs entropy*

$$\boxed{S = -k_B \int d\Gamma\, \rho(P) \ln \rho(P)}$$

has these properties, as we shall show shortly.
Let $\Delta\Gamma_i$ the volume of the phase space element i and ρ_i the average probability density in i. The state of the system is, with the probability

$$p_i = \rho_i \Delta\Gamma_i,$$

in the element i and

$$\sum p_i = 1.$$

We choose the sizes of all elements to be smallest possible, i.e. $\Delta\Gamma_i = 1$. Then

$$
\begin{aligned}
S &= -k_B \sum_i \Delta\Gamma_i \rho_i \ln \rho_i = -k_B \sum_i \rho_i \Delta\Gamma_i \ln \rho_i \Delta\Gamma_i \\
&= -k_B \sum_i p_i \ln p_i,
\end{aligned}
$$

since $\ln \Delta\Gamma_i = 0$. If ρ is smooth in the range $\Delta\Gamma = W$ we have

$$\rho = \frac{1}{W},$$

so that

$$S = -k_B \frac{1}{W} \ln \frac{1}{W} \int d\Gamma.$$

We end up with the *Boltzmann entropy*

$$\boxed{S = k_B \ln W.}$$

Here W is the *thermodynamic probability*: the number of all those states that correspond to the macroscopic state of the system.

A) Let us now show that the maximisation of the Gibbs entropy gives us microcanonical ensemble, when the energy of the system is restricted to $(E, E + \Delta E)$:

$$
\begin{aligned}
\delta S &= -k_B \int_{\Delta\Gamma_E} d\Gamma(\delta\rho \ln \rho + \rho\, \delta \ln \rho) \\
&= -k_B \int_{\Delta\Gamma_E} d\Gamma \delta\rho(\ln \rho + 1) = 0.
\end{aligned}
$$

Because $\delta 1 = \int d\Gamma \delta\rho = 0$, above condition is satisfied if $\ln \rho =$const. or $\rho(P) =$const., when $P \in \Delta\Gamma_E$.
S is indeed maximum:

$$
\begin{aligned}
\delta^2 S &= -k_B \int_{\Delta\Gamma_E} d\Gamma \frac{1}{2}(\delta\rho)^2 \frac{\partial^2(\rho \ln \rho)}{\partial\rho^2} \\
&= -k_B \int_{\Delta\Gamma_E} d\Gamma \frac{1}{2}(\delta\rho)^2 \frac{1}{\rho} \leq 0.
\end{aligned}
$$

B) Additive: if we consider 2 separate systems, the joint probability distribution is $\rho_{12}(P_1, P_2) = \rho_1(P_1)\rho_2(P_2)$, and $d\Gamma_{12} = d\Gamma_1 d\Gamma_2$.

$$
\begin{aligned}
S_{12} &= -k_B \int d\Gamma_{12}\, \rho_{12} \ln \rho_{12} \\
&= -k_B \int d\Gamma_1 d\Gamma_2\, \rho_1 \rho_2(\ln \rho_1 + \ln \rho_2) \\
&= -k_B \left(\int d\Gamma_1 \rho_1 \ln \rho_1 + \int d\Gamma_2 \rho_2 \ln \rho_2 \right) = S_1 + S_2
\end{aligned}
$$

Entropy and disorder

Maximizing the entropy $S \Rightarrow$ minimization of the information about the system. In a microcanonical ensemble complete lack of information (besides the total energy) means that all states with the same total energy are equally probable.
Conversely, losing the information (= non-trivial probability distribution) $\Rightarrow$ maximizing the entropy.
Maximum of entropy $\Leftrightarrow$ maximum of disorder.

5. Quantum mechanical ensembles

5.1. Quantum mechanical concepts

States and Hilbert space

Quantum mechanical states (using Dirac notation, $|\psi\rangle$) of a system form a Hilbert space $\mathcal{H}$, which is a *linear* vector space with *inner (scalar) product* and associated *norm*.
Linearity: if $|\psi\rangle, |\psi'\rangle \in \mathcal{H}$, then $|c\psi + c'\psi'\rangle \in \mathcal{H}$, for $c, c' \in C$.
The inner product $\langle \cdot | \cdot \rangle$ is a mapping $\mathcal{H} \otimes \mathcal{H} \to C$, with

$$\langle \psi | \phi \rangle = \langle \phi | \psi \rangle^*$$
$$\langle \psi | \alpha\phi + \alpha'\phi' \rangle = \alpha \langle \psi | \phi \rangle + \alpha' \langle \psi | \phi' \rangle$$
$$\langle \phi | \phi \rangle \geq 0$$
$$\langle \phi | \phi \rangle = 0 \Leftrightarrow \phi = 0$$

The norm is $||\phi|| = \langle \phi | \phi \rangle^{1/2}$.
Time evolution is defined by Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle .$$

If H does not depend on t, the formal solution is

$$|\psi(t)\rangle = \exp[-\frac{i}{\hbar} H(t - t_0)] |\psi(t_0)\rangle$$

Operators, eigenvalues and trace

- Physical observable $\to$ quantum mechanical operator A, $|\psi\rangle \to A |\psi\rangle$.

- Conjugated operator $A^\dagger$:

$$\langle \psi | A^\dagger | \phi \rangle = \langle \phi | A | \psi \rangle^*$$

- Eigenvalue and -vector: $A |a\rangle = a |a\rangle$. If $A^\dagger = A$ (hermitean), a is real. Eigenvectors form a complete (orthonormal) basis of the Hilbert space.

- Basis of $\mathcal{H}$: any vector can be written as a sum of eigenvectors of some operator:

$$|\psi\rangle = \sum_n \psi_n |n\rangle \quad \text{or} \quad |\psi\rangle = \int da \psi_a |a\rangle$$

depending on whether the eigenvectors form a discrete or continuous set. Here we shall use the former notation.

- Identity operator $I = \sum_n |n\rangle \langle n|$.
Here $P_n = |n\rangle \langle n|$ is the *projection operator* to vector $|n\rangle$.

- Spectral representation of operator: if $A |n\rangle = a_n |n\rangle$,

$$A = \sum_n |n\rangle a_n \langle n| .$$

- Unitary operator U: $UU^\dagger = U \dagger U = 1$. Thus, $||U\psi|| = ||\psi||$ and U correspond to a rotation in Hilbert space, $|n'\rangle = U |n\rangle$. Unitary transformations correspond to a change of eigenbasis.

- Trace of an operator:

$$\text{Tr}\, A = \sum_n \langle n | A | n \rangle = \sum_k a_k ,$$

where the first form is independent of the choice of basis *ketvn*, and the second is obtained by choosing eigenvectors of A.

$$\text{Tr}\, AB = \text{Tr}\, BA, \quad \text{Tr}\, U^\dagger A U = \text{Tr}\, A$$

- If the quantum mechanical state of the system is $|\psi\rangle$, the projection operator corresponding to the state is

$$\rho = |\psi\rangle \langle \psi| .$$

Now expectation values of observables are

$$\langle A \rangle = \text{Tr}\, \rho A .$$

Thus, trace in quantum mechanics corresponds to phase space integral in classical mechanics:

$$\text{Tr}\, A \Longleftrightarrow \int d\Gamma A(q, p).$$

Systems of identical particles

Let $\mathcal{H}^1$ be a Hilbert space for one particle. Then the Hilbert space for N particles is

$$\mathcal{H}^N = \underbrace{\mathcal{H}^1 \otimes \mathcal{H}^1 \otimes \cdots \otimes \mathcal{H}^1}_{N \text{ copies}}.$$

If, for example, $|\boldsymbol{x}_i\rangle \in \mathcal{H}^1$ is a position eigenstate the N-particle state can be written as

$$|\Psi\rangle = \int \int \cdots \int d\boldsymbol{x}_1 \cdots d\boldsymbol{x}_N |\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N\rangle \psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N),$$

where

$$|\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N\rangle = |\boldsymbol{x}_1\rangle \otimes |\boldsymbol{x}_2\rangle \otimes \cdots \otimes |\boldsymbol{x}_N\rangle .$$

There are two kinds of particles:

Bosons The wave function is symmetric with respect to the exchange of particles.

Fermions The wave function is antisymmetric with respect to the exchange of particles.

Note: If the number of translational degrees of freedom is less than 3, e.g. the system is confined to a two dimensional plane, the phase gained by the many particle wave function under the exchange of particles can be other than ± 1. Those kind of particles are called *anyons*.

The Hilbert space of a many particle system is not the whole $\mathcal{H}^N$ but its subspace:

$$\mathcal{H} = \begin{cases} \mathcal{SH}^N & = & \mathcal{S}(\mathcal{H}^1 \otimes \cdots \otimes \mathcal{H}^1) & \text{symm.} \\ \mathcal{AH}^N & = & \mathcal{A}(\mathcal{H}^1 \otimes \cdots \otimes \mathcal{H}^1) & \text{antisymm.} \end{cases}$$

Fock space

Fock space enables us to describe many-particle quantum states with creation and annihilation operators. Formally, Fock space is the direct sum of all (anti)symmetrized N-particle spaces:

$$\mathcal{F} = \mathcal{H}_p^{(0)} \oplus \mathcal{H}_p^{(1)} \oplus \ldots \mathcal{H}_p^{(N)} \oplus \ldots$$

with $\mathcal{H}_p^{(N)} = \mathcal{SH}^{(N)}$ for bosons ($\mathcal{A}$ for fermions). Fock space wave function in coordinate representation is a vector

$$\Psi = (C, \psi_1(\xi_1^{(1)}), \psi_2(\xi_1^{(2)}, \xi_2^{(2)}), \ldots)$$

where C is a complex number, $\xi_i = (x_i, s_i)$ (s_i labels the spin and other internal degrees of freedom), and ψ_N is a fully (anti)symmetric wave function.

Fock space normalized N-particle states can be written as

$$|n_1, n_2, \ldots, n_\ell, \ldots\rangle$$

where $n_1, \ldots$ are 1-particle state occupation numbers. In N-particle state $\sum_\ell n_\ell = N$. In coordinate space representation these states can be written as

$$\langle \xi_1, \ldots, \xi_N | n_1, \ldots \rangle = \frac{1}{\sqrt{N! \prod_i n_i!}}$$
$$\times \sum_{P(\xi_1, \ldots \xi_N)} \epsilon_P \langle \xi_1 | \ell_1 \rangle \ldots \langle \xi_N | \ell_N \rangle,$$

where $\ell_1, \ell_2, \ldots \ell_N$ contain the 1-particle indices of the N-particle state; i.e. it contains n_1 times 1, n_2 times 2 etc. Sum is over all permutations P of N coordinates, and ϵ_P is 1 for bosons, and ± 1 for fermions for even/odd permutations (Slater determinant).

We can define creation and annihilation operators:

$$a_\ell |n_1, \ldots, n_\ell, \ldots\rangle = (-1)^{P_\ell} \sqrt{n_\ell} |n_1, \ldots, n_\ell - 1, \ldots\rangle$$
$$a_\ell^\dagger |n_1, \ldots, n_\ell, \ldots\rangle = (-1)^{P_\ell} \sqrt{1 \pm n_\ell} |n_1, \ldots, n_\ell + 1, \ldots\rangle$$

with upper/lower sign for bosons/fermions, and $P_\ell = 0$ for bosons, and

$$P_\ell = \sum_{k < \ell} n_k$$

for fermions.

The symmetry properties and normalization imply for bosons

$$[a_l, a_k] = [a_l^\dagger, a_k^\dagger] = 0, \qquad [a_l, a_k^\dagger] = \delta_{l,k},$$

and for fermions

$$\{a_l, a_k\} = \{a_l^\dagger, a_k^\dagger\} = 0, \qquad \{a_l, a_k^\dagger\} = \delta_{l,k},$$

($[A, B] \equiv AB - BA$, $\{A, B\} = AB + BA$).

Occupation number operator of state $|\ell\rangle$ is

$$\hat{n}_\ell = a_\ell^\dagger a_\ell$$

with eigenvalues $0, 1, 2, \ldots$ for bosons and $0, 1$ for fermions. Thus, antisymmetry of fermion states $\Rightarrow$ *Pauli exclusion principle.*

For non-interacting systems the Hamilton operator can be expressed as

$$H = \sum_\ell E_\ell \hat{n}_\ell$$

when the 1-particle states are eigenstates of H.

5.2. Density operator and entropy

Let $\mathcal{H}$ be the Hilbert space a many particle system. *The probability measure* tells us the weight that a state $|\psi\rangle \in \mathcal{H}$ represents a system with given macroscopical properties. The density operator ρ tells us the probability of a given state, $p_\phi = \langle \phi | \rho | \phi \rangle$.

Ensemble

The quantum mechanical ensemble or statistical set can be defined in a similar fashion as in classical mechanics. Statistical **macrostate** is the state determined by macroscopic parameters, **microstate** is a particular QM state in Hilbert space.

Pure state and mixed state

If the quantum mechanical state of a system is fully known it is in a **pure state**. In this case the density operator is a (pure) projection operator

$$\rho = |\Psi\rangle \langle \Psi|$$

Statistical mechanics of a pure state reduces into normal quantum mechanics; for example $\langle A \rangle = \text{Tr} \, \rho A = \langle \Psi | A | \Psi \rangle$

Mixed state: only the probability p_i that the system is in state ψ_i is known. Density operator is, in orthonormal base,

$$\rho = \sum_n |\psi_n\rangle p_n \langle \psi_n|$$

Now $\text{Tr} \, \rho = 1$. Ensembe expectation values are

$$\langle A \rangle = \text{Tr} \, \rho A = \sum_i p_i \langle \psi_i | A | \psi_i \rangle = \sum_i p_i \langle A_i \rangle.$$

The a priori probability: if there is no knowledge of the actual state of the system every state in $\mathcal{H}$ can taken with equal weight. Then

$$\rho = \frac{1}{\mathcal{N}} \sum_n |n\rangle \langle n|,$$

where $\mathcal{N} = \dim \mathcal{H}$.

Properties of the density operator

Density operator can be any operator with properties

$$\begin{aligned} \rho^\dagger &= \rho \\ \langle \psi | \rho | \psi \rangle &\geq 0 \qquad \forall \, |\psi\rangle \in \mathcal{H} \\ \text{Tr} \, \rho &= 1. \end{aligned}$$

The density operator associates with every normalized $|\psi\rangle \in \mathcal{H}$ the probability

$$p_\psi = \text{Tr}\,\rho P_\psi = \langle\psi|\rho|\psi\rangle.$$

Since ρ is hermitean there exists an orthonormal basis $\{|\alpha\rangle\}$ for $\mathcal{H}$, where ρ is diagonal

$$\rho = \sum_\alpha p_\alpha |\alpha\rangle\langle\alpha|.$$

Here

$$0 \le p_\alpha \le 1$$

and

$$\sum p_\alpha = 1.$$

In this basis

$$\langle A\rangle = \text{Tr}\,\rho A = \sum_\alpha p_\alpha \langle\alpha|A|\alpha\rangle.$$

The equation of motion
Let us assume that the ensemble gives (and fixes) the probabilities p_α corresponding to the states $|\alpha\rangle$. Now

$$\rho(t) = \sum_\alpha p_\alpha |\alpha(t)\rangle\langle\alpha(t)|.$$

Since the state vectors satisfy the Schrödinger equations

$$i\hbar \frac{d}{dt} |\alpha(t)\rangle = H |\alpha(t)\rangle$$
$$-i\hbar \frac{d}{dt} \langle\alpha(t)| = \langle\alpha(t)| H,$$

we end up with the equation of motion

$$\boxed{i\hbar \frac{d}{dt} \rho(t) = [H, \rho(t)].}$$

It is easy to show that

$$\frac{d\langle A\rangle}{dt} = \left\langle \frac{\partial A}{\partial t} \right\rangle + \frac{1}{i\hbar} \langle[A, H]\rangle.$$

In a **stationary ensemble** the expectation values are independent on time, so $\dot\rho = 0$ or

$$[H, \rho] = 0.$$

This is possible e.g. when $\rho = \rho(H)$.

Entropy
The entropy is defined by

$$\boxed{S = -k_B \text{Tr}\,\rho \ln\rho.}$$

In a base where ρ is diagonal,

$$S = -k_B \sum_\alpha p_\alpha \ln p_\alpha.$$

Entropy has the properties

1. $S \ge 0$, because $0 \le p_\alpha \le 1$.

2. $S = 0$ corresponds to a pure state, i.e. $\exists\alpha:\ p_\alpha = 1$ and $p_{\alpha'} = 0\ \forall\alpha' \ne \alpha$.

3. If the dimension $\mathcal{N}$ of the Hilbert space $\mathcal{H}$ is finite, the entropy has a maximum when

$$\rho = \frac{1}{\mathcal{N}} I$$

or $p_\alpha = \frac{1}{\mathcal{N}}\ \forall |\alpha\rangle \in \mathcal{H}$. Then

$$S = k_B \ln\mathcal{N}.$$

Thus, in this case the entropy fully corresponds to classical Boltzmann entropy $S = k_B \ln W$.

4. The entropy is additive. If we have 2 (independent) systems, the total Hilbert space is

$$\mathcal{H}_{1+2} = \mathcal{H}_1 \otimes \mathcal{H}_2$$

and correspondingly

$$\rho_{1+2} = \rho_1 \otimes \rho_2.$$

If $\rho_i |\alpha^{(i)}\rangle = p_\alpha^{(i)} |\alpha^{(i)}\rangle$, then

$$\rho_{1+2} |\alpha^{(1)}, \beta^{(2)}\rangle = p_\alpha^{(1)} p_\beta^{(2)} |\alpha^{(1)}, \beta^{(2)}\rangle.$$

Now

$$\text{Tr}_{1+2} A = \sum_{\alpha,\beta} \langle\alpha^{(1)}, \beta^{(2)}|A|\alpha^{(1)}, \beta^{(2)}\rangle,$$

so that

$$\begin{aligned}
S_{1+2} &= -k_B \text{Tr}_{1+2}\rho_{1+2} \ln\rho_{1+2} \\
&= -k_B \sum_{\alpha,\beta} p_\alpha^{(1)} p_\beta^{(2)} (\ln p_\alpha^{(1)} + \ln p_\beta^{(2)}) \\
&= -k_B \sum_\alpha p_\alpha^{(1)} \ln p_\alpha^{(1)} - k_B \sum_\beta p_\beta^{(2)} \ln p_\beta^{(2)} \\
&= S_1 + S_2.
\end{aligned}$$

The properties of the statistical entropy above are equivalent to the thermodynamic entropy. This will be shown later.

5.3. Density of states
Let us denote

$$H |n\rangle = E_n |n\rangle,$$

so that

$$H = \sum_n E_n |n\rangle\langle n|.$$

If the volume V of the system is finite the spectrum is discrete and the states can be conveniently normalized like

$$\langle n|m\rangle = \delta_{n,m}.$$

Thermodynamic limit:

$$V \to \infty \text{ and } N \to \infty$$

6

so that N/V remains constant.

The cumulant function of states is defined as

$$J(E) = \sum_n \theta(E - E_n),$$

i.e. the value of J at the point E is the number of those states whose energy is less than E. *The density of states (function)* can be defined as

$$\omega(E) = \frac{dJ(E)}{dE} = \sum_n \delta(E - E_n),$$

since $d\theta(x)/dx = \delta(x)$. However, in macroscopic systems the energy levels are extremely closely spaced, and a more sensible definition for the density of states is

$$\omega(E) = \lim_{\Delta E \to 0} \frac{J(E + \Delta E) - J(E)}{\Delta E}$$

i.e. the number of states in the interval $(E, E + \Delta E)$, where we assume that we do not allow ΔE to become smaller than the interval between energy levels. Density of states becomes a smooth function when the intervals between energy levels $\to 0$ (volume $\to \infty$), as does $J(E)$. We can also write, using the Hamilton operator,

$$\begin{aligned} J(E) &= \operatorname{Tr} \theta(E - H) \\ \omega(E) &= \operatorname{Tr} \delta(H - E). \end{aligned}$$

$\omega(E)$ corresponds to the volume Γ_E of the energy surface of the classical phase space.

Example: 1. Free particle

Let us consider a free particle in a box of size $V = L^3$ with periodic boundary conditions. The Hamiltonian is

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

The eigenfunctions are the plane waves

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}},$$

where the wave vector $\boldsymbol{k} = \boldsymbol{p}/\hbar$ can acquire the values (periodicity)

$$\boldsymbol{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \ n_i \in Z, \ V = L^3.$$

The corresponding energy levels are

$$\epsilon_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}.$$

In the limit of large volume the summation can be transformed to the integration over the wave vector, using

$$\int dk = \sum \Delta k = \frac{2\pi}{L} \sum_n.$$

Thus,

$$\sum_{\boldsymbol{k}} = \int dN_{\boldsymbol{k}} = \frac{V}{(2\pi)^3} \int d^3\boldsymbol{k} = \frac{V}{h^3} \int d^3\boldsymbol{p}.$$

If the particle has spin S, it has $g = 2S + 1$ spin degrees of freedom. Then

$$\begin{aligned} J_1(E) &= g \int dN_{\boldsymbol{k}} \theta\left(E - \frac{p^2}{2m}\right) = g\frac{V}{h^3} 4\pi \int_0^p dp' p'^2 \\ &= g\frac{V}{h^3}\frac{4\pi}{3} p^3. \end{aligned}$$

So we get

$$\begin{aligned} J_1(E) &= \frac{2}{3}C_1 V E^{3/2} \\ \omega_1(E) &= C_1 V E^{1/2} \\ C_1 &= 2\pi g \left(\frac{2m}{h^2}\right)^{3/2}. \end{aligned}$$

Example: 2. Maxwell-Boltzmann gas

Let us consider N free particles. The total energy is

$$E = \sum_j \frac{p_j^2}{2m}$$

and the cumulant function

$$\begin{aligned} &J_N(E) \\ &= \int dN_{\boldsymbol{k}_1} \cdots \int dN_{\boldsymbol{k}_N} \theta\left(E - \frac{p_1^2}{2m} - \cdots - \frac{p_N^2}{2m}\right) \\ &= \int dE_1 \cdots \int dE_N \omega_1(E_1) \cdots \omega_1(E_N) \\ &\qquad \times \theta(E - E_1 - \cdots - E_N). \end{aligned}$$

Thus the corresponding density of states is

$$\begin{aligned} \omega_N(E) &= \frac{dJ_N(E)}{dE} \\ &= \int dE_1 \cdots dE_N \omega_1(E_1) \cdots \omega_1(E_N) \\ &\qquad \times \delta(E - E_1 - \cdots - E_N). \end{aligned}$$

We define the Laplace transforms

$$\begin{aligned} \Omega_1(s) &= \int_0^\infty dE\, e^{-sE} \omega_1(E) \\ \Omega_N(s) &= \int_0^\infty dE\, e^{-sE} \omega_N(E). \end{aligned}$$

Now

$$\begin{aligned} &\Omega_N(s) \\ &= \int_0^\infty dE_1 \cdots dE_N \omega_1(E_1) \cdots \omega_1(E_N) \\ &\quad \times \int_0^\infty dE\, e^{-sE} \delta(E - E_1 - \cdots - E_N) \\ &= \int_0^\infty dE_1 \cdots dE_N \omega_1(E_1)e^{-sE_1} \cdots \omega_1(E_N)e^{-sE_N} \\ &= [\Omega_1(s)]^N. \end{aligned}$$

Since

$$\begin{aligned} \Omega_1(s) &= \int_0^\infty dE\, e^{-sE} C_1 V E^{1/2} = C_1 V \, \Gamma(\tfrac{3}{2})\, s^{-3/2} \\ &= C_1 V \frac{1}{2}\sqrt{\pi} s^{-3/2} \end{aligned}$$

we have

$$\Omega_N(s) = (C_2 V)^N s^{-3N/2},$$

where

$$C_2 = \frac{1}{2}\sqrt{\pi}C_1 = g\left(\frac{2\pi m}{h^2}\right)^{3/2}.$$

Performing the inverse Laplace transforms we get

$$\omega_N(E) = \frac{1}{\Gamma(\frac{3}{2}N)}(C_2 V)^N E^{3/2N-1}.$$

Note: We ignored the permutation symmetry! Thus, for each N-particle states there are $N!$ permutations which are physically equivalent (unless the particles are all different). We can correct the density of states by dividing this by $N!$, which gives us so-called *Boltzmann counting.* Using this we obtain the classical ideal gas or Maxwell-Boltzmann gas theory (will be discussed later):

$$\omega_N(E) = \frac{1}{N!\Gamma(\frac{3}{2}N)}(C_2 V)^N E^{3/2N-1}.$$

Note: This does not take into account the quantum mechanical features of multiple occupation of 1-particle states (bosons, fermions).

Sidebar: inverse Laplace transform
Obviously, if $f(t) = t^\alpha$, then Laplace transform is

$$\int_0^\infty dt\, e^{-ts}t^\alpha = s^{-\alpha-1}\int_0^\infty dy e^{-y}y^\alpha = s^{-\alpha-1}\Gamma(\alpha+1)$$

Thus, if $\alpha = 3N/2 - 1$, we obtain the result for ω_N. Many standard function (inverse) Laplace transformations can be found tabulated (Arfken). More generally, inverse Laplace transforms can be calculated using complex plane integral (see Arfken, for example):

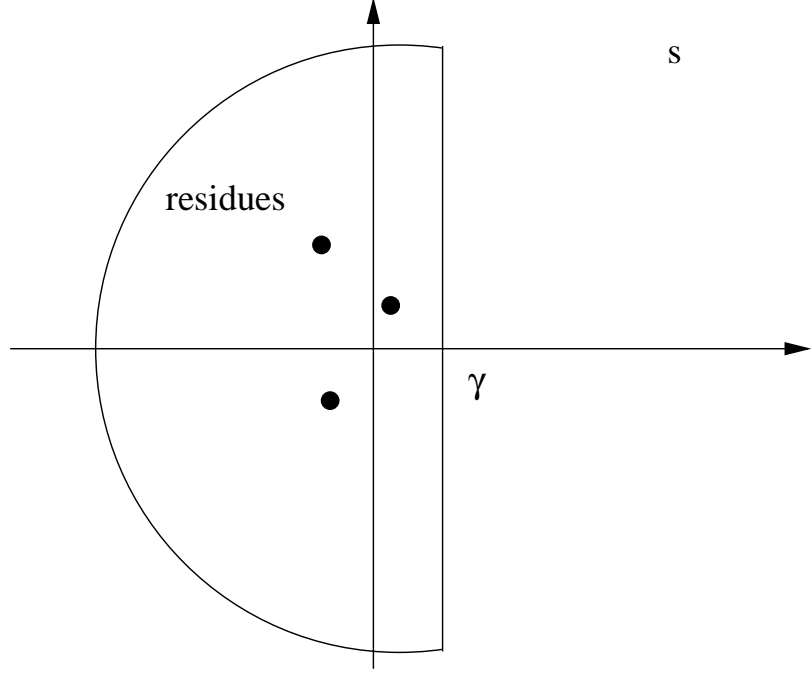$$f(t) = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} ds e^{st}\hat{f}(s)$$

where $\gamma \in R$ is chosen so that the Laplace transform

$$\hat{f}(s) = \int_0^\infty dt e^{-st}f(t)$$

exists when $s \geq \gamma$. It is easy to see that this is inverse Laplace:

$$\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} ds e^{st}\int_0^\infty dt' e^{-st'}f(t')$$

$$= \int_0^\infty dt' f(t')\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} ds e^{s(t-t')}$$

$$= \int_0^\infty dt' f(t')e^{\gamma(t-t')}\frac{1}{2\pi}\int_{-\infty}^\infty dy e^{iy(t-t')} = f(t)$$

The integral can be closed to the left on complex s-plane, and calculated by finding residues within the contour.

5.4. Energy, entropy and temperature
The density of states operator ρ enables us to calculate all thermodynamical properties of the system: for example the moments $\langle E^n \rangle$ and entropy S. We can also define temperature T from properties of ρ. For this we need to define microcanonical ensemble, in analogy with the classical mechanics way done earlier:

Microcanonical ensemble
We require that
a) energy is restricted between $(E, E + \Delta E)$, and
b) the entropy is maximized.
According to 5.2. this is satisfied when all states are equally likely, thus, the density of states operator is

$$\rho_E = \frac{1}{Z_E}\theta(E + \Delta E - H)\theta(H - E),$$

where

$$\begin{aligned} Z_E &= \text{Tr}\,\theta(E + \Delta E - H)\theta(H - E) \\ &= \text{Tr}\left[\theta(E + \Delta E - H) - \theta(E - H)\right] \\ &= J(E + \Delta E) - J(E) \end{aligned}$$

is *microcanonical partition function* or the number of states between $(E, E + \Delta E)$. When ΔE is small, we have

$$Z_E \approx \omega(E)\,\Delta E.$$

Entropy is

$$S_E = -k_B \text{Tr}\,\rho \ln \rho = k_B \ln Z_E.$$

Since Z_E is a positive integer, $S_E \geq 0$ holds. Furthermore we get

$$\begin{aligned} S_E &= k_B \ln[\omega(E)\,\Delta E] \\ &= k_B \ln \omega(E) + S_0, \end{aligned}$$

and we can write

$$S_E = k_B \ln \omega(E),$$

because $\ln \Delta E$ is non-extensive and negligible when V large. (This expression is slightly incorrect dimensionally; we should use $\ln(C\omega(E))$, where C has dimensions of energy.)

Note: As a matter of fact

$$\omega = \omega(E, V, N).$$

Temperature

According to thermodynamics we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}.$$

In the microcanonical ensemble we define the temperature T so that

$$\frac{1}{T} = k_B \frac{\partial}{\partial E} \ln \omega(E, V, N).$$

Denoting

$$\beta = \frac{1}{k_B T},$$

we have

$$\beta = \frac{\partial \ln \omega}{\partial E}.$$

Example: Maxwell-Boltzmann gas
Now

$$\omega_N \propto E^{3/2N-1},$$

so

$$\ln \omega_N = \frac{3}{2} N \ln E + \cdots$$

and

$$\beta = \frac{3N}{2E}$$

or we end up with the equation of state for 1-atomic ideal gas:

$$E = \frac{3}{2} k_B T N.$$

The thermodynamics of a quantum mechanical system can be derived from the density of states $\omega(E, V, N)$. In practice the density of states of a microcanonical ensemble (E and N constant) is difficult to calculate, due to the constraint in total E.

6. Equilibrium distributions

Microcanonical ensemble was discussed in the previous section. That is obtained by maximising entropy with the boundary condition $H = E =$ constant, N constant. Now we shall discuss *canonical* and *grand canonical* ensembles, which are obtained by maximizing entropy with boundary conditions $\langle H \rangle = E$, N const. for canonical ensemble (i.e. energy is allowed to fluctuate) and and $\langle H \rangle = E$, $\langle \hat{N} \rangle = N$ for grand canonical ensemble (i.e. both energy and particle number are allowed to fluctuate).

6.1. Canonical ensemble

Let us now maximise the entropy under the constraints

$$\begin{aligned}
\langle H \rangle &= \text{Tr}\,\rho H = E = \text{constant} \\
\langle I \rangle &= \text{Tr}\,\rho = 1.
\end{aligned}$$

Using Lagrange multipliers, we require that

$$\delta(S - \lambda \langle H \rangle - \lambda' \langle I \rangle) = 0,$$

where λ are λ' are multipliers. We get

$$\delta \text{Tr}\,(-k_B \rho \ln \rho - \lambda \rho H - \lambda' \rho) = \\ \text{Tr}\,(-k_B \ln \rho - k_B I - \lambda H - \lambda' I)\delta\rho = 0.$$

Since $\delta\rho$ is an arbitrary variation, we can solve for ρ and end up (after relabelling the constants) with the *canonical* or *Gibbs distribution*

$$\rho = \frac{1}{Z} e^{-\beta H},$$

where Z is the *canonical sum over states* (or *partition function*, which is determined from the condition $\text{Tr}\,\rho = 1$:

$$Z = \text{Tr}\, e^{-\beta H} = \sum_n e^{-\beta E_n} = \int dE\, \omega(E) e^{-\beta E}.$$

The constant β is yet undetermined! We shall show below that $\beta = 1/k_B T$.

Note: In the canonical ensemble the number of particles is constant, i.e.

$$Z = Z(\beta, V, N, \ldots).$$

The probability for the state ψ is

$$p_\psi = \text{Tr}\,\rho P_\psi = \frac{1}{Z} \langle \psi | e^{-\beta H} | \psi \rangle.$$

Partcularly, in the case of an eigenstate of the Hamiltonian,

$$H |n\rangle = E_n |n\rangle,$$

we have

$$p_n = \frac{1}{Z} e^{-\beta E_n}.$$

For one particle system we get *Boltzmann distribution*

$$p_\nu = \frac{1}{Z} e^{-\beta \epsilon_\nu}; \; Z = \sum_\nu e^{-\beta \epsilon_\nu}.$$

Here ϵ_ν is the one particle energy.

Entropy and temperature

Because in the canonical ensemble we have

$$\ln \rho = -\beta H - \ln Z,$$

the entropy will be

$$
\begin{aligned}
S &= -k_B \mathrm{Tr}\,\rho \ln \rho = -k_B \langle \ln \rho \rangle \\
&= k_B \beta E + k_B \ln Z.
\end{aligned}
$$

Here E is the expectation value of the energy

$$E = \langle H \rangle = \frac{1}{Z}\,\mathrm{Tr}\,H e^{-\beta H}.$$

Let us now calculate $\partial S / \partial E$. Note that the parameter β very well can depend on E! Thus, using the thermodynamical identity we can define T:

$$
\begin{aligned}
\frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)_{V,N} = k_B \beta + k_B E \beta' + k_B \frac{\partial \ln Z}{\partial E} \\
&= k_B(\beta + E\beta' - \beta' \mathrm{Tr}\,H e^{-\beta H}/Z) \\
&= k_B(\beta + E\beta' - \beta' \langle H \rangle) = k_B \beta
\end{aligned}
$$

where $\beta' = \partial \beta / \partial E$. Thus, we obtain the familiar relation

$$\beta = \frac{1}{k_B T}.$$

Free energy

The partition function is the central quantity, and all thermodynamic properties can be derived from it:

$$\frac{\partial Z}{\partial \beta} = -\mathrm{Tr}\,e^{-\beta H} H = -Z\langle H \rangle = -ZE$$

or

$$E = -\frac{\partial}{\partial \beta}\ln Z = k_B T^2 \frac{\partial \ln Z}{\partial T}.$$

Using the expression above we can write

$$S = k_B \frac{\partial}{\partial T}\left(T \ln Z\right).$$

Using the definition for the *Helmholtz free energy* $F = E - TS$, we get

$$\boxed{F = -k_B T \ln Z.}$$

With the help of this the density operator takes the form

$$\boxed{\rho = e^{\beta(F-H)}.}$$

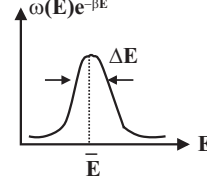Note that F is a number, H operator.

Fluctuations

The probability distribution of the energy E is

$$P(E) = \langle \delta(H-E) \rangle = \mathrm{Tr}\,\rho\,\delta(H-E).$$

This is normalized $\int dE P(E) = 1$, and we get the correct expectation values $\langle H^n \rangle = \int dE E^n P(E)$. Using canonical density ρ, we obtain

$$P(E) = \frac{1}{Z}\omega(E)e^{-\beta E}.$$

When the volume is large, this typcially has a well-defined maximum at $E = \bar{E} \equiv \langle H \rangle$.

Let us write the sum over states as

$$Z = \int dE\,\omega(E)e^{-\beta E} = \int dE\,e^{-\beta E + \ln \omega(E)}.$$

Now we can use the *saddle-point method* to calculate the sharply peaked integral: expand the exponent to second order

$$
\begin{aligned}
\ln \omega(E) - \beta E &= \\
\ln \omega(\bar{E}) &- \beta \bar{E} \\
+ \overbrace{\left(\left.\frac{\partial \ln \omega}{\partial E}\right|_{E=\bar{E}} - \beta\right)}^{=0,\ \text{maximum}}&(E - \bar{E}) \\
+ \frac{1}{2}\left.\frac{\partial^2 \ln \omega}{\partial E^2}\right|_{E=\bar{E}}&(E-\bar{E})^2 + \cdots.
\end{aligned}
$$

Linear term must vanish at $E = \bar{E}$:

$$\beta = \left.\frac{\partial \ln \omega}{\partial E}\right|_{E=\bar{E}} = \frac{1}{k_B}\left.\frac{\partial S(E)}{\partial E}\right|_{E=\bar{E}} = \frac{1}{k_B T(\bar{E})}$$

where we used the microcanonical entropy $S(E) = k_B \ln \omega(E)$ to obtain the microcanonical $T(\bar{E})$. Thus, the temperature of the heat bath in canonical ensemble $= T = T(\bar{E})$, the temperature of the microcanonical ensemble at energy $\bar{E} = \langle H \rangle_{\text{can.}}$. Actually,

$$\rho_{\beta,\text{can.}} = \int dE\,P(E,\beta)\,\rho_{E,\text{microcan.}}$$

and canonical ensemble can be thought as an ensemble of microcanonical ensembles. The 2nd order term in the Taylor series is

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{\partial T}{\partial E} = -\frac{1}{T^2 C_V},$$

so

$$Z \approx \omega(\bar{E})e^{-\beta \bar{E}}\int dE\,\underbrace{e^{-\frac{1}{2k_B T^2 C_V}(E-\bar{E})^2}}_{\text{normal distribution}}.$$

Thus, we find the variance of the normal distribution:

$$(\Delta E)^2 = k_B T^2 C_V$$

or

$$\Delta E = \sqrt{k_B T^2 C_V} = \mathcal{O}(\sqrt{N}),$$

because C_V, as well as E, is extensive ($\mathcal{O}(N)$). Thus the fluctuation of the energy is

$$\frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}}.$$

Note: More straightforward way to calculate the width is to use

$$(\Delta E)^2 = \left\langle (H - \langle H \rangle)^2 \right\rangle = \langle H^2 \rangle - \langle H \rangle^2,$$

which is, using $F = -k_B T \ln \operatorname{Tr} e^{-\beta H}$,

$$
\begin{aligned}
(\Delta E)^2 &= -\frac{\partial^2}{\partial \beta^2}(\beta F) \\
&= -k_B T^2 \frac{\partial}{\partial T} T^2 \frac{\partial}{\partial T} \frac{F}{T} \\
&= -k_B T^3 \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,N} = k_B T^2 C_V
\end{aligned}
$$

Note: Alternative (and perhaps more rigorous) way to derive the density operator for canonical ensemble would be to start from a very large microcanonical system, and divide this into 2 pieces: part I, "system" and II, "heat bath", where volume of II $\gg$ volume of I. Using only microcanonical total density operator, it is straightforward to derive the canonical density for I:

$$\rho_I \propto e^{-\beta_{II} H_I}$$

where $\beta_{II} = 1/k_B T_{II}$.

6.2. Grand canonical ensemble

Let us consider a system where both the energy and the number of particles are allowed to fluctuate. The Hilbert space of the system is then the Fock space, direct sum

$$\mathcal{H} = \mathcal{H}^{(0)} \oplus \mathcal{H}^{(1)} \oplus \cdots \oplus \mathcal{H}^{(N)} \oplus \cdots$$

and the Hamiltonian operator the sum of 1,2,...-particle Hamiltonians:

$$H = H^{(0)} + H^{(1)} + \cdots + H^{(N)} + \cdots.$$

We define the (particle) number operator $\hat{N}$ so that

$$\hat{N} |N\rangle = N |N\rangle$$

for eigenstates of $\hat{N}$.

Grand canonical ensemble can derived by allowing both E and N to fluctuate, and requiring that the expectation values are fixed:

$$
\begin{aligned}
\langle H \rangle &= \bar{E} = \quad \text{given energy} \\
\left\langle \hat{N} \right\rangle &= \bar{N} = \quad \text{given particle number} \\
\operatorname{Tr} \rho &= \langle I \rangle = 1 \quad \text{probability normalization}
\end{aligned}
$$

We can now demand that the entropy $S = -k_B \rho \ln \rho$ is maximized with the above constraints. Thus, using Lagrange multipliers we obtain

$$
\begin{aligned}
0 &= \delta(S + \lambda \langle H \rangle + \lambda' \left\langle \hat{N} \right\rangle + \lambda'' \langle I \rangle) \\
&= \delta \operatorname{Tr} (k_B \rho \ln \rho - \lambda \rho H - \lambda' \rho \hat{N} - \lambda'' \rho) \\
&= \operatorname{Tr} \delta \rho (k_B \ln \rho + k_B - \lambda H - \lambda' \hat{N} - \lambda'')
\end{aligned}
$$

ending up with the *grand canonical distribution*

$$\boxed{\rho = \frac{1}{Z_G} e^{-\beta(H - \mu \hat{N})}}$$

(again relabeling constants). Here

$$\boxed{Z_G = \operatorname{Tr} e^{-\beta(H - \mu \hat{N})}}$$

is the *grand canonical partition function*.
The trace can be split in N-sectors (effectively using eigenstates of $\hat{N}$):

$$
\begin{aligned}
Z_G &= \sum_N \operatorname{Tr}_N e^{-\beta(H - \mu \hat{N})} = \sum_N e^{\beta \mu N} \operatorname{Tr}_N e^{-\beta H^{(N)}} \\
&= \sum_N z^N Z_N,
\end{aligned}
$$

where Z_N is the canonical partition function with N particles, and *fugasity* $\boxed{z \equiv e^{\beta \mu}}$, and $H^{(N)}$ is a N-particle Hamiltonian.
This directly gives the probability distribution of particle number:

$$P(N) \equiv \langle \delta(N - \hat{N}) \rangle = \operatorname{Tr} \rho \hat{N} = \frac{1}{Z_G} z^N Z_N$$

i.e. the grand canonical ensemble is equivalent to the sum of N-particle canonical ensembles where the weight of each N sector is given by z^N.
In the base where the Hamiltonian is diagonal the partition function is

$$Z_G = \sum_N \sum_n e^{-\beta(E_n^{(N)} - \mu N)},$$

where

$$H |N; n\rangle = H^{(N)} |N; n\rangle = E_n^{(N)} |N; n\rangle,$$

when $|N; n\rangle \in \mathcal{H}^{(N)}$ is a state of N particles, i.e.

$$\hat{N} |N; n\rangle = N |N; n\rangle.$$

Particle number and energy
Now

$$
\begin{aligned}
\frac{\partial \ln Z_G}{\partial \mu} &= \frac{1}{Z_G} \operatorname{Tr} e^{-\beta(H - \mu \hat{N})} \beta \hat{N} \\
&= \beta \left\langle \hat{N} \right\rangle = \beta \bar{N}
\end{aligned}
$$

and

$$
\begin{aligned}
\frac{\partial \ln Z_G}{\partial \beta} &= -\frac{1}{Z_G} \operatorname{Tr} e^{-\beta(H - \mu \hat{N})} (H - \mu \hat{N}) \\
&= -\langle H \rangle + \mu \left\langle \hat{N} \right\rangle = -\bar{E} + \mu \bar{N},
\end{aligned}
$$

so that, using $\beta = 1/(k_B T)$,

$$
\begin{aligned}
\bar{N} &= k_B T \frac{\partial \ln Z_G}{\partial \mu} \\
\bar{E} &= k_B T^2 \frac{\partial \ln Z_G}{\partial T} + k_B T \mu \frac{\partial \ln Z_G}{\partial \mu}.
\end{aligned}
$$

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(this is assuming that $\beta = 1/(k_B T)$, which we have not really yet shown!)

Entropy and Grand potential

According to the definition of entropy we have

$$S = -k_B \text{Tr} \, \rho \ln \rho = -k_B \langle \ln \rho \rangle .$$

Now

$$\ln \rho = -\beta H + \beta \mu \hat{N} - \ln Z_G,$$

so that

$$\frac{1}{k_B \beta} S = \bar{E} - \mu \bar{N} + \frac{1}{\beta} \ln Z_G.$$

In thermodynamics we defined the grand potential

$$\Omega = E - TS - \mu N,$$

which agrees with the above expression if we identify $\beta = 1/(k_B T)$ (as expected) and

$$\boxed{\Omega = -k_B T \ln Z_G.}$$

Thus, the density operator can be written as

$$\boxed{\rho = e^{\beta(\Omega - H + \mu \hat{N})}.}$$

Note: The grand canonical partition function depends on variables T, V and μ, i.e.

$$Z_G = Z_G(T, V, \mu).$$

Fluctuations

Now

$$\begin{aligned}
\frac{\partial^2}{\partial \mu^2} \text{Tr} \, e^{-\beta(H - \mu \hat{N})} &= \text{Tr} \, e^{-\beta(H - \mu \hat{N})} \beta^2 \hat{N}^2 \\
&= Z_G \beta^2 \left\langle \hat{N}^2 \right\rangle,
\end{aligned}$$

so

$$\begin{aligned}
(\Delta N)^2 &= \left\langle (\hat{N} - \bar{N})^2 \right\rangle = \left\langle \hat{N}^2 \right\rangle - \bar{N}^2 \\
&= (k_B T)^2 \frac{\partial^2 \ln Z_G}{\partial \mu^2} = k_B T \frac{\partial \bar{N}}{\partial \mu} = \mathcal{O}(\bar{N}),
\end{aligned}$$

because only $\bar{N}$ is extensive in the last expression. Thus the particle number fluctuates like

$$\frac{\Delta N}{\bar{N}} = \mathcal{O}\left(\frac{1}{\sqrt{\bar{N}}}\right).$$

A corresponding expression is valid also for the fluctuations of the energy. For a mole of matter the fluctuations are $\propto 10^{-12}$ or the accuracy $\approx$ the accuracy of the microcanonical ensemble.

6.3. Relation with thermodynamics

In thermodynamics the entropy is a state variable related to the exchange of the heat energy ($dQ = T dS$) between the system and the environment. However, the statistical Gibbs entropy $-k_B \rho \ln \rho$ is constructed in a very different

manner. Let us now study the relation closer. We shall assume that the Hamiltonian H and eigenstates $|\alpha\rangle$ depend on external parameters $\{x_i\}$:

$$H(x_i) |\alpha(x_i)\rangle = E_\alpha(x_i) |\alpha(x_i)\rangle .$$

Now the change in energy of $|\alpha\rangle$:

$$\begin{aligned}
\frac{\partial E_\alpha}{\partial x_i} &= \frac{\partial}{\partial x_i} \langle \alpha| H |\alpha\rangle = \left\langle \alpha \left| \frac{\partial H}{\partial x_i} \right| \alpha \right\rangle + E_\alpha \frac{\partial}{\partial x_i} \langle \alpha| \alpha\rangle \\
&= \left\langle \alpha \left| \frac{\partial H}{\partial x_i} \right| \alpha \right\rangle,
\end{aligned}$$

because $\langle \alpha| \alpha \rangle = 1$ (Feynman-Hellman theorem).

Adiabatic variation

In quantum mechanics it can be shown that, if the variation of the parameters $x(t)$ is slow enough and the initial state of the system is $|\alpha\rangle$, the system will remain in the eigenstate $|\alpha(x(t))\rangle$ and there are no transitions to other Hamiltonian eigenstates (note that this is only true for eigenstates of H).
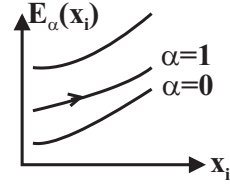
This implies that the probabilities for the states remain constant and the change in the entropy

$$S = -k_B \sum_\alpha p_\alpha \ln p_\alpha$$

is zero.

Let us consider the density operator in an equilibrium state ($[H, \rho] = 0$). We assume N is constant. In the base $\{|\alpha\rangle\}$, where the Hamiltonian is diagonal,

$$H |\alpha\rangle = E_\alpha |\alpha\rangle ,$$

we have

$$\rho = \sum_\alpha p_\alpha P_\alpha, \qquad P_\alpha = |\alpha\rangle \langle \alpha| .$$

We divide the variation of the density operator into two parts:

$$\begin{aligned}
\delta \rho &= \overbrace{\sum_\alpha p_\alpha \delta P_\alpha}^{\text{adiabatic}} + \overbrace{\sum_\alpha \delta p_\alpha P_\alpha}^{\text{nonadiabatic}} \\
&= \delta \rho^{(1)} + \delta \rho^{(2)}.
\end{aligned}$$

The first part corresponds to adiabatic variation (in statistical sense), because the probabilities of the eigenstates remain fixed.

Let us define F_i, the generalized force conjugate to the generalized displacement x_i as

$$F_i = -\text{Tr} \, \rho \frac{\partial H}{\partial x_i} = -\left\langle \frac{\partial H}{\partial x_i} \right\rangle .$$

For example, $F = p$, $x = V$, and $F\delta x$ the work done by the system.

Then the change in energy is

$$
\begin{aligned}
\delta \langle H \rangle &= \mathrm{Tr}\, \delta\rho\, H + \mathrm{Tr}\, \rho\, \delta H \\
&= \mathrm{Tr}\, \delta\rho^{(1)} H + \mathrm{Tr}\, \delta\rho^{(2)} H + \sum_i \delta x_i \mathrm{Tr}\, \rho\, \frac{\partial H}{\partial x_i} \\
&= \sum_\alpha p_\alpha \mathrm{Tr}\, H\, \delta P_\alpha + \mathrm{Tr}\, \delta\rho^{(2)} H - \sum_i F_i \delta x_i.
\end{aligned}
$$

The first term vanishes, because

$$
\begin{aligned}
\mathrm{Tr}\, H\, \delta P_\alpha &= \sum_\beta \langle \beta | H \left(|\alpha\rangle \langle \delta\alpha| + |\delta\alpha\rangle \langle\alpha| \right) |\beta\rangle \\
&= E_\alpha \delta \langle \alpha |\, \alpha \rangle = 0,
\end{aligned}
$$

so that the change in energy becomes

$$
\delta \langle H \rangle = \mathrm{Tr}\, \delta\rho^{(2)} H - \sum_i F_i \delta x_i = \sum_\alpha \delta p_\alpha E_\alpha - \sum_i F_i \delta x_i.
$$

The definition of the statistical Gibbs entropy is

$$
S^{\mathrm{stat}} = -k_b \mathrm{Tr}\, \rho \ln \rho = -k_B \sum_\alpha p_\alpha \ln p_\alpha \,,
$$

and its variation is

$$
\begin{aligned}
\delta S^{\mathrm{stat}} &= -k_B \sum_\alpha \delta p_\alpha \ln p_\alpha - k_B \overbrace{\sum_\alpha \delta p_\alpha}^{=0} \\
&= -k_B \sum_\alpha \delta p_\alpha \ln p_\alpha \\
&= k_B \beta \sum_\alpha \delta p_\alpha E_\alpha,
\end{aligned}
$$

where in the last stage we used the canonical ensemble

$$
p_\alpha = \frac{1}{Z} e^{-\beta E_\alpha}
$$

Thus, if we denote $\beta = 1/(k_B T^{\mathrm{stat}})$, we obtain

$$
\boxed{\delta \langle H \rangle = T^{\mathrm{stat}} \delta S^{\mathrm{stat}} - \sum_i F_i \delta x_i.}
$$

This is equivalent to the first law of the thermodynamics,

$$
\delta U = T^{\mathrm{therm}} \delta S^{\mathrm{therm}} - \delta W,
$$

provided we identify

$$
\begin{aligned}
\langle H \rangle &= \bar{E} = U = \text{internal energy} \\
T^{\mathrm{stat}} &= T^{\mathrm{therm}} \\
S^{\mathrm{stat}} &= S^{\mathrm{therm}} \\
\sum_i F_i \delta x_i &= \delta W = \text{work}.
\end{aligned}
$$

Isolated system and microcanonical ensemble

If the system is microcanonical, then $E_\alpha = E$ for all states. However, when we change x, $E(x)$ can vary! In this case

$$
\begin{aligned}
\delta \langle H \rangle = \delta E &= \sum_\alpha \delta p_\alpha E_\alpha - \sum_i F_i \delta x_i \\
&= -\sum_i F_i \delta x_i \,,
\end{aligned}
$$

which is equivalent to thermodynamical work done by an isolated system

$$
\delta U = -\delta W = -\sum_i F_i \delta x_i
$$

6.4. Einstein's theory of fluctuations

Let us divide a large system into macroscopic parts with weak mutual interactions.

$\Rightarrow \exists$ operators $\{\hat{X}_i\}$, which correspond to the extensive properties of the partial systems so that

$$
\begin{aligned}
[\hat{X}_i, \hat{X}_j] &\approx 0 \\
[\hat{X}_i, H] &\approx 0.
\end{aligned}
$$

$\Rightarrow \exists$ mutual eigenstates $|E, X_1, \ldots, X_n\rangle$, which are macrostates of the system, i.e. for each set of the parameters $(E, X_1, \ldots, X_n)$ there is a macroscopic number of microstates. Let $\Gamma(E, X_1, \ldots, X_n)$ be the number of the microstates corresponding to the state $|E, X_1, \ldots, X_n\rangle$ (the volume of the phase space). The total number of the states is

$$
\Gamma(E) = \sum_{\{X_i\}} \Gamma(E, X_1, \ldots, X_n)
$$

and the relative probability of the state $(E, \{X\})$

$$
f(E, X_1, \ldots, X_n) = \frac{\Gamma(E, X_1, \ldots, X_n)}{\Gamma(E)}.
$$

The entropy of the state $|E, X_1, \ldots, X_n\rangle$ is

$$
S(E, X_1, \ldots, X_n) = k_B \ln \Gamma(E, X_1, \ldots, X_n)
$$

or

$$
f(E, X_1, \ldots, X_n) = \frac{1}{\Gamma(E)} e^{\frac{1}{k_B} S(E, X_1, \ldots, X_n)}.
$$

This is the probability of state X with fixed energy E. In thermodynamic equilibrium the entropy S is maximized:

$$
S^0 = S(E, X_1^{(0)}, \ldots, X_n^{(0)}).
$$

Let us denote by

$$
x_i = X_i - X_i^{(0)}
$$

deviations from the equilibrium positions, and expand the entropy to 2nd order around extremum: the Taylor series of the entropy will be

$$
S = S^0 - \frac{1}{2} k_B \sum_{i,j} g_{ij} x_i x_j + \cdots,
$$

13

where

$$g_{ij} = -\frac{1}{k_B} \left. \left(\frac{\partial^2 S}{\partial X_i \partial X_j} \right) \right|_{\{X_i^{(0)}\}}.$$

We use vector-matrix notation

$$x = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix} \text{ and } g = (g_{ij}).$$

Then the probability becomes

$$f(x) = C e^{-\frac{1}{2} x^T g x},$$

where

$$C = (2\pi)^{-n/2} \sqrt{\det g}.$$

Correlation functions

Correlation functions can be written as

$$\langle x_p \cdots x_r \rangle \equiv \int \mathcal{D}x \, f(x) x_p \cdots x_r$$
$$= \left[\frac{\partial}{\partial h_p} \cdots \frac{\partial}{\partial h_r} F(h) \right]_{h=0},$$

where

$$\mathcal{D}x = dx_1 \cdots dx_n$$

and the generating function is

$$F(h) = C \int \mathcal{D}x e^{-\frac{1}{2} x^T g x + \frac{1}{2}(h^T x + x^T h)} = e^{\frac{1}{2} h^T g^{-1} h}.$$

SVN-system

When studying the stability conditions of matter we found out that the

$$\Delta S = -\frac{1}{2T} \sum_i (\Delta T_i \Delta S_i - \Delta p_i \Delta V_i + \Delta \mu_i \Delta N_i).$$

Let us consider now only one volume element:

$$f = C e^{-\frac{1}{2k_B T}(\Delta T \, \Delta S - \Delta p \, \Delta V + \Delta \mu \, \Delta N)}.$$

We assume that the system is not allowed to exchange particles, i.e. $\Delta N = 0$. Taking now T and V as our independent variables we can employ the definitions of the heat capacity and compressibility:

$$f(\Delta T, \Delta V) \propto e^{-\frac{1}{2} \left[\frac{C_V}{k_B T^2} (\Delta T)^2 + \frac{1}{V k_B T \kappa_T} (\Delta V) \right]}.$$

We can now read out the matrix g:

$$g = \begin{array}{cc} & \begin{array}{cc} T & \quad V \end{array} \\ \begin{array}{c} T \\ V \end{array} & \begin{pmatrix} \frac{C_V}{k_B T^2} & 0 \\ 0 & \frac{1}{V k_B T \kappa_T} \end{pmatrix} \end{array}.$$

The variances are then

$$\langle (\Delta T)^2 \rangle = \frac{k_B T^2}{C_V}$$
$$\langle (\Delta V)^2 \rangle = V k_B T \kappa_T.$$

We can naturally also calculate correlations of other quantities, for example

$$\langle \Delta S \Delta V \rangle = \left(\frac{\partial S}{\partial T} \right)_V \langle \Delta T \Delta V \rangle + \left(\frac{\partial S}{\partial V} \right)_T \langle (\Delta V)^2 \rangle$$
$$= \left(\frac{\partial p}{\partial T} \right)_V V k_B T \kappa_T$$
$$= -\left[\left(\frac{\partial V}{\partial p} \right)_T \left(\frac{\partial T}{\partial V} \right)_p \right]^{-1} V k_B T \kappa_T$$
$$= k_B V T \alpha_p$$

where we used the Maxwell relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$. Note that if we were to origially take other set of variables, say, S, V as the independent ones, the matrix $g = -1/k_B \partial^2 S / \partial \vec{x}^2$ would look different (in this case non-diagonal).

6.5. Reversible minimum work

Another way to calculate the fluctuation probability is to consider the concept of reversible minimum work.
Let $x = X - X^{(0)}$ be the fluctuation of the variable X. For one variable we have

$$f(x) \propto e^{-\frac{1}{2} g x^2}.$$

Let us assume that X is generalized displacement; thus

$$dU = T \, dS - F \, dX - \bar{d}W_{\text{other}}.$$

If we write $S = S(U, X, \ldots)$ we get the partial derivative

$$\frac{\partial S}{\partial X} = \frac{F}{T}.$$

On the other hand we had

$$S = S^0 - \frac{1}{2} k_B \sum_{i,j} g_{ij} x_i x_j$$
$$= S^0 - \frac{1}{2} k_B g x^2,$$

so

$$\frac{\partial S}{\partial X} = -k_B g x$$

and in the limit of small displacement

$$F = -k_B T g x.$$

When there is no action on X from outside, the deviation x fluctuates spontaneously. Let us give rise to the same deviation x by applying *reversible* adiabatic external work:

$$dU = -F \, dX = k_B T \, g \, x \, dx.$$

Integrating this we get

$$(\Delta U)_{\text{rev}} \equiv \Delta R = \frac{1}{2} k_B T g x^2,$$

where ΔR is the minimum reversible work required for the fluctuation $x = \Delta X$. We can write

$$f(\Delta X) \propto e^{-\frac{\Delta R}{k_B T}}.$$

Note that this relates a fluctuation of X at constant $U = E$ ($f(x) \sim e^{\delta^2 S / k_B}$) to the adiabatic work done to achieve same change of X ($\delta S = 0$).

7. Ideal equilibrium systems

In ideal systems there are no interactions between the particles/degrees of freedom. If we know the solution for 1-particle state, N-particle state can be solved by taking into account the correct statistics.

7.1. System of free spins

Let us consider N particles with spin $\frac{1}{2}$. The z-component of the spins are

$$S_{iz} = \pm \tfrac{1}{2}\hbar \quad i = 1, \ldots, N.$$

The z component of the total spin is

$$S_z = \sum_i S_{iz} = \frac{1}{2}\hbar(N^+ - N^-),$$

where

$$N^+ = +\frac{1}{2}\hbar \text{ spin count}$$
$$N^- = -\frac{1}{2}\hbar \text{ spin count}.$$

S_z determines the macrostate of the system. Denoting $S_z = \hbar\nu$ we have

$$N^+ = \frac{1}{2}N + \nu$$
$$N^- = \frac{1}{2}N - \nu$$

and

$$\nu = -\frac{1}{2}N, -\frac{1}{2}N + 1, \ldots, \frac{1}{2}N.$$

Let $W(\nu)$ the number of those microstates for which $S_z = \hbar\nu$, i.e. $W(\nu)$ tells us, how many ways there are to distribute N particles into groups of N^+ and N^- particles so that $N^+ + N^- = N$ and $N^+ - N^- = 2\nu$. From combinatorics we know that this is given by the *binomial distribution:*

$$W(\nu) = \binom{N}{N^+} = \frac{N!}{N^+! N^-!}$$
$$= \frac{N!}{(\frac{1}{2}N + \nu)!(\frac{1}{2}N - \nu)!}.$$

$W(\nu)$ is the *degeneracy* (=number of states) of the macrostate $S_z = \hbar\nu$.
The Boltzmann entropy is

$$S = k_B \ln W(\nu).$$

Using Stirling's formula

$$\boxed{\ln N! \approx N \ln N - N}$$

we get

$$\ln W(\nu) \approx N \ln N - N$$
$$- \left[(\tfrac{1}{2}N + \nu)\ln(\tfrac{1}{2}N + \nu) - (\tfrac{1}{2}N + \nu)\right]$$

$$- \left[(\tfrac{1}{2}N - \nu)\ln(\tfrac{1}{2}N - \nu) - (\tfrac{1}{2}N - \nu)\right]$$

$$= \frac{1}{2}N \ln \frac{N^2}{\frac{1}{4}N^2 - \nu^2} - \nu \ln \frac{\frac{1}{2}N + \nu}{\frac{1}{2}N - \nu}$$

$$= N \ln 2 + \frac{1}{2}N \ln \frac{1}{1 - 4\nu^2/N^2} - \nu \ln \frac{1 + 2\nu/N}{1 - 2\nu/N}$$

$$\approx N \ln 2 - 2\frac{\nu^2}{N}$$

where in the last step we have taken the approximation $|\nu| \ll N$. The maximum of W is clearly at $\nu = 0$.
Thus, the binomial distribution can be approximated by a normal distribution:

$$\boxed{W(\nu) \approx W(0)e^{-2\nu^2/N},} \qquad W(0) \approx 2^N.$$

The mean deviation $\Delta\nu \approx \sqrt{N}/2 \ll N$, i.e. large values of ν are very unlikely.
Note that the total number of states

$$W_{\text{tot}} = \sum_\nu W(\nu) = 2^N$$

Thus, a correct normalization of the gaussian distribution would be

$$W_{\text{tot}} = C \int d\nu e^{-2\nu^2/N} = C\sqrt{N\pi/2} = 2^N$$

which implies $C = 2^N/\sqrt{N\pi/2}$. However, the correction in this case is non-extensive and can be neglected in the large N limit:

$$\ln C = \overbrace{N \ln 2}^{\text{extensive}} - \overbrace{\frac{1}{2}\ln(N\pi/2)}^{\text{non-extensive}}$$

Energy

Let us put the system in an external magnetic field $\boldsymbol{H} = H\hat{z}$, with magnetic flux density

$$\boldsymbol{B} = \mu_0 \boldsymbol{H}.$$

The potential energy is

$$E = -\mu_0 \sum_i \boldsymbol{\mu}_i \cdot \boldsymbol{H} = -\mu_0 H \sum_i \mu_{iz},$$

where $\boldsymbol{\mu}_i$ is the magnetic moment of the particle i.
The magnetic moment of a particle is proportional to its spin:

$$\boldsymbol{\mu} = \gamma \boldsymbol{S},$$

where γ is the gyromagnetic ratio. In classical electrodynamics, with a homogeneously charged solid body of mass m, total charge q and angular momentum $\boldsymbol{S}$, this has the value

$$\gamma_0 = \frac{q}{2m}.$$

However, for elementary particles this is different, and for electrons we have

$$\gamma \approx 2\gamma_0 = -\frac{e}{m},$$

Usually this is given in terms of Bohr magneton

$$\mu_B = \frac{e\hbar}{2m} = 5.79 \cdot 10^{-5} \frac{\text{eV}}{\text{T}}.$$

The energy of the system is

$$E = -\mu_0 H \sum \mu_{iz} = -\mu_0 \gamma H S_z = \epsilon \nu,$$

where

$$\epsilon = -\hbar\gamma\mu_0 H$$

is the energy/particle. For electrons we have

$$\epsilon = 2\mu_0 \mu_B H.$$

Now the change in energy is

$$\Delta E = \epsilon \, \Delta \nu,$$

Changing the variable $\nu \leftrightarrow E$, and using the condition (Jacobi!)

$$\omega(E) \, |\Delta E| = W(\nu) \, |\Delta \nu|$$

we get as the density of states

$$\omega(E) = \frac{1}{|\epsilon|} W\left(\frac{E}{\epsilon}\right).$$

1) Microcanonical ensemble
Let us first consider the spin system at fixed energy. Denoting

$$E_0 = \frac{1}{2}\,\epsilon N,$$

the total energy will lie between $-E_0 \leq E \leq E_0$.
With the help of the energy W can be written as

$$
\begin{aligned}
\ln W(\nu) &= \frac{1}{2} N \ln \frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{\epsilon} \ln \frac{E_0 + E}{E_0 - E} \\
&= \ln \omega(E) + \ln |\epsilon|.
\end{aligned}
$$

As the entropy we get

$$
\begin{aligned}
S(E) &= k_B \ln \omega(E) \\
&= Nk_B \left[\frac{1}{2} \ln \frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{2E_0} \ln \frac{E_0 + E}{E_0 - E}\right] \\
&\quad + \text{non extensive term.}
\end{aligned}
$$

The temperature was defined like

$$\frac{1}{T} = \frac{\partial S}{\partial E},$$

so

$$\beta(E) = \frac{1}{k_B T(E)} = -\frac{N}{2E_0} \ln \frac{E_0 + E}{E_0 - E}.$$

We can solve for the energy:

$$
\begin{aligned}
E &= -E_0 \tanh \frac{\beta E_0}{N} \\
&= -\frac{1}{2} N\mu_0\hbar\gamma H \tanh\left(\frac{\mu_0\hbar\gamma H}{2k_B T}\right).
\end{aligned}
$$

The *magnetization* or the *magnetic polarization* is the magnetic moment per the volume element, i.e.

$$\boldsymbol{M} = \frac{1}{V} \sum_i \boldsymbol{\mu}_i.$$

The z component of the magnetization is

$$
\begin{aligned}
M_z &= -\frac{1}{V} \frac{\epsilon \nu}{\mu_0 H} = \frac{1}{V} \frac{\hbar\gamma\mu_0 H\nu}{\mu_0 H} \\
&= \frac{1}{V} \gamma\hbar\nu.
\end{aligned}
$$

Now

$$E = -\mu_0 H V M_z,$$

so we get for our system as the equation of state

$$M = \frac{1}{2} \rho\hbar\gamma \tanh\left(\frac{\mu_0\hbar\gamma H}{2k_B T}\right),$$

where $\rho = N/V$ is the particle density. **Note:** The relations derived above

$$
\begin{aligned}
E &= E(T, H, N) \\
M &= M(T, H, N)
\end{aligned}
$$

determine the thermodynamics of the system.

2) Canonical ensemble
The canonical partition function is

$$Z = \sum_n e^{-\beta E_n}.$$

Here

$$E_n = -\mu_0 H \sum_{i=1}^{N} \mu_{iz}$$

the energy of a single microstate.
Denote

$$\mu_{iz} = \hbar\gamma\nu_i, \quad \nu_i = \pm\frac{1}{2}.$$

Now

$$
\begin{aligned}
Z &= \sum_{\text{all microstates}} e^{\beta\mu_0 H \sum_i \mu_{iz}} \\
&= \sum_{\nu_1 = -\frac{1}{2}}^{\frac{1}{2}} \cdots \sum_{\nu_N = -\frac{1}{2}}^{\frac{1}{2}} e^{\beta\mu_0\hbar\gamma H \sum_i \nu_i} \\
&= \left[\sum_{\nu = -\frac{1}{2}}^{\frac{1}{2}} e^{\beta\mu_0 H\gamma\hbar\nu}\right]^N = Z_1^N,
\end{aligned}
$$

where Z_1 the one particle state sum

$$
\begin{aligned}
Z_1 &= e^{-\frac{1}{2}\beta\mu_0\hbar H\gamma} + e^{\frac{1}{2}\beta\mu_0\hbar H\gamma} \\
&= 2\cosh \frac{\mu_0\hbar H\gamma}{2k_B T}.
\end{aligned}
$$

The same result can be obtained using $W(\nu)$:

$$
\begin{aligned}
Z &= \sum_{\nu} W(\nu) e^{-\beta E(\nu)} \\
&= \sum_{\nu} W(\nu) e^{-\beta \epsilon \nu} \\
&= \sum_{N^+} \binom{N}{N^+} e^{-\beta \epsilon (N^+ - \frac{1}{2} N)} \\
&= e^{-\frac{1}{2} \beta \epsilon N} \left(1 + e^{-\beta \epsilon}\right)^N .
\end{aligned}
$$

From the partition function we can determine thermodynamic potential, free energy. However, what is the "correct" thermodynamic potential in this case? Naively we might identify

$$
F(T, H) = -k_B T \ln Z
$$

as the Helmholtz free energy (as is done in many textbooks). This is (mostly) OK for thermodynamics, and the simple choice, but it is not fully consistent: Note that H is generalized force ("p"), M is displacement ("V"). Thus, when our set of independent variables is (T, H), the right thermodynamic potential is the Gibbs free energy

$$
\begin{aligned}
G &= G(T, \boldsymbol{H}) = -k_B T \ln Z \\
&= \boxed{-k_B T N \left[\ln 2 + \ln \cosh \frac{\mu_0 H \gamma \hbar}{2 k_B T}\right].}
\end{aligned}
$$

Furthermore, in this case we should identify our energy E as the *enthalpy* of the system:

$$
E = -\mu_0 H V M = U - H \times (\mu_0 V M)
$$

which is related to the true internal energy U by a Legendre transform. In this case internal energy vanishes:

$$
U = 0.
$$

True internal energy U should not depend on external force like H, only on internal properties like M. However, in this case there is no H-independent energy! Thus, the entropy is

$$
\begin{aligned}
S &= -\left(\frac{\partial G}{\partial T}\right)_{\boldsymbol{H}} \\
&= N k_B \left[\ln 2 + \ln \cosh \frac{\mu_0 H \gamma \hbar}{2 k_B T} \right. \\
&\qquad \left. - \frac{\mu_0 \hbar \gamma H}{2 k_B T} \tanh \frac{\mu_0 \hbar \gamma H}{2 k_B T}\right].
\end{aligned}
$$

Differentiating the free energy with respect to the field $\boldsymbol{H}$ we get

$$
\begin{aligned}
-\left(\frac{\partial G}{\partial H_z}\right)_T &= k_B T \frac{1}{Z} \frac{\partial}{\partial H} \sum_{\nu} W(\nu) e^{-\beta \epsilon \nu} \\
&= \mu_0 \gamma \hbar \frac{1}{Z} \sum_{\nu} \nu W(\nu) e^{-\beta \epsilon \nu} \\
&= \mu_0 \gamma \hbar \langle \nu \rangle = \mu_0 V M_z.
\end{aligned}
$$

Thus the differential of the free energy is

$$
\boxed{dG = -S\, dT - \mu_0 V \boldsymbol{M} \cdot d\boldsymbol{H},}
$$

so that the magnetization is

$$
\begin{aligned}
M &= -\frac{1}{\mu_0 V} \left(\frac{\partial G}{\partial H}\right)_T \\
&= -\frac{1}{2} \rho \hbar \gamma \tanh \left(\frac{\mu_0 \hbar \gamma H}{2 k_B T}\right).
\end{aligned}
$$

This is identical with the result we obtained in the microcanonical ensemble.
The microcanonical entropy = the canonical entropy + a non extensive term.

Energy
a) Energy $E(T, H)$ (enthalpy) can be calculated directly from partition function

$$
\begin{aligned}
E &= \langle E(\nu) \rangle = \epsilon \bar{\nu} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z \\
&= -\frac{1}{2} N \epsilon \tanh \left(\frac{1}{2} \beta \epsilon\right) \\
&= \text{the energy of the microcanonical enesmble.}
\end{aligned}
$$

b) Alternatively, using thermodynamic Legendre transformation from enthalpy to Gibbs potential

$$
G = E - TS
$$

or

$$
\begin{aligned}
E &= G + TS = G - T \frac{\partial G}{\partial T} \\
&= G + \beta \frac{\partial G}{\partial \beta} = \frac{\partial}{\partial \beta} (\beta F) \\
&= -\frac{\partial}{\partial \beta} \ln Z
\end{aligned}
$$

Susceptibility
According to the definition the susceptibility is

$$
\begin{aligned}
\chi &= \left(\frac{\partial M}{\partial H}\right)_T = -\frac{1}{\mu_0 V} \left(\frac{\partial^2 G}{\partial H^2}\right) \\
&= \frac{\mu_0 \rho}{k_B T} \frac{\left(\frac{1}{2} \hbar \gamma\right)^2}{\cosh^2 \left(\frac{\hbar \gamma \mu_0 H}{2 K_B T}\right)}.
\end{aligned}
$$

When $H \to 0$ we end up with *Curie's law*

$$
\boxed{\chi = \frac{C}{T},}
$$

where

$$
C = \frac{\mu_0 \rho}{k_B T} \left(\frac{1}{2} \hbar \gamma\right)^2 .
$$

Thermodynamic identifications
Earlier we identified

$$
E^{\text{stat}} \equiv E = \left\langle \hat{H} \right\rangle = \text{enthalpy},
$$

so that

$$
\begin{aligned}
G & = E - TS = G^{\text{therm}} \\
& = \text{the Gibbs free energy} \\
& = U - TS - \mu_0 V \boldsymbol{M} \cdot \boldsymbol{H}.
\end{aligned}
$$

Now using the differentials we get

$$
\begin{aligned}
dU & = dG + d(TS) + d(\mu_0 V \boldsymbol{M} \cdot \boldsymbol{H}) \\
& = TdS + \mu_0 V \boldsymbol{H} \cdot d\boldsymbol{M} \\
& = TdS - dW
\end{aligned}
$$

Thus, the work done by a magnetic system is

$$
\boxed{dW = -\mu_0 V \boldsymbol{H} \cdot d\boldsymbol{M}.}
$$

(compare to pdV).

Example: Adiabatic demagnetization is used to achieve cooling of atomic spins to nanokelvin temperatures. This is due to very large degeneracy of spin states, which means large entropy down to very small temperatures. Removing entropy with magnetic fields can then reduce temperature very effectively. Now

$$
\frac{S}{Nk_B} = \ln 2 + \ln \cosh x - x \tanh x,
$$

where

$$
x = \frac{\mu_0 \hbar H \gamma}{2 k_B T}.
$$

When $T \to 0$, then $x \to \infty$, so that

$$
\begin{aligned}
\ln \cosh x & = \ln \frac{1}{2} e^x (1 + e^{-2x}) \\
& = x - \ln 2 + e^{-2x} + \cdots
\end{aligned}
$$

and

$$
\begin{aligned}
\tanh x & = \frac{e^x (1 - e^{-2x})}{e^x (1 + e^{-2x})} \\
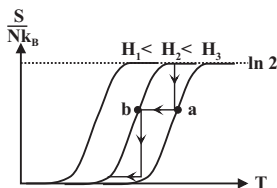& = 1 - 2e^{-2x} + \cdots.
\end{aligned}
$$

Hence

$$
\frac{S}{Nk_B} \to 2x e^{-2x} + \cdots.
$$

When $T \to \infty$, then $x \to 0$, and

$$
\frac{S}{Nk_B} \to \ln 2.
$$

Let us cool down a system by some means at a large field H_a, reaching point a:

We decrease the field adiabatically within the interval $a \to b$. Now $S = S(H/T)$, so that

$$
S_a = S \left(\frac{H_a}{T_a} \right) = S_b = S \left(\frac{H_b}{T_b} \right)
$$

or

$$
\frac{T_b}{T_a} = \frac{H_b}{H_a}.
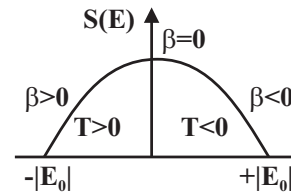$$

Can be serialised to reach even smaller T.

Negative temperature

The entropy of the spin system is

$$
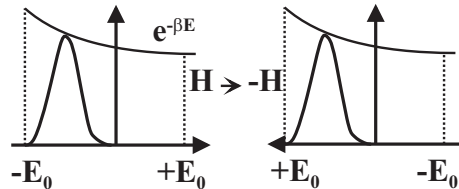S(E) = Nk_B \left[\frac{1}{2} \ln \frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{2E_0} \ln \frac{E_0 + E}{E_0 - E} \right],
$$

where

$$
E_0 = \mu_0 \mu_B H N \text{ ja } -|E_0| < E < |E_0|.
$$

Now

$$
\beta(E) = \frac{1}{k_B} \frac{\partial S}{\partial E} = -\frac{N}{2E_0} \ln \frac{E + E_0}{E - E_0}.
$$

Originally the maximum of $\omega(E) e^{-\beta E}/Z$ is at a negative value E. Reversing the magnetic field abruptly $E \to -E$ and correspondingly $\beta \to -\beta$.

The temperature can be negative if the energy is bounded both above and below.

7.2. Classical ideal gas (Maxwell-Boltzmann gas)

Kinetic gas theory, James Clerk Maxwell (1860): gas of atoms/molecules. Explained many properties of real gases, supporting the atomic hypothesis of matter.

At standard temperature and pressure (STP) most gases are *dilute:*
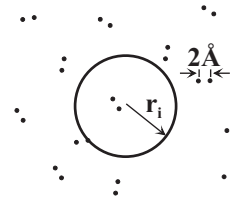
We define r_i so that the volume occupied by one molecule $=$

$$
v_i = \frac{4}{3} \pi r_i^3 = \frac{V}{N} = \frac{1}{\rho}
$$

or

$$
r_i = \sqrt[3]{\frac{3}{4\pi\rho}}.
$$

Typically

- the diameter of an atom or a molecule $d \approx 2\text{Å}$.

- the range of the interaction 2–4Å.

- the mean free path (collision interval) $l \approx 600\text{Å}$.

- at STP ($T = 273\text{K}$, $p = 1\text{atm}$) $r_i \approx 20\text{Å}$.

or

$$
\begin{array}{ccccc}
d & \ll & r_i & \ll & l \\
2 & & 20 & & 600 \quad \text{Å}
\end{array}
$$

The most important effect of collisions is that the system *thermalizes* i.e. attains an equilibrium, which corresponds to a statistical ensemble. Otherwise we can *forget the collisions* and describe the gas as non-interacting molecules. Let us consider a system of *one molecule* which can exchange energy (heat) with its surroundings. Then the suitable ensemble is the canonical ensemble and the distribution the Boltzmann distribution

$$
p_l = \langle l | \rho | l \rangle = \frac{1}{Z} e^{-\beta \epsilon_l},
$$

where the canonical partition function is

$$
Z = \sum_l e^{-\beta \epsilon_l}.
$$

We recall that in $\mathbf{k}$-space the density of 1-particle states is constant: in volume $V = L^3$ the wave function is

$$
\psi_{\mathbf{k}}(\mathbf{x}) \propto e^{i\mathbf{k}\cdot\mathbf{x}}
$$

where, using periodic b.c. $\mathbf{k} = 2\pi\mathbf{n}/L$, $\mathbf{n} \in Z^3$. Thus, in volume element $(\mathbf{k}, \mathbf{k} + \Delta\mathbf{k})$ the number of states is constant independent of $\mathbf{k}$.
For convenience, we shall switch to *velocity space*, with $\mathbf{v} = \mathbf{p}/m = \hbar/m\mathbf{k}$. However, everything would work also in $\mathbf{k}$-space too.
The volume element in velocity space is

$$
d^3v = \frac{1}{m^3} d^3p = \left(\frac{\hbar}{m}\right)^3 d^3k,
$$

i.e. the density of states is also constant. The energy of $\mathbf{k}$-state is

$$
\epsilon_k = \langle \mathbf{k} | H | \mathbf{k} \rangle = \frac{\hbar^2 k^2}{2m} = \frac{1}{2} mv^2,
$$

so that the velocity distribution becomes

$$
f(\mathbf{v}) \propto \langle \mathbf{k} | \rho | \mathbf{k} \rangle = e^{-\frac{mv^2}{2k_BT}}
$$

or

$$
f(\mathbf{v}) = C e^{-\frac{mv^2}{2k_BT}}.
$$

C can be determined from the condition

$$
\begin{aligned}
1 &= \int f(\mathbf{v})\, d^3v = C \left[\int_{-\infty}^{\infty} dv_x e^{-\frac{mv_x^2}{2k_BT}} \right]^3 \\
&= C \left(\frac{2\pi k_BT}{m}\right)^{3/2}.
\end{aligned}
$$

Thus the velocity obeys *Maxwell's distribution*

$$
\boxed{f(\mathbf{v}) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{mv^2}{2k_BT}}.}
$$

From the relation

$$
\int d^3v = \int_0^{\infty} 4\pi v^2 dv
$$

we can obtain for the *speed* (the absolute value of the velocity $v = |\mathbf{v}|$) the distribution function $F(v)$

$$
F(v) = 4\pi v^2 f(v).
$$

- The most likely speed (maximum of the distribution)

$$
v_m = \sqrt{\frac{2k_BT}{m}}.
$$

- The average speed

$$
\langle v \rangle = \int_0^{\infty} dv\, v F(v) = \sqrt{\frac{8k_BT}{\pi m}}.
$$

- The average of the square of the speed

$$
\langle v^2 \rangle = \int_0^{\infty} dv\, v^2 F(v) = \frac{3k_BT}{m}.
$$

Note:

$$
\left\langle \frac{1}{2} mv_x^2 \right\rangle = \left\langle \frac{1}{2} mv_y^2 \right\rangle = \left\langle \frac{1}{2} mv_z^2 \right\rangle = \frac{1}{2} k_BT
$$

and

$$
\left\langle \frac{1}{2} mv^2 \right\rangle = 3 \left\langle \frac{1}{2} mv_x^2 \right\rangle = \frac{3}{2} k_BT,
$$

i.e. the energy is evenly distributed among the 3 (translational) degrees of freedom: the *equipartition* of the energy.

Partition function and thermodynamics
The single particle partition function is

$$
\begin{aligned}
Z_1(\beta) &= \int dE\, \omega(E) e^{-\beta E} \\
&= g \sum_{\mathbf{k}} e^{-\beta \frac{\hbar^2 k^2}{2m}} = g \frac{V}{h^3} \int d^3p\, e^{-\frac{p^2}{2mk_BT}} \\
&= g \frac{V}{h^3} (2\pi m k_BT)^{3/2}.
\end{aligned}
$$

Here g is the spin degeneracy.
When we denote the *thermal de Broglie wave length* by

$$
\lambda_T = \sqrt{\frac{h^2}{2\pi m k_BT}}
$$

we can write the 1 body partition function as

$$
Z_1(\beta) = g \frac{V}{\lambda_T^3}.
$$

In the N particle system the canonical partition function takes the form

$$
\begin{aligned}
Z_N &= \frac{1}{N!} g^N \sum_{\boldsymbol{k}_1} \cdots \sum_{\boldsymbol{k}_N} e^{-\beta(\epsilon_{\boldsymbol{k}_1} + \cdots + \epsilon_{\boldsymbol{k}_1})} \\
&= \frac{1}{N!} g^N \left(\sum_{\boldsymbol{k}} e^{-\beta \epsilon_{\boldsymbol{k}}} \right)^N \\
&= \frac{1}{N!} Z_1^N.
\end{aligned}
$$

Here $N!$ takes care of the fact that each state

$$
|\boldsymbol{k}_1, \ldots, \boldsymbol{k}_N\rangle
$$

is counted only once. Neither the multiple occupation nor the Pauli exclusion principle has been taken into account. Using Stirling's formula $\ln N! \approx N \ln N - N$ the free energy can be written as

$$
\begin{aligned}
F_N &= \\
&= -k_B T \ln Z_N \\
&= N k_B T \left[\ln \frac{N}{V} - 1 - \ln g + h \lambda_T^3 \right] \\
&= \boxed{N k_B T \left[\ln \frac{N}{V} - \frac{3}{2} \ln k_B T - 1 - \ln g + \frac{3}{2} \ln \frac{h^2}{2\pi m} \right]}.
\end{aligned}
$$

Because $dF = -S\, dT - p\, dV + \mu\, dN$, the pressure will be

$$
p = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = N k_B T \frac{1}{V}
$$

i.e. we end up with the *ideal gas equation of state*

$$
pV = N k_B T.
$$

With the help of the entropy

$$
S = -\left(\frac{\partial F}{\partial T} \right)_{V,N} = -\frac{F}{T} + \frac{3}{2} N k_B
$$

the internal energy is

$$
U = F + TS = \frac{3}{2} N k_B T
$$

i.e. the *ideal gas internal energy.*
The heat capacity is

$$
C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{2} N k_B.
$$

Comparing this with

$$
C_V = \frac{1}{2} f k_B N
$$

we see that the number of degrees of freedom is $f = 3$.
We can also calculate the Gibbs function
$G = F + pV = \mu N$, and substuting $N/V = p/(k_B T)$ using

the the equation of state, we obtain μ in terms of the natural variables for the Gibbs ensemble:

$$
\mu(p, T) = T \left(\ln p - \frac{5}{2} \ln k_B T + \frac{3}{2} \ln \frac{h^2}{2\pi m} - \ln g \right).
$$

Grand canonical partition function
According to the definition we have

$$
Z_G = \sum_N \sum_n e^{-\beta(E_n^{(N)} - \mu N)} = \sum_N z^N Z_N,
$$

where

$$
z = e^{\beta \mu}
$$

is called the *fugacity* and Z_N is the partition function of N particles. Thus we get

$$
\boxed{Z_G = \sum_N \frac{1}{N!} z^N Z_1^N = e^{z Z_1} = \exp\left[e^{\beta \mu} \frac{gV}{\lambda_T^3} \right].}
$$

The grand potential is

$$
\boxed{\Omega(T, V, \mu) = -k_B T \ln Z_G = -k_B T e^{\beta \mu} \frac{gV}{\lambda_T^3}.}
$$

Because $d\Omega = -S\, dT - p\, dV - \bar{N}\, d\mu$, we get

$$
p = -\left(\frac{\partial \Omega}{\partial V} \right)_{T,\mu} = -\frac{\Omega}{V} = k_B T e^{\beta \mu} \frac{g}{\lambda_T^3}
$$

and

$$
\bar{N} = -\frac{\partial \Omega}{\partial \mu} = e^{\beta \mu} \frac{gV}{\lambda_T^3} = \frac{pV}{k_B T},
$$

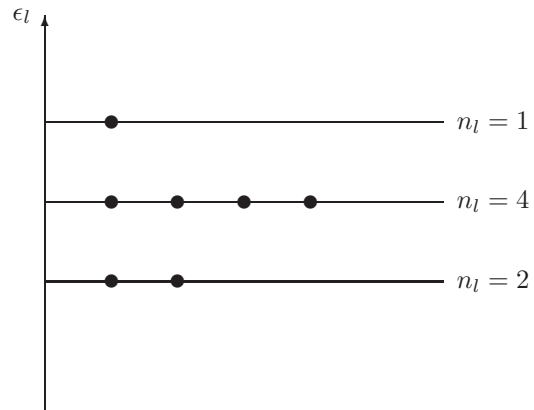and we end up again with the *ideal gas equation of state*

$$
pV = \bar{N} k_B T.
$$

Here

$$
\begin{aligned}
\bar{N} &= \langle N \rangle = \frac{\sum_N N z^N Z_N}{\sum_N z^N Z_N} \\
&= \frac{1}{Z_G} z \frac{\partial Z_G}{\partial z} = \frac{\partial \ln Z_G}{\partial \ln z}.
\end{aligned}
$$

Another way
We distribute N particles among the 1 particle states so that in the state l there are n_l particles.

Now

$$N = \sum_l n_l \text{ and } E = \sum_l \epsilon_l n_l.$$

The number of possible distributions is

$$W = W(n_1, n_2, \ldots, n_l, \ldots) = \frac{N!}{n_1! n_2! \cdots n_l! \cdots}.$$

Since in every distribution $(n_1, n_2, \ldots)$ each of the $N!$ permutatations of the particles gives an identical state the partition function is

$$
\begin{aligned}
Z_{\mathrm{G}} &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \frac{1}{N!} W e^{-\beta(E-\mu N)} \\
&= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \frac{1}{n_1! n_2! \cdots} e^{-\beta \sum_l n_l(\epsilon_l - \mu)} \\
&= \prod_l \left[\sum_{n_l=0}^{\infty} \frac{1}{n_l!} e^{-\beta n_l(\epsilon_l - \mu)} \right] \\
&= \prod_l \exp \left[e^{-\beta(\epsilon_l - \mu)} \right] \\
&= \exp \left[\sum_l e^{-\beta(\epsilon_l - \mu)} \right] \\
&= \exp \left[e^{\beta\mu} Z_1 \right]
\end{aligned}
$$

or exactly as earlier.

Validity range of MB gas law
Now

$$
\begin{aligned}
\frac{\partial \ln Z_{\mathrm{G}}}{\partial \epsilon_l} &= \frac{-\beta \sum_{n=0}^{\infty} n \frac{1}{n!} e^{-\beta n(\epsilon_l - \mu)}}{\prod_m \left[\sum_{n_m=0}^{\infty} \frac{1}{n_m!} e^{-\beta n_m(\epsilon_m - \mu)} \right]} \\
&= -\beta \langle n_l \rangle
\end{aligned}
$$

so the *occupation number* $\bar{n}_l$ of the state l is

$$
\begin{aligned}
\bar{n}_l &= \langle n_l \rangle = -\frac{1}{\beta} \frac{\partial \ln Z_{\mathrm{G}}}{\partial \epsilon_l} = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_l} e^{-\beta(\epsilon_l - \mu)} \\
&= \boxed{e^{-\beta(\epsilon_l - \mu)}.}
\end{aligned}
$$

The Boltzmann distribution gives a wrong result (for real gases) if 1-particle states are multiply occupied. Our approximation is therefore valid if

$$\bar{n}_l \ll 1 \quad \forall l$$

or

$$e^{\beta\mu} \ll e^{\beta\epsilon_l} \quad \forall l.$$

Now $\min \epsilon_l = 0$, so that

$$e^{\beta\mu} \ll 1.$$

On the other hand

$$e^{\beta\mu} = \frac{\bar{N}}{V} \lambda_T^3, \text{ when } g = 1$$

and

$$\frac{\bar{N}}{V} = \frac{1}{v_i} = \frac{3}{4\pi r_i^3},$$
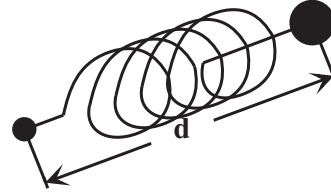
so we must have

$$\lambda_T \ll r_i.$$

Now

$$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

is the minimum diameter of the wave packet of a particle with the typical thermal energy ($\bar{\epsilon}_l = k_B T$) so in other words:
The Maxwell-Boltzmann approximation is valid when the wave packets of individual particles do not overlap.

7.3. Diatomic ideal gas

We classify molecules of two atoms to

- homopolar molecules (identical atoms), e.g. H_2, N_2, O_2, ..., and

- heteropolar molecules (different atoms), e.g. CO, NO, HCl, ...

When the density of the gas is low the intermolecular interactions are minimal and the ideal gas equation of state holds. The internal degrees of freedom, however, change the thermal properties (like C_V). When we assume that the modes corresponding to the internal degrees of freedom are independent on each other, we can write the total Hamiltonian of the molecule as the sum

$$H \approx H^{\mathrm{tr}} + H^{\mathrm{rot}} + H^{\mathrm{vibr}} + H^{\mathrm{el}} + H^{\mathrm{ydin}}.$$

Here

$$H^{\mathrm{tr}} = \frac{\boldsymbol{p}^2}{2m} = \text{kinetic energy}$$

and $m = $ mass of molecule.

$$H^{\mathrm{rot}} = \frac{\boldsymbol{L}^2}{2I} = \frac{\hbar^2 l(l+1)}{2I} = \text{rotational energy}$$

with $\boldsymbol{L} = $ angular momentum and $I = $ moment of inertia. If x_i are distances of atomic nuclei from the center of mass,

$$I = \sum_i m_i x_i^2 = \frac{m_1 m_2}{m_1 + m_2} d^2$$

Example: H_2-molecule $d = 0.75$Å,
$L = \hbar\sqrt{l(l+1)}, \quad l = 0, 1, 2, \ldots$. Now

$$\frac{\hbar^2}{2I k_B} = 85.41\text{K}$$

is the characteristic temperature of rotational d.o.f. Eigenvalues $\frac{\hbar^2}{2I} l(l+1)$ have (2l+1) -fold degeneracy.

$$H^{\mathrm{vibr}} = \hbar\omega_v(\hat{n} + \frac{1}{2}) = \text{vibration energy}$$

The vibrational degrees of freedom of the separation d of nuclei correspond at small amplitudes to a linear harmonic oscillator. $\hat{n} = a^\dagger a = 0, 1, 2, \ldots$ Each energy level is non-degenerate.

$$H^{\text{el}} = \text{electron orbital energy}$$

Corresponds to jumping of electrons from an orbital to another and ionization. Characteristic energy levels are $\gtrsim 1\text{eV} \approx k_B 10^4 \text{K}$, thus, in normal circumstances these degrees of freedom are frozen and can be neglected. H^{nucl} corresponds to energy related to nucleonic spin interactions. The spin degeneracy is $g_y = (2I_1 + 1)(2I_2 + 1)$, where I_1 and I_2 are the spins of the nuclei
Energy terms are effectively decoupled at low temperatures, i.e. the energy E_i of the state i is

$$E_i \approx E_{\text{tr}} + E_{\text{rot}} + E_{\text{vibr}},$$

so the partition sum of one molecule is

$$
\begin{aligned}
Z_1 &= \sum_{\boldsymbol{p}} \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} g_y (2l+1) \times \\
&\quad e^{-\beta \frac{p^2}{2m} - \beta \frac{\hbar^2}{2I} l(l+1) - \beta \hbar \omega_v (n+\frac{1}{2})} \\
&= Z^{\text{tr}} Z^{\text{rot}} Z^{\text{vibr}} Z^{\text{nucl}},
\end{aligned}
$$

i.e. the state sum can be factorized. Above

$$
\begin{aligned}
Z^{\text{tr}} &= \sum_{\boldsymbol{p}} e^{-\beta \frac{p^2}{2m}} = \frac{V}{\lambda_T^3} \\
\lambda_T &= \sqrt{\frac{h^2}{2\pi m k_B T}} \\
Z^{\text{rot}} &= \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \\
T_r &= \frac{\hbar^2}{2I k_B} \\
Z^{\text{vibr}} &= \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_v (n+\frac{1}{2})} \\
&= \left[2 \sinh \frac{T_v}{2T} \right]^{-1} \\
T_v &= \frac{\hbar \omega_v}{k_B} \\
Z^{\text{nucl}} &= g_y = (2I_1 + 1)(2I_2 + 1).
\end{aligned}
$$

Approximatively (neglecting the multiple occupation of states) the state sum of N molecules is

$$Z_N = \frac{1}{N!} Z_1^N,$$

where $1/N!$ takes care of the identity of molecules. We associate this factor with the translational sum. The free energy

$$F = -k_B T \ln Z_N$$

can be divided into terms

$$
\begin{aligned}
F^{\text{tr}} &= -k_B T \ln \left[\frac{1}{N!} (Z^{\text{tr}})^N \right] \\
&= -k_B T \ln \left[\frac{1}{N!} V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2} N} \right] \\
&= -k_B T N \left[\ln \frac{V}{N} + 1 + \frac{3}{2} \ln k_B T + \frac{3}{2} \ln \frac{2\pi m}{h^2} \right] \\
F^{\text{rot}} &= -N k_B T \ln \left\{ \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \right\} \\
F^{\text{vibr}} &= N k_B T \ln \left[2 \sinh \frac{T_v}{2T} \right] \\
F_{\text{nucl}} &= -N k_B T \ln g_y.
\end{aligned}
$$

The internal energy is

$$
\begin{aligned}
U &= F + TS = F - T \frac{\partial F}{\partial T} \\
&= -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right),
\end{aligned}
$$

so the internal energy corresponding to tranlational degrees of freedom is

$$U^{\text{tr}} = -T^2 \frac{\partial}{\partial T} \left(\frac{F^{\text{tr}}}{T} \right) = N \frac{3}{2} k_B T$$

and

$$C_V^{\text{tr}} = \frac{3}{2} N k_B$$

so we end up with the ideal gas result.
Since only F^{tr} depends on volume V the pressure is

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial F^{\text{tr}}}{\partial V} = \frac{N k_B T}{V},$$

i.e. we end up with the ideal gas equation of state

$$pV = N k_B T.$$

Rotation
Typical rotational temperatures

Gas	T_r
H_2	85.4
N_2	2.9
NO	2.4
HCl	15.2
Cl_2	0.36

We see that $T_r \ll$ the room temperature.
$T \ll T_r$
Now

$$Z^{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \approx 1 + 3e^{-2 \frac{T_r}{T}},$$

so the corresponding free energy is

$$F^{\text{rot}} \approx -3 N k_B T e^{-2 \frac{T_r}{T}}$$

22

and the internal energy

$$U^{\text{rot}} = -T^2 \frac{\partial}{\partial T} \left(\frac{F^{\text{rot}}}{T} \right) \approx 6Nk_BT_r e^{-2\frac{T_r}{T}}.$$

Rotations contribute to the heat capacity like

$$C_V^{\text{rot}} \approx 12Nk_B \left(\frac{T_r}{T} \right)^2 e^{-2\frac{T_r}{T}} \underset{T \to 0}{\to} 0.$$

$T \gg T_r$

Now

$$\begin{aligned} Z^{\text{rot}} &\approx \int_0^\infty dl\,(2l+1)e^{-\frac{T_r}{T}\,l(l+1)} \\ &= \left. -\frac{T}{T_r} \middle/ \right._0^\infty e^{-\frac{T_r}{T}\,l(l+1)} = \frac{T}{T_r}, \end{aligned}$$

so the free energy is

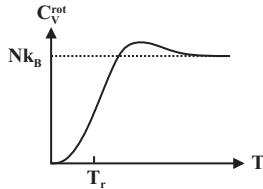$$F^{\text{rot}} \approx -Nk_BT \ln \frac{T}{T_r}$$

and the internal energy

$$U^{\text{rot}} \approx Nk_BT.$$

The contribution to the heat capacity is

$$C_V^{\text{rot}} \approx Nk_B = f^{\text{rot}} \frac{1}{2} Nk_B,$$

or in the limit $T \gg T_r$ there are $f^{\text{rot}} = 2$ rotational degrees of freedom.

Precisely:

Vibration

Typical vibrational temperatures:

Gas	T_v
H_2	6100
N_2	3340
NO	2690
O_2	2230
HCl	4140

We see that $T_v \gg$ the room temperature.

$T \ll T_v$

The free energy is

$$\begin{aligned} F^{\text{vibr}} &= Nk_BT \ln \left[e^{\frac{T_v}{2T}} (1 - e^{-\frac{T_v}{T}}) \right] \\ &\approx \frac{1}{2} Nk_BT_v - Nk_BTe^{-\frac{T_v}{T}}, \end{aligned}$$

so

$$C_V^{\text{vibr}} \approx Nk_B \left(\frac{T_v}{T} \right)^2 e^{-\frac{T_v}{T}}.$$

$T \gg T_v$

Now the free energy is
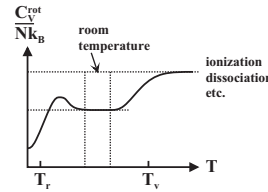
$$F^{\text{vibr}} \approx Nk_BT \ln \frac{T_v}{T}$$

and the internal energy correspondingly

$$U^{\text{vibr}} \approx Nk_BT,$$

so the heat capacity is

$$C_V^{\text{vibr}} \approx Nk_B.$$

We see that in the limit $T \gg T_v$ two degrees of freedom are associated with vibrations like always with harmonic oscillators ($E = \langle T \rangle + \langle V \rangle = 2\langle T \rangle$).

Rotation of homopolar molecules

The symmetry due to the identical nuclei must be taken into account.

Example H_2-gas:

The nuclear spins are

$$I_1 = I_2 = \frac{1}{2},$$

so the nuclei are fermions and the total wave function must be antisymmetric. The total spin of the molecule is $I = 0, 1$. We consider these two cases:

$\uparrow\uparrow$	$\uparrow\downarrow$
$I = 1$	$I = 0$
$I_z = -1, 0, 1$	$I_z = 0$
triplet	singlet
orthohydrogen	parahydrogen
spin wavefunctions symmetric:	spin wave function antisymmetric:

$$\begin{aligned} |1\,1\rangle &= |\uparrow\uparrow\rangle \\ |1\,0\rangle &= \tfrac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1\,{-}1\rangle &= |\downarrow\downarrow\rangle \end{aligned} \qquad |0\,0\rangle = \tfrac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

Space wave function antisymmetric:	Space wave function symmetric:
$(-1)^l = -1$	$(-1)^l = 1$

The corresponding partition functions are

$$\begin{aligned} Z_{\text{ortho}} &= \sum_{l=1,3,5,\ldots} (2l+1)e^{-\frac{T_r}{T}\,l(l+1)} \\ Z_{\text{para}} &= \sum_{l=0,2,4,\ldots} (2l+1)e^{-\frac{T_r}{T}\,l(l+1)} \end{aligned}$$

and the partition function associated with rotation is

$$Z^{\text{rot}} = 3Z_{\text{ortho}} + Z_{\text{para}}.$$

When $T \gg T_r$ collisions cause conversions between ortho and para states so the system is in an equilibrium. In addition $Z_{\mathrm{orto}} \approx Z_{\mathrm{para}}$, so all 4 spin states are equally probable.

When $T \lesssim T_r$ the gas may remain as an *metastable mixture* of ortho and para hydrogens. In the mixture the ratio of the spin populations is $3:1$. Then we must use the partion sum

$$Z_N^{\mathrm{rot}} = Z_{\mathrm{orto}}^{\frac{3N}{4}} Z_{\mathrm{para}}^{\frac{N}{4}}.$$

The internal energy is now

$$U^{\mathrm{rot}} = \frac{3}{4} U^{\mathrm{orto}} + \frac{1}{4} U^{\mathrm{para}}$$

and the heat capacity correspondingly

$$C^{\mathrm{rot}} = \frac{3}{4} C^{\mathrm{orto}} + \frac{1}{4} C^{\mathrm{para}}.$$

7.4. Occupation number representation

Let us recall the Fock space states, which are vectors in Hilbert space

$$\mathcal{F} = \mathcal{H}_p^{(0)} \oplus \mathcal{H}_p^{(1)} \oplus \ldots \mathcal{H}_p^{(N)} \oplus \ldots$$

with $\mathcal{H}_p^{(N)}$ is N-particle Hilbert space. Here actually $\mathcal{H}_p^{(N)} = \mathcal{S}\mathcal{H}^{(N)}$ is symmetrised for bosons and $\mathcal{A}\mathcal{H}^{(N)}$ antisymmetrised for fermions.

Denote by

$$|n_1, n_2, \ldots, n_i, \ldots\rangle$$

the quantum state where there are n_i particles in the 1 particle state i. Let the energy of the state i be ϵ_i. Then

$$
\begin{aligned}
H \left|n_1, n_2, \ldots\right\rangle &= \left(\sum_i n_i \epsilon_i\right) \left|n_1, n_2, \ldots\right\rangle \\
N &= \sum_i n_i.
\end{aligned}
$$

We define the *creation operator* $a_i^\dagger$ so that

$$a_i^\dagger \left|n_1, n_2, \ldots, n_i, \ldots\right\rangle = C \left|n_1, n_2, \ldots, n_i + 1, \ldots\right\rangle$$

i.e. $a_i^\dagger$ creates one particle into the state i.

Correspondingly the *annihilation operator* a_i obeys:

$$a_i \left|n_1, n_2, \ldots, n_i, \ldots\right\rangle = C' \left|n_1, n_2, \ldots, n_i - 1, \ldots\right\rangle,$$

i.e. a_i removes one particle from the state i.

The basis $\{|n_1, n_2, \ldots\rangle\}$ is complete, i.e.

$$\sum_{\{n_i\}} |n_1, n_2, \ldots\rangle \langle n_1, n_2, \ldots| = 1$$

and orthonormal or

$$\langle n_1', n_2', \ldots | n_1, n_2, \ldots\rangle = \delta_{n_1 n_1'} \delta_{n_2 n_2'} \cdots.$$

Bosons

For bosons the creation and annihilation operators obey the commutation relations

$$
\begin{aligned}
[a_i, a_j^\dagger] &= \delta_{ij} \\
[a_i, a_j] &= [a_i^\dagger, a_j^\dagger] = 0.
\end{aligned}
$$

It can be shown that

$$
\begin{aligned}
a_i \left|n_1, \ldots, n_i, \ldots\right\rangle &= \sqrt{n_i} \left|n_1, \ldots, n_i - 1, \ldots\right\rangle \\
a_i^\dagger \left|n_1, \ldots, n_i, \ldots\right\rangle &= \sqrt{n_i + 1} \left|n_1, \ldots, n_i + 1, \ldots\right\rangle.
\end{aligned}
$$

The *(occupation) number operator*

$$\hat{n}_i = a_i^\dagger a_i$$

obeys the relation

$$
\begin{aligned}
\hat{n}_i \left|n_1, \ldots, n_i, \ldots\right\rangle &= a_i^\dagger a_i \left|n_1, \ldots, n_i, \ldots\right\rangle \\
&= n_i \left|n_1, \ldots, n_i, \ldots\right\rangle
\end{aligned}
$$

and $n_i = 0, 1, 2, \ldots$.

An arbitrary one particle operator, i.e. an operator $O^{(1)}$, which in the configuration space operates only on the coordinates on one particle, can be written in the occupation number representation as

$$\hat{O}^{(1)} = \sum_{i,j} \left\langle i\left| O^{(1)} \right| j\right\rangle a_i^\dagger a_j.$$

A two body operator $O^{(2)}$ can be written as

$$\hat{O}^{(2)} = \sum_{ijkl} \left\langle ij\left| O^{(2)} \right| kl\right\rangle a_i^\dagger a_j^\dagger a_l a_k.$$

Example: Hamiltonian

$$H = \sum_i -\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} V(\boldsymbol{r}_i, \boldsymbol{r}_j)$$

takes in the occupation representation the form

$$
\begin{aligned}
H =& \sum_{i,j} \left\langle i\left| -\frac{\hbar^2}{2m} \nabla^2 \right| j\right\rangle a_i^\dagger a_j \\
&+ \frac{1}{2} \sum_{ijkl} \langle ij| V |kl\rangle a_i^\dagger a_j^\dagger a_l a_k,
\end{aligned}
$$

where

$$\left\langle i\left| -\frac{\hbar^2}{2m} \nabla^2 \right| j\right\rangle = -\frac{\hbar^2}{2m} \phi_i^*(\boldsymbol{r}) \nabla^2 \phi_j(\boldsymbol{r}) \, d^3 r$$

and

$$\langle ij| V |kl\rangle = \int \phi_i^*(\boldsymbol{r}_1) \phi_j^*(\boldsymbol{r}_2) V(\boldsymbol{r}_1, \boldsymbol{r}_2) \phi_k(\boldsymbol{r}_2) \phi_l(\boldsymbol{r}_1) \, d^3 r_1 \, d^3 r_2.$$

Fermions

The creation and annihilation operators of fermions satisfy the *anti*commutation relations

$$\{a_i, a_j^\dagger\} = a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}$$
$$\{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0.$$

It can be shown that

$$a_i \left|n_1, \ldots, n_i, \ldots\right\rangle =$$
$$\begin{cases} (-1)^{S_i} \sqrt{n_i} \left|n_1, \ldots, n_i - 1, \ldots\right\rangle, & \text{if } n_i = 1 \\ 0, & \text{otherwise} \end{cases}$$
$$a_i^\dagger \left|n_1, \ldots, n_i, \ldots\right\rangle =$$
$$\begin{cases} (-1)^{S_i} \sqrt{n_i + 1} \left|n_1, \ldots, n_i + 1, \ldots\right\rangle, & \text{if } n_i = 0 \\ 0, & \text{otherwise} \end{cases}$$

Here

$$S_i = n_1 + n_2 + \cdots + n_{i-1}.$$

The number operator satisfies

$$\hat{n}_i \left|n_1, \ldots, n_i, \ldots\right\rangle = n_i \left|n_1, \ldots, n_i, \ldots\right\rangle$$

and $n_i = 0, 1$.

One and two body operators take the same form as in the case of bosons. **Note:** Since a_i and a_j *anticommute* one must be careful with the order of the creation and annihilation operators in $O^{(2)}$.

In the case of non-interacting particles the Hamiltonian operator in the configuration space is

$$H = \sum_i H_1(\boldsymbol{r}_i),$$

where 1-particle Hamiltonian H_1 is

$$H_1(\boldsymbol{r}_i) = -\frac{\hbar^2}{2m} \nabla_i^2 + U(\boldsymbol{r}_i).$$

Let ϕ_j be eigenfunctions of H_1 i.e.

$$H_1 \phi_j(\boldsymbol{r}) = \epsilon_j \phi(\boldsymbol{r}).$$

In the occupation space we have then

$$\hat{H} = \sum_j \epsilon_j a_j^\dagger a_j = \sum_j \epsilon_j \hat{n}_j$$

and

$$\hat{N} = \sum_j a_j^\dagger a_j = \sum_j \hat{n}_j.$$

The grand canonical partition function is now

$$Z_{\mathrm{G}} = \operatorname{Tr} e^{-\beta(\hat{H} - \mu\hat{N})} = \sum_{n_1} \sum_{n_2} \cdots e^{-\beta \sum_l n_l(\epsilon_l - \mu)}.$$

7.5. Bose-Einstein (BE) ideal gas

In relativistic QM it can be shown that the spin of the particle is connected to the statistics: if the spin is integer, $s = 0, 1, \ldots$, the particle is boson and the wave function is symmetric wrt. permutations. If the spin is

$\frac{1}{2}$-integer, the particle is fermion with antisymmetric wave function.

In bosonic systems the occupations of one particle states are $n_l = 0, 1, 2, \ldots$. Only the grand canonical ensemble is simple to calculate. The grand canonical state sum is

$$\begin{aligned} Z_{\mathrm{G,BE}} &= \operatorname{Tr} e^{-\beta(\hat{H} - \mu\hat{N})} \\ &= \sum_{\{n\}=0}^\infty \left\langle n_1 n_2 \cdots \left| e^{-\beta(\hat{H} - \mu\hat{N})} \right| n_1 n_2 \cdots \right\rangle \\ &= \sum_{\{n\}=0}^\infty e^{-\beta \sum_l n_l(\epsilon_l - \mu)} \\ &= \prod_l \left[\sum_{n=0}^\infty e^{-\beta n(\epsilon_l - \mu)} \right] \\ &= \prod_l \frac{1}{1 - e^{-\beta(\epsilon_l - \mu)}}. \end{aligned}$$

Note: In Maxwell-Boltzmann we had $W(\{n\}) = \frac{1}{N!} \frac{N!}{n_1! n_2! \ldots}$; here we effectively have $W(\{n\}) = 1$, which is the correct way to symmetrise multiple occupation numbers.

The grand potential is

$$\Omega_{\mathrm{BE}} = k_B T \sum_l \ln\left[1 - e^{-\beta(\epsilon_l - \mu)}\right].$$

The occupation number of the state l is

$$\begin{aligned} \bar{n}_l &= \langle n_l \rangle = \frac{1}{Z_{\mathrm{G}}} \sum_{n_1} \sum_{n_2} \cdots n_l e^{-\beta \sum_m n_m(\epsilon_m - \mu)} \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_l} \ln Z_{\mathrm{G}} = \frac{\partial \Omega}{\partial \epsilon_l}, \end{aligned}$$

and for the *Bose-Einstein occupation number* we get

$$\boxed{\bar{n}_l = \frac{1}{e^{\beta(\epsilon_l - \mu)} - 1}.}$$

Entropy

Because $d\Omega = -S\,dT - p\,dV - N\,d\mu$ we have

$$\begin{aligned} S &= \left(\frac{\partial \Omega}{\partial T}\right)_{\mu, V} \\ &= -k_B \sum_l \ln\left[1 - e^{-\beta(\epsilon_l - \mu)}\right] \\ &\quad -k_B T \sum_l \frac{1}{1 - e^{-\beta(\epsilon_l - \mu)}} (\epsilon_l - \mu) e^{-\beta(\epsilon_l - \mu)} \frac{-1}{k_B T^2}. \end{aligned}$$

Now

$$e^{\beta(\epsilon_l - \mu)} = 1 + \frac{1}{\bar{n}_l}$$

and

$$\beta(\epsilon_l - \mu) = \ln(1 + \bar{n}_l) - \ln \bar{n}_l,$$

so

$$\begin{aligned} S &= -k_B \sum_l \ln\left(1 - \frac{\bar{n}_l}{\bar{n}_l + 1}\right) \\ &\quad + k_B \sum_l \bar{n}_l \left[\ln(\bar{n}_l + 1) - \ln \bar{n}_l\right] \end{aligned}$$

or

$$S = k_B \sum_l \left[(\bar{n}_l + 1) \ln(\bar{n}_l + 1) - \bar{n}_l \ln \bar{n}_l \right].$$

7.6. Fermi-Dirac ideal gas

The Hamiltonian operator is

$$\hat{H} = \sum_l \epsilon_l a_l^\dagger a_l$$

and the number operator

$$\hat{N} = \sum_l a_l^\dagger a_l.$$

Now

$$\{ a_l, a_{l'}^\dagger \} = \delta_{ll'}$$

and

$$\{ a_l, a_{l'} \} = \{ a_l^\dagger, a_{l'}^\dagger \} = 0.$$

The eigenvalues of the number operator related to the state l,

$$\hat{n}_l = a_l^\dagger a_l,$$

are

$$n_l = 0, 1.$$

The state sum in the grand canonical ensemble is

$$
\begin{aligned}
Z_{\mathrm{G,FD}} \\
&= \mathrm{Tr}\, e^{-\beta(\hat{H} - \mu \hat{N})} \\
&= \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots \left\langle n_1 n_2 \cdots \left| e^{-\beta(\hat{H} - \mu \hat{N})} \right| n_1 n_2 \cdots \right\rangle \\
&= \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots e^{-\beta \sum_l n_l(\epsilon_l - \mu)} \\
&= \prod_l \left\{ \sum_{n=0}^{1} e^{-\beta n(\epsilon_l - \mu)} \right\} \\
&= \prod_l \left[1 + e^{-\beta(\epsilon_l - \mu)} \right].
\end{aligned}
$$

The grand potential is
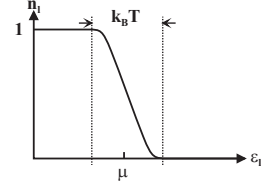
$$\Omega_{\mathrm{FD}} = -k_B T \sum_l \ln \left[1 + e^{-\beta(\epsilon_l - \mu)} \right].$$

The average occupation number of the state l is

$$
\begin{aligned}
\bar{n}_l &= \langle n_l \rangle = \frac{1}{Z_{\mathrm{G,FD}}} \mathrm{Tr}\, \hat{n}_l e^{-\beta(\hat{H} - \mu \hat{N})} \\
&= \frac{1}{Z_{\mathrm{G,FD}}} \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots n_l e^{-\beta \sum_{l'} n_{l'}(\epsilon_{l'} - \mu)} \\
&= -\frac{1}{\beta} \frac{\partial \ln Z_{\mathrm{G,FD}}}{\partial \epsilon_l} = \frac{\partial \Omega_{\mathrm{FD}}}{\partial \epsilon_l} \\
&= \frac{e^{-\beta(\epsilon_l - \mu)}}{1 + e^{-\beta(\epsilon_l - \mu)}}.
\end{aligned}
$$

Thus the *Fermi-Dirac occupation number* can be written as
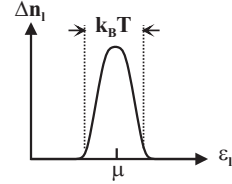
$$\bar{n}_l = \frac{1}{e^{\beta(\epsilon_l - \mu)} + 1}.$$

The expectation value of the square of the occupation number will be

$$
\begin{aligned}
\left\langle n_l^2 \right\rangle &= \frac{1}{Z_{\mathrm{G,FD}}} \mathrm{Tr}\, \hat{n}_l^2 e^{-\beta(\hat{H} - \mu \hat{N})} \\
&= \frac{1}{Z_{\mathrm{G,FD}}} \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots n_l^2 e^{-\beta \sum_{l'} n_{l'}(\epsilon_{l'} - \mu)} \\
&= \frac{1}{\beta^2} \frac{1}{Z_{\mathrm{G,FD}}} \frac{\partial^2 Z_{\mathrm{G,FD}}}{\partial \epsilon_l^2} \\
&= -\frac{1}{\beta} \frac{1}{Z_{\mathrm{G,FD}}} \left(\prod_{l' \neq l} \left[1 + e^{-\beta(\epsilon_{l'} - \mu)} \right] \right) \\
&\quad \times \frac{\partial}{\partial \epsilon_l} e^{-\beta(\epsilon_l - \mu)} \\
&= \frac{e^{-\beta(\epsilon_l - \mu)}}{1 + e^{-\beta(\epsilon_l - \mu)}} = \bar{n}_l.
\end{aligned}
$$

This is natural, since $n_l^2 = n_l$. For the variance we get

$$
\begin{aligned}
(\Delta n_l)^2 &= \left\langle n_l^2 \right\rangle - \langle n_l \rangle^2 = \bar{n}_l - \bar{n}_l^2 \\
&= \bar{n}_l (1 - \bar{n}_l).
\end{aligned}
$$

There are fluctuations only in the vicinity of the chemical potential μ.

The *entropy* is

$$
\begin{aligned}
S &= -\frac{\partial \Omega}{\partial T} \\
&= k_B \sum_l \ln \left[1 + e^{-\beta(\epsilon_l - \mu)} \right] \\
&\quad + \frac{1}{T} \sum_l \overbrace{\frac{e^{-\beta(\epsilon_l - \mu)}}{1 + e^{-\beta(\epsilon_l - \mu)}}}^{= \bar{n}_l} (\epsilon_l - \mu).
\end{aligned}
$$

Now $\beta(\epsilon_l - \mu) = \ln \frac{1 - \bar{n}_l}{\bar{n}_l}$ and $1 + e^{-\beta(\epsilon_l - \mu)} = \frac{1}{1 - \bar{n}_l}$, so

$$S = -k_B \sum_l \left[(1 - \bar{n}_l) \ln(1 - \bar{n}_l) + \bar{n}_l \ln \bar{n}_l \right].$$