Quantum statistics

- When the silver atoms leave the oven in Stern-Gerlach experiment, their spin is randomly oriented.
- $|\alpha\rangle = c_\uparrow|S_z;\uparrow\rangle + c_\downarrow|S_z;\downarrow\rangle$
describes the state of a single atom whose spin is pointing to a definitive direction.
- An ensemble is a collection of identically prepared systems, in which all members (separately) are described with the same ket $|\alpha\rangle$.
- polar and azimuthal angles, α and β, can be solved from

$$\frac{c_\uparrow}{c_\downarrow} = \frac{\cos(\beta/2)}{e^{i\alpha}\sin(\beta/2)}.$$

- only vanishingly small fraction of atoms are in this particular spin state

Let us introduce the concept of *fractional population* by stating that 60% of atoms are characterized with $|S_z;\uparrow\rangle$ and 40% with $|S_z;\downarrow\rangle$ (equally well $|S_x;\uparrow\rangle$ and $|S_x;\downarrow\rangle$). Such an ensemble is specified by assigning fractional populations

$$w_\uparrow = 0.6, \quad w_\downarrow = 0.4.$$

for spin up and down.
Unlike $c_\uparrow$ and $c_\downarrow$, $w_\uparrow$ and $w_\downarrow$ are real and have nothing to do with the relative phase between the spin-up and spin-down ket.
Often such a collection is called an **incoherent mixture**.
The atoms coming from S-G oven form **completely random ensemble** and are said to be **unpolarised**. In contrast, after a selective S-G experiment we have a **pure ensemble** which is polarized since all members of the ensemble are described by the same $|\alpha\rangle$ pointing in some definitive direction.
When the mixed ensemble consist on M different states, there is M different state kets $|\alpha_i\rangle$ with M fractional populations w_i corresponding to these states.
Obviously fractional populations must satisfy normalization

$$\sum_i w_i = 1.$$

$|\alpha_i\rangle$:s do not need to be orthogonal and M can differ from the dimensionality of the ket space N
The ensemble average of an operator A reads

$$\begin{aligned}[A] &\equiv \sum_i w_i\langle\alpha_i|A|\alpha_i\rangle \\ &= \sum_i\sum_{a'} w_i|\langle a'|\alpha_i\rangle|^2 a',\end{aligned}$$

in which $|a'\rangle$ is an eigenstate of A.
Notice the "double probabilistic" nature.
The ensemble average in terms of arbitrary base vectors $\{|b'\rangle\}$

$$\begin{aligned}
[A] &= \sum_i w_i \sum_{b'} \sum_{b''} \langle \alpha_i | b' \rangle \langle b' | A | b'' \rangle \langle b'' | \alpha_i \rangle \\
&= \sum_{b'} \sum_{b''} \left(\sum_i w_i \langle b'' | \alpha_i \rangle \langle \alpha_i | b' \rangle \right) \langle b' | A | b'' \rangle.
\end{aligned}$$

The density operator:

$$\rho \equiv \sum_i w_i |\alpha_i\rangle\langle\alpha_i|$$

and the corresponding density matrix

$$\langle b'' | \rho | b' \rangle = \sum_i w_i \langle b'' | \alpha_i \rangle \langle \alpha_i | b' \rangle.$$

contain all physically significant information about the **ensemble**.
Density operator is hermitean and normalized

$$\rho^\dagger = \rho \qquad ; \qquad \mathrm{tr}\rho = 1.$$

Perhaps useful to remember:
for a pure ensemble
    $\mathrm{tr}(\rho^2)$=1 (and maximal)
while for mixed ensembles
    $\mathrm{tr}(\rho^2) \in [0,1] \in \Re$
Ensemble average in terms of density operator:

$$\begin{aligned}
[A] &= \sum_{b'} \sum_{b''} \langle b'' | \rho | b' \rangle \langle b' | A | b'' \rangle \\
&= \mathrm{tr}(\rho A).
\end{aligned}$$

Recall that trace and thus $[A]$ is independent on representation and can be evaluated in the most convenient basis.
Matrix representations for pure and completely mixed ensembles at blackboard.

Time evolution

$$|\alpha_i\rangle = |\alpha_i; t_0\rangle \longrightarrow |\alpha_i, t_0; t\rangle$$

If the ensemble is left undisturbed, the occupation of states is conserved, i.e.

$$w_i = \text{constant}.$$

and the dynamics of the ρ arises solely by the time evolution of the state kets:

$$\rho(t) = \sum_i w_i |\alpha_i, t_0; t\rangle\langle\alpha_i, t_0; t|,$$

so

$$\begin{aligned} i\hbar \frac{\partial \rho}{\partial t} &= \sum_i w_i \left(i\hbar \frac{\partial}{\partial t} |\alpha_i, t_0; t\rangle \right) \langle\alpha_i, t_0; t| \\ &\quad + \sum_i w_i |\alpha_i, t_0; t\rangle \left(-i\hbar \frac{\partial}{\partial t} |\alpha_i, t_0; t\rangle \right)^\dagger \\ &= H\rho - \rho H = -[\rho, H]. \end{aligned}$$

Like Heisenberg's equation of motion, but wrong sign!
OK, since ρ is not an observable.

Continuum

$$\begin{aligned} [A] &= \sum_{b'} \sum_{b''} \langle b''|\rho|b'\rangle\langle b'|A|b''\rangle \\ &= \mathrm{tr}(\rho A). \end{aligned}$$

For example in position space above transforms to

$$[A] = \int d^3x' \int d^3x'' \, \langle \boldsymbol{x}''|\rho|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|A|\boldsymbol{x}''\rangle.$$

Here the density matrix is

$$\begin{aligned} \langle \boldsymbol{x}''|\rho|\boldsymbol{x}'\rangle &= \langle \boldsymbol{x}''| \left(\sum_i w_i |\alpha_i\rangle\langle\alpha_i| \right) |\boldsymbol{x}'\rangle \\ &= \sum_i w_i \psi_i(\boldsymbol{x}'')\psi_i^*(\boldsymbol{x}'). \end{aligned}$$

Note

$$\langle \boldsymbol{x}'|\rho|\boldsymbol{x}'\rangle = \sum_i w_i |\psi_i(\boldsymbol{x}')|^2.$$

Statistical mechanics
We define

$$\sigma = -\mathrm{tr}(\rho \ln \rho).$$

which in the basis where ρ is diagonal reads

$$\sigma = -\sum_k \rho_{kk} \ln \rho_{kk}.$$

Now $\rho_{kk} \in [0, 1] \in \Re \Rightarrow \sigma$ is a positive definitive and can be implemented to "classify" different ensembles.
One can show that

- for a completely stochastic (random) ensemble

$$\sigma = -\sum_{k=1}^{N} \frac{1}{N} \ln \frac{1}{N} = \ln N,$$

  when N is the number of the independent states in the system.

- for a pure ensemble
$$\sigma = 0.$$

- mixed ensembles something between

Hence σ measures disorder $\Longrightarrow$ it has something to do with the entropy.
The entropy is defined by
$$S = k\sigma.$$

In a thermodynamical equilibrium

$$\frac{\partial \rho}{\partial t} = 0,$$

so
$$-[\rho, H] = 0$$

and the operators ρ and H have common eigenstates $|k\rangle$:

$$\begin{aligned} H|k\rangle &= E_k|k\rangle \\ \rho|k\rangle &= w_k|k\rangle. \end{aligned}$$

Using these eigenstates the density matrix can be represented as

$$\rho = \sum_k w_k |k\rangle\langle k|$$

and
$$\sigma = -\sum_k \rho_{kk} \ln \rho_{kk},$$

where the diagonal elements of the density matrix are

$$\rho_{kk} = w_k.$$

In the equilibrium the entropy is at maximum.
We maximize σ under conditions

- $U = [H] = \mathrm{tr}(\rho H) = \sum_k \rho_{kk} E_k$.

- $\mathrm{tr}\rho = 1$.

Hence

$$\begin{aligned}
\delta\sigma &= -\sum_k \delta\rho_{kk}(\ln\rho_{kk}+1)=0 \\
\delta[H] &= \sum_k \delta\rho_{kk}E_k = 0 \\
\delta(\mathrm{tr}\rho) &= \sum_k \delta\rho_{kk} = 0.
\end{aligned}$$

With the help of Lagrange multipliers we get

$$\sum_k \delta\rho_{kk}\left[(\ln\rho_{kk}+1)+\beta E_k+\gamma\right]=0,$$

so

$$\rho_{kk} = e^{-\beta E_k-\gamma-1}.$$

The normalization ($\mathrm{tr}\rho = 1$) gives

$$\rho_{kk} = \frac{e^{-\beta E_k}}{\sum_l^N e^{-\beta E_l}} \quad \text{(canonical ensemble)}.$$

It turns out that

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

where T is the thermodynamical temperature and k_B the Boltzmann constant. In statistical mechanics we define *the canonical partition function* Z:

$$Z = \mathrm{tr}e^{-\beta H} = \sum_k^N e^{-\beta E_k}.$$

Now

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

The ensemble average can be written as

$$\begin{aligned}
[A] &= \mathrm{tr}\rho A = \frac{\mathrm{tr}\left(e^{-\beta H}A\right)}{Z} \\
&= \frac{\left[\sum_k^N \langle k|A|k\rangle e^{-\beta E_k}\right]}{\sum_k^N e^{-\beta E_k}}.
\end{aligned}$$

In particular we have

$$
\begin{aligned}
U &= [H] = \frac{\sum_k^N E_k e^{-\beta E_k}}{\sum_k^N e^{-\beta E_k}} \\
&= -\frac{\partial}{\partial \beta}(\ln Z).
\end{aligned}
$$

Example Electrons in a magnetic field parallel to z axis.
In the basis $\{|S_z;\uparrow\rangle, |S_z;\downarrow\rangle\}$ of the eigenstates of the Hamiltonian

$$H = \omega_c S_z$$

we have

$$\rho \mapsto \frac{\begin{pmatrix} e^{-\beta\hbar\omega_c/2} & 0 \\ 0 & e^{\beta\hbar\omega_c/2} \end{pmatrix}}{Z},$$

where

$$Z = e^{-\beta\hbar\omega_c/2} + e^{\beta\hbar\omega_c/2}.$$

For example the ensemble averages are

$$
\begin{aligned}
[S_x] &= [S_y] = 0, \\
[S_z] &= -\left(\frac{\hbar}{2}\right)\tanh\left(\frac{\beta\hbar\omega_c}{2}\right).
\end{aligned}
$$