In other words, the diagonal matrix element $< n|\boldsymbol{\rho}|n>$ yields the probability that the state $|n>$ is occupied in the ensemble represented by $\boldsymbol{\rho}$. We can also refer the average of a physical quantity $\mathbf{A}$ to the same basis:

$$[\mathbf{A}] = \mathrm{Tr}\left(\boldsymbol{\rho}\mathbf{A}\right) = \sum_{n,m} < n|\boldsymbol{\rho}|m >< m|\mathbf{A}|n >= \sum_{n,m}\sum_{i} w_i \; a_n^{(i)} a_m^{(i)*} A_{mn} = \sum_{n,m} \overline{a_n a_m^*} \; A_{mn} \; .$$

If an operator $\mathbf{B}$ is diagonal in the given basis, *i.e.* $< m|\mathbf{B}|n >= B_n \delta_{mn}$, its average is given by:

$$[\mathbf{B}] = \sum_i w_i \sum_n P_n^{(i)} B_n = \sum_n B_n \; \overline{|a_n|^2} \; .$$

For the continuous spectrum, we discuss the important cases of the coordinate and momentum representations. The matrix elements of $\boldsymbol{\rho}$ now become two-point functions. For the coordinate representation $\{|\overrightarrow{\mathbf{x}}>\}$, the linear coefficients $< \overrightarrow{\mathbf{x}}|\psi^{(i)} >$ are called 'wave functions' and usually, one writes

$$\psi^{(i)}\left(\overrightarrow{\mathbf{x}}\right) =< \overrightarrow{\mathbf{x}}|\psi^{(i)} > \; ,$$

meaning that they vary continuously with $\tilde{\mathbf{x}}$. Now, we represent the density operator:

$$\begin{aligned} < \; \overrightarrow{\mathbf{x}} \, |\boldsymbol{\rho}| \, \overrightarrow{\mathbf{x}}' >&= \rho\left(\overrightarrow{\mathbf{x}}, \overrightarrow{\mathbf{x}}'\right) = \sum_i w_i < \overrightarrow{\mathbf{x}}|\psi^{(i)} >< \psi^{(i)}|\overrightarrow{\mathbf{x}}' >= \\ =& \; \sum_i w_i \; \psi^{(i)}\left(\overrightarrow{\mathbf{x}}\right) \psi^{(i)*}\left(\overrightarrow{\mathbf{x}}'\right) = \overline{\psi\left(\overrightarrow{\mathbf{x}}\right) \psi^*\left(\overrightarrow{\mathbf{x}}'\right)} \; . \end{aligned} \tag{1.21}$$

Diagonal elements are given by:

$$< \overrightarrow{\mathbf{x}} \, |\boldsymbol{\rho}| \, \overrightarrow{\mathbf{x}} >= \rho\left(\overrightarrow{\mathbf{x}}, \overrightarrow{\mathbf{x}}\right) = \sum_i w_i \; \left|\psi^{(i)}\left(\overrightarrow{\mathbf{x}}\right)\right|^2 = \overline{\left|\psi\left(\overrightarrow{\mathbf{x}}\right)\right|^2} \geqq 0 \; . \tag{1.22}$$

In Quantum Mechanics, $\left|\psi^{(i)}\left(\tilde{\mathbf{x}}\right)\right|^2$ is interpreted as a probability density, since normalization requires

$$\int \mathbf{d}\overrightarrow{\mathbf{x}} \ \left|\psi^{(i)}\left(\overrightarrow{\mathbf{x}}\right)\right|^2 = 1 \ ,$$

where the integral is taken over all space. It follows that diagonal elements of $\boldsymbol{\rho}$, given by (1.22), are also probability densities, with

$$\mathrm{Tr}\left(\boldsymbol{\rho}\right) = \int \mathbf{d}\overrightarrow{\mathbf{x}} \ < \overrightarrow{\mathbf{x}} \left|\boldsymbol{\rho}\right| \overrightarrow{\mathbf{x}} >= \sum_i w_i \ = 1 \ .$$

Average of an observable $\mathbf{A}$ is obtained integrating the two-point function $\rho\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{x}}'\right)$ of (1.21) with the matrix elements of $\mathbf{A}$:

$$\begin{aligned}
[\mathbf{A}] &= \mathrm{Tr}\left(\boldsymbol{\rho}\mathbf{A}\right) = \int \mathbf{d}\overrightarrow{\mathbf{x}} \int \mathbf{d}\overrightarrow{\mathbf{x}}\prime < \overrightarrow{\mathbf{x}} \left|\boldsymbol{\rho}\right| \overrightarrow{\mathbf{x}}\prime >< \overrightarrow{\mathbf{x}}\prime \left|\mathbf{A}\right| \overrightarrow{\mathbf{x}} >= \\
&= \int \mathbf{d}\overrightarrow{\mathbf{x}} \int \mathbf{d}\overrightarrow{\mathbf{x}}\prime \rho\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{x}}\prime\right) \ A\left(\overrightarrow{\mathbf{x}}\prime,\overrightarrow{\mathbf{x}}\right) \ . \qquad (1.23)
\end{aligned}$$

If the observable is local in the coordinate representation, $A\left(\overrightarrow{\mathbf{x}}\prime,\overrightarrow{\mathbf{x}}\right) = A\left(\overrightarrow{\mathbf{x}}\right)\boldsymbol{\delta}\left(\overrightarrow{\mathbf{x}}\prime - \overrightarrow{\mathbf{x}}\right)$, where $\boldsymbol{\delta}\left(\overrightarrow{\mathbf{x}}\prime - \overrightarrow{\mathbf{x}}\right)$ is the Dirac delta function, the double integral (1.23) is reduced to the single integration below:

$$[\mathbf{A}] = \int \mathbf{d}\overrightarrow{\mathbf{x}} \rho\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{x}}\right) \ A\left(\overrightarrow{\mathbf{x}}\right) \ ,$$

i.e. the function $A\left(\overrightarrow{\mathbf{x}}\right)$ is integrated with the probability density $\rho\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{x}}\right)$. Note that for a pure ensemble, $\rho\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{x}}\right)$ is simply given by $\psi^*\left(\overrightarrow{\mathbf{x}}\right)\psi\left(\overrightarrow{\mathbf{x}}\right) = \left|\psi\left(\overrightarrow{\mathbf{x}}\right)\right|^2$, the probability density associated with the wave function $\psi\left(\overrightarrow{\mathbf{x}}\right)$.

We pass to the momentum representation replacing the wave function in real space by the wave function in momentum space:

$$\phi^{(i)}\left(\overrightarrow{\mathbf{p}}\right) = < \overrightarrow{\mathbf{p}}|\psi^{(i)} > \ .$$

All formulae can be translated to the new basis $\{|\overrightarrow{\mathbf{p}}>\}$. For instance, the probability density associated with the diagonal matrix elements of $\boldsymbol{\rho}$ is obtained as:

$$< \overrightarrow{\mathbf{p}}\,|\boldsymbol{\rho}|\,\overrightarrow{\mathbf{p}} >= \rho\left(\overrightarrow{\mathbf{p}},\overrightarrow{\mathbf{p}}\right) = \sum_i w_i \,\left|\phi^{(i)}\left(\overrightarrow{\mathbf{p}}\right)\right|^2 = \overline{\left|\phi\left(\overrightarrow{\mathbf{p}}\right)\right|^2} \geqq 0 \ .$$

Due to the uncertainty principle, we are bound to use one basis only, but we can go from one to the other, say from $|\overrightarrow{\mathbf{x}}>$ to $\overrightarrow{\mathbf{p}}>$, with the transformation matrix [1], [2] :

$$< \overrightarrow{\mathbf{p}}|\overrightarrow{\mathbf{x}}>=\frac{1}{(2\pi\hbar)^{3/2}}\exp\left(-\frac{i\overrightarrow{\mathbf{p}}\cdot\overrightarrow{\mathbf{x}}}{\hbar}\right) \ . \tag{1.24}$$

The classical density function that yields the density of points in phase space, is a function of generalized coordinates and momenta, $\rho(q,p)$. To make connection with the classical case, one has to look for a mixed representation of the operator $\boldsymbol{\rho}$. At first sight, this may seem forbidden by the uncertainty principle, but one can follow a procedure due to Wigner [5] to generate such a function.

Take for instance $\rho\left(\overrightarrow{\mathbf{p}},\overrightarrow{\mathbf{p}}\right)$ and use the transformation (1.24) to pass to the coordinate representation:

$$\rho\left(\overrightarrow{\mathbf{p}},\overrightarrow{\mathbf{p}}\right) = \int \mathbf{d}\overrightarrow{\mathbf{x}} \int \mathbf{d}\overrightarrow{\mathbf{x}}\prime \frac{1}{(2\pi\hbar)^3}\exp\frac{i\overrightarrow{\mathbf{p}}\cdot\left(\overrightarrow{\mathbf{x}}\prime-\overrightarrow{\mathbf{x}}\right)}{\hbar}\ \rho\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{x}}'\right) \ ,$$

then make the change of variables with unit Jacobian:

$$\overrightarrow{\mathbf{r}}=\overrightarrow{\mathbf{x}\prime}-\overrightarrow{\mathbf{x}} \ ,$$

$$\overrightarrow{\mathbf{R}}=\tfrac{1}{2}\left(\overrightarrow{\mathbf{x}}+\overrightarrow{\mathbf{x}\prime}\right) \ .$$

We obtain

$$\rho\left(\overrightarrow{\mathbf{p}},\overrightarrow{\mathbf{p}}\right)=\int \mathbf{d}\overrightarrow{\mathbf{R}}\int \mathbf{d}\overrightarrow{\mathbf{r}}\frac{1}{(2\pi\hbar)^3}\exp\left(\frac{i\overrightarrow{\mathbf{p}}\cdot\overrightarrow{\mathbf{r}}}{\hbar}\right)\ \rho\left(\overrightarrow{\mathbf{R}}-\frac{\overrightarrow{\mathbf{r}}}{2},\overrightarrow{\mathbf{R}}+\frac{\overrightarrow{\mathbf{r}}}{2}\right)\ . \tag{1.25}$$

The integrand in relation to $\overrightarrow{\mathbf{R}}$ defines a function which depends on $\overrightarrow{\mathbf{R}}$ and $\overrightarrow{\mathbf{p}}$, which is of the mixed form and consistent with the uncertainty principle.

Definition 6 *Wigner function, ρ_W*

$$\rho_W\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{p}}\right)\equiv\frac{1}{(2\pi\hbar)^3}\int \mathbf{d}\overrightarrow{\mathbf{r}}\exp\left(\frac{i\overrightarrow{\mathbf{p}}\cdot\overrightarrow{\mathbf{r}}}{\hbar}\right)\ \rho\left(\overrightarrow{\mathbf{x}}-\frac{\overrightarrow{\mathbf{r}}}{2},\overrightarrow{\mathbf{x}}+\frac{\overrightarrow{\mathbf{r}}}{2}\right) \tag{1.26}$$

In our deduction in (1.25), we have proved an important property of the Wigner function, which reads:

$$\rho\left(\overrightarrow{\mathbf{p}},\overrightarrow{\mathbf{p}}\right)=\int \mathbf{d}\overrightarrow{\mathbf{x}}\ \rho_W\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{p}}\right)\ , \tag{1.27}$$

that is, the probability density $\rho\left(\overrightarrow{\mathbf{p}},\overrightarrow{\mathbf{p}}\right)$ is obtained from the Wigner function $\rho_W\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{p}}\right)$ integrating over the space variable $\overrightarrow{\mathbf{x}}$. The complementary relation is also true, and it is left to the reader to prove its validity:

$$\rho\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{x}}\right)=\int \mathbf{d}\overrightarrow{\mathbf{p}}\ \rho_W\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{p}}\right)\ . \tag{1.28}$$

Relations (1.27) and (1.28) are desirable properties for a function to be candidate to represent the classical density. But definition (1.26) is fully quantum mechanical, and one has to take the limit in some non trivial way to get the classical case. In general, one can show that the property

$$\rho_W\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{p}}\right) \geqq 0$$

is not always satisfied in the whole phase space $\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{p}}\right)$. Regions where $\rho_W\left(\overrightarrow{\mathbf{x}},\overrightarrow{\mathbf{p}}\right) < 0$ are said to contain coherent quantum effects, the size of those regions shrinking with $\hbar \to 0$. Formally, it was shown by Wigner [5] that ρ_W satisfies the Liouville equation, when $\hbar \to 0$ (see next subsection). For a system consisting of N particles, definition (1.26) can be generalized to the phase space Γ of a system of particles:

$$\begin{aligned}\rho_W^{(N)}\left(\tilde{\mathbf{x}}_1,\tilde{\mathbf{x}}_2,...,\tilde{\mathbf{x}}_N;\tilde{\mathbf{p}}_1,\tilde{\mathbf{p}}_2,...,\overrightarrow{\mathbf{p}}_N\right) \equiv \frac{1}{(2\pi\hbar)^3}\int\int...\int \mathbf{d}^3\mathbf{r}_1\mathbf{d}^3\mathbf{r}_2...\mathbf{d}^3\mathbf{r}_N \times \\ \times \exp\left(i\frac{\tilde{\mathbf{p}}_1\cdot\tilde{\mathbf{r}}_1+...+\tilde{\mathbf{p}}_N\cdot\tilde{\mathbf{r}}_N}{\hbar}\right)\left\langle\tilde{\mathbf{x}}_1-\tfrac{\tilde{\mathbf{r}}_1}{2},...,\tilde{\mathbf{x}}_N-\tfrac{\tilde{\mathbf{r}}_N}{2}\right|\boldsymbol{\rho}\left|\tilde{\mathbf{x}}_1+\tfrac{\tilde{\mathbf{r}}_1}{2},...,\tilde{\mathbf{x}}_N+\tfrac{\tilde{\mathbf{r}}_N}{2}\right\rangle\ .\end{aligned} \tag{1.29}$$

B

1.5.1 Digression over the Gibbsian ensemble

We discuss here some key concepts concerning the classical density function $\rho(q,p)$, which was the goal of Wigner's approach. In classical Statistical Mechanics, a microstate of a system of N particles is represented by a point in 'phase space' Γ. This is a $6N$ dimensional space spanned by the generalized coordinates and conjugate momenta $\{q_i, p_i\}$, that characterize the system. If we use cartesian coordinates,

$$\{q_i\}_{3N} = (x_1, y_1, z_1, ..., x_N, y_N, z_N) \ .$$

From the macroscopic point of view, we operate with a reduced set of quantities that are compatible with a great number of microstates, as for example the case of a gas occupying a given volume, at standard conditions of temperature and pressure. In Statistical Mechanics, we are not interested in the detailed motion of a system of many particles, but we just want to calculate some average properties (thermodynamic quantities) that we compute using an *ensemble* of ideal replicas of the same system. The ensemble is then represented by a swarm of points in Γ space, being the points interpreted as different microstates corresponding to different initial conditions of the system, all satisfying the same macroscopic constraints. This idea was introduced by Gibbs at the foundations of Statistical Mechanics, with the relevant quantity to characterize the ensemble being the density of points in Γ space. Let $\rho(q_i, p_i, t)$ be such a distribution, with the notation meaning that ρ depends on all generalized coordinates and momenta, and may also depend explicitly on time. In other words,

$$\rho(q_i, p_i, t) dq^{3N} dp^{3N}$$

is the number of representative system points (microstates) contained at time t in the infinitesimal volume $d\Omega = dq^{3N} dp^{3N}$, with $d\Omega$ centered about the point $\{q_i, p_i\}$

in phase space. Those representative points of the ensemble evolve in time, tracing a trajectory in Γ space which is closed (periodic motion) or never autointersects itself. Also, trajectories of different representative points never intersect, since they represent motions with different initial conditions (if two trajectories intersect at a given point, that common point may be chosen as a new initial condition, and the two trajectories should coincide at all times). In Classical Mechanics, one can show that time evolution is a canonical transformation [6], and volume of phase space is a canonical invariant (one of Poincaré's integral invariants). The number of representative points of the ensemble contained in any infinitesimal volume $d\Omega$ is also constant in time. The form of the infinitesimal element changes, but its volume is constant. No representative point can intersect the boundary of $d\Omega$ at any time (same argument as given above). We then can enunciate this result as a theorem:

Theorem 7 (Liouville) *The density $\rho(q, p, t)$ is constant in time, or*

$$\frac{d\rho}{dt} = 0 \ . \tag{1.30}$$

We can rewrite the theorem (1.30) in a different form:

$$0 = \frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_i \left(\dot{q}_i \frac{\partial\rho}{\partial q_i} + \dot{p}_i \frac{\partial\rho}{\partial p_i} \right) \ , \tag{1.31}$$

showing that the explicit dependence on time is cancelled by the implicit dependence through coordinates and momenta. For a Hamiltonian system, Hamilton equations of motion are satisfied, with Hamiltonian H:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \ , \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \ , \tag{1.32}$$

which we substitute in (1.31), yielding:

$$0 = \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i} \right) \ ,$$

which is written in turn, in term of a Poisson bracket [6] as:

$$0 = \frac{\partial \rho}{\partial t} + \{\rho, H\} \ , \tag{1.33}$$

with the Poisson bracket defined as $\{A, B\} \equiv \sum_i \left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i} \right)$. Relation (1.33) is another way to state the Liouville theorem. It can be interpreted geometrically [**huang**]: the motion of representative points in Γ space resembles closely the motion of an incompressible fluid. In fact, relation (1.33) has the form of a continuity equation, if one defines a current density for the flux of points as:

$$\overrightarrow{\mathbf{j}} \equiv \rho \overrightarrow{\mathbf{v}} \ ,$$

with the velocity vector written as

$$\overrightarrow{\mathbf{v}} = (\dot{q}_1, \dot{q}_2, ..., \dot{q}_{3N}; \dot{p}_1, \dot{p}_2 ..., \dot{p}_{3N}) \ .$$

Due to Hamilton equations of motion (1.32), we get

$$0 = \frac{\partial \rho}{\partial t} + \{\rho, H\} = \frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \overrightarrow{\mathbf{j}} \ ,$$

with the 'nabla' operator defined in Γ space as:

$$\boldsymbol{\nabla} \equiv \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, ..., \frac{\partial}{\partial q_{3N}}; \frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, ..., \frac{\partial}{\partial p_{3N}} \right) \ .$$

Then, local variations of ρ are caused by the flux of the density current $\overrightarrow{\mathbf{j}}$, in any neighborhood of representative points of the ensemble. Let $A(q,p)$ be a dynamical quantity of the system of particles. At the macroscopic level, the value of A that we observed is supposed to be the average over the ensemble, calculated as

$$[A]_C\,(t) = \frac{\int dq^{3N} dp^{3N} \rho(q,p,t)\ A(q,p)}{\int dq^{3N} dp^{3N} \rho(q,p,t)} \ ,$$

with the distribution $\rho(q,p,t)$ satisfying Liouville theorem, and the symbol $[...]_C$ standing for the classical average. In principle, the time dependence of $[A]_C\,(t)$ should approach its equilibrium value at the stationary situation:

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

A stationary density distribution $\rho(q,p)$ will only depend on time-independent integrals of the equations of motion. The simplest assumption is to postulate that ρ is a function of the total energy $H = E$, which is a conserved quantity. The equal a priori probability distribution:

$$\rho = \rho(E) = \begin{cases} \text{constant, if } E - \frac{1}{2}\Delta < H < E + \frac{1}{2}\Delta \,, \\ \qquad\qquad 0, \qquad \text{otherwise} \end{cases}$$

is called *microcanonical ensemble*, and represents an isolated system. The quantity Δ is chosen, such that $\Delta \ll E$, and is introduced for convenience in the counting of states. In the thermodynamic limit, macroscopic quantities are independent of Δ.

The question of how the system approaches such equilibrium state, is at the heart of Statistical Mechanics, being one of the central problem in Physics since the time of Boltzmann. We will discuss those issues in the next chapter. ■

CT

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