

## Entropia Estatística e a distribuição de Boltzmann.

Objetivo: obtenção da entropia através de argumentos microscópicos.

Caminho diferente do usual: ponto de partida será a entropia de informações de uma distribuição de probabilidade.

Descrição de um sistema quântico

informações máximas  $\rightarrow |\psi\rangle = |\psi(0)\rangle$

$$\hat{A}_1, \hat{A}_2, \dots, \hat{A}_N \leftrightarrow C O C$$

$$\hat{A}_n |\psi\rangle = a^{(n)} |\psi\rangle \Rightarrow \hat{A}_n |\psi_i^{(n)}\rangle = a_i^{(n)} |\psi_i^{(n)}\rangle; |\psi_i^{(n)}\rangle \equiv |a_i^{(n)}\rangle$$

$$\Rightarrow N \text{ operadores: } |a^{(1)}, a^{(2)}, \dots, a^{(N)}\rangle$$

$$|\psi(t)\rangle = U(t) |\psi(0)\rangle \Rightarrow i\hbar \frac{dU(t)}{dt} = H(t) U(t)$$

$U(t)$  - operador de evolução temporal.

$U$  é unitário pois  $\langle \psi(t) | \psi(t) \rangle = 1 \Rightarrow U^\dagger = U^{-1}$

e satisfaz  $U(t, t_0) = U(t, t_1) U(t_1, t_0)$

Se  $H \neq H(t)$  :  $U(t) = e^{-iHt/\hbar}$

Essa é a versão de Schrödinger.

Versão de Heisenberg :  $|\psi_H\rangle \equiv U^{-1}(t) |\psi(t)\rangle (= |\psi(0)\rangle)$

$$\begin{aligned} \text{e } \hat{A}_H(t) &= U^{-1}(t) \hat{A}(t) U(t) \Rightarrow \langle \psi(t) | \hat{A}(t) | \psi(t) \rangle = \\ &= \langle \psi_H | \hat{A}_H(t) | \psi_H \rangle \end{aligned}$$

$$\Rightarrow \text{se } \hat{A} = \hat{A}(t) \text{ (dependência explícita)} \quad \left( \frac{\partial \hat{A}}{\partial t} \right)_H = U^{-1} \frac{\partial \hat{A}}{\partial t} U$$

$$\Rightarrow \frac{d\hat{A}_H}{dt} = \left( \frac{\partial \hat{A}}{\partial t} \right)_H + \frac{1}{i\hbar} [\hat{A}_H, H]$$

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Definindo  $\hat{\rho} \equiv |\psi\rangle\langle\psi|$  Temos  $\langle\psi|A|\psi\rangle =$   
 $= \sum_n \langle\psi|b_n\rangle \langle b_n|A|\psi\rangle = \sum_n \langle b_n|A|\psi\rangle \langle\psi|b_n\rangle$   
 $= \text{tr } \hat{A} \hat{\rho} = \text{tr } \hat{\rho} \hat{A}$ .

Operadores densidade:

$\hat{\rho} \equiv |\psi\rangle\langle\psi|$  se  $|\psi\rangle = \sum_n c_n |n\rangle$  estado puro

$\Rightarrow \hat{\rho} = \sum_{mn} c_n c_m^* |n\rangle\langle m| \Rightarrow \hat{\rho}_{mn} = c_m c_n^*$

Vamos rotular  $|\psi\rangle \rightarrow |\psi^{(n)}\rangle$   $n$   $\tilde{n}$  é necessariamente discreto.

$\Rightarrow |\psi^{(n)}\rangle = \sum_i c_i^{(n)} |i\rangle$

$\langle\psi^{(n)}|\psi^{(n)}\rangle = 1$  mas  $|\psi^{(n)}\rangle$  e  $|\psi^{(m)}\rangle$  não são necessariamente ortogonais

Distribuição de probabilidades  $\{p_n\} \Rightarrow \sum p_n = 1$

$p_n \geq 0$

$\Rightarrow$  mistura estatística:  $\hat{\rho} = \sum_n p_n |\psi^{(n)}\rangle\langle\psi^{(n)}|$

$= \sum_{ij} p_n c_i^{(n)} c_j^{*(n)} |i\rangle\langle j|$

$\langle\hat{A}\rangle = \sum_n p_n \langle\psi^{(n)}|\hat{A}|\psi^{(n)}\rangle = \sum_n p_n \text{tr } \hat{\rho}_n \hat{A}$

$\Rightarrow \hat{\rho} \equiv \sum_n p_n \hat{\rho}_n$  Temos  $\langle\hat{A}\rangle = \text{tr } \hat{\rho} \hat{A}$

Ex: Stern-Gerlach  $|\psi\rangle = \frac{1}{\sqrt{2}} |\uparrow\rangle + \frac{1}{\sqrt{2}} |\downarrow\rangle = |\psi\rangle_x$

$= \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} \neq \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} = \frac{1}{2} |\uparrow\rangle\langle\uparrow| + \frac{1}{2} |\downarrow\rangle\langle\downarrow|$

Stern-Berlach:

$$|4\rangle = \frac{1}{\sqrt{2}} |↑\rangle + \frac{1}{\sqrt{2}} |↓\rangle$$

$$\Rightarrow \hat{P}_1 = \frac{1}{2} |↑\rangle \langle ↑| + \frac{1}{2} |↓\rangle \langle ↓| + \frac{1}{2} |↑\rangle \langle ↓| + \frac{1}{2} |↓\rangle \langle ↑|$$

$$= \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$$

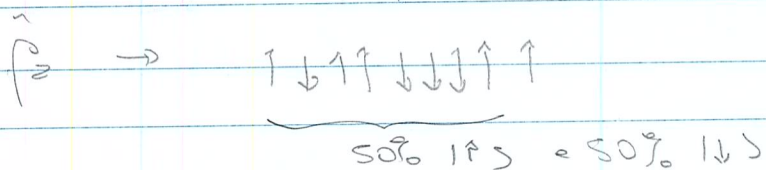
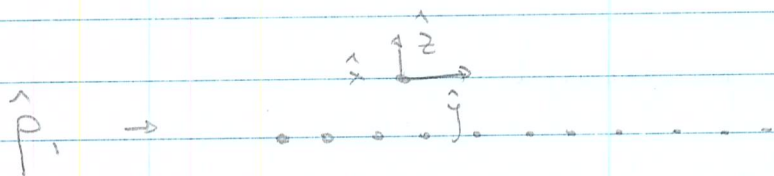
$$\hat{P}_2 = \frac{1}{2} |↑\rangle \langle ↑| + \frac{1}{2} |↓\rangle \langle ↓| = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

$$\langle \sigma_z \rangle_1 = \text{tr} \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \text{tr} \begin{pmatrix} 1/2 & -1/2 \\ 1/2 & -1/2 \end{pmatrix} = 0$$

$$\langle \sigma_z \rangle_2 = \text{tr} \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \text{tr} \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} = 0$$

$$\langle \sigma_x \rangle_1 = \text{tr} \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \text{tr} \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} = 1$$

$$\langle \sigma_x \rangle_2 = \text{tr} \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \text{tr} \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} = 0$$



Representação contínua:

$$\hat{\rho} = \sum_{n,j} p_n c_i^{(n)} c_j^{(n)*} \quad |i\rangle \langle j|$$

$$n \rightarrow \alpha_0 \quad \sum_n \rightarrow \int d\alpha_0 \quad |i\rangle \langle j| \leftrightarrow |x\rangle \langle y| \quad p_n \rightarrow p(\alpha_0)$$

$$|i^{(n)}\rangle \rightarrow |i^{(\alpha_0)}\rangle \quad \text{tal que} \quad |i^{(\alpha_0)}\rangle = \int dx |x\rangle \langle x|i^{(\alpha_0)}\rangle$$

$$\text{funções centradas em } \alpha_0 \Rightarrow \langle x|i^{(\alpha_0)}\rangle = \psi(x-\alpha_0)$$

$$\Rightarrow \hat{\rho} = \iiint_{x_0, x', y'} p(\alpha_0) \psi(x'-\alpha_0) \psi^*(y'-\alpha_0) |x'\rangle \langle y'|$$

$$\Rightarrow \hat{\rho}(x, y) = \langle x|\hat{\rho}|y\rangle = \int_{\alpha_0} p(\alpha_0) \psi(x-\alpha_0) \psi^*(y-\alpha_0)$$

$$\int d\alpha_0 p(\alpha_0) = 1$$

$$\Rightarrow \int_x \hat{\rho}(x, x) dx = \int_{\alpha_0} p(\alpha_0) \psi(x-\alpha_0) \psi^*(x-\alpha_0) dx$$

$$= \int p(\alpha_0) d\alpha_0 = 1 \quad \Rightarrow \text{tr } \hat{\rho} = 1$$

Se  $p(\alpha_0) = \delta(\alpha_0)$ , por exemplo;

$$\Rightarrow \hat{\rho}(x, y) = \psi(x) \psi^*(y) = \langle x|\psi\rangle \langle \psi|y\rangle \rightarrow \text{estado puro.}$$

Propriedades de  $\hat{\rho}$ :

i)  $\hat{\rho} = \hat{\rho}^\dagger$

ii)  $\text{tr} \hat{\rho} = \sum p_n = 1$

iii)  $\langle \psi | \hat{\rho} | \psi \rangle \geq 0$

iv) estado puro:  $\hat{\rho}^2 = \hat{\rho}$

i)  $\hat{\rho}^\dagger = \sum_n p_n (|4^{(n)}\rangle \langle 4^{(n)}|)^\dagger = \sum_n p_n |4^{(n)}\rangle \langle 4^{(n)}|$

ii)  $\text{tr} \hat{\rho} = \sum_n p_n \langle 4^{(n)} | 4^{(n)} \rangle = \sum p_n = 1$

iii)  $\langle \psi | \hat{\rho} | \psi \rangle = \sum_n p_n \langle \psi | 4^{(n)} \rangle \langle 4^{(n)} | \psi \rangle = \sum_n p_n \underbrace{|\langle \psi | 4^{(n)} \rangle|}_{\geq 0} \underbrace{\langle 4^{(n)} | \psi \rangle}_{\geq 0} \geq 0$

iv)  $\hat{\rho} = |4\rangle \langle 4| \Rightarrow \hat{\rho}^2 = |4\rangle \langle 4 | 4 \rangle \langle 4| = |4\rangle \langle 4| = \hat{\rho}$

Dinâmica de  $\hat{\rho}$ :

$\hat{\rho}(t) = \sum_n p_n U(t) |4^{(n)}\rangle \langle 4^{(n)}| U^\dagger(t)$

$\frac{d\hat{\rho}}{dt} = \sum_n p_n \frac{dU}{dt} |4^{(n)}\rangle \langle 4^{(n)}| U^\dagger + \sum_n p_n U |4^{(n)}\rangle \langle 4^{(n)}| \frac{dU^\dagger}{dt}$   
 $= \frac{1}{i\hbar} \sum_n p_n H U |4^{(n)}\rangle \langle 4^{(n)}| U^\dagger - \frac{1}{i\hbar} \sum_n p_n U |4^{(n)}\rangle \langle 4^{(n)}| U^\dagger H$   
 $= \frac{1}{i\hbar} [H, \hat{\rho}] \Rightarrow \boxed{i\hbar \frac{d\hat{\rho}}{dt} = [H, \hat{\rho}]}$

$\hat{\rho}$  na versão de Schrödinger.

Versão de Heisenberg:  $\hat{\rho}_H \equiv U^{-1}(t) \hat{\rho}(t) U(t)$

$\Rightarrow \langle \hat{A}(t) \rangle = \text{tr} [\hat{\rho}_H \hat{A}_H(t)] = \text{tr} [\hat{\rho}(t) \hat{A}(t)]$

Espaço de fase quântico:

Necessidade de se obter macroestados =>

Contagem do # de estados: quando tratamos do estado de partículas numa caixa podemos sempre expandir o estado geral numa base de ondas planas

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

com condições periódicas de contorno  $\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r} + \vec{L})$   
 $\vec{L} = (L_x, L_y, L_z)$

$$\Rightarrow e^{i\vec{k} \cdot \vec{r}} = e^{i\vec{k} \cdot \vec{r}} e^{-i\vec{k} \cdot \vec{L}} \Rightarrow \vec{k}_n = (k_x^{(n)}, k_y^{(n)}, k_z^{(n)})$$
  
$$k_i^{(n)} = \frac{2\pi n_i}{L_i} ; \frac{2\pi}{L_i} \ll 1$$

$$\Rightarrow \bar{\int}_n f(\vec{k}_n) \equiv \sum_{n_x n_y n_z} f(k_x^{(n)}, k_y^{(n)}, k_z^{(n)})$$

$$\rightarrow \bar{\int}_{n_x n_y n_z} f(n_x, n_y, n_z) \Delta n_x \Delta n_y \Delta n_z \quad \Delta n_i = (n+1) - n_i$$

$$= \frac{V}{(2\pi)^3} \sum_{n_x n_y n_z} f(k_x, k_y, k_z) \Delta k_x \Delta k_y \Delta k_z$$

$$\Delta k_i \ll 1 \Rightarrow \bar{\int} \rightarrow \frac{V}{(2\pi)^3} \int \Rightarrow \boxed{\rho(\vec{k}) d^3k = \frac{V d^3k}{(2\pi)^3}}$$

Densidade de níveis de energia:

$$E = \frac{\hbar^2 k^2}{2m} \quad dN(E) = \rho(E) dE = 4\pi k^2 dk \frac{V}{(2\pi)^3}$$

$$k = \frac{\sqrt{2mE}}{\hbar} \Rightarrow dE = \frac{\hbar^2}{m} k dk \Rightarrow dk = \frac{m}{\hbar} \frac{dE}{\sqrt{2mE}}$$

$$\Rightarrow \rho(E) dE = 4\pi \frac{2mE}{\hbar^2} \frac{V}{(2\pi)^3} \frac{m}{\hbar \sqrt{2mE}} dE = \frac{mV}{2\pi^2 \hbar^3} \sqrt{2mE} dE$$

$$\rho(E) = \frac{mV \sqrt{2mE}}{2\pi^2 \hbar^3}$$

Gas ideal monoatômico:

$$E_r = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$$\Rightarrow \langle E_r \rangle = \frac{\hbar^2 \pi^2}{2m} \left( \frac{\langle n_x^2 \rangle}{L_x^2} + \frac{\langle n_y^2 \rangle}{L_y^2} + \frac{\langle n_z^2 \rangle}{L_z^2} \right)$$

isotropia:  $\frac{\langle n_x^2 \rangle}{L_x^2} = \frac{\langle n_y^2 \rangle}{L_y^2} = \frac{\langle n_z^2 \rangle}{L_z^2} = \frac{1}{3} \frac{2m \langle E \rangle}{\hbar^2 \pi^2}$

$$\frac{\partial E_r}{\partial L_x} = - \frac{\hbar^2 \pi^2}{m} \frac{n_x^2}{L_x^3}$$

$$\Rightarrow \frac{\partial \langle E_r \rangle}{\partial L_x} = - \frac{\hbar^2 \pi^2}{m L_x} \frac{\langle n_x^2 \rangle}{L_x^2} = - \frac{\hbar^2 \pi^2}{m L_x} \cdot \frac{1}{3} \frac{2m \langle E_r \rangle}{\hbar^2 \pi^2} = - \frac{2}{3} \frac{\langle E_r \rangle}{L_x}$$

Mudança adiabática de volume:

$$dE = \delta W = - P L_y L_z dL_x \quad E = N \langle E_r \rangle$$

$$= \frac{\partial E}{\partial L_x} dL_x \quad \Rightarrow \quad - P L_y L_z = N \frac{\partial \langle E_r \rangle}{\partial L_x} = - \frac{2}{3} \frac{E}{L_x}$$

$$\Rightarrow \boxed{PV = \frac{2}{3} E} \quad \text{p/gás } \tilde{n}\text{-relativístico (no outro caso } PV = \frac{E}{3})$$

Descrição clássica:  $q_i$  e  $p_i$

$$H = \sum_i \frac{p_i^2}{2m} + \sum_i U(q_i)$$

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \quad \frac{\partial H}{\partial q_i} = - \dot{p}_i$$

microestado:  $(q_i(t), p_i(t))$

$$\Rightarrow \begin{aligned} \dot{q}' &= \dot{q} + \ddot{q} dt = \dot{q} + \partial H / \partial p dt \\ \dot{p}' &= \dot{p} + \ddot{p} dt = \dot{p} - \partial H / \partial q dt \end{aligned}$$

$$\frac{\partial(q', p')}{\partial(q, p)} = \begin{vmatrix} 1 + \partial^2 H / \partial q \partial p dt & \partial^2 H / \partial p^2 dt \\ - \partial^2 H / \partial q^2 dt & 1 - \partial^2 H / \partial p \partial q dt \end{vmatrix}$$

$$= 1 + Q(dt)^2 \Rightarrow J = \frac{\partial(q', p')}{\partial(q, p)}$$

$$\frac{dJ}{dt} = 0 \Rightarrow dq(0) dp(0) = dq(t) dp(t)$$

$\Rightarrow d\Gamma = \prod_{i=1}^N d\vec{r}_i d\vec{p}_i$  é invariante. (tes. Liouville)

Densidade no espaço de fase:

Probabilidade de se observar microestado em  $t=0$ .

$$P^{(N)}(\vec{r}_i, \vec{p}_i, 0) \equiv P_0^{(N)}(\vec{r}_i, \vec{p}_i) \Rightarrow N = \int P_0^{(N)}(\vec{r}_i, \vec{p}_i) \prod_{i=1}^N d\vec{r}_i d\vec{p}_i$$

Se  $P_0 \equiv P_0^{(N)}/N$

$$d\Gamma(\vec{r}_i, \vec{p}_i) = P_0(\vec{r}_i, \vec{p}_i) d\Gamma \Rightarrow \int d\Gamma(\vec{r}_i, \vec{p}_i) = \int P_0(\vec{r}_i, \vec{p}_i) d\Gamma = 1$$

Análogo a  $\hat{p}$  e  $t\hat{p} = 1$

No tempo:  $\vec{r}_i \rightarrow \vec{r}_i(t)$  e  $\vec{p}_i \rightarrow \vec{p}_i(t)$  ( $x \rightarrow y = \varphi_t(x)$ )

$\Rightarrow x = \varphi_t^{-1}(y) \equiv \varphi_{-t}(y)$  e Liouville:  $dx = dy$ .

$x \equiv (\vec{r}_1, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_N)$

Em  $t=0$   $A(0) = A(\vec{r}_i, \vec{p}_i) = A(x)$

$A(t) = A(\vec{r}_i(t), \vec{p}_i(t)) = A(\varphi_t(x))$

$$\langle A(t=0) \rangle = \int dx P_0(x) A(x)$$

$$\langle A(t) \rangle = \int dx P_0(x) A(\varphi_t(x))$$

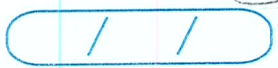
análogo à Heisenberg em MQ.

Analogia c/ Schrödinger.

$$\langle A(t) \rangle = \int dy P_0(\varphi_{-t}(y)) A(y) = \int dx P(x(t), t) A(x)$$

$$P(x(t), t) = P_0(\varphi_{-t}(x))$$





$$\rho(q(t+dt), p(t+dt), t+dt) dq' dp' = \rho(q(t), p(t), t) dq dp$$

$$dq' dp' = dq dp \Rightarrow \frac{\partial \rho}{\partial q} \dot{q} + \frac{\partial \rho}{\partial p} \dot{p} + \frac{\partial \rho}{\partial t} = 0$$

$$\frac{\partial \rho}{\partial t} + \frac{\partial H}{\partial p} \frac{\partial \rho}{\partial q} - \frac{\partial H}{\partial q} \frac{\partial \rho}{\partial p} = 0$$

$$\frac{\partial \rho}{\partial t} - \{H, \rho\} = 0 \quad \text{ou} \quad \frac{\partial \rho}{\partial t} = \{H, \rho\}$$

$$\{A, B\} = \sum_i \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i}$$

eq. quântico-clássico =  $\frac{1}{i\hbar} [ , ] \leftrightarrow \{ , \}$

$$\Rightarrow \frac{dA}{dt} = \{A, H\} + \frac{\partial A}{\partial t}$$

Nota:  $\vec{r} \rightarrow (q_i, p_i)$

Movimento no espaço de fase:  $\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0$

→ conservação do # de cópias

$$\vec{v} = (\dot{q}_i, \dot{p}_i)$$

$$\frac{\partial \rho}{\partial t} + (\vec{v} \cdot \vec{\nabla}) \rho + \rho \vec{\nabla} \cdot \vec{v} = 0$$

mas  $\vec{\nabla} \cdot \vec{v} = \sum_i \frac{\partial \dot{q}_i}{\partial q_i} + \sum_i \frac{\partial \dot{p}_i}{\partial p_i} = \sum_i \frac{\partial^2 H}{\partial q_i \partial p_i} - \sum_i \frac{\partial^2 H}{\partial p_i \partial q_i} = 0$

$$\Rightarrow \frac{\partial \rho}{\partial t} + (\vec{v} \cdot \vec{\nabla}) \rho = 0 \quad \text{ou} \quad \frac{d\rho}{dt} = 0 \quad (\text{fluido incompressível})$$

$$\Rightarrow \frac{\partial \rho}{\partial t} + \sum_i \dot{q}_i \frac{\partial \rho}{\partial q_i} + \sum_i \dot{p}_i \frac{\partial \rho}{\partial p_i} = \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \sum_i \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} = 0$$

$$\Rightarrow \frac{\partial \rho}{\partial t} = \{H, \rho\} \quad \text{caso estacionário } \frac{\partial \rho}{\partial t} = 0 \Rightarrow \begin{cases} \rho = \text{const} \\ \rho = \rho(H) \end{cases}$$

Mais sobre a correspondência quântico-clássico:

$\hat{\rho} \rightarrow \hat{\rho}(x, y) \rightarrow$  elementos de matriz do operador densidade.

Definindo  $q = \frac{x+y}{2}$  e  $\xi = x-y$

$$\text{Temos } \hat{\rho}(x, y) = \hat{\rho}\left(q + \frac{\xi}{2}, q - \frac{\xi}{2}, t\right)$$

Transformada de Wigner:

$$\hat{W}(q, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{ip\xi/\hbar} \hat{\rho}\left(q + \frac{\xi}{2}, q - \frac{\xi}{2}, t\right) d\xi$$

$\hat{W}$  é um operador que depende dos parâmetros  $q$  e  $p$  e é tal que

$$\lim_{\hbar \rightarrow 0} \hat{W}(q, p, t) = \rho(q, p, t)$$

$$\int_{-\infty}^{\infty} dp \hat{W}(q, p, t) = \int_{-\infty}^{\infty} d\xi \hat{\rho}\left(q, \xi, t\right) \underbrace{\int_{-\infty}^{\infty} \frac{1}{2\pi\hbar} dp e^{-ip\xi/\hbar}}_{\delta(\xi)}$$

$$\Rightarrow \int_{-\infty}^{\infty} dp \hat{W}(q, p, t) = \hat{\rho}(q, 0, t) = \hat{\rho}(x, x) = P(x) = \rho(q)$$