Liouville → BBGKY

Born
Bogoliubov
Green
Kirkwood
Yvon

- Liouville's theorem

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

Vs Quantum

$$\boxed{\frac{\partial \hat{\rho}}{\partial t} = \frac{1}{i\hbar}[\hat{H}, \hat{\rho}]}$$

- Partition

$$\underbrace{1 \; 2 \cdots S}_{S} \qquad \underbrace{S+1 \; S+2 \cdots N}_{B}$$

$$\{q_s\, p_s\} \qquad \{q_B\, p_B\}$$

$$H = H_s(q_s p_s) + H_B(q_B p_B) + H_{SB}(q_s q_B \cancel{p_s} \cancel{p_B})$$

- Goal

from $\rho^{TOT}(qpt)$ determine $\rho^{(s)}(q_1 \cdots q_s\, p_1 \cdots q_s\, t)$

as in quantum system

$$\rho^{(s)} = \mathrm{tr}_B\, \rho^{TOT}$$

$$\rho^{(s)} = \int \prod_{s+1}^{N} d^3p_k\, d^3q_k\, \rho^{TOT} \qquad \mathrm{tr}_B \iff \int \prod_{s+1}^{N} d^3p_k\, d^3q_k$$

as in quantum system

$$\frac{\partial \rho^{(s)}}{\partial t} = \mathrm{tr}_B \{H_S, \rho\} + \cancel{\mathrm{tr}_B \{H_B, \rho\}} + \mathrm{tr}_B \{H_{SB}, \rho\}$$

→ generalised Gauss theorem

$$\int d^dx\, \vec{\nabla}\rho \cdot \vec{a}(x) = - \int d^dx\, \rho(x)\, \vec{\nabla} \cdot \vec{a}(x)$$

$$\int dp_B\, dq_B \left[\frac{\partial H_B}{\partial q_B} \frac{\partial \rho}{\partial p_B} - \frac{\partial H}{\partial p_B} \frac{\partial \rho}{\partial q_B} \right]$$

(a) (b)

a) integrating in dp_B

$$- \int dq_B\, dp_B \frac{\partial^2 H}{\partial q_B \partial p_B} \cdot \rho$$

b) integrating in dq_B

$$+ \int dp_B\, dq_B \frac{\partial^2 H}{\partial p_B \partial q_B}\, \rho$$

the difference vanishes

Now consider the third term

$$\int dq_B dp_B \left\{ \frac{\partial H_{SB}}{\partial q_B}\frac{\partial \rho}{\partial p_B} - \cancel{\frac{\partial H_{SB}}{\partial p_B}\frac{\partial \rho}{\partial q_B}} + \right.$$
$$+ \frac{\partial H_{SB}}{\partial q_S}\frac{\partial \rho}{\partial q_S} - \cancel{\frac{\partial H_{SB}}{\partial p_S}\frac{\partial \rho}{\partial q_S}}$$

depends only on coordinates

• **Pairwise interaction**

$$H = \sum_1^N \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} V(|\vec{q}_i - \vec{q}_j|) + \underbrace{\sum_i \phi(q_i)}_{\text{ext potential}}$$

therefore

$$H_{SB} = \sum_1^S{}_i \sum_{S+1}^N{}_j V(|q_i^S - q_j^B|) \quad (\text{no factor } \tfrac{1}{2} \, !!)$$

S B

the third term reads

$$\int \prod_{S+1}^N{}_k d^3p_k d^3q_k \sum_1^S{}_i \sum_{S+1}^N{}_j \frac{\partial V}{\partial q_j}\frac{\partial \rho}{\partial p_j} + \frac{\partial V}{\partial q_i}\frac{\partial \rho}{\partial p_i}$$

$$= \int \prod_{S+1}^N{}_k \underline{d^3p_k d^3q_k} \sum_1^S{}_i \sum_{S+1}^N{}_j \hat{\Theta}_{ij} \rho^{TOT}$$

$$\Theta_{ij} = \frac{\partial V}{\partial \underline{q_j}}\frac{\partial}{\partial \underline{p_j}} + \frac{\partial V}{\partial q_i}\frac{\partial}{\partial p_i}$$

integrated variables on identical particles

$$= \sum_1^S{}_i (N-S) \int \prod_{S+1}^N{}_k d^3p_k d^3q_k \, \Theta_{i\,S+1} \, \rho^{TOT}$$

$$d^3p_{S+1} d^3q_{S+1} \prod_{S+2}^N{}_k d^3p_k d^3q_k$$

$$\mathrm{tr}_B \{H_{SB}, \rho\} = (N-s)\sum_{i=1}^{s} \int d^3q_{s+1}\, d^3p_{s+1}\, \hat{\Theta}_{i\,s+1}\, \rho^{(s+1)}$$

$$\int d^3p_{s+1}\, d^3q_{s+1} \left[\underset{(a)}{\frac{\partial V_{i\,s+1}}{\partial q_i} \frac{\partial \rho^{(s+1)}}{\partial p_i}} + \underset{(b)}{\frac{\partial V_{i\,s+1}}{\partial q_{s+1}} \frac{\partial \rho^{(s+1)}}{\partial p_{s+1}}} \right]$$

generalised Gauss

b) integrate on p_{s+1}

$$- \int d^3q_{s+1}\, d^3p_{s+1}\, \cancel{\frac{\partial^2 V_{i\,s+1}}{\partial p_{s+1}\, \partial q_{s+1}}}\, \rho^{(s+1)}$$

Indep. on p

$$\mathrm{tr}_B \{H_{SB}, \rho\} = \int d^3p_{s+1}\, d^3q_{s+1}\, (N-s) \sum_{i=1}^{s} \underbrace{\frac{\partial V_{i\,s+1}}{\partial \vec{q}_i}}_{-\vec{F}_{i\,s+1}} \frac{\partial \rho^{(s+1)}}{\partial \vec{p}_i}$$

finally

$$\frac{\partial \rho^{(s)}}{\partial t} - \{H_s, \rho^{(s)}\} = -(N-s)\sum_{i=1}^{s} \int d^3p_{s+1}\, d^3q_{s+1}\, \vec{F}_{i\,s+1} \cdot \frac{\partial \rho^{(s+1)}}{\partial \vec{p}_i}$$

K

Examples

$S=1$ cluster of only 1 particle

$$H_S = \frac{\vec{p}^2}{2m} + \phi(\vec{q}) = H^{(1)} \qquad \rho_S = \rho^{(1)}(\vec{p},\vec{q},t)$$

external potential

$$\{H_S, \rho_S\} = \frac{\partial H}{\partial \vec{q}} \cdot \frac{\partial \rho^{(1)}}{\partial \vec{p}} - \frac{\partial H}{\partial \vec{p}} \cdot \frac{\partial \rho^{(1)}}{\partial \vec{q}} = \frac{\partial \phi}{\partial \vec{q}} \cdot \frac{\partial \rho^{(1)}}{\partial \vec{p}} - \frac{\vec{p}}{m} \frac{\partial \rho^{(1)}}{\partial \vec{q}}$$

$$\frac{\partial \rho^{(1)}}{\partial t} - \{H_S, \rho^{(1)}\} = -(N-1) \int d^3\vec{p}_2 d^3\vec{q}_2 \, F(\vec{q}-\vec{q}_2) \cdot \frac{\partial \rho^{(2)}}{\partial \vec{p}}(q_1 q_2 p p_2, t)$$

$$\left\{ \frac{\partial}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{q}} - \frac{\partial \phi(q)}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \right\} \rho^{(1)}(\vec{q}\,\vec{p}\,t) = -(N-1) \int d^3 \bar{p} \int d^3 \bar{q} \, F(q-\bar{q}) \frac{\partial \rho^{(2)}}{\partial \vec{p}}$$

$S=2$

$$H_S = H^{(2)} = \frac{\bar{p}_1^2}{2m} + \frac{\bar{p}_2^2}{2m} + \phi(\bar{q}_1) + \phi(\bar{q}_2) + V(q_1 - q_2)$$

$$\left\{ \frac{\partial}{\partial t} + \sum_i^2 \frac{\vec{p}_i}{m} \frac{\partial}{\partial \vec{q}_i} - \frac{\partial \phi(\vec{q}_i)}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial p_i} - \Theta_{12} \right\} \rho^{(2)}(1\,2,t) =$$

$$= +(N-2) \int d3 \{ \hat{\Theta}_{13} + \hat{\Theta}_{23} \} \rho^{(3)}(1\,2\,3, t)$$

$d^3\vec{p}_3 \, d^3\vec{q}_3$

$$\Theta_{ij} = \frac{\partial V}{\partial \vec{q}_j} \frac{\partial}{\partial \vec{p}_j} + \frac{\partial V}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i}$$