Classical Liouville operator [tln46]

To describe the time evolution of $\rho(\mathbf{X},t)$ we consider a volume V_0 with surface S_0 in Γ-space. The following equations relate the change of probability inside V_0 to the flow of probability through S_0 and use Gauss' theorem.

$$\frac{\partial}{\partial t}\int_{V_0} d^{6N}X\,\rho(\mathbf{X},t) = -\oint_{S_0} d\mathbf{s}\cdot\dot{\mathbf{X}}\rho(\mathbf{X},t) = -\int_{V_0} d^{6N}X\,\nabla_{\mathbf{X}}\cdot[\dot{\mathbf{X}}\rho(\mathbf{X},t)].$$

Balance equation: $\dfrac{\partial}{\partial t}\rho(\mathbf{X},t) + \nabla_{\mathbf{X}}\cdot[\dot{\mathbf{X}}\rho(\mathbf{X},t)] = 0.$

Use $\nabla_{\mathbf{X}}\cdot[\dot{\mathbf{X}}\rho] = \rho\nabla_{\mathbf{X}}\cdot\dot{\mathbf{X}} + \dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}\rho$ and $\nabla_{\mathbf{X}}\cdot\dot{\mathbf{X}} = 0.$

$$\Rightarrow\ \frac{\partial}{\partial t}\rho(\mathbf{X},t) + \dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}\rho(\mathbf{X},t) = 0.$$

Introduce convective derivative: $\dfrac{d}{dt} \equiv \dfrac{\partial}{\partial t} + \dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}.$

Liouville theorem: $\dfrac{d}{dt}\rho(\mathbf{X},t) = 0.$

Use $\dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}\rho = \sum_{i=1}^{3N}\left(\dot{q}_i\dfrac{\partial\rho}{\partial q_i} + \dot{p}_i\dfrac{\partial\rho}{\partial p_i}\right) = \sum_{i=1}^{3N}\left(\dfrac{\partial\rho}{\partial q_i}\dfrac{\partial H}{\partial p_i} - \dfrac{\partial\rho}{\partial p_i}\dfrac{\partial H}{\partial q_i}\right) = \{\rho, H\}.$

Liouville operator: $L \equiv i\{H,\ \} = i\sum_{i=1}^{3N}\left(\dfrac{\partial H}{\partial q_i}\dfrac{\partial}{\partial p_i} - \dfrac{\partial H}{\partial p_i}\dfrac{\partial}{\partial q_i}\right).$

Liouville equation: $i\dfrac{\partial\rho}{\partial t} = i\{H,\rho\} = L\rho.$

Formal solution: $\rho(\mathbf{X},t) = e^{-iLt}\rho(\mathbf{X},0).$

L is a Hermitian operator. Hence all its eigenvalues are real. Hence $\rho(\mathbf{X},t)$ cannot relax to equilibrium in any obvious way. The Liouville equation reflects the time reversal symmetry of the underlying microscopic dynamics. Obtaining the broken time reversal symmetry of irreversible processes from the Liouville equation is a central problem in statistical mechanics (topic of ergodic theory).

Nevertheless: the thermal equilibrium is described by a stationary (time-independent) probability density:

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

A stationary ρ is an eigenfunction of L with eigenvalue zero. If $\rho = \rho(H)$ then $\{H,\rho\} = 0$. Hence ρ is time-independent.