University of Washington
Department of Chemistry
Chemistry 553
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Lecture 16: The Liouville Equation
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Text Reading: Ch. 7.2, 21.7

A. The Liouville Equation

- The function f(X,t) will be the distribution function in phase space. X denotes the set of coordinates and momenta that characterize the system at a point in phase space. We can express a conservation equation for f(X,t) that is analogous to Fick's Law of Diffusion…

$$\frac{\partial f}{\partial t} = -\nabla_X \bullet (V_X f) \tag{16.1}$$

where $\nabla_X \rightarrow \frac{\partial}{\partial X} \rightarrow \left(\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right)$ *and* $V_X \rightarrow \left(\frac{\partial q}{\partial t}, \frac{\partial p}{\partial t}\right)$

- We can also write (16.1) as

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial q} \cdot \left(\frac{dq}{dt} f\right) - \frac{\partial}{\partial p}\left(\frac{dp}{dt} f\right) \tag{16.2}$$

- Recall Hamilton's canonical equations of motion:

$$\left.\begin{aligned} \dot{q}_i &= \frac{dq_i}{dt} = \frac{\partial H(q_i, p_i)}{\partial p_i} \\ \dot{p}_i &= \frac{dp_i}{dt} = -\frac{\partial H(q_i, p_i)}{\partial q_i} \end{aligned}\right\} i = 1, 2 \ldots 3N \tag{16.3}$$

where H is the classical Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m_i} + U(q_1 \ldots q_N) \tag{16.4}$$

- We now substitute Hamilton's equations into (16.4) which directly yields the Liouville equation

$$\begin{aligned} \frac{\partial f}{\partial t} &= -\frac{\partial H}{\partial p} \cdot \frac{\partial f}{\partial q} + \frac{\partial H}{\partial q} \cdot \frac{\partial f}{\partial p} = -Lf \\ where \quad L &= \frac{\partial H}{\partial p} \cdot \frac{\partial}{\partial q} - \frac{\partial H}{\partial q} \cdot \frac{\partial}{\partial p} \end{aligned} \tag{16.5}$$

- (16.5) has the formal solution

$$f(X,t) = e^{-tL} f(X,0) \tag{16.6}$$

- L is called the Liouvillian operator and exp(-tL) is called the time displacement operator.
- (16.5) is also frequently written using Poisson bracket notation:

$$\frac{\partial f}{\partial t} = -\frac{\partial H}{\partial p}\cdot\frac{\partial f}{\partial q} + \frac{\partial H}{\partial q}\cdot\frac{\partial f}{\partial p} = -\{H, f\} = -Lf$$
$$where \quad \{H, f\} = L = \frac{\partial H}{\partial p}\cdot\frac{\partial f}{\partial q} - \frac{\partial H}{\partial q}\cdot\frac{\partial f}{\partial p} \tag{17.5)'}$$

- The Liouvillian is used to determine the time evolution of any dynamical variable, which is any function A of the phase variables X(t):

$$\frac{\partial A}{\partial t} = \left(\frac{\partial q}{\partial t}\right)\left(\frac{\partial A}{\partial q}\right) + \left(\frac{\partial p}{\partial t}\right)\left(\frac{\partial A}{\partial p}\right)$$
$$= \left(\frac{\partial H}{\partial p}\right)\left(\frac{\partial A}{\partial q}\right) - \left(\frac{\partial H}{\partial q}\right)\left(\frac{\partial A}{\partial p}\right) = \{H, A\} = LA \tag{16.7}$$

- Note…some texts, introduce a factor of i into the Liouvillian, thus producing a Liouville equation of the form

$$i\frac{\partial f}{\partial t} = Lf \Rightarrow f(X,t) = e^{-iLt} f(X,0) \tag{16.8}$$

- Note the sign difference between the equations for f(t) and A(t)

$f(t) = e^{-Lt} f(0)$ and $A(t) = e^{Lt} A$ (16.9)

which is a consequence of the equations of motion

$\frac{\partial f}{\partial t} = -Lf = -\{H, f\}$ and $\frac{\partial A}{\partial t} = Lf = \{H, A\}$ (16.10)

- These equations are analogous to the Schroedinger and Heisenberg equations of quantum mechanics.
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B. The Linear Response Function

- Assume the (classical) Hamiltonian of the system has the form

$$H = H_0 - A(X,t)F(t) \tag{16.11}$$

where A is a function of the coordinates of the system and F(t) is the applied force. H_0 is the Hamiltonian of the unperturbed system.

- Suppose f is the ensemble distribution function. In classical mechanics f obeys the Liouville equation

$$\frac{\partial f}{\partial t} = -Lf = \{f, H_0 - A(X,t)F(t)\}$$
$$= \{f, H_0\} - \{f, A(X,t)F(t)\} = -L_0 f - \{f, A(X,t)F(t)\} \tag{16.12}$$
$$\therefore \frac{\partial f}{\partial t} + L_0 f = \{A(X,t)F(t), f\}$$

- Equation (16.12) has the solution:

$$f(t) = e^{-tL_0}\left[f_0 + \int_{-\infty}^{t} e^{t'L_0}\left\{A(X,t'), f(t')\right\} F(t')\,dt' \right]$$
$$f(t) = f_0 + \int_{-\infty}^{t} e^{-(t-t')L_0}\left\{A(X,t'), f(t')\right\} F(t')\,dt' \qquad (16.13)$$

where f_0 is the equilibrium distribution of the ensemble. Note in deriving (16.13) we used the fact that…

$$e^{-L_0 t} f_0 = f_0 \qquad (16.14)$$

- We can use (16.13) to calculate the ensemble response of a system property B to the applied force

$$\int dXf(t)B = \int dXf_0 B + \int_{-\infty}^{t} dt' F(t') \int dX\, B e^{-(t-t')L_0}\left\{A(X,t'), f(t')\right\} \qquad (16.15)$$

where $dX = dq_1 \ldots dp_N$.

- Now (16.15) may be rewritten as

$$\left\langle B(t)\right\rangle = \left\langle B\right\rangle_0 + \int_{-\infty}^{t} dt' F(t') \int dX\, B e^{-(t-t')L_0}\left\{A(X,t'), f(t')\right\}$$
$$or \ldots \Delta B(t) = \left\langle B(t)\right\rangle - \left\langle B\right\rangle_0 = \int_{-\infty}^{t} dt' F(t') \int dX\, B e^{-(t-t')L_0}\left\{A(X,t'), f(t')\right\} \qquad (16.16)$$

- If we assume the applied force is small, the displacement from equilibrium is also small so $f(t) \approx f_0$ and (16.14) becomes

$$\Delta B(t) = \int_{-\infty}^{t} dt' F(t') \int dX\, B e^{-(t-t')L}\left\{A, f\right\}$$
$$= \int_{-\infty}^{t} dt' F(t') \int dX\, e^{(t-t')L} B\left\{A, f\right\} \qquad (16.17)$$
$$\approx \int_{-\infty}^{t} dt' F(t') \int dX\, B(t-t')\left\{A, f_0\right\}$$

- The second step in (16.17) is a result of the unitary nature of the time displacement operator. That is

$$\int dX\, B e^{-(t-t')L}\left\{A, f\right\} = \int dX \left(e^{-(t-t')L}\right)^{\dagger} B\left\{A, f\right\} \qquad (16.18)$$

where $U^{\dagger}$ is the adjoint of U. However the time displacement operator is unitary which by definition means $U^{\dagger} = U^{-1}$, which proves the second step of 16.17.

- After an integration by parts, (16.17) can be rearranged to

$$\Delta B(t) \approx \int_{-\infty}^{t} dt' F(t') \int dXf_0 \left\{B(t-t'), A(t')\right\} = \int_{-\infty}^{t} dt' F(t')\, \phi_{BA}(t-t') \qquad (16.19)$$

where

$$\phi_{BA}(t) = \int dX\ f_0 \{B(t), A(0)\} = \langle \{B(t), A(0)\} \rangle \tag{16.20}$$

$\phi_{BA}(t)$ is the linear response or after-effect function. The after-effect function is causal in the sense that $\phi_{BA}(t-t') = 0$ if $t < t'$. This means the response of the system cannot precede in time the application of the perturbing field F.