A. Introduction.

- When a classical or quantum system is subjected to a sufficiently weak external force, the system exhibits a response that is proportional to the first power of the applied force. The coefficient that determines the magnitude of the response is determined by the fluctuations of the system in the absence of the force.
- The dynamics of the system response to the applied force depends on the decay dynamics of fluctuations in the isolated system. This response is called the linear response. What underlies linear response theory is a fundamental connection between fluctuations in the isolated system and the linear response of certain system properties to the applied force.

B. The Linear Response Function

- Assume the (classical) Hamiltonian of the system has the form
  \[ H = H_0 - A(X,t)F(t) \]  
  (18.1)
  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
  \[ \frac{\partial f}{\partial t} = -Lf = \{f, H_0 - A(X,t)F(t)\} \]  
  (18.2)
  where L is the Liouville operator and satisfies the equation
  \[ Lf = \{H, f\} = \sum_{a=1}^{3N} \left[ \frac{\partial H}{\partial p_a} \frac{\partial f}{\partial q_a} - \frac{\partial f}{\partial p_a} \frac{\partial H}{\partial q_a} \right] \]
  and \(\{\ldots\}\) is a Poisson bracket, defined as
  \[ \{A, B\} = \sum_{a} \left( \frac{\partial A}{\partial p_a} \frac{\partial B}{\partial q_a} - \frac{\partial A}{\partial q_a} \frac{\partial B}{\partial p_a} \right) \]  
  (18.3)
  The Poisson bracket is the classical analog of the commutator of quantum mechanics.
- (18.2) has the formal solution
  \[ \frac{\partial f}{\partial t} = -Lf = \{f, H_0 - A(X,t)F(t)\} = \{f, H_0\} - \{f, A(X,t)F(t)\} \]
  \[ \therefore \frac{\partial f}{\partial t} + L_0 f = \{A(X,t)F(t), f\} \]  
  (18.4)
• Equation (18.4) has the solution:
\[
f(t) = e^{-\tau_0 t} \left[ f_0 + \int_{-\infty}^{t} e^{\tau_0 t'} \left\{ A(X,t'), f(t') \right\} F(t') \, dt' \right]
\]  
(18.5)
\[
f(t) = f_0 + \int_{-\infty}^{t} e^{-(t-t')\tau_0} \left\{ A(X,t'), f(t') \right\} F(t') \, dt'
\]
where \( f_0 \) is the equilibrium distribution of the ensemble. Note in deriving (18.5) we used the fact that...
\[
e^{-\tau_0 t} f_0 = f_0
\]  
(18.6)

• We can use (18.6) to calculate the ensemble response of a system property \( B \) to the applied force
\[
\int dX f(t) B = \int dX f_0 B + \int_{-\infty}^{t} dt' F(t') \int dX B e^{-(t-t')\tau_0} \left\{ A(X,t'), f(t') \right\}
\]  
(18.7)
where \( dX=dq_1...dp_N \).

• Now (18.7) may be rewritten as
\[
\overline{B}(t) = \overline{B}_0 + \int_{-\infty}^{t} dt' F(t') \int dX B e^{-(t-t')\tau_0} \left\{ A(X,t'), f(t') \right\}
\]  
(18.8)
\[
or... \Delta B(t) = \overline{B}(t) - \overline{B}_0 = \int_{-\infty}^{t} dt' F(t') \int dX B e^{-(t-t')\tau_0} \left\{ A(X,t'), f(t') \right\}
\]

• If we assume the applied force is small, the displacement from equilibrium is also small so \( f(t) \approx f_0 \) and (18.8) becomes
\[
\Delta B(t) = \int_{-\infty}^{t} dt' F(t') \int dX B e^{-(t-t')\tau_0} \left\{ A, f \right\}
\]
\[
= \int_{-\infty}^{t} dt' F(t') \int dX e^{(t-t')\tau_0} B \left\{ A, f \right\}
\]  
(18.9)
\[
\approx \int_{-\infty}^{t} dt' F(t') \int dX B(t-t') \left\{ A, f_0 \right\}
\]

• The second step in (18.9) is a result of the unitary nature of the time displacement operator.

• After an integration by parts, (18.9) can be rearranged to
\[
\Delta B(t) \approx \int_{-\infty}^{t} dt' F(t') \int dX f_0 \left\{ B(t-t'), A(t') \right\} = \int_{-\infty}^{t} dt' F(t') \phi_{BA}(t-t')
\]  
(18.10)
where
\[
\phi_{BA}(t) = \int dX f_0 \left\{ B(t), A(0) \right\} = \overline{\{B(t), A(0)\}}
\]  
(18.11)

• \( \phi_{BA}(t) \) is the linear response or after-effect function. A specific form for the after-effect function will be derived later.