Substituting the perturbative form for \( f(x, t) \) into the Liouville equation, one obtains

\[
\frac{\partial}{\partial t}(f_0(x) + \Delta f(x, t)) + (iL_0 + i\Delta L(t))(f_0(x) + \Delta f(x, t)) = 0
\]

Recall \( \partial f_0/\partial t=0 \). Thus, working to linear order in small quantities, one obtains the following equation for \( \Delta f(x, t) \):

\[
\left(\frac{\partial}{\partial t} + iL_0\right)\Delta f(x, t) = -i\Delta L f_0(x)
\]

which is just a first-order inhomogeneous differential equation. This can easily be solved using an integrating factor, and one obtains the result

\[
\Delta f(x, t) = -\int_0^t ds e^{-iL_0(t-s)}i\Delta L(s)f_0(x)
\]

Note that

\[
i\Delta L f_0(x) = iL f_0(x) - iL_0 f_0(x) = iL f_0(x)
\]

But, using the chain rule, we have

\[
\dot{x} \cdot \nabla_x f_0(x) = \frac{\partial f_0}{\partial H} \sum_{i=1}^{3N} \left[ \dot{p}_i \frac{\partial H}{\partial p_i} + \dot{q}_i \frac{\partial H}{\partial q_i} \right]
\]

Define

\[
\mathcal{J}(x) = -\sum_{i=1}^{3N} \left[ D_i(x) \frac{\partial H}{\partial p_i} + C_i(x) \frac{\partial H}{\partial q_i} \right] F_e(t)
\]
which is known as the *dissipative flux*. Thus, for a Cartesian Hamiltonian

\[
H = \sum_{i=1}^{N} \left( \frac{\textbf{p}_i^2}{2m_i} \right) + U(\textbf{r}_1,...,\textbf{r}_N)
\]

where \(\textbf{F}_i(\textbf{r}_1,...,\textbf{r}_N) = -\nabla_iU\) is the force on the \(\underline{i}\)th particle, the dissipative flux becomes:

\[
j(\textbf{x}) = \sum_{i=1}^{N} \left[ \textbf{C}_i(\textbf{x}) \cdot \textbf{F}_i - \textbf{D}_i(\textbf{x}) \cdot \frac{\textbf{p}_i}{m_i} \right]
\]

In general,

\[
\dot{\textbf{x}} \cdot \nabla_{\textbf{x}} f_0(\textbf{x}) = -\frac{\partial f_0}{\partial H} j(\textbf{x}) F_e(t)
\]

Now, suppose \(f_0(\textbf{x})\) is a canonical distribution function

\[
f_0(H(\textbf{x})) = \frac{1}{Q(N,V,T)} e^{-\beta H(\textbf{x})}
\]

then

\[
\frac{\partial f_0}{\partial H} = -\beta f_0(H)
\]

so that

\[
\dot{\textbf{x}} \cdot \nabla_{\textbf{x}} f_0(\textbf{x}) = \beta f_0(\textbf{x}) j(\textbf{x}) F_e(t)
\]

Thus, the solution for \(\Delta f(\textbf{x}, t)\) is

\[
\Delta f(\textbf{x}, t) = -\beta \int_{0}^{t} ds \int d\textbf{x} A(\textbf{x}) e^{-iL_0(t-s)} f_0(\textbf{x}) j(\textbf{x}) F_e(s)
\]

The ensemble average of the observable \(\langle A(\textbf{x}) \rangle\) now becomes

\[
\langle A(\textbf{x}) \rangle = \langle A \rangle_0 - \beta \int d\textbf{x} A(\textbf{x}) \int_{0}^{t} ds \int d\textbf{x} e^{-iL_0(t-s)} f_0(\textbf{x}) j(\textbf{x}) F_e(s)
\]
Recall that the classical propagator is $\exp(iLt)$. Thus the operator appearing in the above expression is a classical propagator of the unperturbed system for propagating backwards in time to $- (t - s)$. An observable $A(x)$ evolves in time according to

$$\frac{dA}{dt} = iLA$$

which implies that forward evolution in time can be achieved by acting to the left on an observable with the time reversed classical propagator. Thus, the ensemble average of $\langle A \rangle$ becomes

$$\langle \langle A \rangle_0 - \beta \int_0^t ds F_e(s) \int d\text{x}_0 f_0(\text{x}_0)A(\text{x}_{t-s}(\text{x}_0))j(\text{x}_0) \rangle_0$$

Now, if we take the complex conjugate of both sides, we find

$$\langle A^*(t) = A^*(0) e^{-iLt} \rangle$$

where now the operator acts to the left on $\langle A^*(0) \rangle$. However, since observables are real, we have

$$\langle A(t) = A(0) e^{-iLt} \rangle$$

which implies that forward evolution in time can be achieved by acting to the left on an observable with the time reversed classical propagator. Thus, the ensemble average of $\langle A \rangle$ becomes

$$\langle \langle A \rangle_0 - \beta \int_0^t ds F_e(s) \langle j(0)A(t-s) \rangle_0 \rangle_0$$

where the quantity on the last line is an object we have not encountered yet before. It is known as an \textit{equilibrium time correlation function}. An equilibrium time correlation function is an ensemble average over the unperturbed (canonical) ensemble of the product of the dissipative flux at $\langle t = 0 \rangle$ with an observable $\langle A \rangle$ evolved to a time $\langle \underline{t - s} \rangle$. Several things are worth noting:
1. The nonequilibrium average $\langle A(t) \rangle$, in the linear response regime, can be expressed solely in terms of equilibrium averages.

2. The propagator used to evolve $A(x)$ to $A(x,t-s)$ is the operator $\exp(iL_0(t-s))$, which is the propagator for the unperturbed, Hamiltonian dynamics with $C_i = D_i = 0$. That is, it is just the dynamics determined by $H$.

3. Since $A(x,t-s) = A(x(t-s))$ is a function of the phase space variables evolved to a time $t-s$, we must now specify over which set of phase space variables the integration $\int dx$ is taken. The choice is actually arbitrary, and for convenience, we choose the initial conditions. Since $x(t)$ is a function of the initial conditions $x(0)$, we can write the time correlation function as:

$$\langle j(0)A(t-s)\rangle_0 = \frac{1}{Q}\int d\{\mathbf{x}_0\} e^{-\beta H(\{\mathbf{x}_0\})}j(\{\mathbf{x}_0\})A(\{\mathbf{x}_0\}(t-s)(\{\mathbf{x}_0\}))$$

Contributors and Attributions

Mark Tuckerman (New York University)