12.5: Perturbative solution of the Liouville equation

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

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

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

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

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

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

Note that

$$i\Delta L f_0(\mathrm{x})=iLf_0(\mathrm{x})-iL_0 f_0(\mathrm{x})=iLf_0(\mathrm{x})=\dot{\mathrm{x}}\cdot\nabla_{\mathrm{x}} f_0(\mathrm{x})$$

But, using the chain rule, we have

$$\begin{aligned}
\dot{\mathrm{x}}\cdot\nabla_{\mathrm{x}} f_0(\mathrm{x}) &= \dot{\mathrm{x}}\cdot\frac{\partial f_0}{\partial H}\frac{\partial H}{\partial \mathrm{x}} \\
&= \frac{\partial f_0}{\partial H}\sum_{i=1}^{3N}\left[\dot{p}_i\frac{\partial H}{\partial p_i}+\dot{q}_i\frac{\partial H}{\partial q_i}\right] \\
&= \frac{\partial f_0}{\partial H}\sum_{i=1}^{3N}\left[\frac{\partial H}{\partial p_i}\left(-\frac{\partial H}{\partial q_i}+D_iF_e(t)\right)+\frac{\partial H}{\partial q_i}\left(\frac{\partial H}{\partial p_i}+C_iF_e(t)\right)\right] \\
&= \frac{\partial f_0}{\partial H}\sum_{i=1}^{3N}\left[D_i(\mathrm{x})\frac{\partial H}{\partial p_i}+C_i(\mathrm{x})\frac{\partial H}{\partial q_i}\right]F_e(t)
\end{aligned}$$

Define

$$j(\mathrm{x})=-\sum_{i=1}^{3N}\left[D_i(\mathrm{x})\frac{\partial H}{\partial p_i}+C_i(\mathrm{x})\frac{\partial H}{\partial q_i}\right]$$

which is known as the *dissipative flux*. Thus, for a Cartesian Hamiltonian

$$H=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}+U(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

where $\mathbf{F}_i(\mathbf{r}_1,\ldots,\mathbf{r}_N)=-\nabla_i U$ is the force on the i th particle, the dissipative flux becomes:

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

In general,

$$\dot{\mathrm{x}}\cdot\nabla_{\mathrm{x}} f_0(\mathrm{x})=-\frac{\partial f_0}{\partial H}j(\mathrm{x})F_e(t)$$

Now, suppose $f_0(x)$ is a canonical distribution function

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

then

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

so that

$$\dot{\rm x} \cdot \nabla_{\rm x} f_0({\rm x}) = \beta f_0({\rm x}) j({\rm x}) F_e(t)$$

Thus, the solution for $\Delta f(x,t)$ is

$$\Delta f({\rm x},t) = -\beta \int_0^t ds e^{-iL_0(t-s)} f_0({\rm x}) j({\rm x}) F_e(s)$$

The ensemble average of the observable $A(x)$ now becomes

$$\begin{aligned} \langle A(t) \rangle &= \langle A \rangle_0 - \beta \int d{\rm x} A({\rm x}) \int_0^t ds e^{-iL_0(t-s)} f_0({\rm x}) j({\rm x}) F_e(s) \\ &= \langle A \rangle_0 - \beta \int_0^t ds \int d{\rm x} A({\rm x}) e^{-iL_0(t-s)} f_0({\rm x}) j({\rm x}) F_e(s) \\ &= \langle A \rangle_0 - \beta \int_0^t ds \int d{\rm x} f_0({\rm x}) A({\rm x}) e^{-iL_0(t-s)} j({\rm x}) F_e(s) \end{aligned}$$

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

$$\begin{aligned} \frac{dA}{dt} &= iLA \\ A(t) &= e^{iLt} A(0) \\ A(-t) &= e^{-iLt} A(0) \end{aligned}$$

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

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

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

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

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 A becomes

$$\begin{aligned} \langle A(t) \rangle &= \langle A \rangle_0 - \beta \int_0^t ds F_e(s) \int d{\rm x}_0 f_0({\rm x}_0) A({\rm x}_{t-s}({\rm x}_0)) j({\rm x}_0) \\ &= \langle A \rangle_0 - \beta \int_0^t ds F_e(s) \langle j(0) A(t-s) \rangle_0 \end{aligned}$$

where the quantity on the last line is an object we have not encountered yet before. It is known as an **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 $t=0$ with an observable A evolved to a time $t-s$. 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 $A({\rm x}, t-s) = A({\rm x}(t-s))$ 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

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