S10.B. Microscopic Linear Response Theory

Consider a system coupled to an external field $\boldsymbol{F}(\boldsymbol{r}, t)$ through the variable density $\boldsymbol{a}(\boldsymbol{r})$. Using the caret ^ to denote an operator, we can write the Hamiltonian as

$$\hat{H}(t) = \hat{H}_0 + \Delta \hat{H}(t) \tag{10.223}$$

where H_0 is the unperturbed Hamiltonian and

$$\Delta \hat{H}(t) = -\int d\boldsymbol{r}\, \hat{a}(\boldsymbol{r}) \cdot \boldsymbol{F}(\boldsymbol{r}, t) \tag{10.224}$$

is the perturbation caused by $\boldsymbol{F}$.

Consider now the Liouville equation [see (6.53), §6.D]

$$i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = \left[\hat{H}(t) ,\ \hat{\rho}(t) \right] \tag{10.225}$$

Let

$$\hat{\rho}(t) = \hat{\rho}_0 + \Delta \hat{\rho}(t) \tag{10.226}$$

where

$$i\hbar \frac{\partial \hat{\rho}_0}{\partial t} = \left[\hat{H}_0 , \hat{\rho}_0 \right] = 0 \tag{10.226a}$$

is the Liouville equation for the unperturbed system.

The solution to (10.226a) is the time-independent equilibrium distribution $\hat{\rho}_0 = \rho_0(\hat{H}_0)$. In the canonical ensemble [see (7.46) of §7.D.1]

$$\hat{\rho}_0 = \frac{1}{Z_0} e^{-\beta \hat{H}_0} \qquad\qquad Z_0 = \mathrm{Tr}\left[e^{-\beta \hat{H}_0} \right] \tag{10.226b}$$

Putting (10.226) into (10.225) gives

$$i\hbar \frac{\partial \Delta \hat{\rho}(t)}{\partial t} = \left[\hat{H}_0 , \Delta \hat{\rho}(t) \right] + \left[\Delta \hat{H}(t) , \rho_0 \right] + \left[\Delta \hat{H}(t) , \Delta \hat{\rho}(t) \right] \tag{10.227}$$

Keeping only 1st order deviations from the equilibrium, we have

$$i\hbar \frac{\partial \Delta \hat{\rho}(t)}{\partial t} \approx \left[\hat{H}_0 , \Delta \hat{\rho}(t) \right] + \left[\Delta \hat{H}(t) , \rho_0 \right] \tag{10.228}$$

Operators in the interaction picture is defined as

$$\hat{O}_{\mathcal{I}}(t) = e^{i \hat{H}_0 t/\hbar}\, \hat{O}(t)\, e^{-i \hat{H}_0 t/\hbar} \tag{10.228a}$$

with

$$\hat{O}_{\mathcal{I}}(0) = \hat{O}(0)$$

Since

$$\left[e^{\pm i \hat{H}_0 t/\hbar}, \hat{H}_0 \right] = 0 \tag{10.228b}$$

differentiating

$$\Delta \hat{\rho}(t) = e^{-i \hat{H}_0 t/\hbar}\, \Delta \hat{\rho}_{\mathcal{I}}(t)\, e^{i \hat{H}_0 t/\hbar}$$

gives

$$i\hbar \frac{\partial \Delta \hat{\rho}(t)}{\partial t} = e^{-i \hat{H}_0 t/\hbar} \left(\hat{H}_0 \Delta \hat{\rho}_{\mathcal{I}}(t) + i\hbar \frac{\partial \Delta \hat{\rho}_{\mathcal{I}}(t)}{\partial t} - \hat{\rho}_{\mathcal{I}}(t)\, \hat{H}_0 \right) e^{i \hat{H}_0 t/\hbar}$$

$$= \left[\hat{H}_0, \Delta\hat{\rho}(t)\right] + i\hbar\, e^{-i\hat{H}_0 t/\hbar} \frac{\partial \Delta\hat{\rho}_{\mathcal{I}}(t)}{\partial t} e^{i\hat{H}_0 t/\hbar}$$

Comparing with (10.228) gives

$$i\hbar \frac{\partial \Delta\hat{\rho}_{\mathcal{I}}(t)}{\partial t} = e^{i\hat{H}_0 t/\hbar}\left[\Delta\hat{H}(t), \rho_0\right] e^{-i\hat{H}_0 t/\hbar}$$

$$= e^{i\hat{H}_0 t/\hbar}\Delta\hat{H}(t)\,\rho_0\, e^{-i\hat{H}_0 t/\hbar} - e^{i\hat{H}_0 t/\hbar}\rho_0\,\Delta\hat{H}(t)\, e^{-i\hat{H}_0 t/\hbar}$$

$$= e^{i\hat{H}_0 t/\hbar}\Delta\hat{H}(t)\, e^{-i\hat{H}_0 t/\hbar}\rho_0 - \rho_0\, e^{i\hat{H}_0 t/\hbar}\Delta\hat{H}(t)\, e^{-i\hat{H}_0 t/\hbar} \qquad \text{[(10.228b) used.]}$$

$$= \left[\Delta\hat{H}_{\mathcal{I}}(t), \rho_0\right] \qquad (10.229)$$

Assuming

$$\Delta\hat{\rho}(-\infty) = 0 \qquad \rightarrow \qquad \Delta\hat{\rho}_{\mathcal{I}}(-\infty) = 0$$

(10.229) gives

$$\Delta\hat{\rho}_{\mathcal{I}}(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} dt' \left[\Delta\hat{H}_{\mathcal{I}}(t'), \rho_0\right] \qquad (10.230)$$

$$\rightarrow \qquad \Delta\hat{\rho}(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} dt'\, e^{-i\hat{H}_0 t/\hbar}\left[\Delta\hat{H}_{\mathcal{I}}(t'), \rho_0\right] e^{i\hat{H}_0 t/\hbar}$$

$$= \frac{1}{i\hbar}\int_{-\infty}^{t} dt' \left[e^{-i\hat{H}_0(t-t')/\hbar}\,\Delta\hat{H}(t')\, e^{i\hat{H}_0(t-t')/\hbar}, \rho_0\right] \qquad (10.231)$$

Putting in (10.224) gives

$$\Delta\hat{\rho}(t) = -\frac{1}{i\hbar}\int_{-\infty}^{t} dt' \int d\boldsymbol{r} \left[e^{-i\hat{H}_0(t-t')/\hbar}\,\hat{a}(\boldsymbol{r})\, e^{i\hat{H}_0(t-t')/\hbar}, \rho_0\right] \cdot \boldsymbol{F}(\boldsymbol{r}, t') \qquad (10.231a)$$

Using

$$\langle\hat{X}\rangle_0 = \mathrm{Tr}\left(\hat{X}\hat{\rho}_0\right)$$

we have

$$\left\langle \hat{a}_i(\boldsymbol{r}, t)\right\rangle \equiv \mathrm{Tr}\left[\hat{a}_i(\boldsymbol{r})\,\hat{\rho}(t)\right] \qquad (10.231b)$$

$$= \left\langle \hat{a}_i(\boldsymbol{r})\right\rangle_0 + \mathrm{Tr}\left[\hat{a}_i(\boldsymbol{r})\,\Delta\hat{\rho}(t)\right] \qquad \text{[(10.226) used.]}$$

Putting in (10.231a) gives

$$\left\langle \hat{a}_i(\boldsymbol{r}, t)\right\rangle = \left\langle \hat{a}_i(\boldsymbol{r})\right\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t} dt' \int d\boldsymbol{r} \qquad (10.232a)$$

$$\times \mathrm{Tr}\left\{\hat{a}_i(\boldsymbol{r})\left[e^{-i\hat{H}_0(t-t')/\hbar}\,\hat{a}_j(\boldsymbol{r})\, e^{i\hat{H}_0(t-t')/\hbar}, \rho_0\right]\right\} F_j(\boldsymbol{r}, t')$$

Using

$$\mathrm{Tr}\left\{\hat{a}_i(\boldsymbol{r})\left[e^{-i\hat{H}_0(t-t')/\hbar}\,\hat{a}_j(\boldsymbol{r})\, e^{i\hat{H}_0(t-t')/\hbar}, \rho_0\right]\right\}$$

$$= \mathrm{Tr}\left\{\hat{a}_i(\boldsymbol{r})\, e^{-i\hat{H}_0(t-t')/\hbar}\,\hat{a}_j(\boldsymbol{r})\, e^{i\hat{H}_0(t-t')/\hbar}\rho_0 - \hat{a}_i(\boldsymbol{r})\,\rho_0\, e^{-i\hat{H}_0(t-t')/\hbar}\,\hat{a}_j(\boldsymbol{r})\, e^{i\hat{H}_0(t-t')/\hbar}\right\}$$

$$= \mathrm{Tr}\left\{\hat{a}_i(\boldsymbol{r})\, e^{-i\hat{H}_0 t/\hbar} e^{i\hat{H}_0 t'/\hbar}\hat{a}_j(\boldsymbol{r})\, e^{-i\hat{H}_0 t'/\hbar}\rho_0\, e^{i\hat{H}_0 t/\hbar} - \hat{a}_i(\boldsymbol{r})\, e^{-i\hat{H}_0 t/\hbar}\rho_0\, e^{i\hat{H}_0 t'/\hbar}\hat{a}_j(\boldsymbol{r})\, e^{-i\hat{H}_0 t'/\hbar} e^{i\hat{H}_0 t/\hbar}\right\}$$

$$= \mathrm{Tr}\Big\{ e^{i\hat{H}_0 t/\hbar}\, \hat{a}_i(\boldsymbol{r})\, e^{-i\hat{H}_0 t/\hbar}\, e^{i\hat{H}_0 t'/\hbar}\, \hat{a}_j(\boldsymbol{r})\, e^{-i\hat{H}_0 t'/\hbar}\, \rho_0 \qquad (\text{ Tr is cyclic. })$$
$$- e^{i\hat{H}_0 t/\hbar}\, \hat{a}_i(\boldsymbol{r})\, e^{-i\hat{H}_0 t/\hbar}\, \rho_0\, e^{i\hat{H}_0 t'/\hbar}\, \hat{a}_j(\boldsymbol{r})\, e^{-i\hat{H}_0 t'/\hbar} \Big\}$$
$$= \mathrm{Tr}\Big\{ \hat{a}_{\mathcal{I}i}(\boldsymbol{r},t)\, \hat{a}_{\mathcal{I}j}(\boldsymbol{r},t')\, \rho_0 - \hat{a}_{\mathcal{I}i}(\boldsymbol{r},t)\, \rho_0\, \hat{a}_{\mathcal{I}j}(\boldsymbol{r},t') \Big\}$$
$$= \mathrm{Tr}\Big\{ \hat{a}_{\mathcal{I}i}(\boldsymbol{r},t)\, \hat{a}_{\mathcal{I}j}(\boldsymbol{r},t')\, \rho_0 - \hat{a}_{\mathcal{I}j}(\boldsymbol{r},t')\, \hat{a}_{\mathcal{I}i}(\boldsymbol{r},t)\, \rho_0 \Big\}$$
$$= \mathrm{Tr}\Big\{ \Big[\hat{a}_{\mathcal{I}i}(\boldsymbol{r},t),\, \hat{a}_{\mathcal{I}j}(\boldsymbol{r},t') \Big] \rho_0 \Big\}$$
$$= \Big\langle \Big[\hat{a}_{\mathcal{I}i}(\boldsymbol{r},t),\, \hat{a}_{\mathcal{I}j}(\boldsymbol{r},t') \Big] \Big\rangle_0 \qquad (10.233)$$

(10.232a) becomes

$$\langle \Delta\, \hat{a}_i(\boldsymbol{r},t) \rangle \equiv \Big\langle \Big\{ \hat{a}_i(\boldsymbol{r},t) - \langle \hat{a}_i(\boldsymbol{r}) \rangle_0 \Big\} \Big\rangle = \langle \hat{a}_i(\boldsymbol{r},t) \rangle - \langle \hat{a}_i(\boldsymbol{r}) \rangle_0$$
$$= -\frac{1}{i\hbar} \int_{-\infty}^{t} dt' \int d\boldsymbol{r} \Big\langle \Big[\hat{a}_{\mathcal{I}i}(\boldsymbol{r},t),\, \hat{a}_{\mathcal{I}j}(\boldsymbol{r},t') \Big] \Big\rangle_0 F_j(\boldsymbol{r},t') \qquad (10.232)$$

= average deviation of $a_i(\boldsymbol{r})$ from its equilibrium value.

(10.232) is known as the Kubo formula. In matrix form,

$$\langle \Delta\, \hat{\mathbf{a}}(\boldsymbol{r},t) \rangle = -\frac{1}{i\hbar} \int_{-\infty}^{t} dt' \int d\boldsymbol{r} \Big\langle \Big[\hat{\mathbf{a}}_{\mathcal{I}}(\boldsymbol{r},t),\, \hat{\mathbf{a}}_{\mathcal{I}}(\boldsymbol{r},t') \cdot \boldsymbol{F} \Big] \Big\rangle_0 \qquad (10.232a)$$

Caution: the difference between $\langle \hat{a}_i(\boldsymbol{r},t) \rangle$ & $\langle \hat{a}_{\mathcal{I}i}(\boldsymbol{r},t) \rangle$ was lost in Reichl's narrative [see Reichl's (10.234)].

The linear response formula (10.133) of §10.E.2 can be generalized to the spatially dependent case as

$$\langle \Delta\, \hat{\mathbf{a}}(\boldsymbol{r},t) \rangle = 2i \int_{-\infty}^{t} dt' \int d\boldsymbol{r}'\ \mathbb{K}''(\boldsymbol{r},\boldsymbol{r}';t-t') \cdot \boldsymbol{F}(\boldsymbol{r}',t') \qquad (10.235)$$

Comparing with (10.232) gives a microscopic expression for the imaginary (or dissipative) part of the response matrix as

$$\mathbb{K}''_{ij}(\boldsymbol{r},\boldsymbol{r}';t-t') = \frac{1}{2\hbar} \Big\langle \Big[\hat{a}_{\mathcal{I}i}(\boldsymbol{r},t),\, \hat{a}_{\mathcal{I}j}(\boldsymbol{r},t') \Big] \Big\rangle_0 \qquad (10.236)$$

Note: Reichl writes $\mathbb{K}''_{ij}$ as $\mathbb{K}''_{a_i a_j}$, which is more in line with the notations used in previous sections.

Consider now the spatially dependent correlation function of a translationally invariant system

$$C_{ij}(\boldsymbol{r}-\boldsymbol{r}';\ \tau) = \langle \hat{a}_{\mathcal{I}i}(\boldsymbol{r},\tau)\, \hat{a}_{\mathcal{I}j}(\boldsymbol{r}') \rangle_0$$
$$= \langle \hat{a}_{\mathcal{I}i}(\boldsymbol{r},\tau)\, \hat{a}_j(\boldsymbol{r}') \rangle_0 \qquad (10.237)$$

Its Fourier transform is

$$G_{ij}(\boldsymbol{k},\tau) = \int d\rho\, e^{-i\boldsymbol{k}\cdot\boldsymbol{\rho}}\, C_{ij}(\boldsymbol{\rho};\tau) \qquad \boldsymbol{\rho} = \boldsymbol{r}-\boldsymbol{r}'$$
$$= \frac{1}{V} \int d\boldsymbol{r} \int d\boldsymbol{r}'\, e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \langle \hat{a}_{\mathcal{I}i}(\boldsymbol{r},\tau)\, \hat{a}_j(\boldsymbol{r}') \rangle_0$$
$$= \frac{1}{V} \langle \hat{a}_{\mathcal{I}i}(\boldsymbol{k},\tau)\, \hat{a}_j(-\boldsymbol{k}) \rangle_0$$
$$= \frac{1}{V} \langle \hat{a}_{\mathcal{I}i}(\boldsymbol{k},\tau)\, \hat{a}_j^{+}(\boldsymbol{k}) \rangle_0 \qquad [\ \hat{\mathbf{a}}(\boldsymbol{r}) \text{ is Hermitian.}\ ] \qquad (10.238)$$

Similarly, the Fourier transform of (10.236) gives

$$\mathbb{K}''_{ij}(\boldsymbol{k},\,\tau) = \frac{1}{2\,\hbar\,V}\left\langle \left[\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau)\,,\,\hat{a}^{+}_{\mathcal{I}\,j}(\boldsymbol{k}\,)\right]\right\rangle_0$$
$$= \frac{1}{2\,\hbar\,V}\left\langle \left[\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau)\,,\,\hat{a}^{+}_{j}(\boldsymbol{k}\,)\right]\right\rangle_0 \qquad (10.239)$$

Now,

$$\left\langle\,\hat{a}^{+}_{j}(\boldsymbol{k}\,)\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau)\,\right\rangle_0 = \mathrm{Tr}\Big[\,\hat{a}^{+}_{j}(\boldsymbol{k})\,e^{i\,\hat{H}_0\,\tau/\hbar}\,\hat{a}_{i}(\boldsymbol{k})\,e^{-i\,\hat{H}_0\,\tau/\hbar}\,\rho_0\,\Big]$$
$$= \frac{1}{Z_0}\,\mathrm{Tr}\Big[\,\hat{a}^{+}_{j}(\boldsymbol{k})\,e^{i\,\hat{H}_0\,\tau/\hbar}\,\hat{a}_{i}(\boldsymbol{k})\,e^{-i\,\hat{H}_0\,\tau/\hbar}\,e^{-\beta\,\hat{H}_0}\,\Big]$$
$$= \frac{1}{Z_0}\,\mathrm{Tr}\Big[\,\hat{a}^{+}_{j}(\boldsymbol{k})\,e^{-\beta\,\hat{H}_0}\,e^{i\,\hat{H}_0(\,\tau-i\,\beta\,\hbar)\big/\hbar}\,\hat{a}_{i}(\boldsymbol{k})\,e^{-i\,\hat{H}_0(\,\tau-i\,\beta\,\hbar)\big/\hbar}\Big]$$
$$= \frac{1}{Z_0}\,\mathrm{Tr}\Big[\,\hat{a}^{+}_{j}(\boldsymbol{k})\,e^{-\beta\,\hat{H}_0}\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau-i\,\beta\,\hbar)\Big]$$
$$= \mathrm{Tr}\big[\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau-i\,\beta\,\hbar)\,\hat{a}^{+}_{j}(\boldsymbol{k})\,\rho_0\big]$$
$$= \left\langle\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau-i\,\beta\,\hbar)\,\hat{a}^{+}_{j}(\boldsymbol{k})\right\rangle_0 \qquad (10.240a)$$

Using

$$f(\tau+a) = \sum_{n=0}^{\infty}\frac{a^n}{n!}\,\frac{d^n f(\tau)}{d\,\tau^n} = e^{a\,d/d\,\tau}\,f(\tau)$$

(10.240a) becomes

$$\left\langle\,\hat{a}^{+}_{j}(\boldsymbol{k}\,)\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau)\,\right\rangle_0 = \left\langle\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau-i\,\beta\,\hbar)\,\hat{a}^{+}_{j}(\boldsymbol{k})\right\rangle_0$$
$$= e^{-i\,\beta\,\hbar\,\partial/\partial\,\tau}\left\langle\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau)\;\hat{a}^{+}_{j}(\boldsymbol{k})\right\rangle_0 \qquad (10.240)$$

(10.239) thus becomes

$$\mathbb{K}''_{ij}(\boldsymbol{k},\,\tau) = \frac{1}{2\,\hbar\,V}\left(1-e^{-i\,\beta\,\hbar\,\partial/\partial\,\tau}\right)\left\langle\,\hat{a}_{\mathcal{I}\,i}(\boldsymbol{k},\,\tau)\;\hat{a}^{+}_{j}(\boldsymbol{k})\right\rangle_0$$
$$= \frac{1}{2\,\hbar}\left(1-e^{-i\,\beta\,\hbar\,\partial/\partial\,\tau}\right)G_{ij}(\boldsymbol{k},\,\tau) \qquad [\,(10.238)\text{ used.}\,] \qquad (10.241)$$

Taking the Fourier transform of (10.241) gives

$$\chi''_{ij}(\boldsymbol{k},\,\omega) \equiv \int_{-\infty}^{\infty} d\,\tau\,e^{i\,\omega\,\tau}\,\mathbb{K}''_{ij}(\boldsymbol{k},\,\tau)$$
$$= \frac{1}{2\,\hbar}\int_{-\infty}^{\infty} d\,\tau\,e^{i\,\omega\,\tau}\left(1-e^{-i\,\beta\,\hbar\,\partial/\partial\,\tau}\right)G_{ij}(\boldsymbol{k},\,\tau)$$
$$= \frac{1}{2\,\hbar}\int_{-\infty}^{\infty} d\,\tau\,e^{i\,\omega\,\tau}\left[\,G_{ij}(\boldsymbol{k},\,\tau)-G_{ij}(\boldsymbol{k},\,\tau-i\,\beta\,\hbar)\,\right]$$
$$= \frac{1}{2\,\hbar}\left[\,\int_{-\infty}^{\infty} d\,\tau\,e^{i\,\omega\,\tau}\,G_{ij}(\boldsymbol{k},\,\tau)-e^{-\beta\,\hbar\,\omega}\int_{-\infty}^{\infty} d\,\tau'\,e^{i\,\omega\,\tau'}\,G_{ij}(\boldsymbol{k},\,\tau')\,\right]$$
$$= \frac{1}{2\,\hbar}\left(1-e^{-\beta\,\hbar\,\omega}\right)\int_{-\infty}^{\infty} d\,\tau\,e^{i\,\omega\,\tau}\,G_{ij}(\boldsymbol{k},\,\tau)$$
$$= \frac{1}{2\,\hbar}\left(1-e^{-\beta\,\hbar\,\omega}\right)S_{ij}(\boldsymbol{k},\,\omega) \qquad (10.242)$$

where [c.f. (10.108) of §10.D.2]

$$S_{ij}(\boldsymbol{k},\,\omega) = \int_{-\infty}^{\infty} d\,\tau\,e^{i\,\omega\,\tau}\,G_{ij}(\boldsymbol{k},\,\tau) \qquad (10.242a)$$

is the spectral density matrix.

Using the Kramers-Kronig relation [see (10.129) of §10.E.2], (10.242) becomes

$$\chi_{ij}(\boldsymbol{k},\,\omega) = \lim_{\eta\to 0}\int \frac{d\,\omega'}{\pi}\,\frac{\chi''_{ij}(\boldsymbol{k},\,\omega')}{\omega' - \omega - i\,\eta}$$

$$= \lim_{\eta\to 0}\int \frac{d\,\omega'}{2\,\pi\,\hbar}\,\frac{\left(1 - e^{-\beta\hbar\omega'}\right) S_{ij}(\boldsymbol{k},\,\omega')}{\omega' - \omega - i\,\eta} \tag{10.243}$$