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### 10.E.3. The Fluctuation-Dissipation Theorem

The fluctuation-dissipation theorem relates the dynamic susceptibility  $\chi(\omega)$  with the spectral density matrix  $\mathfrak{S}_{\alpha\alpha}(\omega)$ .

Note that  $\chi(\omega)$  &  $\mathfrak{S}_{\alpha\alpha}(\omega)$  are the Fourier transforms of the response matrix  $\mathbb{K}(\tau)$  and the correlation matrix  $\mathbf{C}_{\alpha\alpha}(\tau)$ , respectively [see (10.117) & (10.108)]. Now,  $\mathbf{C}_{\alpha\alpha}(\tau)$  describes the correlation of the fluctuations  $\alpha$ , while  $\mathbb{K}(\tau)$  controls their decay (or dissipation). Hence the name of the theorem.

The decay of  $\alpha$  can be studied in two ways. First, it can be expressed as [see (10.88)]

$$\alpha(t) = e^{-\mathbb{M}|t|} \cdot \alpha \quad [\alpha = \alpha(0)] \quad (10.149)$$

so that [see (10.100)]

$$\mathbf{C}_{\alpha\alpha}(t) = \langle \alpha(t) \alpha^T \rangle = k_B e^{-\mathbb{M}|t|} \cdot \mathbf{g}^{-1} \quad [\mathbf{g}^{-1} = \frac{1}{k_B} \langle \alpha \alpha^T \rangle] \quad (10.152)$$

Secondly, as shown in §10.E.2, using the step force [see (10.134)]

$$\mathbf{F}(t) = \mathbf{F} \theta(-t) = \begin{cases} \mathbf{F} & t < 0 \\ 0 & t \geq 0 \end{cases}$$

we get [see (10.146)]

$$\begin{aligned} \alpha &= \chi(0) \cdot \mathbf{F} \\ &= \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\chi''(\omega)}{\omega} \cdot \mathbf{F} \quad [(10.144a) \text{ used.}] \end{aligned}$$

so that, for  $t \geq 0$ ,

$$\begin{aligned} \alpha(t) &= e^{-\mathbb{M}t} \cdot \chi(0) \cdot \mathbf{F} \\ &= \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \cos \omega t \frac{\chi''(\omega)}{\omega} \cdot \mathbf{F} \quad [\text{See (10.147).}] \end{aligned} \quad (10.150)$$

Since  $\mathbf{F}$  is arbitrary, we have

$$\begin{aligned} e^{-\mathbb{M}|t|} \cdot \chi(0) &= \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \cos \omega t \frac{\chi''(\omega)}{\omega} \quad (10.151) \\ &= \frac{1}{k_B} \mathbf{C}_{\alpha\alpha}(t) \cdot \mathbf{g} \cdot \chi(0) \quad [(10.152) \text{ used.}] \end{aligned}$$

$$\rightarrow \mathbf{C}_{\alpha\alpha}(t) = k_B \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \cos \omega t \frac{\chi''(\omega)}{\omega} \cdot \chi^{-1}(0) \cdot \mathbf{g}^{-1} \quad (10.153a)$$

In Exercise 10.5, we shall show that

$$\mathbf{g} \cdot \chi(0) = \frac{1}{T} \quad (10.153b)$$

so that (10.153a) becomes

$$\mathbf{C}_{\alpha\alpha}(t) = k_B T \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \cos \omega t \frac{\chi''(\omega)}{\omega} \quad (10.154)$$

Since  $\mathfrak{S}_{\alpha\alpha}(\omega)$  is real [see (10.112a) of §10.D.2], we have,

$$\mathbf{C}_{\alpha\alpha}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \mathfrak{S}_{\alpha\alpha}(\omega)$$

$$\begin{aligned}
 &= \int_0^\infty \frac{d\omega}{2\pi} (e^{-i\omega t} + e^{i\omega t}) \mathbb{S}_{\alpha\alpha}(\omega) \\
 &= \int_0^\infty \frac{d\omega}{\pi} \mathbb{S}_{\alpha\alpha}(\omega) \cos \omega t \\
 &= \mathcal{P} \int_{-\infty}^\infty \frac{d\omega}{2\pi} \mathbb{S}_{\alpha\alpha}(\omega) \cos \omega t
 \end{aligned} \tag{10.154a}$$

Comparing with (10.154) then gives

$$\mathbb{S}_{\alpha\alpha}(\omega) = 2 k_B T \frac{\chi''(\omega)}{\omega} \quad [\omega \neq 0] \tag{10.154b}$$

which is known as the **fluctuation-dissipation theorem**.

### Exercise 10.5

Prove that  $\mathbf{g} \cdot \chi(0) = \frac{1}{T}$ , where  $g_{ij} = -\left(\frac{\partial^2 S}{\partial A_i \partial A_j}\right)_U$ .

### Answer

Consider a system with extensive variable  $\mathbf{A} = \mathbf{A}_0 + \boldsymbol{\alpha}$  so that the 1st law becomes

$$\begin{aligned}
 dU &= T dS + \mathbf{F} \cdot d\mathbf{A} \\
 &= T dS + \mathbf{F} \cdot d\boldsymbol{\alpha}
 \end{aligned} \tag{1a}$$

where  $\mathbf{F}$  is the intensive variable or external force. Note that [see (2.23) of §2.D.2]

$$\begin{aligned}
 \mathbf{F} \cdot d\mathbf{A} &= \text{work done on the system by } \mathbf{F} \\
 &= -dW
 \end{aligned}$$

(1a) can be written as

$$\begin{aligned}
 dS &= \frac{1}{T} dU - \frac{1}{T} \mathbf{F} \cdot d\mathbf{A} \\
 &= \left(\frac{\partial S}{\partial U}\right)_A dU + \left(\frac{\partial S}{\partial \mathbf{A}}\right)_U \cdot d\mathbf{A} \quad [S = S(U, \mathbf{A})] \tag{2} \\
 &= \left(\frac{\partial S}{\partial U}\right)_A dU + \left(\frac{\partial S}{\partial \boldsymbol{\alpha}}\right)_U \cdot d\boldsymbol{\alpha} \tag{2a}
 \end{aligned}$$

$$\rightarrow \left(\frac{\partial S}{\partial U}\right)_A = \frac{1}{T} \quad \left(\frac{\partial S}{\partial \mathbf{A}}\right)_U = -\frac{1}{T} \mathbf{F} \tag{2b}$$

In the equilibrium state with  $U = U_0$ ,  $S$  can be expanded as a Taylor series in the fluctuations  $\boldsymbol{\alpha}$  [see (7.22) of §7.C.1],

$$S = S_0 + \frac{1}{2} \alpha_i \alpha_j \left(\frac{\partial^2 S}{\partial A_i \partial A_j}\right)_0 + \dots \tag{2c}$$

where the subscript 0 indicates  $\mathbf{A} = \mathbf{A}_0$ .

$$\rightarrow dS = -\frac{1}{2} \boldsymbol{\alpha}^T \cdot \mathbf{g} \cdot \boldsymbol{\alpha} + \dots$$

Since  $\mathbf{g}^T = \mathbf{g}$ , we have

$$\begin{aligned}
 \left(\frac{\partial S}{\partial \mathbf{A}}\right)_U &= \left(\frac{\partial S}{\partial \boldsymbol{\alpha}}\right)_U = -\frac{1}{2} \frac{\partial}{\partial \alpha_i} (\alpha_j g_{jk} \alpha_k) + \dots = -\frac{1}{2} (\delta_{ij} g_{jk} \alpha_k + \alpha_j g_{jk} \delta_{ik}) + \dots \\
 &= -\frac{1}{2} (g_{ik} \alpha_k + \alpha_j g_{ji}) + \dots = -\mathbf{g} \cdot \boldsymbol{\alpha} + \dots
 \end{aligned} \tag{2d}$$

Equating (2a) with (2d) gives, to 1st order in  $\boldsymbol{\alpha}$ ,

$$\begin{aligned}
 \frac{1}{T} \mathbf{F} &= \mathbf{g} \cdot \boldsymbol{\alpha} \\
 &= \mathbf{g} \cdot \boldsymbol{\chi}(0) \cdot \mathbf{F} \quad [ (10.146) \text{ used. } ] \\
 \rightarrow \frac{1}{T} &= \mathbf{g} \cdot \boldsymbol{\chi}(0) \quad \text{QED.}
 \end{aligned} \tag{6}$$

Note that our proof is valid only for linear responses.