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10.E.3. The Fluctuation-Dissipation Theorem

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

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

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

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

so that [see (10.100)]

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

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

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

we get [see (10.146)]

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

so that, for $t \geq 0$,

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

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

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

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

In Exercise 10.5, we shall show that

$$\mathbb{g} \cdot \boldsymbol{\chi}(0) = \frac{1}{T} \qquad (10.153\text{b})$$

so that (10.153a) becomes

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

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

$$\begin{aligned} \mathbb{C}_{\alpha\alpha}(t) &= \int_{-\infty}^{\infty} \frac{d\,\omega}{2\,\pi} e^{-i\,\omega\,t}\, \mathbb{S}_{\alpha\alpha}(\omega) \\ &= \int_{0}^{\infty} \frac{d\,\omega}{2\,\pi} \left(e^{-i\,\omega\,t} + e^{i\,\omega\,t} \right) \mathbb{S}_{\alpha\alpha}(\omega) \\ &= \int_{0}^{\infty} \frac{d\,\omega}{\pi} \mathbb{S}_{\alpha\alpha}(\omega) \cos\omega\,t \qquad (10.154\text{a}) \end{aligned}$$

Comparing with (10.154) then gives

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

which is known as the fluctuation-dissipation theorem.

Exercise 10.5

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

Answer

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

$$\begin{aligned} dU &= T\,dS + \boldsymbol{F}\cdot d\boldsymbol{A} \\ &= T\,dS + \boldsymbol{F}\cdot d\boldsymbol{\alpha} \qquad (1a) \end{aligned}$$

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

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

(1a) can be written as

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

$$\rightarrow \quad \left(\frac{\partial S}{\partial U}\right)_{\boldsymbol{A}} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial \boldsymbol{A}}\right)_U = -\frac{1}{T} \boldsymbol{F} \qquad (2b)$$

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],

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

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

$$\rightarrow \quad dS = -\frac{1}{2} \boldsymbol{\alpha}^T \cdot \mathbb{g} \cdot \boldsymbol{\alpha} + \ldots$$

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

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

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

$$\begin{aligned} \frac{1}{T} \boldsymbol{F} &= \mathbb{g} \cdot \boldsymbol{\alpha} \\ &= \mathbb{g} \cdot \chi(0) \cdot \boldsymbol{F} \qquad [\ (10.146) \text{ used.}\ ] \end{aligned}$$

$$\rightarrow \quad \frac{1}{T} = \mathbb{g} \cdot \chi(0) \qquad \text{QED.} \qquad (6)$$

Note that our proof is valid only for linear responses.