University of Washington
Department of Chemistry
Chemistry 553
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Lecture 18: Currents and the Classical Fluctuation Dissipation Theorem
Text Reading: Ch 21,22

A. Currents

- A common calculation is the linear current which flows in response to application of a field E(t). Common expression for a current is $\dot{A} = \frac{dA}{dt}$
- A useful property of Poisson brackets is that

$$\{f_0, B\} = \frac{f_0}{kT}\{B, H\} = -\frac{f_0 \dot{B}}{kT} \qquad (18.1)$$

Then

$$\phi_{BA}(t) = \langle\{B(t), A(0)\}\rangle = \int dX\,\{B(t), A(0)\}\, f_0 = \int dX\, A(0)\{f_0, B(t)\}$$
$$= -\frac{1}{kT}\langle A(0)\dot{B}(t)\rangle = \int dX\, B(t)\{A(0), f_0\} = \frac{1}{kT}\langle \dot{A}(0) B(t)\rangle$$

Now we will obtain some expressions useful for calculating a linear current. This means that we assume $B(t) = \dot{A}(t)$

$$\phi_{\dot{A}A}(t) = \int dX f_0\{\dot{A}(t), A(0)\} = \int dX\,\{A(0), f_0\}\,\dot{A}(t) = \beta\int dX\, f_0 \dot{A}(0)\,\dot{A}(t)$$
$$\chi_{BA}(\omega) \equiv \chi_{\dot{A}A}(\omega) \equiv \int_0^\infty dt\,\phi_{\dot{A}A}(t)\, e^{-i\omega t} = \beta\int_0^\infty dt\,\langle \dot{A}(0)\,\dot{A}(t)\rangle e^{-i\omega t} \qquad (18.2)$$

Note: In electrical engineering the Greek letter sigma (σ) is usually used to designate the complex susceptibility in problems relating to current flow. We will stay with chi (χ)..

- Then the in-phase and out-of-phase components are

$$\chi'_{\dot{A}A}(\omega) = \frac{1}{kT}\int_0^\infty dt\,\langle \dot{A}(0)\,\dot{A}(t)\rangle \cos\omega t$$
$$and \ldots \chi''_{\dot{A}A}(\omega) = \frac{1}{kT}\int_0^\infty dt\,\langle \dot{A}(0)\,\dot{A}(t)\rangle \sin\omega t \qquad (18.3)$$

- Note that the average rate of dissipation (i.e. Joule heating) is given by

(18.4)

$$\bar{D}_\omega = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} dsF(s)\left(\Delta\dot{A}\right) = \frac{\omega}{2\pi}F_\omega^{\ 2}\int_0^{2\pi/\omega}\cos\omega s\left[\chi'_{\dot{A}A}(\omega)\cos\omega s + \chi''_{\dot{A}A}(\omega)\sin\omega s\right]ds$$

$$= \frac{F_\omega^{\ 2}}{2}\chi'_{\dot{A}A}(\omega) = \frac{F_\omega^{\ 2}}{2kT}\int_0^\infty dt\left\langle \dot{A}(0)\dot{A}(t)\right\rangle\cos\omega t$$

(18.5)

- Note the difference with expression given for the dissipation in the last lecture). Equation (18.5) says that the rate of dissipation resulting from the application of the field F(t) is related to the Fourier cosine transform of the auto-correlation function of the current. This is just a consequence of the fact that B=dA/dt.
- In electrical circuits, the current density J is $J = \dot{A}$. . In linear response theory the current density is

$$J_k(t) = \sum_\ell \int_{-\infty}^{t} dsE_\ell(s)\phi_{\ell,k}(t-s) \quad k,\ell = x,y,z \tag{18.6}$$

where J_k is the current that flows in the k direction in response to an applied electrical field E_ℓ. The response function is defined as

$$\phi_{k,\ell}(t) = \frac{1}{k_BT}\left\langle J_k(0)J_\ell(t)\right\rangle \tag{18.7}$$

- Case 1: $E = (E_x, 0, 0)$

$$J_x(t) = \int_{-\infty}^{t} dsE_x\phi_{xx}(t-s) = \int_0^\infty dsE_x\phi_{xx}(\tau) \quad = E_x\int_0^\infty ds\phi_{xx}(\tau)$$

$$= \frac{E_x}{2k_BT}\int_{-\infty}^{+\infty}\left\langle J_x(0)J_x(s)\right\rangle = \chi_{xx}E_x \tag{18.8}$$

When the applied field is constant in time we obtain Ohm's Law and σ_{xx}, is the electrical conductivity and is related to the current autocorrelation function.

- Case 2: $E = (E_x\cos\omega t, 0, 0)$

$$J_x(t) = \mathrm{Re}\left[e^{i\omega t}\int_0^\infty d\tau E_x e^{-i\omega\tau}\phi_{xx}(\tau)\right] \quad = \frac{E_x}{2k_BT}\mathrm{Re}\left[e^{i\omega t}\int_{-\infty}^{+\infty} d\tau e^{-i\omega\tau}\left\langle J_x(0)J_x(\tau)\right\rangle\right]$$

$$= E_x\,\mathrm{Re}\left[e^{i\omega t}\chi_{xx}(\omega)\right] = E_x\left(\chi'_{xx}\cos\omega t + \chi''_{xx}\sin\omega t\right)$$

(18.9)

where

$$\chi_{xx}(\omega) = \frac{1}{2k_BT}\int_{-\infty}^{+\infty} d\tau e^{-i\omega\tau}\left\langle J_x(0)J_x(\tau)\right\rangle \tag{18.10}$$

- Equations (18.8) and (18.10) relate the rate of current dissipation to the one-sided Fourier transform of the autocorrelation function of the current J. These equations are special cases of the fluctuation-dissipation theorem.

B. Classical Form of the Fluctuation-Dissipation Theorem

- We now obtain the fluctuation-dissipation theorem for a general classical system. Recall the expression for the linear response function…

$$\langle \Delta B \rangle \approx \int_{-\infty}^{t} dt' F(t') \phi_{BA}(t-t') \tag{18.11}$$

$$\begin{aligned} where \ldots \phi_{BA}(t) &= \int dX \, B(t) \{A(0), f_0\} \\ &= \int dX \, f_0 \{B(t), A(0)\} = \langle \{B(t), A(0)\} \rangle \end{aligned} \tag{18.12}$$

As in the last lecture we remove the Poisson bracket…

$$\begin{aligned} \phi_{BA}(t) &= \int dX \, f_0 \{B(t), A(0)\} = -\int dX \, f_0 \{A(0), B(t)\} = -\int dX \, B(t) \{ f_0, A(0)\} \\ &= \frac{1}{kT} \int dX \, f_0 B(t) \dot{A}(0) = -\frac{1}{kT} \langle \dot{B}(t) A(0) \rangle \end{aligned} \tag{18.13}$$

- From (18.13) we obtain after an integration by parts

$$\begin{aligned} \chi_{BA}(\omega) &= \chi'_{BA}(\omega) - i\chi''_{BA}(\omega) = \int_0^{\infty} dt \, \phi_{BA}(t) e^{-i\omega t} = -\frac{1}{kT} \int_0^{\infty} dt \langle A(0) \dot{B}(t) \rangle e^{-i\omega t} \\ &= -\frac{1}{kT} \left\{ \langle A(0) B(t) \rangle e^{-i\omega t} \Big|_0^{\infty} - \int_0^{\infty} dt \langle A(0) B(t) \rangle (-i\omega) e^{-i\omega t} \right\} \\ &= \frac{\langle A(0) B(0) \rangle}{kT} - \frac{i\omega}{kT} \int_0^{\infty} dt \langle A(0) B(t) \rangle (\cos \omega t - i \sin \omega t) \end{aligned} \tag{18.14}$$

- We can also obtain expression for the in-phase and out-of-phase responses…

$$\chi'_{BA}(\omega) = \frac{\langle A(0) B(0) \rangle}{kT} - \frac{\omega}{kT} \int_0^{\infty} dt \langle A(0) B(t) \rangle \sin \omega t$$

$$or \quad \chi'_{BA}(\omega) = -\frac{\omega}{kT} \int_0^{\infty} dt \langle A(0) B(t) \rangle \sin \omega t \tag{18.15}$$

$$and \ldots \chi''_{BA}(\omega) = \frac{\omega}{kT} \int_0^{\infty} dt \langle A(0) B(t) \rangle \cos \omega t$$

  - Recall that the rate of dissipation is given by

$$\bar{D}_{\omega} = \frac{\omega}{2} |F_{\omega}|^2 \chi''_{AA}(\omega) \tag{18.16}$$

so (18.16) gives a relationship between the rate of dissipation and the fluctuations of the system, which is an example of the fluctuation-dissipation theorem…

$$\bar{D}_\omega = \frac{\omega}{2}|F_\omega|^2 \chi''_{AA}(\omega) = \frac{\omega^2}{2}\frac{|F_\omega|^2}{kT}\int_0^\infty dt \langle A(0)A(t)\rangle \cos\omega t$$
$$\text{or } \chi''_{AA}(\omega) = \frac{\omega}{kT}\int_0^\infty dt \langle A(0)A(t)\rangle \cos\omega t \qquad (18.17)$$

(18.17) means that there is a direct relationship between the fluctuations of the system, embodied by $\int_0^\infty dt \langle A(0)A(t)\rangle \cos\omega t$, and the dissipation of the system, embodied by $\chi''_{AA}(\omega)$.

C. Kramer-Kronig Relations

- χ'_{BA} and χ''_{BA} quantify the absorption and dispersion, respectively of energy from an applied field F(t). These two components of the complex susceptibility are directly related as a result of the causal nature of the linear response function $\phi_{BA}(t) = \langle\{B(t), A(0)\}\rangle$. From now on we will drop the BA subscript.
- Derivation of the Kramer-Kronig relations is left as an exercise.
- The in-phase response $\chi'(\omega)$ is related to the out-of-phase response $\chi''(\omega)$ by:

$$\chi'(\omega) = -\frac{2}{\pi}\int_0^{+\infty} \frac{y\chi''(y)}{\omega^2 - y^2} dy \qquad (18.18)$$

- The inverse relationship is:

$$\chi''(\omega) = \frac{2\omega}{\pi}\int_0^{+\infty} \frac{\chi'(y)}{\omega^2 - y^2} dy \qquad (18.19)$$

- Equations (18.18) and (18.19) are called Kramer-Kronig relations. In mathematics they are called a Hilbert transform pair. The real and imaginary components of the complex Fourier transform of a causal function are related by a Hilbert transform.
- The KK relations will be derived in the next lecture and applications will be given,.