University of Washington
Department of Chemistry
Chemistry 553
Spring Quarter 2010

Lecture 17: Linear Response Theory: Complex Susceptibility
05/04/11
Text Reading: Ch 21

A. The Complex Susceptibility

- In the last lecture we found that the linear response to a force F(t) is given by

$$\Delta B(t) = \int_{-\infty}^{t} dt' F(t')\phi_{BA}(t-t') \tag{17.1}$$

where the after effect or linear response function is given by

$$\phi_{BA}(t) = \int dX\ f_0 \{B(t), A(0)\} = \langle \{B(t), A(0)\} \rangle \tag{17.2}$$

- The after-effect or linear response function $\phi_{BA}(t-t')$ has a property called causality. If t' is the time of application of the perturbation and t is the time of response, $\phi_{BA}(t-t') = 0$ if t<t'. That is, the effect cannot precede the cause. Causal functions have important properties called Kramer-Kronig relations, discussed below.
- Assume the applied force has the form

$$F(t) = F_\omega \cos\omega t = F_\omega \operatorname{Re}\left(e^{i\omega t}\right) \tag{17.3}$$

then (17.1) assumes the form…

$$\Delta B(t) = \int_{-\infty}^{t} dt' F(t')\phi_{BA}(t-t') = F_\omega \operatorname{Re}\left[\int_{-\infty}^{t} dt' e^{i\omega t'}\phi_{BA}(t-t')\right] \tag{17.4}$$

- Now we apply the change of variable $\tau = t - t'$ and (17.4) becomes

$$\Delta B(t) = F_\omega \operatorname{Re}\left[\int_{-\infty}^{t} dt' e^{i\omega t'}\phi_{BA}(t-t')\right] = F_\omega \operatorname{Re}\left[e^{i\omega t}\int_{0}^{\infty} d\tau e^{-i\omega\tau}\phi_{BA}(\tau)\right] \tag{17.5}$$

- Finally (17.5) can be reduced to

$$\Delta B(t) = F_\omega \operatorname{Re}\left[e^{i\omega t}\int_{0}^{\infty} d\tau e^{-i\omega\tau}\phi_{BA}(\tau)\right] = F_\omega \operatorname{Re}\left[e^{i\omega t}\chi_{BA}(\omega)\right] \tag{17.6}$$

$where\ldots \chi_{BA}(\omega) = \int_{0}^{\infty} d\tau e^{-i\omega\tau}\phi_{BA}(\tau)$ is called the complex susceptibility.

- We identify two components of the susceptibility…

$$\chi_{BA}(\omega) = \chi'_{BA}(\omega) - i\chi''_{BA}(\omega)$$

$$where\ldots \chi'_{BA}(\omega) = \int_0^\infty d\tau\, \phi_{BA}(\tau)\cos\omega\tau \;\; and \;\; \chi''_{BA}(\omega) = \int_0^\infty d\tau\, \phi_{BA}(\tau)\sin\omega\tau \quad (17.7)$$

so that

$$\Delta B(t) = F_\omega\left[\chi'_{BA}(\omega)\cos\omega\tau + \chi''_{BA}(\omega)\sin\omega\tau\right] \quad (17.8)$$

- The term $\chi'_{BA}(\omega)$ is called the in-phase response because it is in phase with the applied force. The term $\chi''_{BA}(\omega)$ is the out-of-phase response.

B. Absorption/Dissipation

The physical meaning of the two components of the complex susceptibility χ will now be discussed. The potential (free) energy of the system in the field of the applied force at time t for A=B and

- The reversible work performed over one cycle at angular frequency ω is

$$\begin{aligned}
\bar{U}_\omega &= \frac{1}{T}\int_0^T ds F(s)\Delta B(s) = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} ds F(s)\Delta B(s) \\
&= \frac{\omega}{2\pi}F_\omega^2\int_0^{2\pi/\omega} ds\cdot\cos\omega s\cdot\left[\chi'_{BA}(\omega)\cos\omega s + \chi''_{BA}(\omega)\sin\omega s\right] \\
&= \frac{\omega}{2\pi}F_\omega^2\int_0^{2\pi/\omega} ds\cdot\left[\chi'_{BA}(\omega)\cos^2\omega s + \chi''_{BA}(\omega)\cos\omega s\sin\omega s\right] \\
&= \frac{\omega}{2\pi}F_\omega^2\frac{1}{\omega}\left[\chi'_{BA}(\omega)\frac{\omega s}{2}\Bigg|_0^{2\pi/\omega} + \chi''_{BA}(\omega)\frac{\sin^2\omega s}{2\omega}\Bigg|_0^{2\pi/\omega}\right] = \frac{|F_\omega|^2}{2}\cdot\chi'_{BA}(\omega)
\end{aligned} \quad (17.9)$$

- If the perturbation to the system is -F(t)ΔB(t)the average rate of energy dissipation over one cycle is –dF/dtΔB(t)

$$\begin{aligned}
\bar{D}_\omega &= -\frac{\omega}{2\pi}\int_0^{2\pi/\omega} ds\,\Delta B(s)\left(\frac{dF}{ds}\right) \\
&= \frac{\omega}{2\pi}\int_0^{2\pi/\omega} ds\,F(s)\left(\frac{d\Delta B}{ds}\right) = \frac{\omega}{2}|F_\omega|^2\,\chi''_{BA}(\omega)
\end{aligned} \quad (17.10)$$

- The second line is obtained by integrating the first line by parts and neglecting the boundary conditions. In the second line in (17.10) the integrant is clearly the rate of work done on the system per unit time and thus is the energy absorbed by the system from the field per unit time..