University of Washington
Department of Chemistry
Chemistry 553
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Lecture 22: Quantum Form for the Fluctuation-Dissipation Theorem
05/16/11
McQuarrie: Ch. 21-8
R. Kubo "The Fluctuation-Dissipation Theorem" *Rep. Prog. Phys.* **29**, 255 1966.
R. Kubo, Statistical Mechanical Theory of Irreversible Processes I. *J. Phys. Soc. Jpn.* **12(6)**, 570 1957.

A. Kubo's Theorem: Quantum Form

- In the last lecture we derived the expression for the quantum mechanical linear response function:

$$\phi_{BA}(t) = \frac{i}{\hbar} Tr\left(Be^{-L_0 t}\left[A(0),\rho_0\right]\right) = \frac{i}{\hbar} Tr\left(e^{L_0 t} B\left[A(0),\rho_0\right]\right) = \frac{i}{\hbar} Tr\left(B(t)\left[A(0),\rho_0\right]\right) \quad (22.1)$$

- Expand the trace in an eigenbasis of H_0:

$$\begin{aligned}\phi_{BA}(t) &= -\frac{1}{i\hbar} Tr\left\{Be^{-L_0 t}\left[A(0),\rho_0\right]\right\} = -\frac{1}{i\hbar Q} Tr\left\{Be^{-L_0 t}\left[A(0),e^{-\beta H_0}\right]\right\} \\ &= -\frac{1}{i\hbar Q} Tr\left\{e^{L_0 t} B\left[A(0),e^{-\beta H_0}\right]\right\} = -\frac{1}{i\hbar Q} Tr\left\{e^{iH_0 t/\hbar} B(0) e^{-iH_0 t/\hbar}\left[A(0),e^{-\beta H_0}\right]\right\} \\ &= -\frac{1}{i\hbar Q} Tr\left\{e^{iH_0 t/\hbar} B(0) e^{-iH_0 t/\hbar} A e^{-\beta H_0} - e^{iH_0 t/\hbar} B(0) e^{-iH_0 t/\hbar} e^{-\beta H_0} A\right\} \\ &= -\frac{1}{i\hbar Q}\sum_{m,n}\left\{e^{i\omega_n t} B_{nm} e^{-i\omega_m t} A_{mn} e^{-\beta\hbar\omega_n} - e^{i\omega_n t} B_{nm} e^{-i\omega_m t} e^{-\beta\hbar\omega_m} A_{mn}\right\}\end{aligned} \quad (22.2)$$

- (22.2) can be re-arranged to yield

$$\begin{aligned}\phi_{BA}(t) &= -\frac{1}{i\hbar Q}\sum_{m,n}\left\{e^{-it(\omega_m-\omega_n)} B_{nm} A_{mn} e^{-\beta\hbar\omega_n} - e^{-it(\omega_m-\omega_n)} B_{nm} e^{-\beta\hbar\omega_m} A_{mn}\right\} \\ &= -\frac{1}{i\hbar Q}\sum_{m,n} e^{-it(\omega_m-\omega_n)} B_{nm} A_{mn}\left\{e^{-\beta\hbar\omega_n} e^{-\beta\hbar\omega_m} e^{\beta\hbar\omega_m} - e^{-\beta\hbar\omega_m}\right\} \\ &= \frac{1}{i\hbar Q}\sum_{m,n} e^{-\beta\hbar\omega_m}\left(1-e^{\beta\hbar\omega_{mn}}\right) e^{-i\omega_{mn} t} A_{mn} B_{nm}\end{aligned} \quad (22.3)$$

where $\omega_{mn} = \omega_m - \omega_n$

- Now we consider the Fourier transform of the response function…

$$\chi_{BA}(\omega)=\int_0^{+\infty} dte^{-i\omega t}\phi_{BA}(t)$$

$$\begin{aligned}\therefore \chi_{BA}(\omega) &= \frac{1}{i\hbar Q}\int_0^{+\infty} dte^{-i\omega t}\sum_{m,n} e^{-\beta\hbar\omega_m}\left(1-e^{\beta\hbar\omega_{mn}}\right)e^{-i\omega_{mn}t}A_{mn}B_{nm} \\ &= \frac{1}{i\hbar Q}\int_{-\infty}^{+\infty} dt\sum_{m,n} e^{-\beta\hbar\omega_m}\left(1-e^{\beta\hbar\omega_{mn}}\right)e^{-i(\omega-\omega_{nm})t}A_{mn}B_{nm} \\ &= \frac{\pi}{i\hbar Q}\left(1-e^{-\beta\hbar\omega}\right)\sum_{m,n} e^{-\beta\hbar\omega_m}A_{mn}B_{nm}\delta(\omega-\omega_{nm})\end{aligned} \tag{22.4}$$

Where the last line follows because the integral definition of the delta function $\delta(\omega-\omega_{nm})=\frac{1}{2\pi}\int_{-\infty}^{+\infty} dte^{-i(\omega-\omega_{nm})t}$

- Now we consider the quantum mechanical correlation function…

$$g_{BA}(t)=Tr\left(\rho_0\left(\frac{B(t)A(0)+A(0)B(t)}{2}\right)\right) \tag{22.5}$$

- We similarly consider the Fourier transform of (22.5)…

$$\tilde{G}_{BA}(\omega)=\int_{-\infty}^{+\infty} dte^{-i\omega t}g_{BA}(t) \tag{22.6}$$

- Combining (22.5) and (22.6), and proceeding analogously as in (22.2)-(22.4) we obtain

$$\tilde{G}_{BA}(\omega)=\frac{\pi\left(1+e^{-\beta\hbar\omega}\right)}{Q}\sum_{m,n} e^{-\beta\hbar\omega_m}\delta(\omega-\omega_{nm})A_{mn}B_{nm} \tag{22.7}$$

- Combining (22.4) and (22.7) we get

$$\chi_{BA}(\omega)=\frac{1}{i\hbar}\frac{\left(1-e^{-\beta\hbar\omega}\right)}{\left(1+e^{-\beta\hbar\omega}\right)}\tilde{G}_{BA}(\omega)=\frac{1}{i\hbar}\tilde{G}_{BA}(\omega)\tanh\left(\frac{\hbar\omega}{2kT}\right) \tag{22.8}$$

where we have used the definition $\tanh(x)=\frac{e^x-e^{-x}}{e^x+e^{-x}}$

Equation (22.8) is Kubo's theorem. It shows that the Fourier transform of the response function is related by a factor of $\tanh\left(\frac{\hbar\omega}{2kT}\right)$ to the Fourier transform of the correlation function.

- Combine (22.5) and (22.8)

$$\chi_{BA}(\omega) = \chi'_{BA}(\omega) - i\chi''_{BA}(\omega) = -\frac{i}{\hbar}\tanh\left(\frac{\hbar\omega}{2kT}\right)\int_{-\infty}^{+\infty} dt\, g_{BA}(t)\left(\cos\omega t - i\sin\omega t\right)$$

$$\therefore \chi''_{BA}(\omega) = \frac{1}{\hbar}\tanh\left(\frac{\hbar\omega}{2kT}\right)\int_{-\infty}^{+\infty} dt g_{BA}(t)\cos\omega t \qquad (22.9)$$

- Equation (22.9) is the quantum mechanical fluctuation-dissipation theorem. We can recover the classical limit by evaluating (22.9) at infinite temperature. Using the fact that $\lim_{T\to\infty}\tanh(x) = x$

$$\lim_{T\to\infty}\chi''_{BA}(\omega) = \frac{1}{\hbar}\left(\frac{\hbar\omega}{2kT}\right)\int_{-\infty}^{+\infty} dt g_{BA}(t)\cos\omega t = \frac{\omega}{kT}\int_{0}^{+\infty} dt g_{BA}(t)\cos\omega t \qquad (22.10)$$

which is identical to the classical fluctuation-dissipation theorem obtained earlier…