**University of Washington**
**Department of Chemistry**
**Chemistry 553**
**Spring Quarter 2011**

Lecture 20: Kramer-Kronig Relations
Text Reading: Ch 21,22

## A. Kramer-Kronig Relations

- In the last lecture we found that if a causal function is Fourier transformed, the real and imaginary parts of the Fourier transform are related. In other words…if

$$F(\omega) = F'(\omega) - iF''(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt \qquad (20.1)$$

where f(t) is causal then

$$F'(\omega) = -\frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{F''(y)}{(\omega - y)} dy \qquad (20.2)$$

- In physics Equation (20.2) is called a Kramer-Kronig Relation. Because the after-effect function is causal, equation (20.2) applies to the components of the complex susceptibility. When applied to the complex susceptibility it has the form

$$\chi'(\omega) = -\frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\chi''(y)}{(\omega - y)} dy \qquad (20.3)$$

- Because $\chi'(\omega)$ is an even function we can say

$$\chi'(\omega) = \chi'(-\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\chi''(y)}{(\omega + y)} dy$$

$$\therefore 2\chi'(\omega) = \chi'(\omega) + \chi'(-\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \chi''(y) \left[ \frac{1}{(\omega + y)} - \frac{1}{(\omega - y)} \right] dy \qquad (20.4)$$

$$so\ \chi'(\omega) = -\frac{2}{\pi} \int_{0}^{+\infty} \frac{y\chi''(y)}{(\omega^2 - y^2)} dy = \frac{2}{\pi} \int_{0}^{+\infty} \frac{y\chi''(y)}{(y^2 - \omega^2)} dy$$

- It is also possible to show that

$$f(t) = f_e(t) + f_o(t) = f_e(t) + f_e(t)\,\mathrm{sgn}(t) \qquad (20.5)$$

and following the same procedure as outlined in the last lecture we obtain:

$$\chi''(\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\chi'(y)}{\omega - y} dy = \frac{2\omega}{\pi} \int_{0}^{+\infty} \frac{\chi'(y)}{\omega^2 - y^2} dy = -\frac{2\omega}{\pi} \int_{0}^{+\infty} \frac{\chi'(y)}{y^2 - \omega^2} dy \qquad (20.6)$$

- In mathematics Equations (20.3) and (20.6) are called 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.
- We conclude that as a consequence of the causal nature of the after-effect function $\phi_{BA}(\tau)$, the real and imaginary components of its Fourier transform $\chi'(\omega)$ and $\chi''(\omega)$ are not independent. Conversely, if the real and imaginary components of the Fourier transform of a function are related by a Hilbert transform, the function must be causal. The KK relations are therefore a statement of causality in the frequency domain.
- There are alternative versions of the KK relations in the literature. Sometimes one sees:

$$\begin{aligned} \chi'(\omega) &= \frac{2}{\pi} \wp \int_0^{+\infty} \frac{y\chi''(y)}{y^2-\omega^2} dy \\ \chi''(\omega) &= -\frac{2\omega}{\pi} \wp \int_0^{+\infty} \frac{\chi'(y)}{y^2-\omega^2} dy \end{aligned} \tag{20.7}$$

- The script P "$\wp$" means Cauchy principal value of the integral. Notice that when you do the integrals in (20.7) you will encounter singularities at $y = \pm\omega$. Integration in the complex can be used to avoid these problems and the part of the integral that excludes these singularities is the called the Cauchy principal value. You often see this notation when the KK relations are proven by performing a complex line integral using the Cauchy Integral Theorem. The proof is elegant but little physical insight is obtained.
- Finally, one often sees the KK relations in the form:

$$\begin{aligned} \chi'(\omega) &= \chi_\infty + \frac{2}{\pi} \wp \int_0^{+\infty} \frac{y\chi''(y)}{y^2-\omega^2} dy \\ \chi''(\omega) &= -\frac{2\omega}{\pi} \wp \int_0^{+\infty} \frac{\chi'(y)-\chi_\infty}{y^2-\omega^2} dy \end{aligned} \tag{20.8}$$

- The form of the KK relations in equations (20.7) assumes that at infinite frequency the imaginary part of the susceptibility $\chi''(\omega)$ goes to zero. This can be justified on physical grounds because otherwise the system would absorb energy to an infinite extent…the system would never "saturate". But the real part of the susceptibility does not necessarily vanish, and its value at infinite frequency is $\chi_\infty$.