University of Washington
Department of Chemistry
Chemistry 553
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Lecture 7: The Wiener-Khinchine Theorem
4/11/11
Background Reading: McQ 22.2

A. Time and Ensemble Averages

- Assume some property of a system is described by a random variable x(t). by random variable we mean that the value of this property at any time can only be assessed statistically.
- Assume the underlying process that makes x(t) vary randomly is stationary. Stationary means that the probability distributions that we use to calculate averages of x(t) do not vary with a shift in time coordinate.
- A consequence of the stationary nature of a random process is that if we observe x(t) over a long period T, which exceeds any periodicities in the in the process, observing x(t) for a large number N of such periods T is equivalent to observing N arbitrarily chosen systems from an ensemble of similarly prepared systems. This is called the Ergodic hypothesis.
- Consider the average of a property x observed over a peiod of time T:

$$\overline{x(t)} = \underset{T\to\infty}{Lim}\frac{1}{T}\int_{-T/2}^{+T/2} x(t)dt \tag{7.1.1}$$

- We can also define the ensemble average as

$$\langle x(t)\rangle = \int_{-\infty}^{+\infty} xf(x)\,dx = \int_{-\infty}^{+\infty} xW_1(x)\,dx \tag{7.1.2}$$

- In (7.2) W_1 is the probability of a value occurring between x and x+dx. W_1 is independent of time if the process is stationary.
- According to the ergodic hypothesis $\langle x\rangle = \overline{x}$
- We can similarly define a correlation function for a stationary random process:

$$C(\tau) = \underset{T\to\infty}{Lim}\frac{1}{T}\int_{-T/2}^{+T/2} x(t)x(t+\tau)dt \tag{7.1.3}$$

- We have heretofore treated the correlation function as an ensemble average

$$K(\tau) = \langle x(t)x(t+\tau)\rangle = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} x_1x_2W_2(x_2,\tau;x_1)\,dx_1dx_2 \tag{7.1.4}$$

  where $W_2(x_2,\tau;x_1)$ is the joint probability, i.e. the probability that a value of x_1 is initially observed and at a time τ later a value of x_2 is observed. Also according to the ergodic hypothesis C(t)=K(t).

B. Wiener-Khinchin (W-K) Theorem

- Consider the average and correlation function for a random stationary process:

$$\overline{y(t)} = \langle y(t)\rangle = \underset{T\to\infty}{Lim}\frac{1}{T}\int_{-T/2}^{+T/2} y(t)dt \text{ and } C(\tau) = \underset{T\to\infty}{Lim}\frac{1}{T}\int_{-T/2}^{+T/2} y(t)\,y(t+\tau)dt \qquad (7.1.5)$$

- Define the Fourier transform of y(t):

$$\tilde{Y}(\omega) = \int_{-\infty}^{+\infty} y(t)e^{i\omega t}dt \qquad (7.1.6)$$

where also

$$y(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\tilde{Y}(\omega)e^{-i\omega t}d\omega \qquad (7.1.7)$$

- Substitute (7.1.7) into the correlation function expression

$$\begin{aligned}
C(\tau) &= \underset{T\to\infty}{Lim}\frac{1}{T}\int_{-T/2}^{+T/2} y(t)\,y(t+\tau)dt = \underset{T\to\infty}{Lim}\frac{1}{T}\int_{-T/2}^{+T/2}\left[\frac{1}{2\pi}\int_{-\infty}^{+\infty}\tilde{Y}(\omega_1)e^{-i\omega_1 t}d\omega_1\right]\left[\frac{1}{2\pi}\int_{-\infty}^{+\infty}\tilde{Y}(\omega_2)e^{-i\omega_2(t+\tau)}d\omega_2\right]dt \\
&= \underset{T\to\infty}{Lim}\frac{1}{T}\left[\frac{1}{2\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\tilde{Y}(\omega_1)\tilde{Y}(\omega_2)e^{-i\omega_2\tau}\left[\frac{1}{2\pi}\int_{-T/2}^{+T/2}e^{-i(\omega_1+\omega_2)t}dt\right]d\omega_2 d\omega_1\right] \\
&= \underset{T\to\infty}{Lim}\frac{1}{T}\left[\frac{1}{2\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\tilde{Y}(\omega_1)\tilde{Y}(\omega_2)e^{-i\omega_2\tau}\delta(\omega_1+\omega_2)\,d\omega_2 d\omega_1\right] \\
&= \frac{1}{2\pi}\int_{-\infty}^{+\infty}\left[\underset{T\to\infty}{Lim}\frac{1}{T}\tilde{Y}(\omega_1)\tilde{Y}(-\omega_1)\right]e^{-i\omega_1\tau}d\omega_1 = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\left[\underset{T\to\infty}{Lim}\frac{1}{T}\tilde{Y}(\omega_1)\tilde{Y}^*(\omega_1)\right]e^{-i\omega_1\tau}d\omega_1 \\
&= \frac{1}{2\pi}\int_{-\infty}^{+\infty}S(\omega)e^{-i\omega\tau}d\omega
\end{aligned}$$

(7.1.8)

- The quantity

$$S(\omega) = \underset{T\to\infty}{Lim}\frac{1}{T}\tilde{Y}(\omega)\tilde{Y}^*(\omega) = \underset{T\to\infty}{Lim}\frac{1}{T}\left|\tilde{Y}(\omega)\right|^2 \qquad (7.1.9)$$

is called the spectral density. It can be shown that the spectral density is an even function so the Fouier transform expression is finally

$$\begin{aligned}
C(\tau) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty}S(\omega)e^{-i\omega\tau}d\omega = \frac{1}{2\pi}\int_{-\infty}^{+\infty}S(\omega)\cos\omega\tau d\omega = \\
\therefore S(\omega) &= 2\int_{0}^{+\infty}C(\tau)\cos\omega\tau d\tau
\end{aligned} \qquad (7.1.10)$$

C. Solution of Free Diffusion Langevin Equation Using the W-K Theorem

- Recall the Langevin Equation for free diffusion:

$$\frac{dv}{dt} + \frac{v}{\tau} = A(t) \qquad (7.1.11)$$

- Define the Fourier transform of the velocity:

$$\tilde{V}(\omega) = \int_{-\infty}^{+\infty} v(t) e^{i\omega t} dt \tag{7.1.12}$$

- Fourier transform both sides of (7.1.11)

$$\begin{aligned} i\omega\tilde{V}(\omega) + \frac{\tilde{V}(\omega)}{\tau} &= \int_{-\infty}^{+\infty} A(t) e^{i\omega t} dt = \tilde{A}(\omega) \\ \therefore \tilde{V}(\omega) &= \frac{\tilde{A}(\omega)}{i\omega + \frac{1}{\tau}} = \tilde{\chi}(\omega)\tilde{A}(\omega) \end{aligned} \tag{7.1.13}$$

where $\tilde{\chi}(\omega)$ is called the response function.

- Now by definition

$$\Phi_v(\omega) = \lim_{T\to\infty} \frac{1}{T}\left|\tilde{V}(\omega)\right|^2 = \left|\tilde{\chi}(\omega)\right|^2 \lim_{T\to\infty}\frac{1}{T}\left|\tilde{A}(\omega)\right|^2 = \frac{1}{\omega^2+\tau^{-2}}\Phi_A(\omega) \tag{7.1.14}$$

- Now $\Phi_A(\omega)$ is the Fourier transform of the correlation function of the fluctuating force…

$$\Phi_A(\omega) = \int_{-\infty}^{+\infty} K_A(s) e^{i\omega s} ds = \alpha \int_{-\infty}^{+\infty} \delta(s) e^{i\omega s} ds = \alpha = \frac{6k_BT}{\tau M} \tag{7.1.15}$$

- We now put the result from (7.1.15) into (7.1.14):

$$\Phi_v(\omega) = \frac{1}{\omega^2+\tau^{-2}}\Phi_A(\omega) = \frac{6k_BT}{\tau M}\frac{1}{\omega^2+\tau^{-2}} \tag{7.1.16}$$

- Now use the result from (7.1.16) to determine the velocity autocorrelation function:

$$\begin{aligned} C_v(s) = K_v(s) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty}\Phi_v(\omega)e^{-i\omega s}d\omega = \frac{1}{2\pi}\frac{6k_BT}{\tau M}\int_{-\infty}^{+\infty}\frac{e^{-i\omega s}}{\omega^2+\tau^{-2}}d\omega \\ &= \frac{1}{\pi}\frac{6k_BT}{\tau M}\int_{0}^{+\infty}\frac{\cos\omega s}{\omega^2+\tau^{-2}}d\omega = \frac{1}{\pi}\frac{6k_BT}{M}\frac{\pi}{2}e^{-|s|/\tau} = \frac{3k_BT}{M}e^{-|s|/\tau} \end{aligned} \tag{7.1.17}$$