Lecture 6: Langevin Theory: The Velocity Autocorrelation Function
10/13/04

A. Limit of Delta-Function Correlated Processes.
   o We can further reduce (3.20) by assuming a specific form for \( K \). Let us assume that \( K \) falls off very rapidly as \( s \) increases. Another way of saying this is that the random force at \( t_1 \) is uncorrelated with its value at a time \( t_2 \) unless the two times are close together. Let us model this behavior with the function

\[
K(u_1, u_2) = \alpha \delta(u_1 - u_2)
\]

where \( \delta(u_1 - u_2) \) is the delta function. The property follows if we assume a Markovian Process. We can use (4.1) to evaluate (3.20)...

\[
\left\langle v^2(t) \right\rangle = e^{-2t/\tau} \left\{ v^2(0) + \int_0^t \int_0^t du_1 du_2 e^{(u_1+u_2)/\tau} K(u_1, u_2) \right\}
\]

\[
= e^{-2t/\tau} \left\{ v^2(0) + \alpha \int_0^t du_1 du_2 e^{(u_1+u_2)/\tau} \delta(u_1 - u_2) \right\}
\]

\[
= e^{-2t/\tau} \left\{ v^2(0) + \alpha \int_0^t e^{2u_1/\tau} \right\}
\]

\[
= e^{-2t/\tau} \left\{ v^2(0) + \frac{\alpha \tau}{2} \left( e^{2t/\tau} - 1 \right) \right\} = e^{-2t/\tau} v^2(0) + \frac{\alpha \tau}{2} \left( 1 - e^{-2t/\tau} \right)
\]

• It remains to evaluate the parameter \( \alpha \). We can do this by requiring that (6.2) approach the equipartition value for large \( t \)…i.e.

\[
\left\langle v^2(t \to \infty) \right\rangle = \frac{3kT}{M} = \frac{\alpha \tau}{2} \Rightarrow \alpha = \frac{6kT}{\tau M}
\]

• Therefore

\[
\left\langle v^2(t) \right\rangle = e^{-2t/\tau} v^2(0) + \frac{3kT}{M} \left( 1 - e^{-2t/\tau} \right)
\]

• From (5.10) and (6.4) we can obtain the equation for the mean squared displacement of a B-particle...

\[
\frac{d^2}{dt^2} \left\langle r^2 \right\rangle + \frac{1}{\tau} \frac{d}{dt} \left\langle r^2 \right\rangle = 2 \left\langle v^2 \right\rangle = 2 \left\{ e^{-2t/\tau} v^2(0) + \frac{3kT}{M} \left( 1 - e^{-2t/\tau} \right) \right\}
\]

which has the solution...

\[
\left\langle r^2 \right\rangle = v^2(0) \tau^2 \left( 1 - e^{-t/\tau} \right)^2 - \frac{3kT}{M} \tau^2 \left( 1 - e^{-t/\tau} \right) \left( 3 - e^{-t/\tau} \right) + \frac{6kT \tau}{M} t
\]

Homework 3: Solve (6.5) and show the solution is (6.6)
• Note again for
\[ t \ll \tau \ldots \langle r^2 \rangle \approx v^2(0)t^2 \]
\[ t \gg \tau \ldots \langle r^2 \rangle \approx (6BkT)t = \left(\frac{6kT}{f}\right)t = 6Dt \]  \hspace{1cm} (6.7)

• These limiting values clearly indicate what we have already established about the Langevin theory. For times short compared to the relaxation time, (3.12) reduces to a reversible, deterministic expression. However, for times long compared to the relaxation time, the displacement is that expected for an irreversible diffusive motion.

B. The Velocity Autocorrelation Function

• Thus far we have only discussed the role of the autocorrelation function for the random force in Brownian motion. An important relationship also exists between the diffusion coefficient \( D \) and an autocorrelation function. A basic definition of \( r(t) \) is

\[ r(t) - r(0) = \int_0^t v(u)du \]  \hspace{1cm} (6.8)

where \( v(u) \) is the velocity at time \( u \). Then we can extend (6.8) to include the mean squared displacement…

\[ \langle r^2 \rangle = \int_0^t \int_0^t dv_1dv_2 \langle v(u_1)v(u_2) \rangle \]  \hspace{1cm} (6.9)

**Homework 3: Derive (6.9)**

where \( \langle v(u_1)v(u_2) \rangle = K_v(u_1,u_2) \) is the velocity autocorrelation function. Note the velocity autocorrelation function has the same properties as the autocorrelation function for the fluctuating force…it is sensitive only to \( u_1-u_2 \) Because the motion is a stationary Markov process. Therefore

\[ K_v(u_1,u_2) = K_v(s) \text{ where } s = u_1 - u_2 \]  \hspace{1cm} (6.10)

Therefore we change variables in (6.9)... \( s = u_1 - u_2 \) and \( S = \frac{1}{2}(u_1 + u_2) \). We note that for \( 0 \leq S \leq t/2 \), \( s \) varies from \(-2S\) to \(+2S\). Also for \( t/2 \leq S \leq t \), \( s \) varies from \( s = -2(t-S) \) to \( 2(t-S) \). Then (6.9) becomes

\[ \langle r^2 \rangle = \int_{t/2}^{t/2} dS \int_{-2S}^{+2S} ds K_v(s) + \int_{t/2}^{+2(t-S)} dS \int_{-2(t-S)}^{+2(t-S)} ds K_v(s) \]  \hspace{1cm} (6.11)

• We have already noted that correlation functions drops off very rapidly once \( s \) becomes large. Therefore we can extend the integration limits for \( K(s) \) to negative and positive infinity and (6.11) becomes…
\[
\langle r^2 \rangle = \int_{-\infty}^{\infty} dS \int_{-\infty}^{\infty} ds K_v(s) + \int_{0}^{t} dt \int_{-\infty}^{\infty} ds K_v(s) \\
= \int_{0}^{t} dt \int_{-\infty}^{\infty} ds K_v(s) = t \int_{-\infty}^{\infty} ds K_v(s) \tag{6.12}
\]

- Therefore there is a relatively simple relationship between the diffusion coefficient and the velocity autocorrelation function. It can be derived in this way...recall
\[
\langle r^2 \rangle = 6Dt \Rightarrow \frac{d}{dt} \langle r^2 \rangle = 6D \tag{6.13}
\]

- But from (6.12) we have that
\[
\frac{d}{dt} \langle r^2 \rangle = \int_{-\infty}^{\infty} ds K_v(s) \tag{6.14}
\]

- Then we combine (6.13) and (6.14) to obtain...
\[
D = \frac{1}{6} \int_{-\infty}^{\infty} ds K_v(s) = \frac{1}{3} \int_{-\infty}^{\infty} ds K_v(s) \tag{6.15}
\]

- (6.15) means that if we graph the velocity autocorrelation function versus s for s>0, the area under the curve equals 3D.

C. The Fluctuation-Dissipation Theorem for Brownian Motion

- Recall the expression for the mean squared velocity of a Brownian particle:
\[
\langle v^2(t) \rangle = e^{-\frac{v}{\tau}} \left\{ v^2(0) + \int_{0}^{t} du_1 du_2 e^{(u_1-u_2)/\tau} K(u_1, u_2) \right\} \tag{6.16}
\]

where the correlation function of the random force is
\[
K(u_1, u_2) = \langle A(u_1) \cdot A(u_2) \rangle = \frac{\langle F(u_1) \cdot F(u_2) \rangle}{M^2} \tag{6.17}
\]

- For a stationary process the correlation function only depends on the time difference \(s = u_1 - u_2\) and so
\[
K(u_1, u_2) = \langle A(u_1) \cdot A(u_1 + s) \rangle = \langle A(0) \cdot A(s) \rangle = K(s) \tag{6.18}
\]

- Therefore (6.16) is rewritten as
\[
\langle v^2(t) \rangle = e^{-\frac{v}{\tau}} v^2(0) + \frac{\tau}{2} \left(1 - e^{-\frac{v}{\tau}}\right) \int_{-\infty}^{\infty} ds K(s) \tag{6.19}
\]

- In the infinite time limit we can invoke the equipartition theorem:
\[
\lim_{t \to \infty} \langle v^2(t) \rangle = \frac{3kT}{M} = \frac{\tau}{2} \int_{-\infty}^{\infty} ds K(s) \tag{6.20}
\]

- We finally obtain
\[
\frac{6kT}{\tau M} = \frac{6fM}{M^2} = \int_{-\infty}^{\infty} ds K(s) \Rightarrow f = \frac{M^2}{6kT} \int_{-\infty}^{\infty} ds K(s) \tag{6.21}
\]
• (6.21) states that the drag force on a Brownian particle, described by the friction coefficient \( f \), is related to the area under the curve of the correlation function of the fluctuating force. This particular form of the fluctuation-dissipation theorem was derived assuming the random force is a stationary process and the friction is Markovian (i.e. no memory).