Lecture 5: Langevin Theory: The Velocity Autocorrelation Function
03/06/07

A. Limit of Delta-Function Correlated Processes.

- We can further reduce (5.20) 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

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

(5.1)

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)...

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

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

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

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

(5.2)

- It remains to evaluate the parameter \( \alpha \). We can do this by requiring that (5.2) approach the equipartition value for large \( t \) ...i.e.

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

(5.3)

- Therefore

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

(5.4)

- From (5.10) and (5.4) we can obtain the equation for the mean squared displacement of a B-particle...

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

(5.5)

which has the solution...

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

(5.6)
• Note again for
\[ t \ll \tau \ldots \left\langle r^2 \right\rangle \approx v^2(0)t^2 \]
\[ t \gg \tau \ldots \left\langle r^2 \right\rangle \approx (6BkT)t = \left( \frac{6kT}{f} \right)t = 6Dt \]  \hfill (5.7)

• 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
\[ r(t) - r(0) = \int_0^t v(u)\,du \] \hfill (5.8)
where \( v(u) \) is the velocity at time \( u \). Then we can extend (5.8) to include the mean squared displacement...
\[ \left\langle r^2 \right\rangle = \int_0^t \int_0^t du_1 du_2 \left\langle v(u_1) \cdot v(u_2) \right\rangle \] \hfill (5.9)
where \( \left\langle v(u_1) \cdot v(u_2) \right\rangle = K_v(u_1, u_2) \) 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
\[ K_v(u_1, u_2) = K_v(s) \text{ where } s = u_1 - u_2 \] \hfill (5.10)

Therefore we change variables in (5.9)... \( s = u_1 - u_2 \) 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 \(-2(t-S)\) to \(+2(t-S)\). Then (5.9) becomes

\[ \left\langle r^2 \right\rangle = \int_0^{t/2} ds \int_{-2S}^{+2S} dS \, K_v(s) + \int_{t/2}^{t} dS \int_{-2(t-S)}^{+2(t-S)} ds \, K_v(s) \] \hfill (5.11)

• 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 (5.11) becomes...
\[ \langle r^2 \rangle = \int_0^{t/2} dS \int ds K_v(s) + \int_0^t dS \int ds K_v(s) \]
\[ = \int_0^t dS \int ds K_v(s) = t \int ds K_v(s) \]  \hspace{1cm} (5.12)

- Therefore there is a relatively simple relationship between the diffusion coefficient and the velocity autocorrelation function. It can be derived in this way...recall

\[ \langle r^2 \rangle = 6Dt \Rightarrow \frac{d}{dt} \langle r^2 \rangle = 6D \]  \hspace{1cm} (5.13)

- But from (5.12) we have that

\[ \frac{d}{dt} \langle r^2 \rangle = \int ds K_v(s) \]  \hspace{1cm} (5.14)

- Then we combine (5.13) and (5.14) to obtain...

\[ D = \frac{1}{6} \int ds K_v(s) = \frac{1}{3} \int_0^\infty ds K_v(s) \]  \hspace{1cm} (5.15)

- (5.15) 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:

\[ \langle v^2(t) \rangle = e^{-2t/\tau} \left\{ v^2(0) + \int_0^t du_1 du_2 e^{\frac{u_1+u_2}{\tau}} K(u_1, u_2) \right\} \]  \hspace{1cm} (5.16)

where the correlation function of the random force is

\[ K(u_1, u_2) = \left\{ A(u_1) \cdot A(u_2) \right\} = \frac{\langle F(u_1) \cdot F(u_2) \rangle}{M^2} \]  \hspace{1cm} (5.17)

- For a stationary process the correlation function only depends on the time difference \( s = u_1 - u_2 \) and so

\[ K(u_1, u_2) = \langle A(u_1) \cdot A(u_1 + s) \rangle = \langle A(0) \cdot A(s) \rangle = K(s) \]  \hspace{1cm} (5.18)

- Therefore (5.16) is rewritten as

\[ \langle v^2(t) \rangle = e^{-2t/\tau} v^2(0) + \frac{\tau}{2} \left( 1 - e^{-2t/\tau} \right) \int_{-\infty}^\infty ds K(s) \]  \hspace{1cm} (5.19)

- In the infinite time limit we can invoke the equipartition theorem:

\[ \lim_{t \to \infty} \langle v^2(t) \rangle = \frac{3kT}{M} = \frac{\tau}{2} \int_{-\infty}^\infty ds K(s) \]  \hspace{1cm} (5.20)

- We finally obtain
\[ \frac{6kT}{\tau M} = \frac{6f kT}{M^2} = \int_{-\infty}^{\infty} ds K(s) \Rightarrow f = \frac{M^2}{6kT} \int_{-\infty}^{\infty} ds K(s) \quad (5.21) \]

- (5.21) 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).