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Department of Chemistry
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Lecture 5: Langevin Theory: Diffusion and the Velocity Autocorrelation Function
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Chandrasekhar: Ch. 2.2

A. Limit of Delta-Function Correlated Processes.

- We can further explore the Langevin equation by assuming a specific form for the autocorrelation function K(s). 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

$$K(u_1,u_2) = K(u_1-u_2) = \alpha\delta(u_1-u_2) \tag{5.1}$$

where $\delta(u_1-u_2)$ is the delta function.

- Property (5.1) follows if we assume a stationary Markovian Process. Stationary means that the process depends only upon the length or duration of the process…$s=u_1-u_2$ in this case.
- Markov refers to the fact that the process has short "memory", i.e. that the current condition of the system depends upon prior events to a very small extent. Formally, for a Markov process composed of discrete jumps, the condition of the system at any instant depends upon prior history only one jump time back. This fact is simulated in (5.1) by a delta function…which de-correlates the system rapidly.
- Given (5.1) the force F(t) is said to be delta-function correlated. The force is also called a "white noise" force because the Fourier transform of a delta function is a constant in frequency space. We can use (4.1) to evaluate $\langle v^2(t)\rangle$

$$\begin{aligned}
\langle v^2(t)\rangle &= e^{-2t/\tau}\left\{v^2(0)+\int_0^t\int_0^t du_1du_2\, e^{(u_1+u_2)/\tau}K(u_1,u_2)\right\}\\
&= e^{-2t/\tau}\left\{v^2(0)+\alpha\int_0^t\int_0^t du_1du_2\, e^{(u_1+u_2)/\tau}\delta(u_1-u_2)\right\}\\
&= e^{-2t/\tau}\left\{v^2(0)+\alpha\int_0^t du_1 e^{2u_1/\tau}\right\}\\
&= e^{-2t/\tau}\left\{v^2(0)+\frac{\alpha\tau}{2}\left(e^{2t/\tau}-1\right)\right\} = e^{-2t/\tau}v^2(0)+\frac{\alpha\tau}{2}\left(1-e^{-2t/\tau}\right)
\end{aligned} \tag{5.2}$$

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

$$\left\langle v^2\left(t\to\infty\right)\right\rangle = \frac{3kT}{M} = \frac{\alpha\tau}{2} \Rightarrow \alpha = \frac{6kT}{\tau M} \tag{5.3}$$

- Therefore

$$\left\langle v^2\left(t\right)\right\rangle = e^{-2t/\tau}v^2\left(0\right) + \frac{3kT}{M}\left(1-e^{-2t/\tau}\right) \tag{5.4}$$

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

$$\frac{d^2}{dt^2}\left\langle r^2\right\rangle + \frac{1}{\tau}\frac{d}{dt}\left\langle r^2\right\rangle = 2\left\langle v^2\right\rangle = 2\left\{e^{-2t/\tau}v^2\left(0\right) + \frac{3kT}{M}\left(1-e^{-2t/\tau}\right)\right\} \tag{5.5}$$

which has the solution…

$$\left\langle r^2\right\rangle = v^2\left(0\right)\tau^2\left(1-e^{-t/\tau}\right)^2 - \frac{3kT}{M}\tau^2\left(1-e^{-t/\tau}\right)\left(3-e^{-t/\tau}\right) + \frac{6kT\tau}{M}t \tag{5.6}$$

- Note again for

$$\begin{aligned} &t \ll \tau \ldots \left\langle r^2\right\rangle \approx v^2\left(0\right)t^2 \\ &t \gg \tau \ldots \left\langle r^2\right\rangle \approx \left(6BkT\right)t = \left(\frac{6kT}{f}\right)t = 6Dt \end{aligned} \tag{5.7}$$

- 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

$$r\left(t\right) - r\left(0\right) = \int_0^t v\left(u\right)du \tag{5.8}$$

where v(u) is the velocity at time u. Then we can extend (5.8) to include the mean squared displacement…

$$\left\langle r^2\right\rangle = \int_0^t\int_0^t ds_1 ds_2 \left\langle v\left(s_1\right)\cdot v\left(s_2\right)\right\rangle \tag{5.9}$$

where $\left\langle v\left(u_1\right)\cdot v\left(u_2\right)\right\rangle = K_v\left(u_1,u_2\right)$ 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 . Using the expression for the velocity:

$$v(t) = v(0)e^{-t/\tau} + e^{-t/\tau}\int dse^{s/\tau}A(s) \tag{5.10}$$

- Using the same reasoning as before we obtain for the velocity correlation function

$$\langle v(t_1)v(t_2)\rangle = v_0^2 e^{-(t_1+t_2)/\tau} + e^{-(t_1+t_2)/\tau}\int_0^{t_1} ds_1 \int_0^{t_2} ds_2 e^{(s_1+s_2)/\tau}\langle A(s_1)A(s_2)\rangle \tag{5.11}$$

- Assuming again that the fluctuation is a stationary Markov process, we assume the correlation function $\langle A(s_1)A(s_2)\rangle$ is sensitive only to s_1-s_2.

  Assuming again that the langevin force A(t) is delta-function correlated:

$$\langle v(t_1)v(t_2)\rangle = v_0^2 e^{-(t_1+t_2)/\tau} + \alpha e^{-(t_1+t_2)/\tau}\int_0^{t_1} ds_1 \int_0^{t_2} ds_2 e^{(s_1+s_2)/\tau}\delta(s_1 - s_2) \tag{5.12}$$

- Integrate wrt s_2 first. The s_1 integration runs from zero to t_1 or t_2 which ever is less.

$$\langle v(t_1)v(t_2)\rangle = v_0^2 e^{-(t_1+t_2)/\tau} + \alpha e^{-(t_1+t_2)/\tau}\int_0^{t_1} ds_1 e^{2s_1/\tau}$$

$$= v_0^2 e^{-(t_1+t_2)/\tau} + \alpha e^{-(t_1+t_2)/\tau}\int_0^{\min(t_1,t_2)} ds_1 e^{2s_1/\tau} \tag{5.13}$$

$$= v_0^2 e^{-(t_1+t_2)/\tau} + \frac{\alpha\tau}{2}e^{-(t_1+t_2)/\tau}\left(e^{2t/\tau}\Big|_0^{\min(t_1,t_2)}\right) = v_0^2 e^{-(t_1+t_2)/\tau} + \frac{\alpha\tau}{2}\left(e^{-|t_1-t_2|/\tau} - e^{-(t_1+t_2)/\tau}\right)$$

- Assume t_1,t_2>>t. Then only the first term in parentheses survives:

$$\langle v(t_1)v(t_2)\rangle = v_0^2 e^{-(t_1+t_2)/\tau} + \frac{\alpha\tau}{2}\left(e^{-|t_1-t_2|/\tau} - e^{-(t_1+t_2)/\tau}\right) \approx \frac{\alpha\tau}{2}e^{-|t_1-t_2|/\tau}$$

$$or\ldots \tag{5.14}$$

$$\langle v(t_1)v(t_2)\rangle = \langle v(t_1)v(t_1 - s)\rangle = K_v(s) = \frac{\alpha\tau}{2}e^{-|s|/\tau}$$

- Note that we can determine alpha by letting t_1=t_2

$$\langle v^2(t)\rangle = K_v(s=0) = \frac{\alpha\tau}{2} = \frac{3k_BT}{M} \Rightarrow \alpha = \frac{6k_BT}{M\tau}$$

$$K_v(s) = \left(v_0^2 - \frac{3k_BT}{M}\right)e^{-(t_1+t_2)/\tau} + \frac{3k_BT}{M}e^{-|t_1-t_2|/\tau} \tag{5.15}$$

$$\therefore \lim_{t\to\infty} K_v(s) = \frac{3k_BT}{M}e^{-|t_1-t_2|/\tau} = \frac{3k_BT}{M}e^{-|s|/\tau}$$

- To calculate the mean-squared displacement we require a change of variables $S = (s_1 + s_2)/2$ and $s = s_1 - s_2$. Note dSds=ds_1ds_2.

$$\langle r^2\rangle = \int_0^t\int_0^t ds_1 ds_2 K_v(s) \approx \int_0^t dS \int_{-\infty}^{+\infty} ds K_v(s) = \frac{3k_BT}{M}t\int_{-\infty}^{+\infty} e^{-|s|/\tau}ds = \frac{6k_BT}{M}t\int_0^{+\infty} e^{-|s|/\tau}ds$$

$$= \frac{6k_BT\tau}{M}t = 6Bk_BTt = 6Dt \tag{5.16}$$

From (5.16) $$D = \frac{1}{6}\int_{-\infty}^{+\infty} ds\, K_v(s) = \frac{1}{3}\int_{0}^{+\infty} ds\, K_v(s) \qquad (5.17)$$

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

D. The Fluctuation-Dissipation Theorem for Brownian Motion

- Recall the expression for the mean squared velocity of a Brownian particle:

$$\left\langle v^2(t)\right\rangle = e^{-2t/\tau}\left\{ v^2(0) + \int_0^t\int_0^t du_1 du_2\, e^{(u_1+u_2)/\tau} K_A(u_1,u_2)\right\} \qquad (5.18)$$

where the correlation function of the random force is

$$K_A(u_1,u_2) = \left\langle A(u_1)\cdot A(u_2)\right\rangle = \frac{\left\langle F(u_1)\cdot F(u_2)\right\rangle}{M^2} = \frac{K_F(u_1,u_2)}{M^2} \qquad (5.19)$$

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

$$K_A(u_1,u_2) = \left\langle A(u_1)\cdot A(u_1+s)\right\rangle = \left\langle A(0)\cdot A(s)\right\rangle = K_A(s) \qquad (5.20)$$

- Therefore (5.18) is rewritten as

$$\begin{aligned}\left\langle v^2(t)\right\rangle &\approx e^{-2t/\tau}v^2(0) + e^{-2t/\tau}\left\{\int_0^t dSe^{2S/\tau}\int_{-\infty}^{\infty} dsK_A(s)\right\} \\ &= e^{-2t/\tau}v^2(0) + \frac{\tau}{2}\left(1-e^{-2t/\tau}\right)\left\{\int_{-\infty}^{\infty} dsK_A(s)\right\}\end{aligned} \qquad (5.21)$$

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

$$\underset{t\to\infty}{Lim}\left\langle v^2(t)\right\rangle = \frac{3k_BT}{M} \approx \frac{\tau}{2}\left\{\int_{-\infty}^{\infty} dsK_A(s)\right\} \qquad (5.22)$$

- We finally obtain

$$\begin{aligned}\frac{6k_BT}{\tau M} &= \frac{6k_BT}{BM^2} = \int_{-\infty}^{\infty} dsK_A(s) \\ \therefore \zeta &= \frac{1}{B} = \frac{M^2}{6kT}\int_{-\infty}^{\infty} dsK_A(s) = \frac{1}{6kT}\int_{-\infty}^{\infty} dsK_F(s)\end{aligned} \qquad (5.23)$$

- (5.23) 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).