University of Washington
Department of Chemistry
Chemistry 553
Spring Quarter 2010

Lecture 4: Langevin Theory: The Autocorrelation Function of the Fluctuating Force

04/04/11

Reading: McQ Ch 20, Chandrasekhar: Ch. 2.1

A. Langevin Theory

- Einstein's theory of Brownian motion is valid only after a large number of jumps is executed by the B-particle. Langevin theory is valid over a much wider time range.
- The basis for Langevin theory is Newton's equation of motion…*F=ma*. The force acting on the Brownian particle is the result of the drag force and the incessant collisions of solvent particles with the B-particle. Hence…

$$M\frac{dv(t)}{dt} = \Im(t) \tag{4.1}$$

- The force $\Im(t)$ is written as the sum of two parts.

$$\Im(t) = -\frac{v}{B} + F(t) \text{ where } \overline{F(t)} = \langle F(t)\rangle = 0 \tag{4.2}$$

- The term –v/B corresponds to the viscous drag. B is called the mobility and is inversely related to the coefficient of friction ζ.. F(t) is a rapidly fluctuating force that corresponds to the incessant collisions with solvent. We then write the equation of motion…

$$M\frac{dv}{dt} = -\frac{v}{B} + F(t) \tag{4.3}$$

- We now take the ensemble average of (3.3)…

$$M\frac{d\langle v\rangle}{dt} = -\frac{\langle v\rangle}{B} + \langle F(t)\rangle = -\frac{\langle v\rangle}{B} \tag{4.4}$$

the solution of which is

$$\langle v(t)\rangle = v(0)e^{-t/\tau} \text{ where } \tau = MB \tag{4.5}$$

- We note that the "drift" velocity decays at a rate determined by the relaxation time τ. This fact was established in the last lecture.
- Now we consider the instantaneous position of the B-particle…we divide (4.5) by M…

$$\frac{dv}{dt} = -\frac{v}{\tau} + A(t) \text{ where } A(t) = \frac{F(t)}{M}. \tag{4.6}$$

and take the inner product of both sides of (3.6) with r…

$$r\bullet\frac{dv}{dt} = -\frac{r\bullet v}{\tau} + r\bullet A(t) \tag{4.7}$$

- Now we use the relationships

$$r \bullet v = \frac{1}{2}\frac{d}{dt}r^2 \ and \ r \bullet \frac{dv}{dt} = \frac{1}{2}\frac{d^2}{dt^2}r^2 - v^2 \tag{4.8}$$

$$\frac{1}{2}\frac{d^2}{dt^2}r^2 - v^2 + \frac{1}{2\tau}\frac{d}{dt}r^2 = r \bullet A(t) \tag{4.9}$$

- We now take the ensemble average of both sides of (3.9)

$$\begin{aligned}&\frac{1}{2}\frac{d^2}{dt^2}\left\langle r^2\right\rangle - \left\langle v^2\right\rangle + \frac{1}{2\tau}\frac{d}{dt}\left\langle r^2\right\rangle = \left\langle r \bullet A(t)\right\rangle = 0\\ &or\ldots\frac{d^2}{dt^2}\left\langle r^2\right\rangle + \frac{1}{\tau}\frac{d}{dt}\left\langle r^2\right\rangle = 2\left\langle v^2\right\rangle\end{aligned} \tag{4.10}$$

where we have used the fact that $\left\langle r \bullet A(t)\right\rangle = 0$.

- The differential equation (4.10) can be simplified by recalling the equipartition principle for translations in three dimensions…

$$\frac{1}{2}M\left\langle v^2\right\rangle = \frac{3kT}{2} \Rightarrow \left\langle v^2\right\rangle = \frac{3kT}{M} \tag{4.11}$$

which results in the following inhomogeneous differential equation…

$$\frac{d^2}{dt^2}\left\langle r^2\right\rangle + \frac{1}{\tau}\frac{d}{dt}\left\langle r^2\right\rangle = \frac{6kT}{M} \tag{4.12}$$

which has the solution…

$$\left\langle r^2\right\rangle = \frac{6kT\tau^2}{M}\left\{\frac{t}{\tau} - \left(1 - e^{-t/\tau}\right)\right\} \tag{4.13}$$

We consider two limits of this equation

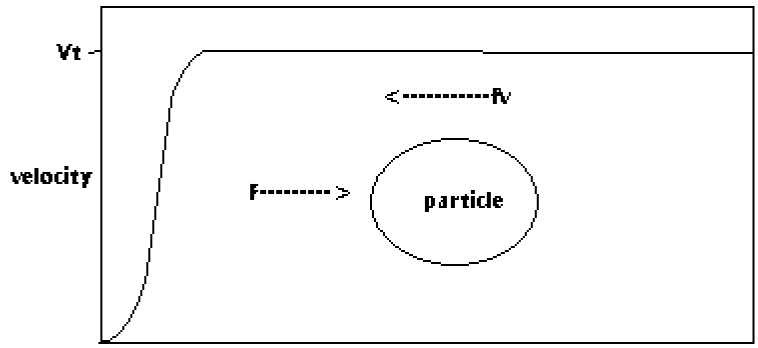
1. t<<τ : $\left\langle r^2\right\rangle \approx \frac{3kT}{M}t^2 = \left\langle v^2\right\rangle t^2$. This means that for times much shorter than the relaxation time of the system (3.13) reverts to a reversible equation of motion r(t)=vt.
2. t>>τ: $\left\langle r^2\right\rangle \approx \frac{6kT\tau}{M}t = \left(6BkT\right)t$. Note that D=BkT, where D is the diffusion coefficient. The mobility B is defined as the terminal velocity per unit force. To understand this imagine a B-particle subjected to an external force. It will initially accelerate but as the applied force is opposed by a drag or frictional force $F_D = -\zeta v = -\frac{v}{B}$, a steady state velocity will be quickly established. The parameter f is the coefficient of friction and B=1/f. At steady state we have (see figure)

$$F + F_D = 0 \ or \ F = -F_D = \zeta v_T \Rightarrow B = \frac{1}{f} = \frac{v_T}{F} \tag{4.14}$$

$$\therefore D = BkT = \frac{kT}{f} \tag{4.15}$$

B. The Auto-correlation Function

- Thus far we have not obtained a relationship for any average B-particle property



associated with the fluctuating force F(t) or A(t)=F(t)/M.

- To find such a relationship we have to consider the average of $v^2(t)$. We begin by obtaining the formal solution of the equation of motion…

$$\frac{dv}{dt} = -\frac{v}{\tau} + A(t) \tag{4.16}$$

- We integrate (4.16) to obtain

$$v(t) = v(0)e^{-t/\tau} + e^{-t/\tau}\int_0^t du\, e^{u/\tau} A(u) \tag{4.17}$$

- Now we square (4.17) to obtain $v^2(t)$...then we take the average…

$$\begin{aligned}\left\langle v^2(t)\right\rangle &= v^2(0)e^{-2t/\tau} + 2e^{-2t/\tau}\left\{v(0)\cdot\int_0^t du\, e^{u/\tau}\left\langle A(u)\right\rangle\right\} \\ &+ e^{-2t/\tau}\int_0^t\int_0^t du_1 du_2\, e^{(u_1+u_2)/\tau}\left\langle A(u_1)\cdot A(u_2)\right\rangle\end{aligned} \tag{4.18}$$

- The second term in (4.18) is zero. Therefore the average squared velocity is

$$\begin{aligned}\left\langle v^2(t)\right\rangle &= v^2(0)e^{-2t/\tau} + e^{-2t/\tau}\int_0^t\int_0^t du_1 du_2\, e^{(u_1+u_2)/\tau}\left\langle A(u_1)\cdot A(u_2)\right\rangle \\ &= e^{-2t/\tau}\left\{v^2(0) + \int_0^t\int_0^t du_1 du_2\, e^{(u_1+u_2)/\tau}\left\langle A(u_1)\cdot A(u_2)\right\rangle\right\} \\ &= e^{-2t/\tau}\left\{v^2(0) + \int_0^t\int_0^t du_1 du_2\, e^{(u_1+u_2)/\tau} K(u_1,u_2)\right\}\end{aligned} \tag{4.19}$$

- The quantity $K(u_1,u_2) = \left\langle A(u_1)\cdot A(u_2)\right\rangle$ is called the autocorrelation function. K has the following properties
  - For a stationary ensemble (i.e. no change in macroscopic behavior in time) K is only dependent on u_1-u_2. That is

$$K\left(u_1, u_2\right) = K\left(u_1, u_1 + s\right) = K\left(s\right) \tag{4.20}$$

- For s=0…K(0)>0.
- For s>0, K(s) cannot exceed K(0). The behavior of K(s) is shown below…

- A sketch of K(s) is given below…