Chapter 20 Brownian Motion

Brownian motion discovered in 1827

Basic Idea:

Split force on the particle into two parts

(a) frictional due to drag

(b) fluctuating force $\vec{A}'(t)$

frictional force given by Stokes law

$$-\gamma'\vec{u} \quad \begin{cases} \vec{u} = \text{velocity} \\ \gamma' = \text{friction const.} = 6\pi a\eta \end{cases}$$

particle radius (a) ↗ ↖ viscosity of medium (η)

$\vec{A}'(t)$ changes rapidly compared to $\vec{u}$

Langevin equation

$$m\frac{d\vec{u}}{dt} = -\gamma'\vec{u} + \vec{A}'(t)$$

$$\frac{d\vec{u}}{dt} = -\zeta\vec{u} + \vec{A}(t)$$

Stochastic diff. eq.

$W\left(u,t:u_0\right)$: Prob. of *u(t)* given $u = u_0$ at $t = 0$

$$W \to \delta\left(u_x - u_{x0}\right)\delta\left(u_y - u_{y0}\right)\delta\left(u_z - u_{z0}\right) \text{ as } t \to 0$$

as $t \to \infty$, the particle will be at equil.

And *W* evolves into a Maxwellian distrib.

$$W = \left(\frac{m}{2\pi kT\left(1-e^{-2\zeta t}\right)}\right)^{3/2} \exp\left[\frac{m\left|\vec{u}-\vec{u}_0 e^{-\zeta t}\right|^2}{2kT\left(1-e^{-2\zeta t}\right)}\right]$$

$$W \to \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mu^2/kT}$$

$$\vec{U} \equiv \vec{u}\left(t\right) - \vec{u}_0 e^{-\zeta t} = e^{-\zeta t}\int_0^t e^{\zeta\zeta}\vec{A}\left(\zeta\right)d\zeta$$

The Langevin eq. is a first-order differential equation for which the formal solution can be written (see derivation below)

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first-order linear diff. eq.

$$\frac{dy}{dt} + p\left(t\right)y = q\left(t\right)$$

$$y = \frac{\int s\left(t\right)q\left(t\right)dt + C}{s\left(t\right)}$$

where

$$s\left(t\right) = e^{\int p\left(t\right)dt}$$

for our case

$$s(t) = e^{\int \zeta dt} = e^{\zeta t}$$

$$u = \frac{\int e^{\zeta t'} A(t') dt' + C}{e^{\zeta t}}$$

$$u - \frac{C}{e^{\zeta t}} = \frac{\int e^{\zeta t'} A(t') dt'}{e^{\zeta t}}$$

$$\boxed{u - Ce^{-\zeta t} = e^{-\zeta t} \int e^{\zeta t'} A(t') dt'}$$

$$t = 0 \quad u \to u_0 \Rightarrow C = u_0$$

$$U = u - u_0 e^{-\zeta t} = e^{-\zeta t} \int_0^t e^{\zeta t'} A(t') dt'$$

At this point, the symbols for vectors has been dropped

square and then ensemble average

now take ensemble average

$$\langle u \rangle = u_0 e^{-\zeta t} \text{ since } \langle A(t) \rangle = 0$$

$$\langle U^2 \rangle = \langle u^2 \rangle - u_0^2 e^{-2\zeta t} = e^{-2\zeta t} \int_0^t \int_0^t e^{\zeta (t' + t'')} \underbrace{\langle A(t') A(t'') \rangle}_{\text{correlation function}} dt' dt''$$

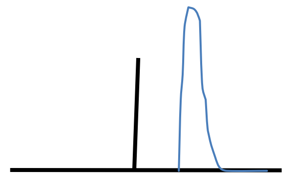
correlation function

assume $\langle A(t')\cdot A(t'')\rangle$

function of $|t'-t''|$ only

and is 0 except when t' close to t''

$$\langle A(t')\cdot A(t'')\rangle = \phi(|t'-t''|)$$



strongly peaked

$$\langle U\rangle^2 = \frac{1}{2}e^{-2\zeta t}\int_0^{2t} e^{\zeta x}dx\int_{-\infty}^{\infty}\phi(y)\,dy$$

$x = t'+t''$

$y = t'-t''$

$\int_{-\infty}^{\infty}\phi(y)\,dy = \tau$ assumed

$$\rightarrow \langle U^2\rangle = \frac{\tau}{2\zeta}\left(1-e^{-2\zeta t}\right)$$

$$\langle U^2\rangle = \frac{3kT}{m}\left(1-e^{-2\zeta t}\right)$$

equipartition holds as $t\rightarrow\infty$

$$\langle u^2\rangle = \frac{3kT}{m}+\left(u_0^2-\frac{3kT}{m}\right)e^{-2\zeta t}$$

$\Rightarrow$ Probability distribution W is Gaussian $\rightarrow$ Maxwellian distribution as $t\rightarrow\infty$

The above focused on the velocity of the particle. Analogous results can be derived for the displacement

$\vec{r}-\vec{r}_o = \int_0^t \vec{u}(t')\,dt$ which allows us to evaluate $\vec{r}-\vec{r}_o$

$$\left\langle \left| r - r_0 \right|^2 \right\rangle = \frac{u_0^2}{\zeta^2}\left(1 - e^{-\zeta t}\right)^2 + \frac{3kT}{m\zeta^2}\left(2\zeta t - 3 + 4e^{-\zeta t} - e^{-2\zeta t}\right)$$

for short time

$$\left\langle \left| r - r_0 \right|^2 \right\rangle \rightarrow \frac{u_0}{\zeta^2}(\zeta t)^2 + \frac{3kT}{m\zeta}\left(2\zeta t - 3 + 4\left(1 - \zeta t\right) - \left(1 - 2\zeta t\right)\right)$$

$$\rightarrow u_0 t^2 + \frac{3kT}{m\zeta}\left[2\zeta t - 4\zeta t + 2\zeta t\right]$$

$$\left\langle \left| r - r_0 \right|^2 \right\rangle = \left| u_0 \right|^2 t^2$$

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if $t >> \xi^{-1}$, mean sq. displ. becomes linear in time

at long time

$$\left\langle \left| r - r_0 \right|^2 \right\rangle = \frac{6kT}{m\zeta} t = 6Dt$$

where D is the diffusion constant $\left(\frac{kT}{m\zeta}\right)$

and

$$W = \frac{1}{\left(4\pi Dt\right)^{3/2}} e^{-\frac{\left|r-r_0\right|^2}{4Dt}}$$

solution to diffusion eq.

$$\frac{\partial W}{\partial t} = D\nabla_r^2 W$$

Diffusion eq.

$$\frac{\partial W}{\partial t} = \zeta\, div_u\left(W\vec{u}\right) + \frac{\zeta kT}{m}\nabla_u^2 W$$

Fokker-Planck eq