Correlation function and diffusion in Langevin Eq.

Correlation Function of the momenta

$$p(t) = e^{-\gamma t} p_0 + \int_0^t dt' \, e^{-\gamma(t-t')} \xi(t')$$

Ornstein Uhlenbeck process where

$$\langle \xi(t) \rangle = 0 \quad \langle \xi(t)\, \xi(t') \rangle = \frac{2m}{\beta} \gamma\, \delta(t-t')$$

$$C(t,t') = \langle p(t)\, p(t') \rangle$$

$$C(t,t') = p_0^2 e^{-\gamma(t+t')} + \frac{m}{\beta}\left[e^{-\gamma|t-t'|} - e^{-\gamma(t+t')} \right]$$

which can be recast as

$$C(t,t') = \left(p_0^2 - \frac{m}{\beta}\right) e^{-\gamma(t+t')} + \frac{m}{\beta} e^{-\gamma|t-t'|}$$

The pre factor of the first term has indeed the meaning of $C(0,0)$

$$\langle p^2(0) \rangle = p_0^2 - \frac{m}{\beta} + \frac{m}{\beta} = p_0^2$$

while averaging only on histories of ξ

$$\langle p(t) \rangle = e^{-\gamma t} p_0 \quad \rightarrow \langle p(0) \rangle^2 = p_0^2$$

if p_0 has no fluctuations i.e. is fixed then $\langle p^2(0) \rangle = \langle p(0) \rangle^2$

if on the other hand we average over initial conditions

$$C(t,t') = \left[\langle p^2(0) \rangle - \frac{m}{\beta} \right] e^{-\gamma(t+t')} + \frac{m}{\beta} e^{-\gamma|t-t'|}$$

Mean Square Displacement & Displacement

$$\langle |X(t)-X(0)|^2\rangle = \frac{1}{m^2}\int_0^t dt' \int_0^t dt'' \, C(t,t')$$

$$\int_0^t dt' \int_0^t dt'' \, e^{-\gamma(t+t')} = \left(\frac{1-e^{-\gamma t}}{\gamma}\right)^2$$

$$\int_0^t dt' \int_0^t dt'' e^{-\gamma|t-t'|} = 2\int_0^t dt' \int_0^{t'} dt'' \, e^{-\gamma(t'-t'')} =$$

$$= 2\int_0^t dt' e^{-\gamma t'} \frac{e^{\gamma t'}-1}{\gamma} = \frac{2}{\gamma} t - \frac{2}{\gamma^2}(1-e^{-\gamma t})$$

$$\langle |X(t)-X(0)|^2\rangle = \frac{1}{m^2}\left[C(0,0)-\frac{m}{\beta}\right]\left(\frac{1-e^{-\gamma t}}{\gamma}\right)^2 +$$

$$+ \frac{2}{m\beta\gamma}\left[t - \frac{(1-e^{-\gamma t})}{\gamma}\right]$$

$\boxed{\text{as } \gamma t \gg 1}$ **Diffusive Regime**

$$\langle |X(t)-X(0)|^2\rangle = \frac{1}{m^2}\left[C(\infty)-\frac{m}{\beta}\right]\frac{1}{\gamma^2} - \frac{2}{m\beta\gamma^2} +$$

$$+ \frac{2}{m\beta\gamma} t$$

the leading dependence in t is linear and give rise to Diffusive behaviour

$$\langle |X(t)-X(0)|^2\rangle \sim 2Dt$$

$$D = \frac{k_B T}{m\gamma}$$

$\boxed{\text{as } \gamma t \ll t}$ **Ballistic Regime**

$$\langle |X(t)-X(0)|^2\rangle = \frac{1}{m^2}\left(C(00)-\frac{m}{\beta}\right)\left(\frac{\gamma t}{\gamma}\right)^2 +$$

$$+\frac{2}{m\beta\gamma}\left[t-\frac{\left(1-1+\gamma t-\frac{\gamma^2 t^2}{2}\right)}{\gamma}\right]$$

$$\langle |X(t)-X(0)|^2\rangle = \frac{1}{m^2}\left(C(00)-\frac{m}{\beta}\right)t^2 +$$

$$+\frac{2}{m\beta\gamma}\left[\frac{\gamma^2 t^2}{2\gamma}\right]$$

$$\langle |X(t)-X(0)|^2\rangle = \frac{1}{m^2}C(0,0)\,t^2$$

this is the ballistic regime independent on the damping γ.

Diffussive regime can be easily obtaind using the overdamped limit of the Langevin equation.

$$P(t) = \frac{1}{\gamma} \xi(t)$$

$$\langle |X(t) - X(0)|^2 \rangle = \frac{1}{m^2\gamma^2} \int_0^t dt' \int_0^t dt'' \langle \xi(t')\xi(t'') \rangle$$

$$\langle |X(t) - X(0)|^2 \rangle = \frac{1}{m^2\gamma^2} \frac{2m\gamma}{\beta} t = \frac{2}{m\gamma\beta} t$$

Ballistic regime can be easily obtained neglecting the damping

$$X(t) = X(0) + \frac{P(0)}{m} t$$

$$\langle |X(t) - X(0)|^2 \rangle = \frac{C(0,0)}{m^2} t^2$$

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Diffusion

$$\langle |X(t)-X(0)|^2\rangle = \frac{1}{M^2}\left(C(0,0)-\frac{M}{\beta}\right)\overset{(1)}{\left(\frac{1-e^{-\gamma t}}{\gamma}\right)^2} + \frac{2}{M\gamma\beta}\overset{(2)}{\left[t-\frac{(1-e^{-\gamma t})}{\gamma}\right]}$$

Ballistic $\gamma t \ll 1$ (* see below)

Compensation btw terms (1) & (2) gives

$$\langle |X(t)-X(0)|^2\rangle \simeq \frac{1}{M^2} C(0,0)\, t^2 \qquad C(0,0) = p_{(0)}^2 \quad \text{if } p_{(0)}^2 \neq 0$$

Diffusive $\gamma t \gg 1$

$$\langle |X(t)-X(0)|^2\rangle \simeq \underbrace{\frac{1}{M^2}\left(C(0,0)-\frac{M}{\beta}\right)\overset{(1)}{\frac{1}{\gamma^2}} - \overset{(2)}{\frac{2}{M\beta\gamma^2}}}_{\text{pre asympt}} + \frac{2}{M\beta\gamma}\, t$$

the pre-asymptotic term reads

$$\frac{C(0,0)}{M^2\gamma^2} - \frac{1}{M\beta\gamma^2} - \frac{2}{M\beta\gamma^2} = \frac{p_{(0)}^2}{M^2\gamma^2} - \frac{3}{M\beta\gamma^2}$$

which gives several units for MSD

- one related to initial data $\frac{p_{(0)}^2}{M^2\gamma^2}$ which is singular when $p(0)=0$

- one related to diffusive MSD at time γ^{-1}

$$\langle \Delta X^2(t)\rangle \underset{\text{Diffusive}}{\sim} \frac{2}{M\beta\gamma}\, t \quad \text{at } t\sim\gamma^{-1} \qquad \frac{1}{M\beta\gamma^2}$$

(*)
when $p(0)=0$ the ballistic regime gives

$$\langle \Delta x^2(t)\rangle \sim -\frac{t^2}{\beta M} + \frac{\cancel{2}}{M\beta\cancel{\gamma}}\frac{\cancel{\gamma^2} t^2}{\cancel{2\gamma}} \quad \mathcal{O}(t^4)$$

we should go to third order

$$\langle \Delta x^2(t)\rangle = \frac{p(0)^2}{M^2}t^2 - \frac{(3p(0)^2 - 2\frac{M}{\beta})\gamma t^3}{3M^2}$$

which gives

$$\langle \Delta x^2(t)\rangle \simeq \frac{2\gamma}{3M\beta}t^3 \quad \text{when } t\simeq\gamma^{-1} \quad \frac{2\gamma}{3M\beta}\frac{1}{\gamma^3} \propto \frac{1}{M\beta\gamma^2}$$

it is thus convenient to scale MSD with the unit $\frac{1}{M\beta\gamma^2}$

$$\langle \Delta x^2(t)\rangle M\beta\gamma^2 =$$

$$\frac{\cancel{M\beta\gamma^2}}{\cancel{M^2}}\left(C(0,0)-\frac{M}{\beta}\right)\left(\frac{1-e^{-\gamma t}}{\cancel{\gamma}}\right)^2 + \frac{2\cancel{M\beta}\gamma^{\cancel{2}}}{\cancel{M\gamma\beta}}\left[t - \frac{(1-e^{-\gamma t})}{\gamma}\right]$$

$$\langle \Delta x^2\rangle M\beta\gamma^2 = \left(\frac{\beta p(0)^2}{M}-1\right)(1-e^{-\gamma t})^2 + 2\left[\gamma t - (1-e^{-\gamma t})\right]$$

which is a function of $\beta E(0) = \frac{\beta p(0)^2}{2M}$ and γt

let

$x = \beta\frac{p(0)^2}{2M}$ the fraction of initial energy to k_BT

$$\boxed{\langle \Delta x^2\rangle M\beta\gamma^2 = (2x-1)(1-e^{-\gamma t})^2 + 2\left[\gamma t - 1 + e^{-\gamma t}\right]}$$

Ballistic regime $\gamma t \ll 1$

$$\langle \Delta x^2 \rangle M\beta\gamma^2 \simeq 2x t^2 - \frac{(6x-2)t^3}{3}$$ time γ^{-1} units

Diffusive regime $\gamma t \gg 1$

$$\langle \Delta x^2 \rangle M\beta\gamma^2 \simeq 2t - 2 + 2x - 1 = 2t + 2x - 3$$