Tentative Syllabus

- Introduction to stochastic processes
  - Random Walk Model of Brownian Motion
  - Brief review of standard continuous time random variables
  - Brief review of Normal Variables
  - Einsteins Brownian Motion
  - OrnsteinUhlenbeck Processes
  - Langevin's Brownian Motion
  - Stochastic Damped Harmonic Oscillator
  - Fluctuations without Dissipation
- Statistical mechanics and Thermal statistics
- Single Molecule Physics
- Instrumentation for single molecule investigation
- Other topics

Grading Policy

- Homeworks (50%)
- Final Project (50%)

References

- An Introduction to Stochastic Processes in Physics (Don S. Lemons)
- Fundamentals of Statistical and Thermal Physics (Reif)
- Stochastic Processes in Physics and Chemistry (Van Kampen)

Some Notation:

- $\langle x \rangle$; denotes the mean of the random variable x.
- $\mathrm{Var}\{x\} = \langle x^2 \rangle - \langle x \rangle^2$
- $\mathrm{Cov}\{X, Y\} = \langle (X - \langle X \rangle)(Y - \langle Y \rangle) \rangle$

  where X and Y are random variables

- $\mathrm{Cor}\{X, Y\} = \dfrac{\mathrm{Cov}\{X, Y\}}{\sqrt{\mathrm{Var}\{X\}\,\mathrm{Var}\{Y\}}}$

Mean Sum theorem:

$$\left\langle \sum_{i=1}^{N} x_i \right\rangle = \sum_{i=1}^{N} \langle x_i \rangle$$

Variance Sum theorem

$$\mathrm{Var}\left\{ \sum_{i=1}^{N} x_i \right\} = \sum_{i=1}^{N} \mathrm{Var}\{x_i\}$$

if x_i are all independent.

Random Walk model of Brownian Motion

- Imagine a Brownian particle that starts at the origin and can move in either direction on the horizontal axis with a uniform step size Δx every Δt seconds.

- Let X_i be the random variable describing the i^{th} step. that are independent
- Let the random variable describing the position of the particle after n steps be $X(n)$ given by

$$X(n) = \sum_{i=1}^{n} X_i$$

Then

Mean and Variance

- $$\langle X(n)\rangle = \left\langle \sum_{i=1}^{n} X_i \right\rangle$$

$$= \sum_{i=1}^{n} \langle X_i \rangle$$

$$= 0$$

- Variance

$$\mathrm{Var}\{X(n)\} = \mathrm{Var}\left\{\sum_{i=1}^{n} X_i\right\}$$

$$= \sum_{i=1}^{n} \mathrm{Var}\{X_i\}$$

$$\mathrm{Var}\{X_i\} = \langle X_i^2 \rangle - \langle X_i \rangle^2$$

$$= \left(\frac{1}{2}\Delta x^2 + \frac{1}{2}\Delta x^2\right) - 0$$

$$= \Delta x^2$$

$$\therefore \quad \mathrm{Var}\{X(n)\} = n\,\Delta x^2$$

Now, n steps are taken in $t = n\Delta t$ time

Thus,

$$\mathrm{Var}\{X(n)\} = \left(\frac{\Delta x^2}{\Delta t}\right) t.$$

Variance

Thus

$$\mathrm{Var}\{x(t)\} = \left(\frac{\Delta x^2}{\Delta t}\right) t$$

and

$$\langle x(t) \rangle = 0$$

- Thus, the mean of the random walk is zero for all time t
- The variance grows linearly with time
  - if $\frac{\Delta x^2}{\Delta t}$ is some meaningful characteristic described by the physics of the particle undergoing Brownian motion.
  - otherwise, the variance depends on the fineness of the spatial and temporal discretization.

Variance

- Indeed it will be shown later that $\left(\frac{\Delta x^2}{\Delta t}\right)$ is equal to twice the diffusion constant

Another issue:

- The random walk model does not connect with Newtons Laws of motion. Consider

$$V(t) = V(0) + \frac{1}{M}\int_0^t F(t')\,dt'$$

where $F(t')$ is the force felt by the particle. One can imagine that in the time interval t' to $t'+\Delta t$ the impulsive force

$$\int_{t'}^{t'+\Delta t} F(t')\,dt'$$ are

delivered randomly. Then

Critique

One can model the Brownian particle as

$$v(t) = \sum_{i=0}^{n} v_i \quad ; \quad n = t/\Delta t$$

where v_i are independent random variables with mean 0 and variance Δv^2. Thus

$$\langle v(t)^2 \rangle = \left(\frac{\Delta v^2}{\Delta t}\right) t$$

and if $\left(\frac{\Delta v^2}{\Delta t}\right)$ is a physical constant then $\frac{M\langle v^2\rangle}{2}$ grows linearly with time, which is not possible.

Moment generating function

→ Suppose X is a random variable with pdf $p(x)$. Then

$$M_X(t) := \langle e^{tX} \rangle = \int e^{tx} p(x) dx.$$

Note that

$$\langle x^n \rangle = \int x^n p(x) dx.$$

- $\frac{d}{dt}\left(M_X(t)\right) = \frac{d}{dt} \int e^{tx} p(x) dx = \int x e^{tx} p(x) dx$

$\therefore \quad \frac{d}{dt} M_X(t) \Big|_{t=0} = \langle x \rangle$

- $\frac{d^2}{dt^2} M_X(t) = \int x^2 e^{tx} p(x) dx$

$\Rightarrow \quad \frac{d^2}{dt^2} M_X(t) \Big|_{t=0} = \langle x^2 \rangle$

$$\therefore \quad \boxed{\frac{d^n M_X(t)}{dt^n} \Big|_{t=0} = \langle x^n \rangle .}$$

Uniform Random Variable

- X is a uniform random variable $U(m,a)$ if it has a probability density

$$p(x) = \frac{1}{2a} \quad \text{if} \quad m-a \le x \le m+a$$
$$= 0 \quad \text{otherwise.}$$

- $$\langle X \rangle = \int x\, p(x)\, dx = \int_{m-a}^{m+a} x \frac{1}{2a}\, dx$$
$$= \frac{1}{2a} \frac{1}{2}\left[(m+a)^2 - (m-a)^2 \right]$$
$$= m.$$

$$\mathrm{Var}\{x\} = \langle \cancel{x}^2 \rangle - m^2 = \frac{a^2}{3}.$$

- $$\langle (X - \langle x \rangle)^n \rangle = \frac{a^{n+1} - (-a)^{n+1}}{2a(n+1)}$$

The uniform random variable is a good model when the only characterization available of X is that it lies between $m-a$ and $m+a$.

Uniform Random Variable

$$\rightarrow \quad M_u(t) = \int e^{tx} p(x)\, dx$$

$$= \int_{m-a}^{m+a} e^{tx} \frac{1}{2a}\, dx$$

$$= \frac{1}{2a} \int_{m-a}^{m+a} e^{tx} dx$$

$$= \frac{1}{2a} \frac{1}{t} \Big[e^{tx} \Big]_{m-a}^{m+a}$$

$$= \frac{1}{2at} \left[e^{(m+a)t} - e^{(m-a)t} \right].$$

Normal Random Variable

- $N(m, a^2)$ has a pdf

$$p(x) = \frac{1}{\sqrt{2\pi a^2}} e^{-\frac{(x-m)^2}{2a^2}} \qquad -\infty < x < \infty$$

- The moment generating function is given by

$$M_X(t) = \langle e^{tx} \rangle = \int_{-\infty}^{\infty} e^{tx} \frac{1}{\sqrt{2\pi a^2}} e^{-\frac{(x-m)^2}{2a^2}} dx$$

$$= \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{\infty} e^{\left(tx - \frac{(x-m)^2}{2a^2}\right)} dx.$$

$$= e^{mt + \frac{a^2t^2}{2}}.$$

$\therefore \quad \langle (X-m)^n \rangle = 1 \cdot 3 \cdot 5 \cdots (n-1) a^n$ if n even
$= 0$ for odd n.

Kurtosis

$$\text{Kurtosis}(X) = \frac{\langle (X-m)^4 \rangle}{\langle (X-m)^2 \rangle^2} = 3.$$

is taken as the standard of kurtosis.

Normal random Variable

Leptokurtic Random Variable:

when the kurtosis of a random variable is greater than 3 it is said to be leptokurtic

Platykurtic:

when the kurtosis of a random variable is less than 3 it is said to be Platykurtic. The uniform random variable is Platykurtic.

Normal Variable theorems

① Suppose $X \sim N(m, a^2)$

and $Y = \alpha + \beta X$

Then Y is a normal variable

with mean $\alpha + \beta m$ and variance $\beta^2 a^2$

② Suppose $X \sim N_1(m_1, a_1^2)$ and

$Y \sim N_2(m_2, a_2^2)$

with X and Y statistically independent

Then

$X+Y$ is normal with mean $m_1 + m_2$ and variance

$a_1^2 + a_2^2$

JOINTLY NORMAL VARIABLES

Definition: Two random variables are jointly normal if both of them are linear combinations of the same set of independent normal variables.

Suppose

$$Y_1 = a_0 + \sum_{i=1}^{M} a_i N_i(0,1)$$

$$Y_2 = b_0 + \sum_{i=1}^{M} b_i N_i(0,1)$$

Then, the joint distribution of Y_1 and Y_2; $P_{Y_1,Y_2}(y_1,y_2)$ is completely determined by

$$\langle Y_1 \rangle = a_0; \quad \langle Y_2 \rangle = b_0$$

$$\langle Y_1^2 \rangle = \sum_{i=1}^{M} a_i^2; \quad \langle Y_2^2 \rangle = \sum_{i=1}^{m} b_i^2$$

and $\text{Cov}\{Y_1, Y_2\} = \sum_{i=1}^{M} a_i b_i$

EVEN if $m > 5$.

Jointly normal Variables

The joint distribution of two jointly normal variables Y_1 and Y_2 is given by

$$p(y_1, y_2) = \frac{1}{2\pi \sigma_1 \sigma_2 \sqrt{1-\rho^2}} e^{-\frac{1}{(1-\rho^2)}\left[\frac{(y_1-\mu_1)^2}{2\sigma_1^2} + \frac{(y_2-\mu_2)^2}{2\sigma_2^2} - \rho\frac{(y_1-\mu_1)(y_2-\mu_2)}{\sigma_1\sigma_2}\right]}$$

where $Var(Y_1) = \sigma_1$, $Var\{Y_2\} = \sigma_2$

$\mu_1 = mean\{Y_1\}$; $\mu_2 = mean\{Y_2\}$

$\rho = Cor\{Y_1, Y_2\}$

Central Limit theorem

Suppose $\{X_i\}$ are all independent random variables that have the same pdf (identically distributed) with mean μ_0 and variance σ_0.

Also assume that the moment generating function $M_{X_i}(t)$ exists

Let

$$S_m = X_1 + X_2 + \cdots + X_m.$$

$$\mu_m \doteq \sum_{i=1}^{m} \langle X_i \rangle = m\mu_0$$

$$\sigma_m^2 \doteq \sum_{i=1}^{m} \mathrm{Var}\{X_i\} = m\sigma_0^2$$

Let $Z_m = \dfrac{S_m - \mu_m}{\sigma_m}$

$$= \frac{S_m - m\mu_0}{\sqrt{m\sigma_0^2}} = \sum_{i=1}^{m} \frac{(X_i - \mu_0)}{\sqrt{m\sigma_0^2}}$$

Let $Y_i = \dfrac{X_i - \mu_0}{\sigma_0}$ with $\langle Y_i \rangle = 0;\ \mathrm{Var}\{Y_i\} = 1$

Central limit theorem

Then

$$Z_m = \frac{1}{\sqrt{m}} \sum_{i=1}^{m} Y_i$$

$$M_{Z_m}(t) = M_{\frac{1}{\sqrt{m}}\sum_{i=1}^{m} Y_i}(t)$$

$$= \left\langle e^{t \frac{1}{\sqrt{m}} \sum_{i=1}^{m} Y_i} \right\rangle$$

$$= \left\langle e^{\frac{t}{\sqrt{m}} Y_1 + \frac{t}{\sqrt{m}} Y_2 \cdots + \frac{t}{\sqrt{m}} Y_m} \right\rangle$$

$$= \left\langle e^{\frac{t}{\sqrt{m}} Y_1} \right\rangle \left\langle e^{\frac{t}{\sqrt{m}} Y_2} \right\rangle \cdots$$

$$\cdots \left\langle e^{\frac{t}{\sqrt{m}} Y_m} \right\rangle$$

$$= \left[\left\langle e^{\frac{t}{\sqrt{m}} Y_1} \right\rangle \right]^m$$

$$= \left[\left\langle 1 + \frac{t Y_1}{\sqrt{m}} + \frac{t^2 Y_1^2}{2! m} + \frac{t^3 Y_1^3}{3! m^{3/2}} + \cdots \right\rangle \right]^m$$

$$= \left[1 + \frac{t \langle Y_1 \rangle}{\sqrt{m}} + \frac{t^2 \langle Y_1^2 \rangle}{2m} + \frac{t^3 \langle Y_1^3 \rangle}{3! m^{3/2}} + \cdots \right]^m$$

$$= \left[1 + 0 + \frac{t^2}{2m} + 0 + \cdots \right]^m$$

Central limit theorem

$\therefore$

$$M_{Z_m}(t) = \left[1 + \frac{t^2}{2m} + \frac{t^3}{3!\, m^{3/2}} + \cdots\right]^m$$

and

$$\lim_{m\to\infty} M_{Z_m}(t) = \lim_{m\to\infty} \left[1 + \frac{t^2}{2m} + \frac{t^3}{3!\, m^{3/2}} + \cdots\right]^m$$

$$= \lim_{m\to\infty} \left[1 + \frac{t^2}{2m}\right]^m$$

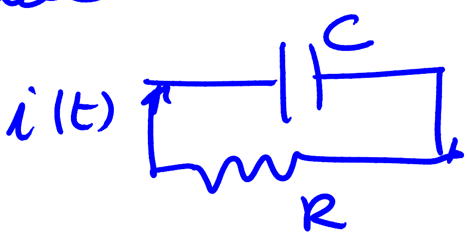
$$= e^{t^2/2}$$

and thus, $\lim_{m\to\infty} M_{Z_m}(t)$ is a normal distribution with mean 0 and variance 1.

Thus, the sum of i.i.d variables becomes Normal as the sum is taken over a large number of i.i.d variables.

EINSTEIN'S BROWNIAN MOTION.

Consider the RC circuit shown below



which is governed by

$$i(t)R + \frac{q(t)}{C} = 0$$

$$\Rightarrow \quad dq(t) + \frac{q(t)}{RC}\,dt = 0$$

which can also be written as

$$q(t+dt) - q(t) = -\frac{q(t)}{RC}\,dt$$

* Since t is arbitrary is dt can be made arbitrarily small the dynamical equation is time domain continuous.

* Since $\lim_{dt \to 0} q(t+dt) = q(t)$ the dynamical equation is process-variable continuous.

Continuity

of course

$$\lim_{dt \to 0} \frac{q(t+dt) - q(t)}{dt} = -\frac{q(t)}{RC}$$

exists and therefore the related process is smooth.

Wiener Process

* A random variable $X(t)$ has a pdf $p(x,t)$ which is parametrized by the time variable t.

* $X(t+dt)$ and $X(t)$ are different random variables

* A markov-process relates $X(t+dt)$ and $X(t)$ by

$$X(t+dt) - X(t) = F(X(t), dt)$$

where $F[X(t), dt]$ is called the Markov propagator function.

* We will assume time-domain continuity and thus $dt \to 0$ and we will restrict ourselves to process variable continuity i.e.

$$X(t+dt) - X(t) \to 0 \text{ as } dt \to 0.$$

Wiener Process.

Thus as

$$\lim_{dt\to 0} F(X(t), dt) = \lim_{dt\to 0}(X(t+dt) - X(t))$$

it follows that we need to have $F(X(t), dt) \to 0$ as $dt \to 0$.

The Wiener Process is defined by having $F(X(t), dt) = \sqrt{\delta^2 dt}\, N_t^{t+dt}(0,1)$

So that

$$X(t+dt) - X(t) = \sqrt{\delta^2 dt}\, N_t^{t+dt}(0,1)$$

where $N_t^{t+dt}(0,1)$ is a unit Normal associated with the time interval $(t, t+dt)$.

The equation

$$X(t+dt) = X(t) + \sqrt{\delta^2 dt}\, N_t^{t+dt}(0,1)$$

Wiener Process

Simply means that if

$X(t)$ has a realized value

$x(t)$ then

$$X(t+dt) = x(t) + \sqrt{\delta^2 dt}\; N_t^{t+dt}(0,1)$$

is a random variable with distribution

$$N(x(t), \delta^2 dt)$$

Comment on $\sqrt{dt}$ presence

(*) In deterministic differential equations it is $\sqrt{dt}$ terms are not present together with dt terms, as $\sqrt{dt}$ is infinitely larger that dt as $dt \to 0$

However, the term

$\sqrt{\delta^2 dt}\; N_t^{t+dt}(0,1)$ where the Normal N_t^{t+dt} assumes positive and negative values so that the cumulative

Self - Consistency

effect of $\sqrt{\delta^2 dt}\, N_t^{t+dt}(0,1)$ in forming $x(t)$ is of the order dt.

(*) The fact that we have time domain continuity imposes some important structure on $N_t^{t+dt}(0,1)$ for different t.

Indeed:

$$x(t+dt) - x(t) = x(t+dt) - x(t+dt/2) + x(t+dt/2) - x(t)$$

$$\Leftrightarrow \quad \sqrt{\delta^2 dt}\, N_t^{t+dt}(0,1) = \sqrt{\delta^2 \tfrac{dt}{2}}\, N_{t+\frac{dt}{2}}^{t+dt}(0,1)$$

$$\sqrt{\delta^2 \tfrac{dt}{2}}\, N_t^{t+dt/2}(0,1)$$

a condition that is called self consistency

Of course if $N_{t+dt/2}^{t+dt}(0,1)$ and $N_t^{t+dt/2}(0,1)$ are statistically independent random variables then the above equation holds, but it can be shown that it holds only if

$$N_t^{t+dt/2}(0,1) \text{ and } N_{t+dt/2}^{t+dt}(0,1)$$

are independent.

Thus, if the time-intervals are disjoint the associated normals are independent. This is a remarkable conclusion of simply imposing time-domain continuity.

Therefore

$$X(t+dt) - X(t) = \sqrt{\delta^2 dt}\; N_t^{t+dt}(0,1)$$

where $N_t^{t+dt}(0,1)$ is such that

$N_{t_1}^{t_2}(0,1)$ is independent of $N_{t_1'}^{t_2'}(0,1)$ if

$$[t_1, t_2] \cap [t_1', t_2'] = \phi.$$

(*) Note that $\lim_{dt \to 0} X(t+dt) - X(t) = 0$

but $$\frac{X(t+dt) - X(t)}{dt} = \sqrt{\frac{\delta^2}{dt}}\; N_t^{t+dt}(0,1)$$

and $$\lim_{dt \to 0} \frac{X(t+dt) - X(t)}{dt} \to \infty \text{ for all } t$$

The way to generate Brownian Motion

$$X(dt) = X(0) + \sqrt{\delta^2 dt}\, N_t^{t+dt}(0,1)$$

$$X(2dt) = X(dt) + \sqrt{\delta^2 dt}\, N_{t+dt}^{t+2dt}(0,1)$$

$$= X(0) + N_t^{t+dt}(0,\delta^2 dt) + N_{t+dt}^{t+2dt}(0,\delta^2 dt)$$

|||ly

$$X(Ndt) = X(0) + \sum_{i=0}^{N-1} N_{t+idt}^{t+(i+1)dt}(0,\delta^2 dt)$$

Each one of these is independent

$$= X(0) + N(0, N\delta^2 dt)$$

If $t = Ndt$ then

$$\boxed{X(t) = X(0) + N_0^t(0,\delta^2 t)}$$

Note that unlike the discrete random walk that depended on two independent entities Δx^2 and Δt; the above derivation does not depend on time discretization; The

Continuous time Wiener Process.

relationship

$$X(t) - X(0) = N(0, \delta^2 t)$$

depends on only one parameter δ^2.

Note also that in the derivation dt can be chosen to be as small as possible and t can thus be approximated as finely as needed.

Simulating Brownian Motion:

Step0 Assume $a = X(0)$ and a time-step Δt : let $x = a$;
$N = 0$

Step1: Obtain a realization of a normal r.v. $N(0,1)$
be α

Step2: Let $x = x + \alpha$

step3: $N = N + 1$

Repeat until N reaches the value $t/\Delta t$

Note that

$$X(t) - X(0) = N(0, \delta^2 t)$$

and thus assuming $X(0)=0$

$X(t)$ has a pdf

$$p(x,t) = \frac{1}{\sqrt{2\pi\delta^2 t}} e^{-x^2/2\delta^2 t}$$

- It can be easily verified that $p(x,t)$ satisfies

$$\frac{\partial p(x,t)}{\partial t} = \frac{\delta^2}{2} \frac{\partial^2 p(x,t)}{\partial x^2}$$

or in other words

$$\frac{\partial p(x,t)}{\partial t} - \frac{\delta^2}{2} \frac{\partial^2 p(x,t)}{\partial x^2} = 0$$

which is the diffusion Equation.

Brownian Motion with Drift and sedimentation

Consider the equation

$$x(t+dt) - x(t) = \alpha\, dt + \sqrt{\sigma^2 dt}\, N_t^{t+dt}(0,1)$$

that describes Brownian motion superimposed on a steady drift of rate α. Let $x(0) = 0$.

We will now find the pdf $p(x,t)$.

pdf

- Consider the dynamical equation

$$x(t+dt) - x(t) = \alpha dt + \sqrt{\delta^2 dt}\, N_t^{t+dt}(0,1).$$

$$x(dt) = x(0) + \alpha dt + \sqrt{\delta^2 dt}\, N_0^{dt}(0,1).$$

$$= x(0) + \alpha dt + N_0^{dt}(0, \delta^2 dt)$$

$$x(2dt) = x(dt) + \alpha dt + \sqrt{\delta^2 dt}\, N_{dt}^{2dt}(0,1)$$

$$= x(0) + 2\alpha dt + N_0^{dt}(0, \delta^2 dt) + N_{dt}^{2dt}(0, \delta^2 dt)$$

$$= x(0) + 2\alpha dt + N_0^{2dt}(0, 2\delta^2 dt)$$

$$x(3dt) = x(2dt) + N_{2dt}^{3dt}(0, \delta^2 dt)$$

$$= x(0) + \alpha 3dt + N_0^{3dt}(0, \delta^2 3dt)$$

$$\therefore x(Ndt) = x(0) + \alpha(Ndt) + N_0^{Ndt}(0, \delta^2 Ndt)$$

$$\Rightarrow x(t) = x(0) + \alpha t + N_0^t(0, \delta^2 t).$$

If $x(0) = 0$

$$x(t) = \alpha t + N_0^t(0, \delta^2 t)$$

$$= N_0^t(\alpha t, \delta^2 t).$$

Thus, the pdf is described by

$$p(x,t) = \frac{1}{\sqrt{2\pi\delta^2 t}}\, e^{-(x-\alpha t)^2/2\delta^2 t}.$$

Sedimentation.

(c) $\arg\max_x p(x,t) = \arg\max (\ln p(x,t))$

$$= \arg\max \ln e^{-(x-\alpha t)^2/2\delta^2 t}$$

$$= \arg\max -\frac{(x-\alpha t)^2}{2\delta^2 t}$$

which occurs at $x_{max} = \alpha t$.

The maximum value is given by

$$p(x_{max}, t) = \frac{1}{\sqrt{2\pi\delta^2 t}} e^0 = \frac{1}{\sqrt{2\pi\delta^2 t}}$$

$$p(x_{\frac{1}{2}}, t) = \frac{1}{2\sqrt{2\pi\delta^2 t}} = \frac{1}{\sqrt{2\pi\delta^2 t}} e^{-(x_{\frac{1}{2}}-\alpha t)^2/2\delta^2 t}$$

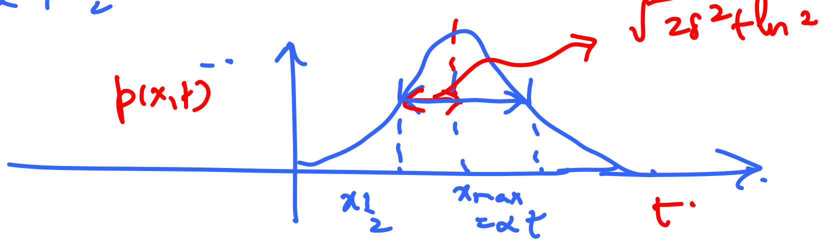
$$\Rightarrow \quad \frac{1}{2} = e^{-(x_{\frac{1}{2}}-x_{max})^2/2\delta^2 t}$$

$$\Rightarrow -\ln 2 = -(x_{\frac{1}{2}}-x_{max})^2/2\delta^2 t$$

$$\Rightarrow \quad 2\delta^2 t \ln 2 = (x_{\frac{1}{2}}-x_{max})^2$$

$$\Rightarrow |x_{\frac{1}{2}}-x_{max}| = \sqrt{2\delta^2 t \ln 2}$$

$$\Rightarrow 2|x_{\frac{1}{2}}-x_{max}| = 2\sqrt{2\delta^2 t \ln 2}$$



Because the center evolves as αt and its full width at half maximum evolves more slowly as $2\sqrt{2\sigma^2 t \ln 2}$ it is possible to separate different species of Brownian particles with different rates α. In a similar manner electrophoresis employs an electrical field to separate charged particles.