複雑液体・ソフトマター論：
コロイドの物理
Physics of colloidal worlds

ST

広島大総合科

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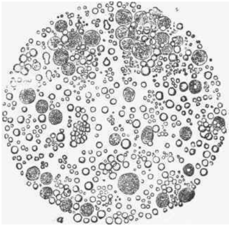
Overview

Outline

Examples of colloids

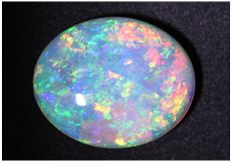
micro	meso	macro
Atoms·Molecules	Colloids	Objects
~ 1 nm	$1 \sim 10\ \mu$m	$10\ \mu$m $\sim$

Milk : Fat particles in water



https://www.quora.com/If-you-mix-skim-milk-and-whole-milk-will-they-stay-mixed

Opal : Crystal of silica particles

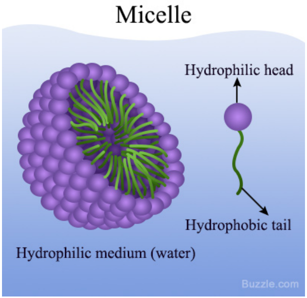


http://www.luxrender.net/forum/viewtopic.php?f=36&t=12547

Silica

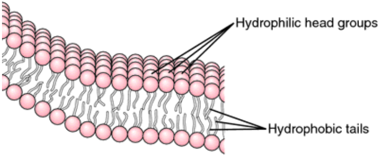
http://www.silicagelmanufacturer.com/white-silica-gel.htm

Micelles : Aggregates of surfactants



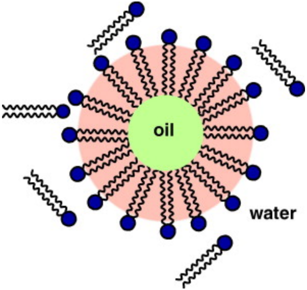
https://socratic.org/questions/what-are-micelles

Bilayers : Two dimensional aggregates of surfactants



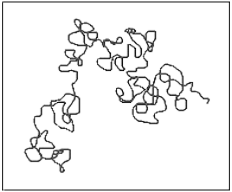
http://medical-dictionary.thefreedictionary.com/bilayers

Microemulsions : Droplets stabilized by surfactants



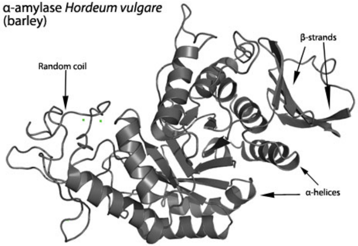
https://www.researchgate.net/publication/215475567_Microemulsion_method_A_novel_route_to_synthesize_orga

Synthetic polymers :



http://pslc.ws/macrog/property/solpol/ps5.htm

Natural polymers : Proteins, DNAs, RNAs, $\cdots$



http://www.homebrewtalk.com/showthread.php?t=111819

Inside a cell

$$\text{(A cell)} = \text{(A space surrounded by membranes,} \sim 10\ \mu\text{m)}$$

$$+$$

$$\text{(Many types of colloids, 1 nm} \sim 1\ \mu\text{m)}$$

Proteins (molecular machines), DNA/RNA (molecular information strages), Bilayers (molecular frameworks), $\cdots$

It's a small colloidal world!

Ingredients of life

Three major ingredients of life

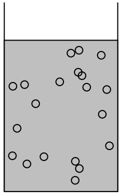
Nucleic acids	:	Information
Protein	:	Functionality
Lipids	:	Frameworks

All of them are Colloids!

Large interfaces

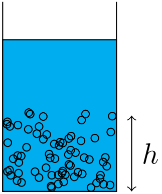
Exercise 1 : Calculate the total surface area of n colloidal particles of the diameter d.

Exercise 2 : Then calculate the total surface area in 1 l of colloidal suspension containing 10%(v/v) of colloids of 1 μm in diameter.



Colloidal suspension

Importance of fluctuation



Sedimentation equilibrium

The number $n(h)$ of colloids at the height h:

$$\frac{n(h)}{n(0)} = \exp\left\{-\frac{(m-m_w)gh}{k_B T}\right\} \quad (1)$$

m : the mass of a colloid

m_w : the mass of water of the same volume with a colloid

$$= \exp\left(-\frac{h}{\lambda}\right), \quad (2)$$

$$\lambda = \frac{k_B T}{(m-m_w)g} \quad \cdots \text{ The hight where } n(\lambda)/n(0) = \mathrm{e}^{-1}. \quad (3)$$

Exercise 3 : Calulate λ for silica particles of the density $\rho = 2.2$ g/cm^3 and the radius r below.

r (μm)	λ
0.1	
1	
10	
100	

When does λ become larger than r?

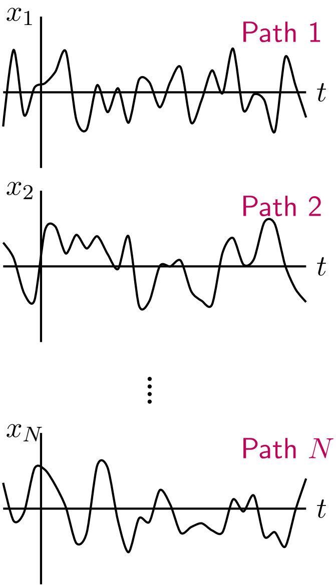
Summary

- Colloids are particles of size 1 nm $\sim$ 10 μm.
- It is mesoscopic world in between micro and macro.
- The interface always plays important role in colloids.
- Also fluctuation is always important in colloidal world.

Outline

Ensemble

One dimensional Brownian motion: N times observation



- Each sample is different.
- But statistical properties are common.

$\Longrightarrow$ No use of deterministic.

$\Longrightarrow$ Need of statistic.

Ensemble

$x_1, x_2, \cdots, x_N$: samples

Variables change randomly

$\cdots$ Random variables

- Random variable: $x_1, x_2, \cdots, x_N$
- Random process: $x(t)$

  The process that changes every time sampled.
- Ensemble average: Averaged quantity over the ensemble.

$$\langle x(t) \rangle = \frac{1}{N} \sum_{\text{path}} x_i(t) \tag{4}$$

This is different from the time average,

$$\langle x_i \rangle_{\text{time}} = \frac{1}{T} \int_{-T/2}^{T/2} x_i(t) dt \tag{5}$$

Ergodic hypothesis

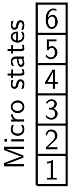
The ergodic hypothesis assumes for a safficiently long time,

$$\langle x \rangle = \langle x \rangle_{\text{time}} \tag{6}$$

, if the system is in a steady state.

$\parallel$

All the microstates the system can access has the same probability to be visited by the system.



Example: An average of a hundreds dice vs. an average of a die cast a hundred times.

The central limit theorem

Let's consider the random variables $x_1(t), x_2(t), \cdots, x_n(t)$ with $\langle x_i \rangle (t) = 0$, and its sum,

$$X_n(t) = \sum_{i=1}^{n} x_i(t). \tag{7}$$

Then the mean and variance are

$$\langle X_n \rangle = \left\langle \sum_i x_i \right\rangle = \sum_i \langle x_i \rangle = 0 \tag{8}$$

$$\left\langle X_n^2 \right\rangle = \sum_i \left\langle x_i^2 \right\rangle \equiv \sum_i \sigma_i^2 \tag{9}$$

Exercise 4 : Confirm eq. (9).

The central limit theorem

If $x_1, x_2, \cdots, x_n$ are similar random variables, the probability distribution function $P(X_n)$ becomes a Gaussian distribution,

$$P(X_n) \xrightarrow[n\to\infty]{} \frac{1}{\sqrt{2\pi s_n^2}} \exp\left(-\frac{X_n^2}{2s_n^2}\right) \tag{10}$$

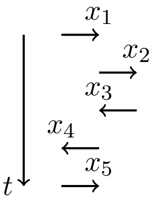
$$s_n^2 = \sum_i \sigma^2. \tag{11}$$

This is called the central limit theorem.

Brownian motion & Gaussian distribution

Let $x_1, x_2, \cdots x_n$ be displacement at the step i of Brownian motion.

Random walk model



$$\langle x_i \rangle = 0 \tag{12}$$

$$\left\langle x_i^2 \right\rangle = \sigma_i^2 \tag{13}$$

Then the distribution of $X_n = \sum_n x_i$ becomes Gaussian because of the central limit theorem.

Exercise 5 : Calculate

$$\langle X_n \rangle = \int_{-\infty}^{\infty} X_n P(X_n) dX_n \tag{14}$$

$$\langle X_n^2 \rangle = \int_{-\infty}^{\infty} X_n^2 P(X_n) dX_n, \tag{15}$$

$$\text{with } P(X_n) = \frac{1}{\sqrt{2\pi s_n^2}} \exp\left(-\frac{X_n^2}{2s_n^2}\right) \tag{16}$$

$$\text{and } \int_{-\infty}^{\infty} x^2 \mathrm{e}^{-\alpha x^2} dx = \frac{1}{2\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2} \tag{17}$$

Mean square displacement

If $\sigma^2 \equiv \sigma_1^2 = \sigma_2^2 = \cdots \sigma_n^2$,

$$s_n^2 = \sum_i \sigma_i^2 = n\sigma^2. \tag{18}$$

Then

$$\left\langle X_n^2 \right\rangle = n\sigma \propto n \text{ (the number of steps)}. \tag{19}$$

Then with $n = \frac{t}{\Delta t}$, ($\Delta t =$ Time needed for a step),

$$\left\langle X_n^2 \right\rangle = \frac{\sigma^2}{\Delta t} t \propto t \tag{20}$$

$$= 2Dt, \qquad D = \frac{\sigma^2}{2\Delta t}. \tag{21}$$

D is the diffusion coefficient.

Exercise 6 : Calsulate $\langle X_n^2 \rangle$ directly from

$$\langle X_n^2 \rangle = \langle (x_1 + x_2 + \cdots + x_n)^2 \rangle \tag{22}$$

by assuming the independency between x_i and x_j if $i \neq j$.

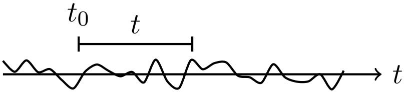
Correlation function

For a random process $x(t)$,

$$\phi(t_0, t) \equiv \langle x(t)x(t_0+t)\rangle_{\text{time}} \tag{23}$$

$$= \lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{T} x_k(t_0)x(t_0+t)dt_0 \tag{24}$$

is called the correlation function.



How much similar is $x(t_0+t)$ with $x(t_0)$?

Under the ergodic hypothesis, the ensemble average

$$\langle x(t_0)(x(t_0+t))\rangle = \frac{1}{N}\sum_{k=1}^{N} x_k(t_0)x_k(t_0+t) \qquad (25)$$

is the same as $\phi(t)$. Thus

$$\phi(t_0,t) = \langle x(t_0)x(t_0+t)\rangle \,. \qquad (26)$$

Reversibility & Stationarity

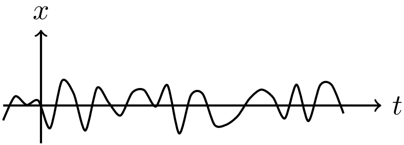
- If the system is in steady state, $\phi(t)$ does not depend on t_0.

$$\phi(t_0, t) = \phi(t) = \langle x(0)x(t)\rangle \,. \tag{27}$$

- If the system is reversible, $\phi(t_0, t)$ does not change when $t \to -t$.

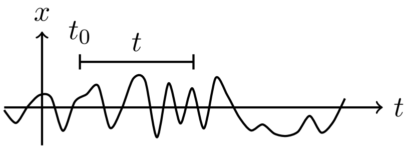
$$\phi(t_0, t) = \langle x(t_0)x(t_0 + t)\rangle = \langle x(t_0)x(t_0 - t)\rangle = \phi(t_0, -t) \tag{28}$$

$$\therefore \quad \phi(t_0, t) \text{ is an even function of } t. \tag{29}$$



It is impossible to determin the direction of time from the data like this.

Physics of the correlation function



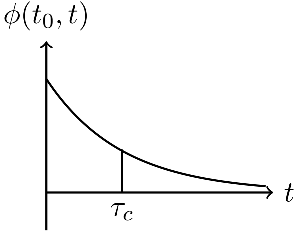
- $t \to 0$: Always,

$$\langle x(t_0)x(t_0+t)\rangle = \left\langle x(t_0)^2 \right\rangle > 0. \tag{30}$$

- $t \to \infty$: $x(t_0)$ and $x(t_0+t)$ is independent. Therefore,

$$\langle x(t_0)x(t_0+t)\rangle \xrightarrow[t\to\infty]{} \langle x(t_0)\rangle \langle x(t_0+t)\rangle = 0 \tag{31}$$

Thus, $\phi(t_0, t)$ is the reducing function of t.



The time at which

$$\phi(t_0, t)/\phi(t_0, 0) = \mathrm{e}^{-1} \tag{32}$$

is the correlation time, τ_c.

Fourier transformation

The Fourier integral or Fourier transform of $x(t)$ is

$$x(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\hat{x}(\omega)\mathrm{e}^{i\omega t}d\omega \tag{33}$$

$\hat{x}(\omega)$: The Fourier transform or spectral composition. (34)

Since $x(t)$ is real, $x^*(t) = x(t)$.
Exercise 7 : Then show the relation,

$$\hat{x}^*(\omega) = \hat{x}(-\omega). \tag{35}$$

Problem of divergence

Inverse Fourier transform of $x(t)$ gives

$$\hat{x}(\omega) = \int_{-\infty}^{\infty} x(t)\mathrm{e}^{-i\omega t} dt. \tag{36}$$

But this will sometimes diverge, because $x(t)$ always has a value. So it is necessary to define $x_T(t)$ as

$$x_T(t) = \begin{cases} x(t) & -T \leq t \leq T \\ 0 & \text{otherwise} \end{cases} \tag{37}$$

then its inverse Fourier transform

$$\hat{x}_T(\omega) = \int_{-\infty}^{\infty} x_T(t)\mathrm{e}^{-i\omega t} dt. \tag{38}$$

does not diverge.

Spectrum of the correlation function

The definition of $\phi(t)$ (under the stationarity assumption) is

$$\phi(t) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} x_T(t_0) x_T^*(t_0 + t) dt_0. \tag{39}$$

Exercise 8 : Show the relation

$$\phi(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \lim_{T\to\infty} \frac{1}{2T} \left|\hat{x}_T(\omega)\right|^2 \mathrm{e}^{i\omega t} d\omega, \tag{40}$$

using

$$x_T(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{x}_T(\omega) \mathrm{e}^{i\omega t} d\omega \tag{41}$$

$$\delta(\omega - \omega') = \lim_{T\to\infty} \frac{1}{2\pi} \int_{-T}^{T} \mathrm{e}^{i(\omega-\omega')t} dt. \tag{42}$$

Power spectrum

The power spectrum or spectrum density is defined as

$$J(\omega) = \lim_{T \to \infty} \frac{1}{2T} \left| \hat{x}_T(\omega) \right|^2 . \tag{43}$$

Then

$$\phi(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} J(\omega) \mathrm{e}^{i\omega t} d\omega. \tag{44}$$

On the other hand, by Fourier inverse transform

$$J(\omega) = \int_{-\infty}^{\infty} \phi(t) \mathrm{e}^{-i\omega t} dt. \tag{45}$$

Wiener-Khinchin theorem

Thus there is a relation

$$\phi(t) \underset{\text{Fourier inverse transform}}{\overset{\text{Fourier transform}}{\rightleftharpoons}} J(\omega). \tag{46}$$

This is called Wiener-Khinchin theorem.

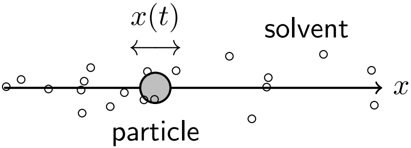
Exercise 9 : Express $\phi(0) = \left\langle x^2 \right\rangle$ using $J(\omega)$.

Exercise 10 : Show that $J(\omega)$ is real.

Outline

Equation of motion for Brownian motion

Let's consider one-dimensional Brownian motion.



The equation of motion is

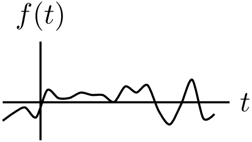
$$m\frac{dv}{dt} = F(t) + f(t) \tag{47}$$

$$F(t) \ : \ \text{External force} \tag{48}$$

$$f(t) \ : \ \text{Force exerted by solvent} \tag{49}$$

$f(t)$: Approximated as a random function of t

$\therefore$ Random variable



Force exerted by solvent

$f(t)$ can be splitted into two parts

$$f(t) = -\zeta v + f'(t) \tag{50}$$

$$-\zeta v \ : \ \text{Viscous resistance} \cdots \text{dissipation} \tag{51}$$

$$f'(t) \ : \ \text{Random force} \cdots \text{fluctuation.} \tag{52}$$

Both come from the interaction to solvent molecules.

$\therefore$ Strong correlation between dissipation and fluctuation

$\longrightarrow$ the fluctuation-dissipation theorem

Langevin equation

Then the equation of motion amounts to

$$m\frac{dv}{dt} = F(t) - \zeta v + f'(t). \tag{53}$$

This is called the Langevin equation. It is a stochastic differential equation.

Random walk model

Let $x(t)$ to be the position of the particle at t, and

$$\frac{dx}{dt} = v \tag{54}$$

$$x(0) = 0 \ \therefore \ \langle x(t) \rangle = 0 \tag{55}$$

$$\left\langle f'(t) \right\rangle = 0 \tag{56}$$

$$\left\langle xf' \right\rangle = \langle x \rangle \left\langle f' \right\rangle = 0 \ \because \ \text{No correlation} \tag{57}$$

$$F(t) = 0. \tag{58}$$

Then the Langevin equation becomes

$$m\frac{dv}{dt} = -\zeta v + f'(t). \tag{59}$$

Multiply x to both sides and transform,

$$m x \frac{dv}{dt} = -\zeta x v + x f'(t) \tag{60}$$

$$\therefore \; m \left\{ \frac{d}{dt}(xv) - v^2 \right\} = -\zeta x v + x f'(t). \tag{61}$$

Then take the ensemble average of both sides,

$$m \frac{d}{dt} \langle xv \rangle - m \left\langle v^2 \right\rangle = -\zeta \langle xv \rangle + \left\langle x f'(t) \right\rangle . \tag{62}$$

With the equipartition law,

$$\frac{m \left\langle v^2 \right\rangle}{2} = \frac{k_B T}{2} \tag{63}$$

and

$$\left\langle x f' \right\rangle = 0, \tag{64}$$

the equation is simplified to

$$m \frac{d}{dt} \langle xv \rangle = k_B T - \zeta \langle xv \rangle . \tag{65}$$

Exercise 11 : Solve Eq. (65) under the initial condition, $\langle x(0) \rangle = 0$.

With

$$\langle xv \rangle = \frac{1}{2}\frac{d}{dt}\left\langle x^2 \right\rangle, \tag{66}$$

the solution of Eq. (65) is

$$\frac{1}{2}\frac{d}{dt}\left\langle x^2 \right\rangle = \frac{k_B T}{\zeta}\left(1 - \mathrm{e}^{-t/\tau}\right),\ \tau = \frac{m}{\zeta}. \tag{67}$$

Exercise 12 : Solve Eq. (67) under the initial condition, $\left\langle x^2(0) \right\rangle = 0$.

The solution of Eq. (67) is

$$\left\langle x^2(t)\right\rangle = \frac{2k_BT}{\zeta}\left\{t-\tau\left(1-\mathrm{e}^{-t/\tau}\right)\right\},\ \tau=\frac{m}{\zeta}. \qquad (68)$$

Exercise 13 : Calculate the limit of Eq. (68) when $t \ll \tau$ (the short time limit).

Exercise 14 : Calculate the limit of Eq. (68) when $t \gg \tau$ (the long time limit).

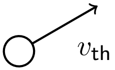
In the short time limit ($t \ll \tau$),

$$\left\langle x^2(t)\right\rangle = \frac{k_B T}{\zeta\tau} t^2 \tag{69}$$

$$\therefore \; \sqrt{\langle x^2(t)\rangle} = \sqrt{\frac{k_B T}{m}} t \tag{70}$$

$\therefore$ In this regime, the particle moves ballistically with the thermal velocity,

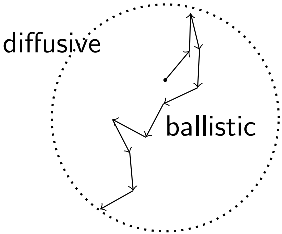
$$v_{\text{th}} = \frac{d}{dt}\sqrt{\langle x^2\rangle} = \frac{k_B T}{m}. \tag{71}$$



In the long time limit ($t \gg \tau$),

$$\langle x^2(t) \rangle = \frac{2k_B T}{\zeta} t. \tag{72}$$

$\langle x^2(t) \rangle \propto t$ indicates diffusive motion (= the random walk model).



Einstein relation

If compared with the result from the random walk model,

$$\left\langle x^2(t) \right\rangle = 2Dt, \tag{73}$$

the Einstein relation is obtained,

$$D = \frac{k_B T}{\zeta}. \tag{74}$$

$$D \; : \; \text{Characteristics of fluctuation} \tag{75}$$

$$\zeta \; : \; \text{Characteristics of dissipation} \tag{76}$$

$\therefore$ This relation is one of fluctuation-dissipation theorem.

Spectrum of velocity fluctuation

Let $F(t) = 0$,

$$m\frac{dv}{dt} = -\zeta v + f'(t). \tag{77}$$

Multiply $v(0)$ and average,

$$m\frac{d}{dt}\langle v(0)v(t)\rangle = -\zeta\langle v(0)v(t)\rangle + \underbrace{\langle v(0)f'(t)\rangle}_{\langle v(0)\rangle\langle f'(t)\rangle = 0} \tag{78}$$

$$\therefore\ m\frac{d\phi_v}{dt} = -\zeta\phi_v, \tag{79}$$

$$\phi_v = \langle v(0)v(t)\rangle \ \text{: velocity correlation function} \tag{80}$$

Exercise 15 : Solve Eq. (79) with $\langle v^2(0)\rangle = k_B T/m$ (equipartition law).

Thus the velocity correlation function is

$$\phi_v = \frac{k_B T}{m} \mathrm{e}^{-t/\tau_c}, \; \tau_c = \frac{m}{\zeta} \tag{81}$$

Since $\phi_v(t) = \phi_v(-t)$,

$$\phi_v = \frac{k_B T}{m} \mathrm{e}^{-|t|/\tau_c} \tag{82}$$

The spectrum of v, $J_v(\omega)$, can be obtained using Wiener-Khinchin theorem,

$$\phi_v(t) \underset{\text{Fourier}}{\overset{\text{inverse Fourier}}{\rightleftharpoons}} J_v(\omega) \tag{83}$$

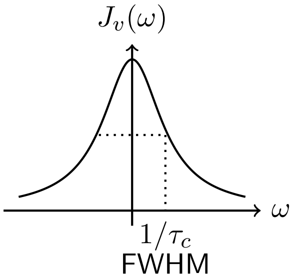
$$J_v(\omega) = \int_{-\infty}^{\infty} \phi_v(t) \mathrm{e}^{-i\omega t} dt \tag{84}$$

Exercise 16 : Solve Eq. (84) using Euler's formula,

$$\mathrm{e}^{i\theta} = \cos\theta + i\sin\theta. \tag{85}$$

Debye relaxation spectrum

$$J_v(\omega) = \frac{2k_BT}{\zeta}\frac{1}{1+\omega^2\tau_c^2}. \tag{86}$$



Spectrum of random force

Fourier transform $v(t)$, $f'(t)$,

$$v(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \hat{v}(\omega)\mathrm{e}^{i\omega t}d\omega$$
$$f'(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \hat{f}'(\omega)\mathrm{e}^{i\omega t}d\omega \tag{87}$$

Exercise 17 : Substitute Eqs. (87) into the Langevin equation ($F(t) = 0$) and obtain the relation between $\hat{v}$ and $\hat{f}'$.

From the relation,

$$\hat{v} = \frac{\hat{f}'}{im\omega + \zeta} \tag{88}$$

the power spectrum can be obtained,

$$J_v(\omega) = |\hat{v}|^2 = \frac{|\hat{f}'|^2}{|im\omega + \zeta|^2} = \frac{J_{f'}(\omega)}{|im\omega + \zeta|^2}. \tag{89}$$

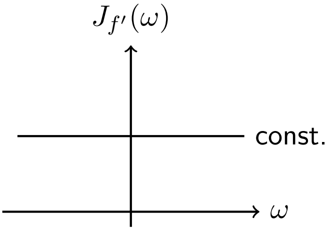
Exercise 18 : Using

$$J_v(\omega) = \frac{2k_B T}{\zeta} \frac{1}{1 + \omega^2 \tau_c^2}, \tag{90}$$

calculate $J_{f'}(\omega)$.

White spectrum

$$J_{f'}(\omega) = 2\zeta k_B T \tag{91}$$

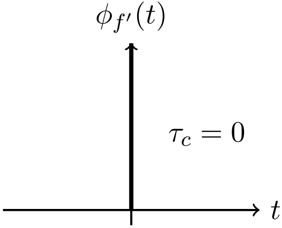


It is also called white noise.

Exercise 19 : Calculate the correlation function, $\langle f'(0) f'(t) \rangle$, using the definition of δ function,

$$\delta(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{e}^{i\omega t} d\omega \tag{92}$$

$$\left\langle f'(0)f'(t)\right\rangle = 2\zeta k_B T\delta(t) \tag{93}$$

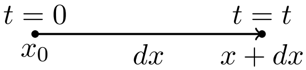


$\tau_c = 0$ No correlation except $t = 0$.

Outline

Transition probability

Let's consider the transition probability, $P(x, t|x_0)dx$.



Initial condition:

$$P(x, 0|x_0) = \delta(x - x_0) \tag{94}$$

Markov process

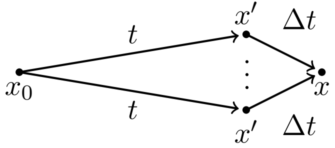
The Markov process:

If each step of a random process depends only on the state a step ago, the process is the Markov process.

Then,

$$P(x, t + \Delta t | x_0) = \int_{-\infty}^{\infty} P(x, \Delta t | x') P(x', t | x_0) dx', \qquad (95)$$

which is called Chapman-Kolmogorov equation.



Kramers-Moyal expansion

When $\Delta t \ll 1$, the left-hand side of Eq. (95) can be expanded,

$$P(x,t|x_0) + \frac{\partial P}{\partial t}\Delta t = \int_{-\infty}^{\infty} P(x,\Delta t|x-\Delta x)P(x-\Delta x,t|x_0)d\Delta x, \tag{96}$$

with a change of variables, $\Delta x = x - x'$, where $\Delta x \ll 1$ for $\Delta t \ll 1$.

Expansion of $P(x, \Delta t|x - \Delta x)P(x - \Delta x, t|x_0)$ around $x + \Delta x$ yields,

$$P(x, \Delta t|x - \Delta x)P(x - \Delta x, t|x_0) = \sum_{n=0}^{\infty} \frac{(-\Delta x)^n}{n!} \frac{\partial^n}{\partial x^n} P(x + \Delta x, \Delta t|x)P(x, t|x_0) \tag{97}$$

Exercise 20 : Confirm Eq. (97).

$$\therefore\ P(x,t|x_0) + \frac{\partial P}{\partial t}\Delta t = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} P(x,t|x_0) \int_{-\infty}^{\infty} (\Delta x)^n P(x+\Delta x, \Delta t|x) d\Delta x.$$

At $n = 0$,

$$P(x,t|x_0) \underbrace{\int_{-\infty}^{\infty} P(x+\Delta x, \Delta t|x) d\Delta x}_{=1} = P(x,t|x_0). \qquad (98)$$

Then,

$$\frac{\partial P}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} \left[\alpha_n(x) P(x, t|x_0)\right] \tag{99}$$

$$\alpha_n(x) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_{-\infty}^{\infty} (\Delta x)^n P(x + \Delta x, \Delta t|x) d\Delta x \tag{100}$$

$$= \lim_{\Delta t \to 0} \frac{\langle (\Delta x)^n \rangle}{\Delta t} \tag{101}$$

$\langle (\Delta x)^n \rangle \cdots$ nth moment of Δx.

This is called Kramers-Moyal expansion.

Exercise 21 : Confirm Eq. (99).

Fokker-Planck equation

When a change of x is induced by many random events (such as diffusion), $P(x,t|x_0)$ becomes Gaussian for the central limit theorem. Then

$$\alpha_n = 0 \ (n \geq 3). \tag{102}$$

Then

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}(\alpha_1 P) + \frac{1}{2}\frac{\partial^2}{\partial x^2}(\alpha_2 P). \tag{103}$$

Simplified a lot!

1st and 2nd moment

Calculate α_1, α_2 using the Langevin equation:

$$m\frac{d^2x}{dt^2} + \zeta\frac{dx}{dt} = F(x,t) + f'(t). \tag{104}$$

Assuming (inertia) $\ll$ (viscous resistance),

$$\frac{dx}{dt} = \frac{1}{\zeta}F(x,t) + \frac{1}{\zeta}f'(t). \tag{105}$$

Then integrate both sides,

$$\underbrace{\int_t^{t+\Delta t}\frac{dx}{dt}dt'}_{A} = \frac{1}{\zeta}\underbrace{\int_t^{t+\Delta t}F(x,t')dt'}_{B} + \frac{1}{\zeta}\int_t^{t+\Delta t}f'(t')dt'. \tag{106}$$

$$\therefore \quad \mathsf{A} = x(t+\Delta t) - x(t) = \Delta x \tag{107}$$

$$\mathsf{B} = \frac{1}{\zeta} F(x,t)\Delta t. \tag{108}$$

(assuming $F(x,t)$ is slowly changing.)

Then

$$\Delta x = \frac{1}{\zeta} F(x,t)\Delta t + \frac{1}{\zeta}\int_t^{t+\Delta t} f'(t')dt'. \tag{109}$$

Exercise 22 : Calculate α_1 and α_2 using Eq. (109).

$$\alpha_1 = \frac{F(x,t)}{\zeta} \tag{110}$$

$$\alpha_2 = \frac{2k_B T}{\zeta}. \tag{111}$$

Then with $P = P(x, t|x_0)$,

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left(\frac{F}{\zeta}P\right) + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left(\frac{2k_B T}{\zeta}P\right). \tag{112}$$

Using the Einstein relation,

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial P}{\partial x} - \frac{F}{k_B T}P\right). \tag{113}$$

This is called the Fokker-Planck equation.

Exercise 23 : Confirm Eq. (113).

Diffusion equation

Let

$$\rho(x,t)dx \;\; : \text{Probability to find a particle at } x \sim x+dx \text{ at } t, \tag{114}$$

then $\rho(x,t)$ is the normalized density, and

$$\rho(x,t) = \int_{-\infty}^{\infty} P(x,t|x_0)\rho(x_0,0)dx_0 \tag{115}$$

where $\rho(x_0,0)$ is the initial density.Time derivative yields,

$$\frac{\partial \rho}{\partial t} = \int_{-\infty}^{\infty} \frac{\partial P}{\partial t}\rho(x_0,0)dx_0 \tag{116}$$

Exercise 24 : Substitute the Fokker-Planck equation and simplify Eq. (116).

Answer:

$$\frac{\partial \rho}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial \rho}{\partial x} - \frac{F}{k_B T}\rho\right) \tag{117}$$

Thus ρ itself is the Fokker-Planck equation. This is called diffusion equation.

Flux

The flux, j, is defined as

$$\frac{\partial \rho}{\partial t} = -\frac{\partial j}{\partial x}. \tag{118}$$

This is called Continuity equation. Using j, the diffusion equation is rewritten as

$$j = \frac{\rho}{\zeta}\left(-k_B T \frac{\partial \ln \rho}{\partial x} \ + \ F\right). \tag{119}$$

Diffusion force External force

Thus, the flux is proportional to (density)×(force).

Exercise 25 : Confirm Eq. (119).

If F is a potential force,

$$F = -\frac{\partial U}{\partial x} \tag{120}$$

with the potential U. Then

$$j = -\frac{\rho}{\zeta}\frac{\partial}{\partial x}\left(U + k_B T \ln \rho\right), \tag{121}$$

where

$$\mu = U + k_B T \ln \rho \tag{122}$$

is the chemical potential. Thus the flux is proportial to the chemical potential gradient.

Exercise 26 : Confirm Eq. (121).

Stationary state

When $U(x,t) = U(x)$, the stationary state $(\partial\rho/\partial t = 0)$ is given by

$$\frac{\partial \rho}{\partial x} + \frac{\rho}{k_B T}\frac{\partial U}{\partial x} = 0. \tag{123}$$

Exercise 27 : Solve Eq. (123) to calculate the stationary density distribution $\rho(x)$.

Answer:

$$\rho \propto \exp\left(-\frac{U}{k_B T}\right) \tag{124}$$

Then

$$j = -\frac{\rho}{\zeta}\frac{\partial}{\partial x}\left(U + k_B T \ln \rho\right) = 0. \tag{125}$$

Thus there is no flux in the stationary state.