Mathematical Statistics

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http://ishiken.free.fr/lecture.html

Oct. 18 Combination and probability
Oct. 25 Random variables and probability distributions
Nov. 1 Representative probability distributions
Nov. 8 (First half) Random walk and gambler's ruin problem
(Latter half) Brownian motion and diffusion
Nov. 22 Noise theory

Stochastic process

Only exercises are provided on Nov. 15.

Reference books

[1] Satsuma, J. (2001). *“Probability /Statistics”* -- *Beginning course of mathematics of science and technology 7*, Iwanami Shoten

[2] Kolmogorov, A.N., Žurbenko, I. G., Prokhorov, A.V. (2003). *“Beginning of Kolmogorov’s Probability Theory”.* (Trans. Murayama , T. & Baba, Y.): Morikita Shuppan

[3] Kitahara, K. (1997). *“Nonequilibrium Statistical Mechanics” – Iwanami Fundamental Physics Series 8*, Iwanami Shoten

Mathematical Statistics

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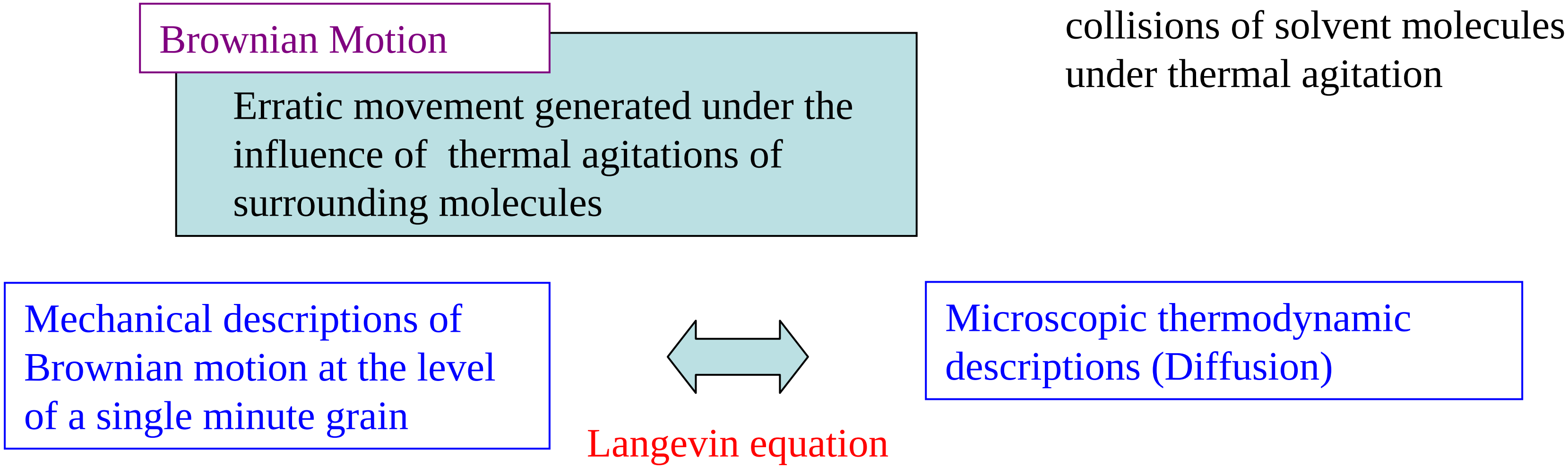
Nov. 8 (Latter half) Brownian motion and diffusion

- Autocorrelation function
- Langevin equation

5-1 Brownian Motion

- Robert Brown, English botanist, 1827
  - Observed pollen grains suspended in water performing an erratic movement under a microscope.

Movement in response to collisions of solvent molecules under thermal agitation



Brownian Motion

Erratic movement generated under the influence of thermal agitations of surrounding molecules

Mechanical descriptions of Brownian motion at the level of a single minute grain

Microscopic thermodynamic descriptions (Diffusion)

Langevin equation

Autocorrelation Function

- Generally, the random variable $x(t)$ takes each different value; $x(t)$ and $x(t+t)$, at each different time; t *and* $t+t$ in most cases.
  - $t \rightarrow 0$: $x(t)$ and $x(t+t)$ are the values approximate to one another.
  - $t \rightarrow$ Infinite: $x(t)$ and $x(t+t)$ completely independent of each another.
- Correlation between successive events → Depends on time interval t

⇨ Autocorrelation Function

$$G(\tau)=\langle x(t)x(t+\tau)\rangle=\lim_{T\to\infty}\frac{1}{T}\int_0^T x(t)x(t+\tau)dt$$

Time average

4-3 Random Walk And Diffusion

- Random walk and diffusion phenomenon

$$P(t,x)=\sqrt{\frac{1}{4\pi Dt}}\exp\left[-\frac{x^2}{4Dt}\right]$$

Fluctuation-dissipation theorem

Fluctuation (in equilibrium)

Dissipation/
Transportation]

$$D=\frac{l^2}{2\tau} \Rightarrow \left\langle x^2\right\rangle = 2Dt$$

Variance of position σ_x^2

- Initial Conditions
  - What will concentration distribution be at $t = 0$?

$$\left.\begin{array}{l} \int_{-\infty}^{\infty} P(t,x)dx = 1 \\ x\neq 0 \Rightarrow P(t\to +0,x)=0 \\ x=0 \Rightarrow P(t\to +0,x=0)=\infty \end{array}\right\}$$

Dirac’s delta function

$$\delta(x)=\lim_{t\to +0}\sqrt{\frac{1}{4\pi Dt}}\exp\left[-\frac{x^2}{4Dt}\right]$$

⇨ Distribution concentrating on $x = 0$

Random walk is one model of one-dimensional

diffusion equation $\frac{\partial P}{\partial t}=D\frac{\partial^2 P}{\partial x^2}$ $P(t=0,x)=\delta(x)$

5-2 Langevin Equation

→ Reference book [3], p.90

- Equation of motion of fine particles in a solvent
  - Introducing stochastic force → Langevin equation

$$m\frac{d^2\mathbf{x}}{dt^2}=\mathbf{F} \qquad \mathbf{F}=-m\gamma\frac{d\mathbf{x}}{dt}+\mathbf{R}(t)$$

Viscous resistance force

Random Force

$$\langle\mathbf{R}(t)\rangle=0$$

$$\langle R_\alpha(t)R_\beta(t')\rangle\propto\delta_{\alpha\beta}\delta(t-t')$$

Random forces are not correlated with each other, if:

- Directional elements are different,
- Time elements are different.

Also the random force differs depending on each fine particle.

$$m\frac{d\mathbf{u}}{dt}=\mathbf{F} \qquad \mathbf{F}=-m\gamma\mathbf{u}+\mathbf{R}(t)$$

$$\Downarrow$$

Averaged, in regard to fine particles

$$m\frac{d}{dt}\langle\mathbf{u}\rangle=-m\gamma\langle\mathbf{u}\rangle$$

5-2 Langevin Equation

- Relation with diffusion coefficient

$$m\frac{d^2\mathbf{x}}{dt^2} = -m\gamma\frac{d\mathbf{x}}{dt} + \mathbf{R}(t)$$

Consider by focusing on element *x* only.

$$m\frac{d^2x}{dt^2} = -m\gamma\frac{dx}{dt} + R(t)$$

Multiply both sides by *x*.

$$mx\frac{d^2x}{dt^2} = -m\gamma x\frac{dx}{dt} + xR(t)$$

Averaged, in regard to time average or fine particles

$$m\left\langle x\frac{d^2x}{dt^2}\right\rangle = -m\gamma\left\langle x\frac{dx}{dt}\right\rangle$$

$$x\frac{dx}{dt} = \frac{1}{2}\frac{d\left(x^2\right)}{dt} \Rightarrow x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2\left(x^2\right)}{dt^2} - \left(\frac{dx}{dt}\right)^2$$

At a temperature *T*; $\frac{1}{2}m\left\langle\left(\frac{dx}{dt}\right)^2\right\rangle = \frac{kT}{2}$

$$\frac{1}{2}m\frac{d^2\left\langle x^2\right\rangle}{dt^2} - kT = -\frac{1}{2}m\gamma\frac{d\left\langle x^2\right\rangle}{dt}$$

5-2 Langevin Equation

- Relation with diffusion coefficient

$$\frac{1}{2}m\frac{d^2\langle x^2\rangle}{dt^2} - kT = -\frac{1}{2}m\gamma\frac{d\langle x^2\rangle}{dt} \qquad f = \frac{d\langle x^2\rangle}{dt}$$

$$\frac{1}{2}m\frac{df}{dt} - kT = -\frac{1}{2}m\gamma f \Rightarrow \frac{df}{dt} + \gamma f - \frac{2kT}{m} = 0$$

$$\Rightarrow f = \frac{2kT}{m\gamma}\left(1 - e^{-\gamma t}\right) \Rightarrow \langle x^2\rangle = \frac{2kT}{m\gamma^2}\left(\gamma t + e^{-\gamma t} - 1\right)$$

Attenuated on a 10^{-13} sec - basis

If we take t large enough, then; $\langle x^2\rangle = \dfrac{2kT}{m\gamma}t$

According to diffusion equation; $\langle x^2\rangle = 2Dt$

Einstein’s relation, 1905 $D = \dfrac{kT}{m\gamma}$

Boltzmann constant k can be fixed through measurement of macroscopic quantum.

5-2 Langevin Equation

- Summary: Equation of motion of fine particles in a solvent
  - Introducing stochastic force → Langevin Equation

$$m\frac{d^2\mathbf{x}}{dt^2} = \mathbf{F} \qquad \mathbf{F} = -m\gamma\frac{d\mathbf{x}}{dt} + \mathbf{R}(t)$$

Viscous resistance force

Random Force

$$\langle \mathbf{R}(t) \rangle = 0$$

$$\langle R_\alpha(t) R_\beta(t') \rangle \propto \delta_{\alpha\beta}\delta(t-t')$$

Random forces are not correlated with each other, if:

- Directional elements are different,
- Time elements are different.

Also the random force differs depending on each fine particle.

$$\langle x^2 \rangle = \frac{2kT}{m\gamma}t + \frac{2kT}{m\gamma^2}\left(e^{-\gamma t} - 1\right)$$

Attenuated on a 10^{-13} sec basis

If we take t large enough, then; $\langle x^2 \rangle = \frac{2kT}{m\gamma}t$

According to diffusion equation,

$$\langle x^2 \rangle = 2Dt$$

Einstein's relation, 1905 $D = \frac{kT}{m\gamma}$

The Special Theory of Relativity and the Light Quantum Hypothesis were also published in the same year !

5-3 Representation based on velocity correlation function

→ Reference book [3], p. 95

Velocity Correlation Function $\phi(\tau) = \langle u(t_1)u(t_2)\rangle == \langle u(t_1)u(t_1+\tau)\rangle$

Average of large amount of fine particles

Mean square displacement of particles

If we take t large enough; $\langle x^2 \rangle = 2Dt$

⇨ Regard $D = \lim_{t\to\infty} \frac{1}{2t}\langle x^2\rangle$ as the definition of diffusion constant.

$$x = \int_0^t u(t')dt' \quad ⇨ \quad D = \lim_{t\to\infty}\frac{1}{2t}\int_0^t dt_1 \int_0^t dt_2 \langle u(t_1)u(t_2)\rangle$$

Diffusion coefficient is represented as the time integration of velocity correlation function.

$\langle u(t_1)u(t_2)\rangle$ in equilibrium serves as a function of time difference only. ⇨ $\phi(t_1 - t_2) = \langle u(t_1)u(t_2)\rangle$

$$D = \lim_{t\to\infty}\frac{1}{2t}\int_0^t dt_1 \int_0^t dt_2 \phi(t_1 - t_2)$$

5-3 Representation based on velocity correlation function

$$D = \lim_{t\to\infty} \frac{1}{2t} \int_0^t dt_1 \int_0^t dt_2 \phi(t_1 - t_2) \quad \Longrightarrow \quad D = \lim_{t\to\infty} \int_0^t \left(1 - \frac{\tau}{t}\right) \phi(\tau) d\tau$$

[Proof]

$$\begin{aligned}
\int_0^t dt_1 \int_0^t dt_1 \phi(t_1 - t_2) &= \int_0^t dt_1 \int_0^{t_1} dt_2 \phi(t_1 - t_2) + \int_0^t dt_1 \int_{t_1}^t dt_2 \phi(t_1 - t_2) \\
&= \int_0^t dt_1 \int_0^{t_1} dt_2 \phi(t_1 - t_2) + \int_0^t dt_2 \int_0^{t_2} dt_1 \phi(t_1 - t_2) \\
&= \int_0^t dt_1 \int_0^{t_1} dt_2 \phi(t_1 - t_2) + \int_0^t dt_1 \int_0^{t_1} dt_2 \phi(t_2 - t_1) \\
&= \int_0^t dt_1 \int_0^{t_1} d\tau [\phi(\tau) + \phi(-\tau)] = 2 \int_0^t dt_1 \int_0^{t_1} d\tau \phi(\tau) \\
&= 2 \int_0^t d\tau \int_\tau^t dt_1 \phi(\tau) = 2 \int_0^t (t - \tau) \phi(\tau) d\tau
\end{aligned}$$

$$\tau = t_1 - t_2$$

$$\phi(-\tau) = \phi(\tau)$$

$$\therefore\ D = \lim_{t\to\infty} \int_0^t \left(1 - \frac{\tau}{t}\right) \phi(\tau) d\tau$$

If $\phi(\tau)$ is a rapidly decaying function, then;

$$\boxed{D = \int_0^\infty \phi(\tau) d\tau}$$

5-3 Representation based on velocity correlation function

$$\phi(\tau)=\langle u(t_1)u(t_2)\rangle==\langle u(t_1)u(t_1+\tau)\rangle$$ Velocity Correlation Function

If $\phi(\tau)$ is a rapidly decaying function, then:

$$\boxed{D=\int_0^\infty \phi(\tau)d\tau}$$

Diffusion coefficient is a coefficient obtained by integrating velocity correlation function.

$$\phi(\tau)=\frac{k_BT}{m}e^{-\tau/\tau_c}$$ τ_c : Correlation Time

$$\Rightarrow \quad D=\frac{k_BT}{m}\tau_c$$

Einstein’s relation, 1905 $$D=\frac{k_BT}{m\gamma}$$

$$\Rightarrow$$

Correlation Time $\tau_c=\gamma^{-1}$ Resistance Coefficient