Part 5 The theory of Brownian motion

Typical experiment

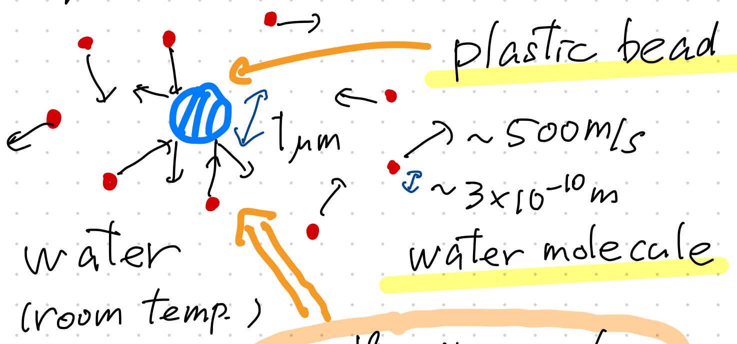
Basic symmetry and the transition probability

Kramers equation

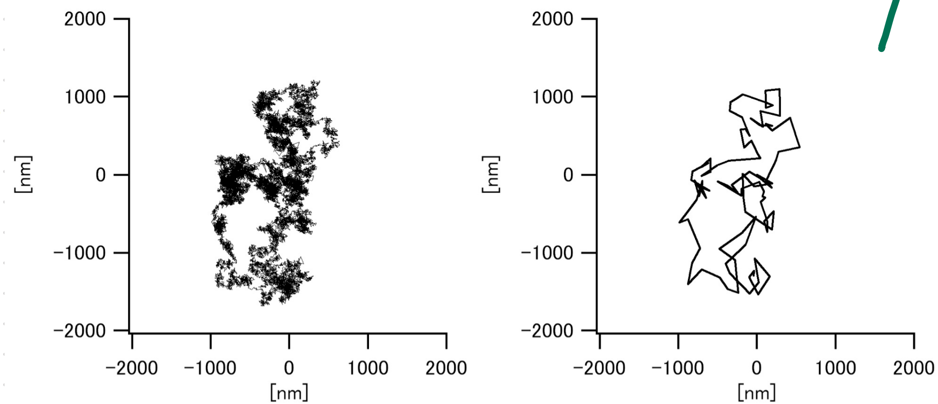
Langevin equation

Einstein’s theory of Brownian motion

§ Typical experiment

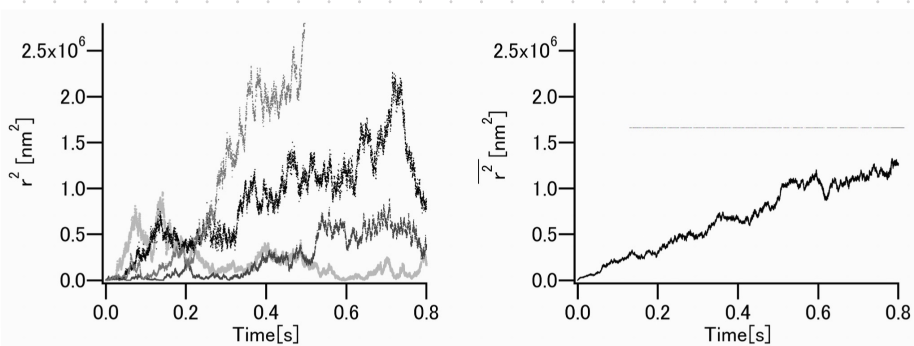


$\sim 10^{19}$ collisions/sec



the bead exhibits a random motion observable by an optical microscope.

Brownian motion



peculiar behavior

$\begin{pmatrix}\text{displacement} \\ \text{of the bead}\end{pmatrix}^2 \propto \text{time}$

(experimental data by Takayuki Nishizaka)

§ basic symmetry and the transition probability → part 1 - p29 ~ 2

■ setting

$X = (\mathbb{r}, \mathbb{p}, X_w)$

$\mathbb{r}, \mathbb{p}$ the position and momentum of the bead

$\mathbb{r} \in \Lambda \subset \mathbb{R}^d, \quad \mathbb{p} \in \mathbb{R}^d \qquad (d = 1, 2, 3)$

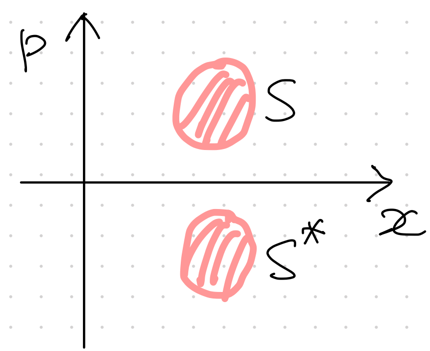
$X_w = (\mathbb{r}_1, \cdots, \mathbb{r}_N; \mathbb{p}_1, \cdots, \mathbb{p}_N)$ describes water molecules

Hamiltonian (1) $H(X) = \dfrac{\mathbb{p}^2}{2m} + V(\mathbb{r}) + H_w(X_w) + H_{int}(\mathbb{r}, X_w)$

assume (2) $H(X^*) = H(X)$

S arbitrary finite region in the phase space $\Lambda \times \mathbb{R}^d$ of the bead

time-reversal (3) $S^* = \{(\mathbb{r}, -\mathbb{p}) \mid (\mathbb{r}, \mathbb{p}) \in S\}$

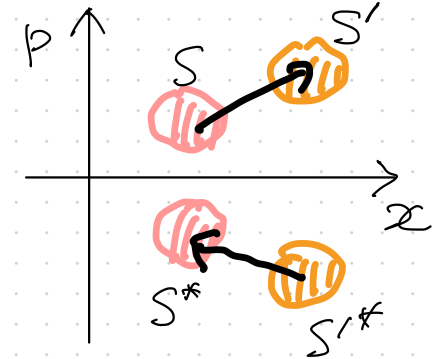


(4) $$\chi_S(X) = \begin{cases} 1 & (\mathbb{r}, \mathbb{p}) \in S \\ 0 & (\mathbb{r}, \mathbb{p}) \notin S \end{cases}$$

detailed balance condition

restricted partition function

(1) $$Z_S(\beta) = \int dX\, e^{-\beta H(X)} \chi_S(X)$$



for $\tau > 0$ and two regions $S, S' \subset \Lambda \times \mathbb{R}^d$

(2) $$p^{(\tau)}(S \to S') := \int dX\, \frac{e^{-\beta H(X)}}{Z_S(\beta)} \chi_S[X]\, \chi_{S'}[\mathcal{J}_\tau(X)]$$

the probability that the state of the bead is in S' at $t = \tau$ when the whole system is initially in equlibrium with the constraint that the state of the bead in S

by repeating the derivation in part 1-p32, we get

detailed balance condition

(3) $$\boxed{Z_S(\beta)\, p^{(\tau)}(S \to S') = Z_{S'}(\beta)\, p^{(\tau)}(S'^* \to S^*)}$$

▷ transition probability in the short time scale

τ small $\rightarrow$ $\begin{cases} \text{essentially no changes in } \mathbf{r} \\ \text{only } \mathbf{p} \text{ changes because of collisions} \end{cases}$

S small region including $(\mathbf{r}, \mathbf{p})$, S' small region including $(\mathbf{r}, \mathbf{p}')$

(1) $$\frac{Z_S(\beta)}{Z_{S'}(\beta)} = e^{-\beta\left\{\frac{|\mathbf{p}|^2}{2m} - \frac{|\mathbf{p}'|^2}{2m}\right\}}$$

(2) $$e^{-\frac{\beta}{2m}|\mathbf{p}|^2}\, p^{(\tau)}(S \to S') = e^{-\frac{\beta}{2m}|\mathbf{p}'|^2}\, p^{(\tau)}(S'^* \to S^*)$$

simple exponential form (3) $$p^{(\tau)}(S \to S') = A\, e^{\alpha \frac{\beta|\mathbf{p}|^2}{2m} - (1-\alpha)\frac{\beta|\mathbf{p}'|^2}{2m}}$$

set $\boxed{\alpha = \frac{1}{2}}$ "independent of $\mathbf{p}$ when $\mathbf{p} = \mathbf{p}'$ only if $\alpha = 1/2$"

plausible form

(4) $$p^{(\tau)}(S \to S') = A\, e^{\frac{\beta}{4m}\{|\mathbf{p}|^2 - |\mathbf{p}'|^2\}} = \boxed{A\, e^{\frac{\beta m}{4}\{|\mathbf{v}|^2 - |\mathbf{v}'|^2\}}}$$

§ Kramerse equation

Corresponding stochastic process

$\mathbb{P} = m v$

determines the time evolution of the probability density $P(\mathbb{r}, v, t)$

the position and the velocity of the bead

Cosider the d=1 case for simplicity (x, v)

⚠ the effect of collisions

→ we only focus on the prob. density for v

one gets the same result from more complicated models

discretized version $v = j\delta$, $t = n\varepsilon$ $\quad j, n \in \mathbb{Z}$

$P_v(t)$ the probability that the velocity is v at time t

as $t \to t+\varepsilon$ the velocity may change by $\pm\delta$ ← the simplest model

the transition probability $p(v \to v \pm \delta)$ ⇐ the same as $p^{(\tau)}(S \to S')$

master equation (part 2 p.29)

$$(1) \quad P_v(t+\varepsilon) - P_v(t) = -\{p(v \to v+\delta) + p(v \to v-\delta)\} P_v(t)$$
$$+ p(v+\delta \to v) P_{v+\delta}(t) + p(v-\delta \to v) P_{v-\delta}(t)$$

from P4-(4)

(1) $P(v \to v \pm \delta) = A\, e^{\frac{\beta m}{4}\{v^2 - (v \pm \delta)^2\}} = A\, e^{\frac{\beta m}{4}\{\mp 2v\delta - \delta^2\}}$

$$= A\left\{1 \mp \frac{\beta m v}{2}\delta - \frac{\beta m}{4}\delta^2 + \boxed{\frac{(\beta m v)^2}{8}\delta^2} + O(\delta^3)\right\}$$

(2) $P(v \pm \delta \to v) = A\left\{1 \pm \frac{\beta m v}{2}\delta + \frac{\beta m}{4}\delta^2 + \boxed{\frac{(\beta m v)^2}{8}\delta^2} + O(\delta^3)\right\}$

(can be neglected because this always has the same sign as 1)

substitute these into P5-(1)

(3) $\underbrace{P_v(t+\varepsilon) - P_v(t)}_{\varepsilon \dot{P}} = A\Big[-2\left(1 - \frac{\beta m}{4}\delta^2\right)P_v(t)$

$$+ \left(1 + \frac{\beta m v}{2}\delta + \frac{\beta m}{4}\delta^2\right)P_{v+\delta}(t) + \left(1 - \frac{\beta m v}{2}\delta + \frac{\beta m}{4}\delta^2\right)P_{v-\delta}(t)\Big]$$

$$= A\Big[\underbrace{\{P_{v+\delta}(t) + P_{v-\delta}(t) - 2P_v(t)\}}_{\delta^2 P''} + \frac{\beta m v}{2}\delta\underbrace{\{P_{v+\delta}(t) - P_{v-\delta}(t)\}}_{2\delta P'}$$

$$+ \frac{\beta m}{4}\delta^2\underbrace{\{2P_v(t) + P_{v+\delta}(t) + P_{v-\delta}(t)\}}_{4P + O(\delta)}\Big]$$

(4) $\boxed{A = \text{const}\,\frac{\varepsilon}{\delta^2}}$

write (1) $A = \dfrac{\gamma}{m^2\beta}\dfrac{\varepsilon}{\delta^2}$

this expression will be justified in p16-(2)

p6-(3) becomes

$$(2)\quad \frac{P_v(t+\varepsilon)-P_v(t)}{\varepsilon} = \frac{\gamma}{m^2\beta}\frac{1}{\delta^2}\{P_{v+\delta}(t)+P_{v-\delta}(t)-2P_v(t)\}$$

$$+\frac{\gamma}{m}v\frac{1}{2\delta}\{P_{v+\delta}(t)-P_{v-\delta}(t)\}+\frac{\gamma}{m}\{P_v(t)+O(\delta)\}$$

continuum limit $\varepsilon, \delta \to 0$ (3) $\dfrac{P_v(t)}{\delta} \to P(v,t)$ = probability density

$$(4)\quad \frac{\partial}{\partial t}P(v,t) = \frac{\gamma}{m^2\beta}\frac{\partial^2}{\partial v^2}P(v,t)+\frac{\gamma}{m}v\frac{\partial}{\partial v}P(v,t)+\frac{\gamma}{m}P(v,t)$$

$$= \frac{\gamma}{m^2\beta}\frac{\partial^2}{\partial v^2}P(v,t)+\frac{\gamma}{m}\frac{\partial}{\partial v}\{v\,P(v,t)\}$$

⑩ the final form

the change in $P(x,v,t)$ due to the Hamiltonian dynamics is described by Liouville's equation → part 1-p12-(6)

(1) $$\frac{\partial}{\partial t}P(x,v,t) = -v\frac{\partial}{\partial x}P(x,v,t) - \frac{f(x)}{m}\frac{\partial}{\partial v}P(x,v,t)$$

((2) $f(x) = -\dfrac{\partial V(x)}{\partial x}$ for the potential force)

(1) + p7-(4)

the Kramers equation

(3) $$\boxed{\frac{\partial}{\partial t}P(x,v,t) = -v\frac{\partial}{\partial x}P(x,v,t) - \frac{f(x)}{m}\frac{\partial}{\partial v}P(x,v,t) + \frac{\gamma}{m^2\beta}\frac{\partial^2}{\partial v^2}P(x,v,t) + \frac{\gamma}{m}\frac{\partial}{\partial v}\{v\,P(x,v,t)\}}$$

(for $d=3$

(4) $$\frac{\partial}{\partial t}P(\mathbf{r},\mathbf{v},t) = -\mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}}P(\mathbf{r},\mathbf{v},t) - \frac{\mathbf{f}(\mathbf{r})}{m}\cdot\frac{\partial}{\partial \mathbf{v}}P(\mathbf{r},\mathbf{v},t) + \frac{\gamma}{m^2\beta}\Delta_{\mathbf{v}}P(\mathbf{r},\mathbf{v},t) + \frac{\gamma}{m}\frac{\partial}{\partial \mathbf{v}}\cdot\{\mathbf{v}\,P(\mathbf{r},\mathbf{v},t)\}$$)

§ Langevin equation

what is the equation of motion that corresponds to the Kramers equation?

Liouville's equation

$$(1)\quad \frac{\partial}{\partial t}P(x,v,t) = \boxed{-v\frac{\partial}{\partial x}P(x,v,t) - \frac{f(x)}{m}\frac{\partial}{\partial v}P(x,v,t)}$$

$$\boxed{+\frac{\gamma}{m}\frac{\partial}{\partial v}\{vP(x,v,t)\} + \frac{\gamma}{m^2\beta}\frac{\partial^2}{\partial v^2}P(x,v,t)}$$

the effect of collisions

leads to $\begin{cases} \text{deterministic resistance} \\ \text{random force} \end{cases}$

Newton's equations

$$(2)\quad \dot{x} = v$$

$$(3)\quad m\dot{v} = f$$

This too

- resisted motion

$$(4)\quad m\dot{v} = -\gamma v$$

- diffusion-like behavior

$$(5)\quad m\dot{v} = \xi$$

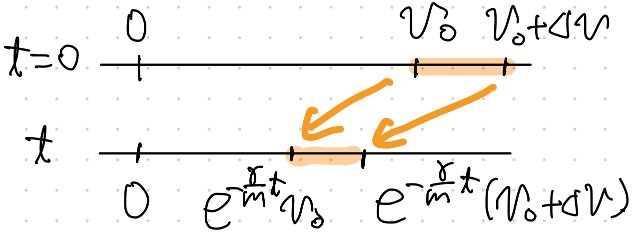
random force

(diffusion equation

$$(6)\quad \frac{\partial}{\partial t}f(t,x) = D\frac{\partial^2}{\partial x^2}f(t,x)$$
)

ii resisted motion

$$(1)\quad m\dot{v}(t) = -\gamma v(t) \longrightarrow (2)\quad v(t) = e^{-\frac{\gamma}{m}t}v(0)$$



probability conservation

$$(3)\quad P(v_0,0)\,\Delta v = \underbrace{P\left(e^{-\frac{\gamma}{m}t}v_0,\ t\right)e^{-\frac{\gamma}{m}t}}_{=(*)}\,\Delta v$$

$$(4)\quad \frac{\partial}{\partial t}(*) = \left[-\frac{\gamma}{m}v\frac{\partial}{\partial v}P(v,t)\,e^{-\frac{\gamma}{m}t} + \frac{\partial}{\partial t}P(v,t)\,e^{-\frac{\gamma}{m}t} - \frac{\gamma}{m}P(v,t)\,e^{-\frac{\gamma}{m}t}\right]_{v\to e^{-\frac{\gamma}{m}t}v_0} = 0$$

$\therefore$

$$(5)\quad \frac{\partial}{\partial t}P(v,t) = \frac{\gamma}{m}\frac{\partial}{\partial v}\{v\,P(v,t)\}$$

we get the desired equation

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(iii) random force

discrete time (1) $t = n\varepsilon \quad (n \in \mathbb{Z}) \qquad (\varepsilon > 0)$

- difference equation

(2) $m \dfrac{\hat{v}(t+\varepsilon) - \hat{v}(t)}{\varepsilon} = \hat{\xi}_t^{(\varepsilon)} \iff$ (3) $\hat{v}(t+\varepsilon) = \hat{v}(t) + \dfrac{\varepsilon}{m} \hat{\xi}_t^{(\varepsilon)}$

$\hat{\xi}_t^{(\varepsilon)}$: random variable for each $t = n\varepsilon \ (n \in \mathbb{Z})$

$\hat{\xi}_t^{(\varepsilon)}$ and $\hat{\xi}_{t'}^{(\varepsilon)}$ are independent if $t \neq t'$

the probability density that $\hat{\xi}_t^{(\varepsilon)}$ takes value $\xi \in \mathbb{R}$ (4) $\tilde{P}_\varepsilon(\xi) = \sqrt{\dfrac{\beta\varepsilon}{4\pi\gamma}}\, e^{-\frac{\beta\varepsilon}{4\gamma}\xi^2}$

(5) $\int d\xi\, \tilde{P}_\varepsilon(\xi) = 1$ (6) $\int d\xi\, \xi\, \tilde{P}_\varepsilon(\xi) = 0$ (7) $\int d\xi\, \xi^2\, \tilde{P}_\varepsilon(\xi) = \dfrac{2\gamma}{\beta\varepsilon}$

we thus have (8) $\langle\langle \hat{\xi}_{n\varepsilon}^{(\varepsilon)} \hat{\xi}_{m\varepsilon}^{(\varepsilon)} \rangle\rangle = \dfrac{2\gamma}{\beta\varepsilon} \delta_{n,m}, \quad \langle\langle \hat{\xi}_{n\varepsilon}^{(\varepsilon)} \rangle\rangle = 0$

- master equation

(1) $P(v,t+\varepsilon) - P(v,t)$

$$= -P(v,t)\overbrace{\left\{\int_{-\infty}^{\infty} d\xi\, \tilde{P}_\varepsilon(\xi)\right\}}^{1} + \int_{-\infty}^{\infty} d\xi\, P\left(v - \frac{\varepsilon}{m}\xi, t\right) \tilde{P}_\varepsilon(\xi)$$

$$\simeq \int_{-\infty}^{\infty} d\xi \left\{ -P(v,t) + P\left(v - \frac{\varepsilon}{m}\xi, t\right) \right\} \tilde{P}_\varepsilon(\xi)$$

$$= \int_{-\infty}^{\infty} d\xi \left\{ -\frac{\varepsilon}{m}\xi \frac{\partial}{\partial v} P(v,t) + \frac{1}{2}\left(\frac{\varepsilon}{m}\xi\right)^2 \frac{\partial^2}{\partial v^2} P(v,t) + \cdots \right\} \tilde{P}_\varepsilon(\xi)$$

$$= \frac{1}{2}\left(\frac{\varepsilon}{m}\right)^2 \left(\frac{2\gamma}{\beta\varepsilon}\right) \frac{\partial^2}{\partial v^2} P(v,t) + o(\varepsilon)$$

(2) $$\frac{1}{\varepsilon}\left\{ P(v,t+\varepsilon) - P(v,t) \right\} = \frac{\gamma}{m^2\beta} \frac{\partial^2}{\partial v^2} P(v,t) + \frac{o(\varepsilon)}{\varepsilon}$$

letting $\varepsilon \to 0$ (3) $$\frac{\partial}{\partial t} P(v,t) = \frac{\gamma}{m^2\beta} \frac{\partial^2}{\partial v^2} P(v,t)$$

desired diffusion-type equation

- continuum limit of the equation of motion

$$(1)\quad m\,\frac{\hat{v}(t+\varepsilon)-\hat{v}(t)}{\varepsilon}=\hat{\xi}^{(\varepsilon)}_t \xrightarrow{\varepsilon\to 0} (2)\quad \boxed{m\frac{d}{dt}\hat{v}(t)=\hat{\xi}(t)}$$

$$(3)\quad \left\langle\!\left\langle \hat{\xi}^{(\varepsilon)}_{n\varepsilon}\,\hat{\xi}^{(\varepsilon)}_{m\varepsilon}\right\rangle\!\right\rangle=\frac{2\gamma}{\beta\varepsilon}\delta_{n,m} \quad\longrightarrow\quad (4)\quad \left\langle\!\left\langle \hat{\xi}(t)\,\hat{\xi}(s)\right\rangle\!\right\rangle=0 \text{ if } s\neq t$$

$$(5)\quad \sum_{m\in\mathbb{Z}}\varepsilon\left\langle\!\left\langle \hat{\xi}^{(\varepsilon)}_{n\varepsilon}\,\hat{\xi}^{(\varepsilon)}_{m\varepsilon}\right\rangle\!\right\rangle=\frac{2\gamma}{\beta} \quad\longrightarrow\quad (6)\quad \int_{-\infty}^{\infty}ds\left\langle\!\left\langle \hat{\xi}(t)\,\hat{\xi}(s)\right\rangle\!\right\rangle=\frac{2\gamma}{\beta}$$

$$(7)\quad \boxed{\left\langle\!\left\langle \hat{\xi}(t)\,\hat{\xi}(s)\right\rangle\!\right\rangle=\frac{2\gamma}{\beta}\delta(t-s)} \qquad (8)\quad \boxed{\left\langle\!\left\langle \hat{\xi}(t)\right\rangle\!\right\rangle=0}$$

(fluctuation-dissipation relation of the 2nd kind)

$\hat{\xi}(t)$ Gaussian white noise

$$(9)\quad \hat{W}^{(\varepsilon)}_t:=\sum_{n=0}^{[t/\varepsilon]}\varepsilon\,\hat{\xi}^{(\varepsilon)}_{n\varepsilon} \xrightarrow{\varepsilon\to 0} \hat{W}(t)\quad \text{Wiener process}$$

mathematically better object

Langevin equation

to sum up, the Kramerse equation

(1) $$\frac{\partial}{\partial t}P(x,v,t) = -v\frac{\partial}{\partial x}P(x,v,t) - \frac{f(x)}{m}\frac{\partial}{\partial v}P(x,v,t) - \frac{\gamma}{m^2\beta}\frac{\partial^2}{\partial v^2}P(x,v,t) + \frac{\gamma}{m}\frac{\partial}{\partial v}\{vP(x,v,t)\}$$

is equivalent to

the Lagevin equation

stochastic differential equation

(2) $$\frac{d}{dt}\hat{x}(t) = \hat{v}(t)$$

(3) $$m\frac{d}{dt}\hat{v}(t) = f(\hat{x}(t)) - \gamma\hat{v}(t) + \hat{\xi}(t)$$

(4) $$\langle\langle \hat{\xi}(t)\,\hat{\xi}(s)\rangle\rangle = \frac{2\gamma}{\beta}\delta(t-s)$$

(fluctuation-dissipation relation of the 2nd kind)

(5) $$\langle\langle \hat{\xi}(t)\rangle\rangle = 0$$

$\hat{\xi}(t)$ Gaussian white noise

§ Einstein's theory of Brownian motion

① free Brownian motion

(1) $$m\frac{d}{dt}\hat{v}(t) = -\gamma\hat{v}(t) + \hat{\xi}(t)$$

usual ODE (2) $$m\dot{v}(t) = -\gamma v(t) + f(t)$$

(3) $$v(t) = e^{-\frac{\gamma}{m}(t-t_0)}v(t_0) + \frac{1}{m}\int_{t_0}^{t} ds\, e^{-\frac{\gamma}{m}(t-s)} f(s)$$

$t_0 \to -\infty$

(4) $$v(t) = \frac{1}{m}\int_{-\infty}^{t} ds\, e^{-\frac{\gamma}{m}(t-s)} f(s)$$

formal solution of (1)

(5) $$\hat{v}(t) = \frac{1}{m}\int_{-\infty}^{t} ds\, e^{-\frac{\gamma}{m}(t-s)} \hat{\xi}(s)$$

our treatment here is mathematically not rigorous

but the results are correct

- correlation function of $\hat{v}(t)$

(1) $$\hat{v}(t) = \frac{1}{m}\int_{-\infty}^{t} ds\, e^{-\frac{\gamma}{m}(t-s)}\hat{\xi}(s)$$

(2) $$\langle\!\langle \hat{v}(t) \rangle\!\rangle = \frac{1}{m}\int_{-\infty}^{t} ds\, e^{-\frac{\gamma}{m}(t-s)}\langle\!\langle \hat{\xi}(s) \rangle\!\rangle = 0$$

$t \le t'$

(3) $$\langle\!\langle \hat{v}(t)\,\hat{v}(t') \rangle\!\rangle = \frac{1}{m^2}\int_{-\infty}^{t} ds \int_{-\infty}^{t'} ds'\, e^{-\frac{\gamma}{m}\{t+t'-(s+s')\}}\langle\!\langle \hat{\xi}(s)\,\hat{\xi}(s') \rangle\!\rangle$$

$$\langle\!\langle \hat{\xi}(s)\,\hat{\xi}(s') \rangle\!\rangle = \frac{2\gamma}{\beta}\delta(s-s')$$

$t \le t'$ is crucial

$$= \frac{1}{m^2}\frac{2\gamma}{\beta}\int_{-\infty}^{t} ds\, e^{-\frac{\gamma}{m}\{t+t'-2s\}}$$

$$= \frac{1}{m\beta} e^{-\frac{\gamma}{m}(t'-t)}$$

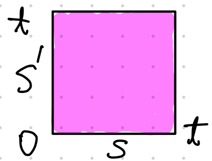
$t = t'$

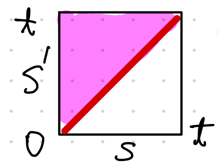
(4) $$\langle\!\langle \frac{m}{2}\{\hat{v}(t)\}^2 \rangle\!\rangle = (2\beta)^{-1} = \frac{1}{2}k_B T$$ → the choice of A in p7-(1) is justified!

- expectation value of $(\hat{x}(t)-\hat{x}(0))^2$

$t>0$ (1) $\hat{x}(t)-\hat{x}(0)=\int_0^t ds\,\hat{v}(s)$

(2) $\langle\langle \hat{x}(t)-\hat{x}(0)\rangle\rangle=\int_0^t ds\,\langle\langle \hat{v}(s)\rangle\rangle = 0$





$s'\geq s$ $\quad \frac{1}{m\beta}e^{-\frac{\gamma}{m}(s'-s)}$

$\parallel$

(3) $\langle\langle (\hat{x}(t)-\hat{x}(0))^2\rangle\rangle$

$$=\int_0^t ds\int_0^t ds'\,\langle\langle \hat{v}(s)\,\hat{v}(s')\rangle\rangle = 2\int_0^t ds\int_s^t ds'\,\langle\langle \hat{v}(s)\,\hat{v}(s')\rangle\rangle$$

$$=\frac{2}{m\beta}\int_0^t ds\int_s^t ds'\,e^{-\frac{\gamma}{m}(s'-s)}=\boxed{\frac{2}{\beta\gamma}t}-\frac{2m}{\beta\gamma^2}\left\{1-e^{-\frac{\gamma}{m}t}\right\}$$

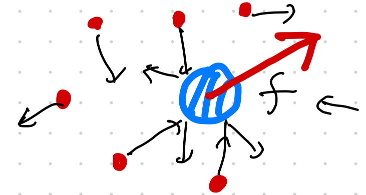
diffusion constant

(4) $\boxed{D}=\lim_{t\to\infty}\frac{1}{2t}\langle\langle (\hat{x}(t)-\hat{x}(0))^2\rangle\rangle=\boxed{\frac{1}{\beta\gamma}}$

diffusive behavior

(5) $\langle\langle (\hat{x}(t)-\hat{x}(0))^2\rangle\rangle \simeq 2Dt$

Brownian motion under a constant force



(1) $m\frac{d}{dt}\hat{v}(t) = -\gamma\hat{v}(t) + \boxed{f} + \hat{\xi}(t)$

(2) $m\frac{d}{dt}\hat{u}(t) = -\gamma\hat{u}(t) + \hat{\xi}(t)$ with (4) $\hat{u}(t) = \hat{v}(t) - \frac{f}{\gamma}$

since (4) $\langle\langle \hat{u}(t) \rangle\rangle = 0$

terminal velocity (5) $\langle\langle \hat{v}(t) \rangle\rangle = \mu f$ with moblity (6) $\mu = \frac{1}{\gamma}$

from P17-(4) Einstein's relation.

(7) $\boxed{\mu = \beta D}$ (8) $\boxed{D = k_B T \mu}$

linear response relation

(10) $L = \lim_{\tau\to\infty} \frac{1}{2t}\int_0^t\int_0^t ds\,ds' \langle\langle \hat{J}(s)\hat{J}(s') \rangle\rangle_0$

part 4-p12-(1)

(9) $\mu = \beta \lim_{t\to\infty} \frac{1}{2t}\int_0^t ds \int_0^t ds' \langle\langle \hat{v}(s)\hat{v}(s') \rangle\rangle$

▷ Einstein's relation

"count" the number of molecules by observing the Brownian motion

(1) $\boxed{D = k_B T \mu}$

(2) $k_B = \dfrac{R}{N_A}$

R: gas constant

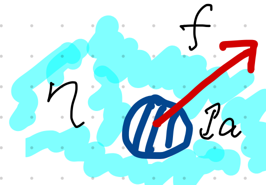
N_A: Avogadro's constant

Stokes' law (fluid dynamics)

(3) $\mu = \dfrac{1}{6\pi\eta a}$

a: radius

η: viscocity

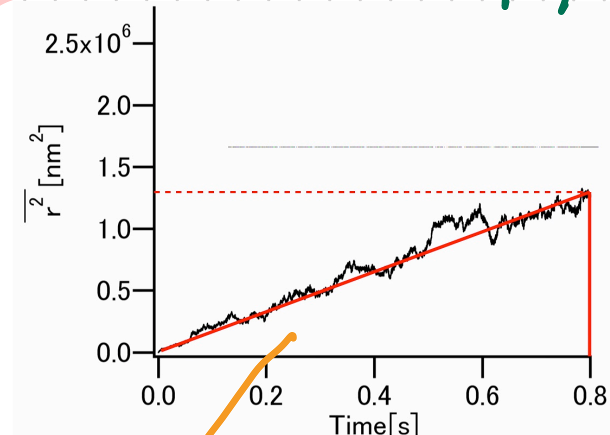


$$D = \frac{RT}{N_A}\,\frac{1}{6\pi\eta a}$$

determined by macroscopic experiments

the number of molecules

measured by a microscope



$$D \simeq \frac{1}{4}\,\frac{1.3\times10^{6}\,(\mathrm{nm})^2}{0.8\,\mathrm{s}}$$

$a \simeq 0.5\,\mu\mathrm{m}$ $(d=2)$

$R \simeq 8.3\,\dfrac{\mathrm{J}}{\mathrm{K\,mol}}$

$\eta \simeq 0.8\times10^{-3}\,\dfrac{\mathrm{kg}}{\mathrm{m\,s}}$

$T \simeq 300\mathrm{K}$

$N_A \simeq 8.1\times10^{23}\,/\mathrm{mol}$

Incomplete references

Detailed balance condition

C. Maes and K. Netocny, “Time-Reversal and Entropy”, J. Stat. Phys. **110**, 269 (2003).

Einstein’s theory of Brownian motion

A. Einstein, “The theory of the Brownian movement”, Ann. der Physik **17**, 549 (1905).

Many textbooks on nonequilibrium statistical mechanics start by talking about the Langevin equation as if it is something you understand intuitively (but I never did). Now you (and I) can read these books with confidence!