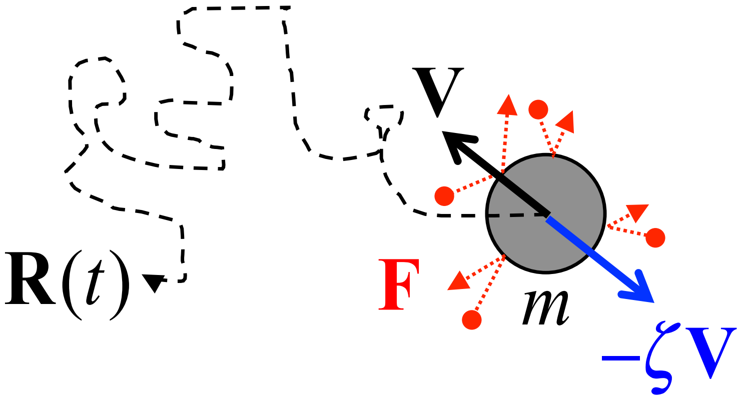
Brownian motion 1: basic theories

Brownian motion and the Langevin equation

Brownian motion and the Langevin equation

Equation of motion of a Brownian particle:

Particle radius:	a
Particle mass:	m
Solvent viscosity:	η
Friction constant:	$\zeta = 6\pi\eta a$
Particle position:	$\mathbf{R}(t)$
Particle velocity:	$\mathbf{V}(t) = d\mathbf{R}/dt$
Friction force:	$-\zeta\mathbf{V}(t)$
Random force:	$\mathbf{F}(t)$



Langevin Equation:

$$\boxed{m\frac{d\mathbf{V}}{dt} = -\zeta\mathbf{V} + \mathbf{F}} \qquad (21)$$

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Random force:

$$\mathbf{F}(t) = \left(F_x(t), F_y(t), F_z(t)\right)$$

White noise:

$$\left\langle F_\alpha(t) \right\rangle = 0 \qquad (22)$$

$$\varphi_F(t) \equiv \left\langle F_\alpha(\tau) F_\beta(\tau + t) \right\rangle = 2\tilde{D}\delta_{\alpha\beta}\delta(t) \qquad (23)$$

where $\alpha, \beta \in x, y, z$, and

$$\delta_{\alpha\beta} = 1 \quad (\alpha = \beta), \quad \delta_{\alpha\beta} = 0 \quad (\alpha \neq \beta)$$

$$\delta(t) = \infty \quad (t = 0), \quad \delta(t) = 0 \quad (t \neq 0)$$

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Power spectrum of random force $\mathbf{F}(t)$:

$$
\begin{aligned}
S_F(\omega) &= \lim_{T\to\infty} \frac{1}{T}\left|\tilde{\mathbf{F}}_T(\omega)\right|^2 \\
&= \int_{-\infty}^{\infty} dt \varphi_F(t) e^{i\omega t} \\
&= \int_{-\infty}^{\infty} dt \left\langle \mathbf{F}(\tau) \bullet \mathbf{F}(\tau + t) \right\rangle e^{i\omega t} \\
&= \int_{-\infty}^{\infty} dt 6\tilde{D}\delta(t) e^{i\omega t} \\
&= 6\tilde{D}
\end{aligned}
\tag{24}
$$

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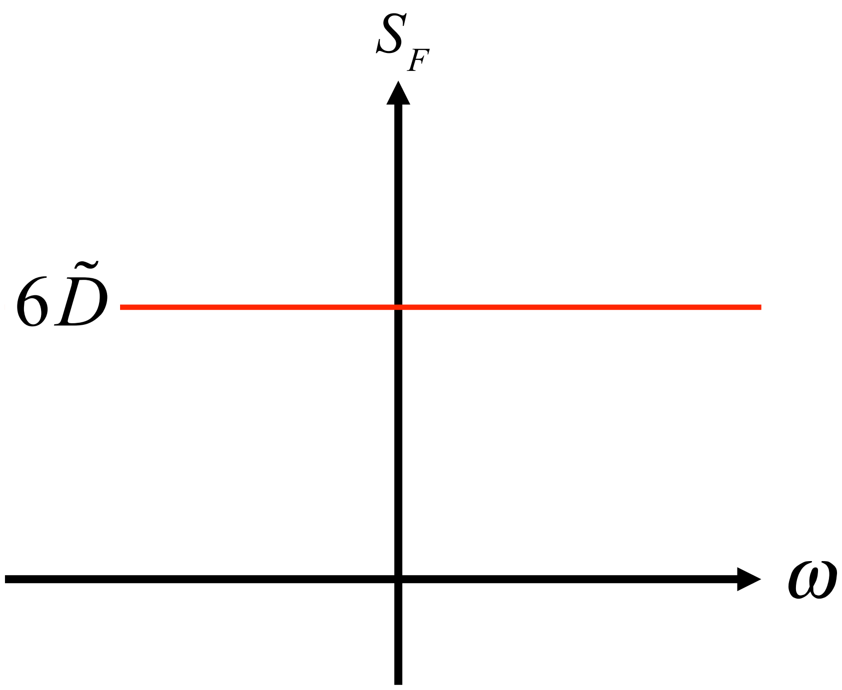
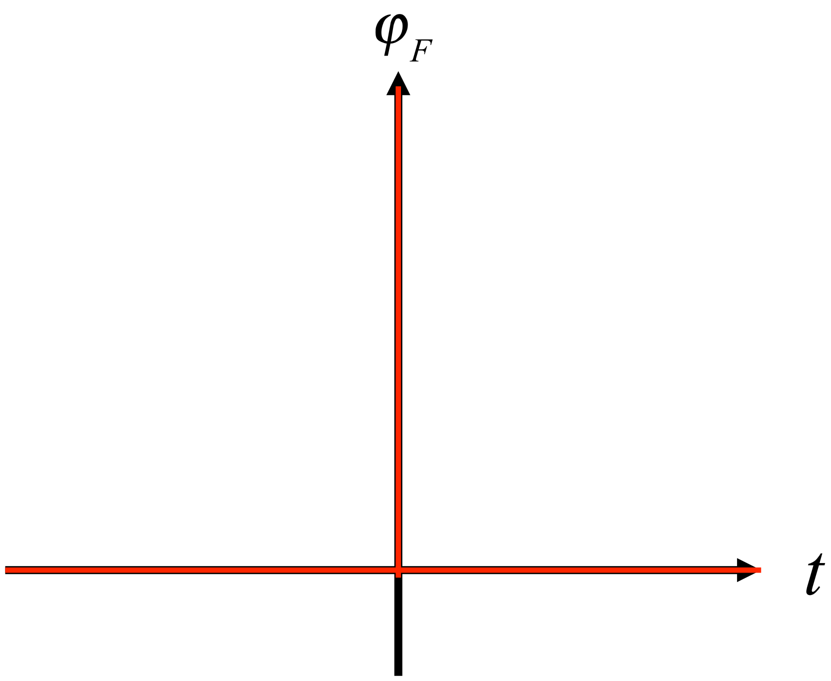
Property of random force $\mathbf{F}(t)$:



$$S_F(\omega) = 6\tilde{D}$$



$$\varphi_F(t) = 6\tilde{D}\delta(t)$$

Brownian motion and the Langevin equation

Fourier transform Eq.(1)

$$-i\omega m\tilde{\mathbf{V}}_T(\omega) = -\zeta\tilde{\mathbf{V}}_T(\omega) + \tilde{\mathbf{F}}_T(\omega)$$

$$\tilde{\mathbf{V}}_T(\omega) = \frac{\tilde{\mathbf{F}}_T(\omega)}{-i\omega m + \zeta}$$

Power Spectrum of particle velocity $\mathbf{V}(t)$:

$$S_V(\omega) = \lim_{T\to\infty}\frac{1}{T}\left|\tilde{\mathbf{V}}_T(\omega)\right|^2$$

$$= \lim_{T\to\infty}\frac{1}{T}\left|\tilde{\mathbf{F}}_T(\omega)\right|^2 \frac{1}{m^2\omega^2+\zeta^2} = \frac{6\tilde{D}}{m^2\omega^2+\zeta^2} \qquad (25)$$

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Auto-correlation function of particle velocity $\mathbf{V}(t)$:

Using Winner-Khintchine theorem and Eq.(6)

$$\begin{aligned}\varphi_V(t) \equiv \langle \mathbf{V}(\tau)\bullet\mathbf{V}(\tau+t)\rangle &= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega S_V(\omega)e^{-i\omega t} \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \frac{6\tilde{D}}{m^2\omega^2+\zeta^2}e^{-i\omega t} \\ &= \frac{3\tilde{D}}{\zeta m}\exp\left(-\frac{\zeta}{m}|t|\right) \end{aligned} \tag{26}$$

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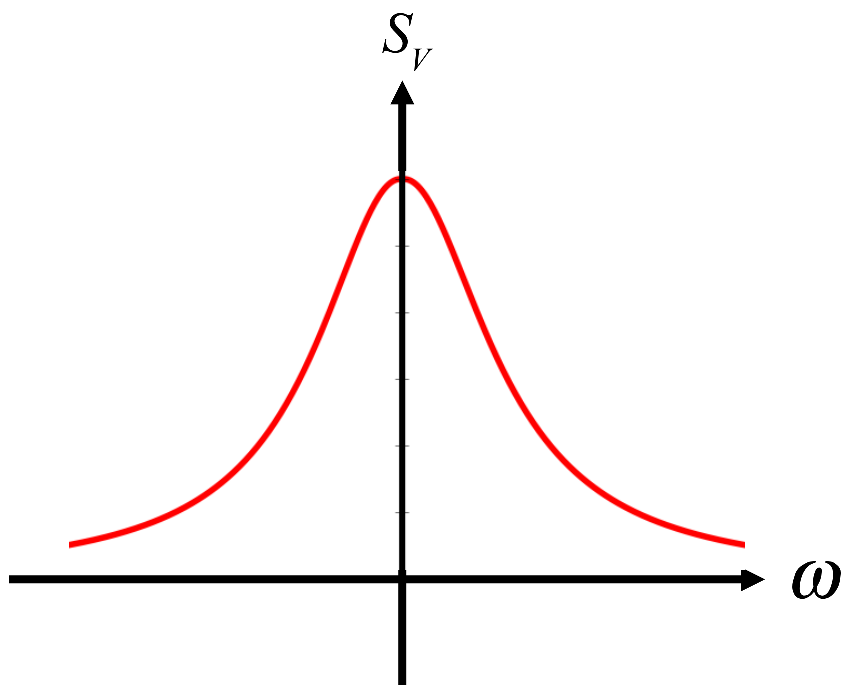
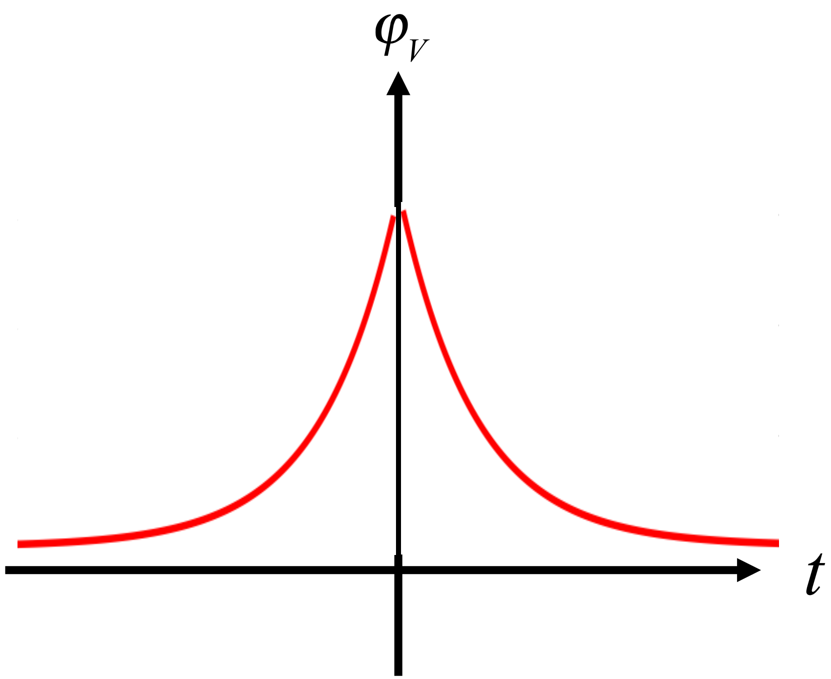
Property of particle velocity $\mathbf{V}(t)$:



$$S_V = \frac{6\tilde{D}}{m^2\omega^2 + \zeta^2}$$



$$\varphi_V = \frac{3\tilde{D}}{\zeta m}\exp\left(-\frac{\zeta}{m}|t|\right)$$

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From Eq.(26) $\quad \varphi_V(t=0) = \langle \mathbf{V}^2 \rangle = \dfrac{3\tilde{D}}{\zeta m}$

Equipartition of energy $\quad \langle \mathbf{V}^2 \rangle = \dfrac{3k_B T}{m}$

$$\therefore \frac{3\tilde{D}}{\zeta m} = \frac{3k_B T}{m} \quad \rightarrow \quad \boxed{\tilde{D} = k_B T \zeta} \qquad (29)$$

Fluctuation-dissipation theorem

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Displacement: $\Delta\mathbf{R}(t) \equiv \mathbf{R}(t) - \mathbf{R}(0) = \int_0^t \mathbf{V}(t_1)\,dt_1$

Mean square displacement:

$$\left\langle \left|\Delta\mathbf{R}(t)\right|^2 \right\rangle = \int_0^t dt_1 \int_0^t dt_2 \left\langle \mathbf{V}(t_1)\bullet\mathbf{V}(t_2)\right\rangle$$

$$= \int_0^t dt_1 \int_0^t dt_2 \frac{3\tilde{D}}{\zeta} \exp\left(-\frac{\zeta}{m}\left|t_2 - t_1\right|\right)$$

$$= 2\int_0^t dt_1 \int_{t_1}^t dt_2 \frac{3\tilde{D}}{\zeta} \exp\left(-\frac{\zeta}{m}\left(t_2 - t_1\right)\right) = \frac{6\tilde{D}}{\zeta^2} t + Cons.$$

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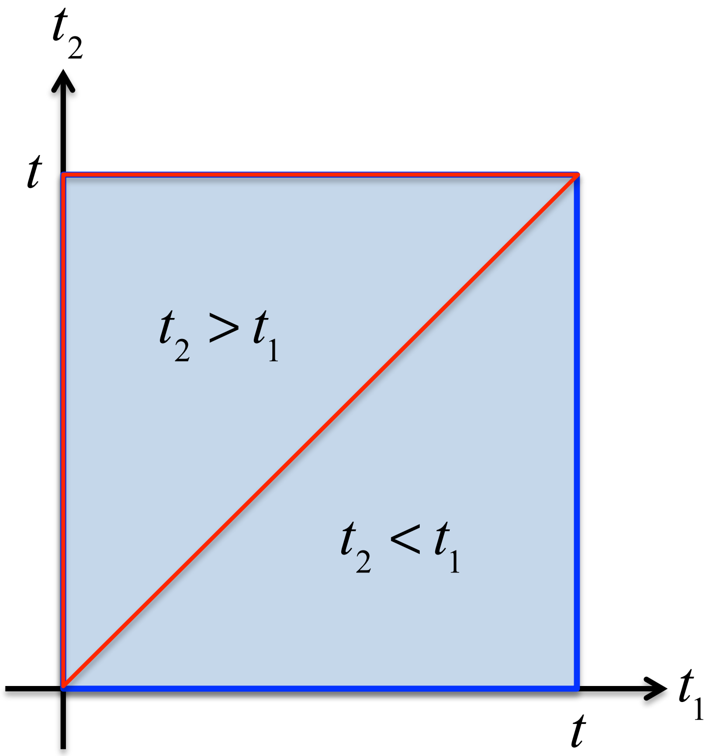

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$$= \int_0^t dt_1 \int_0^t dt_2 \frac{3\tilde{D}}{\zeta} \exp\left(-\frac{\zeta}{m}\left|t_2 - t_1\right|\right)$$

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Self diffusion constant:

$$D \equiv \lim_{t\to\infty} \frac{\left\langle \left| \Delta\mathbf{R}(t) \right|^2 \right\rangle}{6t} = \frac{\tilde{D}}{\zeta^2} \tag{30}$$

Einstein relation: (from Eq.(29) and (30))

$$D = \frac{k_B T}{\zeta} \tag{31}$$

Stokes-Einstein relation: (from Eq.(31) and Stokes law $\zeta = 6\pi a\eta$)

$$D = \frac{k_B T}{6\pi a\eta} \tag{32}$$