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08. Brownian Motion

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Abstract

Part eight of course materials for Nonequilibrium Statistical Physics (Physics 626), taught by Gerhard Müller at the University of Rhode Island. Entries listed in the table of contents, but not shown in the document, exist only in handwritten form. Documents will be updated periodically as more entries become presentable.
Updated with version 2 on 5/3/2016.

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Brownian Motion [nln63]

Early experimental evidence for atomic structure of matter. Historically important in dispute between 'atomicists' and 'energeticists' in late 19th century.

Brown 1828:
Observation of perpetual, irregular motion of pollen grains suspended in water. The particles visible under a microscope (pollen) are small enough to be manifestly knocked around by even smaller particles that are not directly visible (molecules).

Einstein, Smoluchowski 1905:
Correct interpretation of Brownian motion as caused by collisions with the molecules of a liquid. Theoretical framework of thermal fluctuations grounded in the assumption that matter has a molecular structure and with aspects that are experimentally testable.

Perrin 1908:
Systematic observations of Brownian motion combined with quantitative analysis. Confirmation of Einstein's predictions. Experimental determination of Avogadro's number.

Langevin 1908:
Confirmation of Einstein's results via different approach. Langevin's approach provided more detailed (less contracted) description of Brownian motion. Langevin equation proven to be generalizable. Foundation of general theory of fluctuations rooted in microscopic dynamics.

Relevant Time Scales [nln64]

Conceptually, it is useful to distinguish between *heavy* and *light* Brownian particles. For the most part, only Brownian particles that are heavy compared to the fluid molecules are large enough to be visible under a microscope.
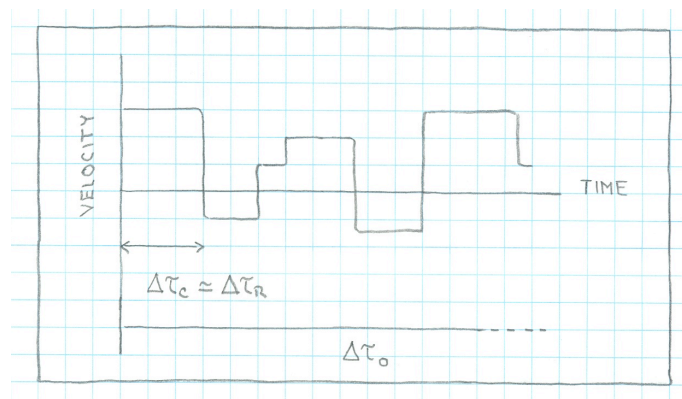
Time scales relevant in the observation and analysis of Brownian particles:

- $\Delta\tau_C$: time between collisions,
- $\Delta\tau_R$: relaxation time,
- $\Delta\tau_O$: time between observations.

Heavy Brownian particles: $\Delta\tau_C \ll \Delta\tau_R \ll \Delta\tau_O$.
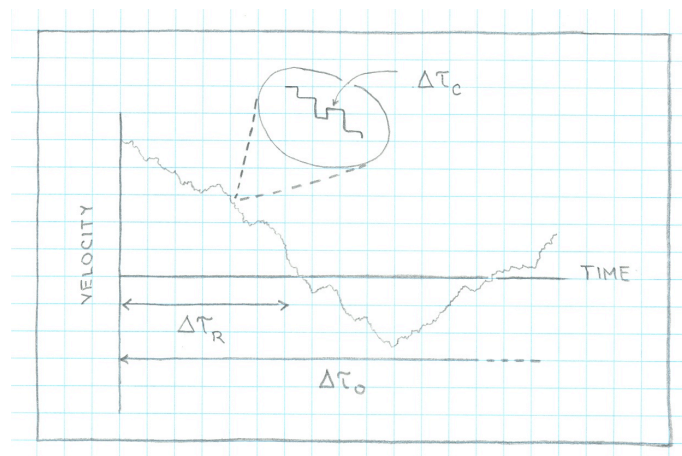
Light Brownian particles: $\Delta\tau_C \simeq \Delta\tau_R \ll \Delta\tau_O$.

Einstein's Theory [nln65]

Theory operates on time scale dt, where $\Delta\tau_R \ll dt \ll \Delta\tau_O$.
Focus on one space coordinate: x.
Local number density of Brownian particles: $n(x, t)$.
Brownian particles experience shift of size s in time dt.
Probability distribution of shifts: $P(s)$.
Successive shifts are assumed to be statistically independent.
Assumption justified by choice of time scale: $\Delta\tau_R \ll dt$.

Effect of shifts on profile of number density:

$$n(x, t + dt) = \int_{-\infty}^{+\infty} ds\, P(s) n(x + s, t).$$

Expansion of $n(x, t)$ in space and in time:

$$n(x + s, t) = n(x, t) + s\frac{\partial}{\partial x}n(x, t) + \frac{1}{2}s^2\frac{\partial^2}{\partial x^2}n(x, t) + \cdots,$$

$$n(x, t + dt) = n(x, t) + dt\frac{\partial}{\partial t}n(x, t) + \cdots$$

Integrals (normalization, reflection symmetry, diffusion coefficient):

$$\int_{-\infty}^{+\infty} ds\, P(s) = 1, \quad \int_{-\infty}^{+\infty} ds\, sP(s) = 0, \quad \frac{1}{2}\int_{-\infty}^{+\infty} ds\, s^2 P(s) \doteq Ddt.$$

Substitution of expansions with these integrals yields diffusion equation:

$$\frac{\partial}{\partial t}n(x, t) = D\frac{\partial^2}{\partial x^2}n(x, t).$$

Solution with initial condition $n(x, 0) = N\delta(x - x_0)$ and no boundaries:

$$n(x, t) = \frac{N}{\sqrt{4\pi Dt}}\exp\left(-\frac{(x - x_0)^2}{4Dt}\right),$$

No drift: $\langle\langle x \rangle\rangle = 0$.

Diffusive mean-square displacement: $\langle\langle x^2 \rangle\rangle = 2Dt$.

Diffusion Equation Analyzed [nln73]

Here we present two simple and closely related methods of analyzing the diffusion equation,

$$\frac{\partial}{\partial t}\rho(x,t) = D\frac{\partial^2}{\partial x^2}\rho(x,t), \tag{1}$$

in one dimension and with no boundary constraints.

Fourier transform:

Ansatz for plane-wave solution: $\rho(x,t)_k = \tilde{\rho}_k(t)\,e^{ikx}$.

Substitution of ansatz into PDE (1) yields ODE for Fourier amplitude $\tilde{\rho}_k(t)$, which is readily solved:

$$\frac{d}{dt}\tilde{\rho}_k(t) = -Dk^2\tilde{\rho}_k(t) \quad \Rightarrow \quad \tilde{\rho}_k(t) = \tilde{\rho}_k(0)\,e^{-Dk^2t}.$$

Initial Fourier amplitudes from initial distribution:

$$\tilde{\rho}_k(0) = \int_{-\infty}^{+\infty} dx\,e^{-ikx}\rho(x,0). \tag{2}$$

Time-dependence of distribution as superposition of plane-wave solutions:

$$\rho(x,t) = \int_{-\infty}^{+\infty} \frac{dk}{2\pi}\,e^{ikx}\tilde{\rho}_k(0)\,e^{-Dk^2t}. \tag{3}$$

Green's function:

Green's function $G(x,t)$ describes time evolution of point source at $x=0$:

$$G(x,0) = \delta(x) \quad \Rightarrow \quad \tilde{G}_k(0) \doteq \int_{-\infty}^{+\infty} dx\,e^{-ikx}G(x,0) = 1 \quad \Rightarrow \quad \tilde{G}_k(t) = e^{-Dk^2t}.$$

$$\Rightarrow \quad G(x,t) = \int_{-\infty}^{+\infty} \frac{dk}{2\pi}\,e^{ikx-Dk^2t} = \frac{1}{\sqrt{4\pi Dt}}\,e^{-x^2/4Dt}. \tag{4}$$

Superposition of point-source solutions in the form of a convolution integral:

$$\rho(x,t) = \int_{-\infty}^{+\infty} dx'\rho(x',0)G(x-x',t). \tag{5}$$

[nex128] Release of Brownian particle from box confinement

Consider a physical ensemble of Brownian particles uniformly distributed inside a one-dimensional box. The initial density is

$$\rho(x,0) = \frac{1}{2}\theta\big(1 - |x|\big),$$

where $\theta(x)$ is the step function. At time $t = 0$ the particles are released to diffuse left and right. Use the two methods presented in [nln73] to calculate the analytic solution,

$$\rho(x,t) = \frac{1}{4}\left[\mathrm{erf}\left(\frac{x+1}{\sqrt{4Dt}}\right) - \mathrm{erf}\left(\frac{x-1}{\sqrt{4Dt}}\right)\right],$$

of the diffusion equation, where the error function is defined as follows:

$$\mathrm{erf}(x) \doteq \frac{2}{\sqrt{\pi}}\int_0^x du\, e^{-u^2}.$$

(a) In the Fourier analysis of [nln73] first calculate the initial Fourier amplitudes via (2) and then use the result in the integration (3).
(b) In the Green's function analysis of [nln73] perform the involution integral (5) with the point-source solution (4) and the initial rectangular initial distribution pertaining to this application.
(c) Plot $\rho(x,t)$ versus x for $-3 \leq x \leq +3$ and $Dt = 0, 0.04, 0.2, 1, 5$.

Solution:

Smoluchowski Equation [nln66]

Einstein's result derived from different starting point.

Two laws relating number density and flux of Brownian particles:

(a) Conservation law: $\dfrac{\partial}{\partial t}n(x,t) = -\dfrac{\partial}{\partial x}j(x,t)$ (continuity equation);
   local change in density due to net flux from or to vicinity.

(b) Constitutive law: $j(x,t) = -D\dfrac{\partial}{\partial x}n(x,t)$ (Fick's law);
   flux driven by gradient in density.

Combination of (a) and (b) yields diffusion equation for density:

$$\frac{\partial}{\partial t}n(x,t) = D\frac{\partial^2}{\partial x^2}n(x,t). \tag{1}$$

Solution of (1) yields flux via (b).

Extension to include drift.

Brownian particles subject to external force $F_{\text{ext}}(x,t)$.

Resulting drift velocity v, averaged over time scale dt identified in [nln65], produces drag force $F_{\text{drag}} = -\gamma v$ due to front/rear asymmetry of collisions.

Damping constant: γ;   mobility: γ^{-1}.

Drift contribution to flux $j(x,t)$ has general form $n(x,t)v(x,t)$.

On time scale dt of [nln65], forces are balanced: $F_{\text{ext}} + F_{\text{drag}} = 0$.

Drift velocity has reached terminal value: $v_{\text{T}} = -F_{\text{ext}}/\gamma$.

(c) Extended constitutive law: $j(x,t) = -D\dfrac{\partial}{\partial x}n(x,t) + \gamma^{-1}F_{\text{ext}}(x,t)n(x,t)$.

Substitution of (c) into (a) yields Smoluchowski equation:

$$\frac{\partial}{\partial t}n(x,t) = D\frac{\partial^2}{\partial x^2}n(x,t) - \gamma^{-1}\frac{\partial}{\partial x}\big[n(x,t)F_{\text{ext}}(x,t)\big]. \tag{2}$$

The two terms on the rhs represent diffusion and drift, respectively.

Einstein's Fluctuation-Dissipation Relation

Consider a colloid of volume V suspended in a fluid.

Excess mass: $m = V(\rho_{\text{coll}} - \rho_{\text{fluid}})$.

External (gravitational) force directed vertically down: $F_{\text{ext}} = -mg$.

Smoluchowski equation [nln66]:

$$\frac{\partial}{\partial t} n(z, t) = D \frac{\partial^2}{\partial z^2} n(z, t) + \gamma^{-1} \frac{\partial}{\partial z} \big[n(z, t) mg \big].$$

Stationary solution: $\partial n / \partial t = 0 \quad \Rightarrow \quad n = n_{\text{s}}(z)$.

$$\Rightarrow \quad \frac{d}{dz} \left[D \frac{dn_{\text{s}}}{dz} + \frac{mg}{\gamma} n_{\text{s}} \right] = 0; \quad n_{\text{s}}(\infty) = 0, \quad \left. \frac{dn_{\text{s}}}{dz} \right|_{z=\infty} = 0.$$

$$\Rightarrow \quad n_{\text{s}}(z) = n_{\text{s}}(0) \exp\left(-\frac{mg}{\gamma D} z \right).$$

Comparison with law of atmospheres (thermal equilibrium state) [tex150],

$$n_{\text{eq}}(z) = n_{\text{eq}}(0) \exp\left(-\frac{mg}{k_{\text{B}} T} z \right),$$

implies

$$D = \frac{k_{\text{B}} T}{\gamma} \qquad \text{(Einstein relation)}.$$

This is an example of a relation between a quantity representing fluctuations (D) and a quantity representing dissipation (γ).

The Einstein relation was used to estimate Avogadro's number N_{A}:

- Colloid in the shape of a solid sphere of radius a.
- Motion in incompressible fluid with viscosity η.
- Stokes' law for drag force: $F_{\text{drag}} = -6\pi \eta a v = -\gamma v$.
- Damping constant $\gamma = 6\pi \eta a$ (experimentally accessible).
- Diffusion constant D (experimentally accessible).
- Ideal gas constant $R = N_{\text{A}} k_{\text{B}}$ (experimentally accessible).
- Avogadro's number: $N_{\text{A}} = \dfrac{RT}{6\pi \eta a D}$.

Smoluchowski vs Fokker-Planck

The Smoluchowski equation [nln66] as derived from a conservation law and constitutive law can be transcribed into a Fokker-Planck equation [nln57] if density and flux of particles are replaced by density and flux of probability.

Here we use generic notation:

- density: $\rho(x, t)$,
- flux: $J(x, t)$,
- diffusivity: $D(x)$,
- mobility: Γ,
- external force: $F(x)$.

Conservation law: $\dfrac{\partial}{\partial t}\rho(x, t) = -\dfrac{\partial}{\partial x}J(x, t)$.

Constitutive law: $J(x, t) = -D(x)\dfrac{\partial}{\partial x}\rho(x, t) + \Gamma F(x)\rho(x, t)$.

$$\Rightarrow \frac{\partial}{\partial t}\rho(x, t) = -\frac{\partial}{\partial x}\Big[\Gamma F(x)\rho(x, t)\Big] + \underbrace{\frac{\partial}{\partial x}\Big[D(x)\frac{\partial}{\partial x}\rho(x, t)\Big]}.$$

$$\frac{\partial^2}{\partial x^2}\Big[D(x)\rho(x, t)\Big] = \frac{\partial}{\partial x}\Big[D'(x)\rho(x, t)\Big] + \overbrace{\frac{\partial}{\partial x}\Big[D(x)\frac{\partial}{\partial x}\rho(x, t)\Big]}.$$

$$\Rightarrow \frac{\partial}{\partial t}\rho(x, t) = -\frac{\partial}{\partial x}\Big[\Big(\underbrace{\Gamma F(x) + D'(x)}_{A(x)}\Big)\rho(x, t)\Big] + \frac{\partial^2}{\partial x^2}\Big[\underbrace{D(x)}_{B(x)}\rho(x, t)\Big].$$

$A(x)$ and $B(x)$ represent drift and diffusion in the Fokker-Planck equation.

Fourier's Law for Heat Conduction

Heat conduction inside a solid involves three field quantities:

- energy density: $\epsilon(x,t)$,
- heat current: $J(x,t)$,
- local temperature: $T(x,t)$.

Relations between field quantities:

(a) conservation law: $\dfrac{\partial}{\partial t}\,\epsilon(x,t) = -\dfrac{\partial}{\partial x}\,J(x,t)$ (continuity equation),

(b) constitutive law: $J(x,t) = -\lambda\dfrac{\partial}{\partial x}\,T(x,t)$ (Fourier's law),

(c) thermodynamic relation: $\epsilon(x,t) = c_V T(x,t)$.

Material constants:

- specific heat: c_V,
- thermal conductivity: λ,
- thermal diffusivity: $D_T = \lambda/c_V$.

Diffusion equation from (a)-(c):

$$\frac{\partial}{\partial t}\,T(x,t) = D_T \frac{\partial^2}{\partial x^2}\,T(x,t).$$

Applications:

▷ Temperature profile inside wall [nex117]

[nex117] Thermal diffusivity

A solid wall of very large thickness and lateral extension (assumed to occupy all space at $z > 0$) is brought into contact with a heat source at its surface ($z = 0$). The wall is initially in thermal equilibrium at temperature T_0. The heat source is kept at the higher temperature T_1. The contact is established at time $t = 0$. Show that the temperature profile inside the wall depends on time as follows:

$$T(z) = T_0 + (T_1 - T_0)\text{erfc}\left(\frac{z}{2\sqrt{D_T t}}\right),$$

where $D_T = \lambda/c_V$ is the thermal diffusivity, λ the thermal conductvity, and c_V the specific heat. Then plot $T(z)/T_0$ versus z for $0 \le z \le 5$, $T_1/T_0 = 3$, and $D_T t = 0.2, 1, 5$. Describe the meaning of the three curves in relation to each other. The complementary error function is defined as follows:

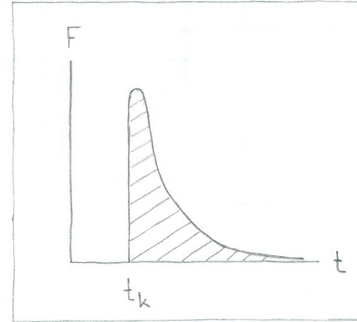$$\text{erfc}(x) \doteq \frac{2}{\sqrt{\pi}} \int_x^\infty du\, e^{-u^2}.$$

Solution:

Shot Noise

Electric current in a vacuum tube or solid state device described as a random sequence of discrete events involving microscopic charge transfer:

$$I(t) = \sum_k F(t - t_k).$$

Assumptions:

- uniform event profile $F(t)$ characteristic of process (e.g. as sketched),
- event times t_k randomly distributed,
- average number events per unit time: λ.

Attributes characteristic of Poisson process: [nex25] [nex16]

- probability distribution: $P(n, t) = e^{-\lambda t}(\lambda t)^n/n!$,
- mean and variance: $\langle\langle n \rangle\rangle = \langle\langle n^2 \rangle\rangle = \lambda t$.

Probability that n events have taken place until time t reinterpreted as probability that stochastic variable $N(t)$ assumes value n at time t:
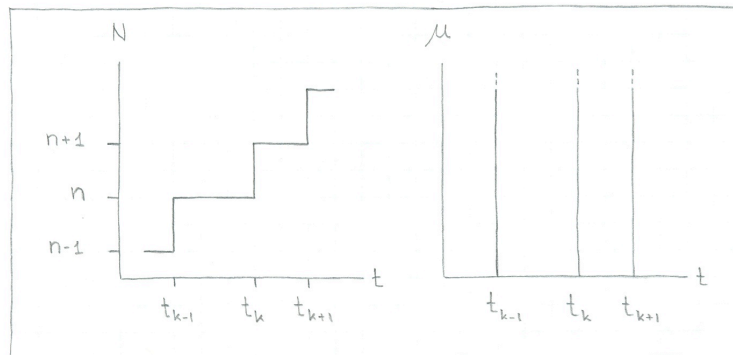
$$P(n, t) = \text{prob}\{N(t) = n\}.$$

Sample path of $N(t)$ and its derivative:

$$N(t) = \sum_k \theta(t - t_k), \quad \mu(t) \doteq \frac{dN}{dt} = \sum_k \delta(t - t_k).$$

Sample path of electric current:

$$I(t) = \sum_k F(t - t_k) = \int_{-\infty}^{+\infty} dt' F(t - t')\mu(t').$$

Event profile: $F(t) = q\,e^{-\alpha t}\theta(t)$ with charge $q_0 = q/\alpha$ per event.

Electric current: $I(t) = \displaystyle\int_{-\infty}^{t} dt'q\,e^{-\alpha(t-t')}\mu(t')$.

Stochastic differential equation:

$$\frac{dI}{dt} = -\alpha I(t) + q\mu(t). \tag{1}$$

Attributes of Poisson process: $\langle\langle dN(t)\rangle\rangle = \langle\langle [dN(t)]^2\rangle\rangle = \lambda dt$.

Fluctuation variable: $d\eta(t) = dN(t) - \lambda dt \quad \Rightarrow \langle d\eta(t)\rangle = 0,\ \langle [d\eta(t)]^2\rangle = \lambda dt$.

Average current from (1):[1]

$$dI(t) = \big[\lambda q - \alpha I(t)\big]dt + q\,d\eta(t) \quad \Rightarrow\ \langle dI(t)\rangle = \big[\lambda q - \alpha\langle I(t)\rangle\big]dt$$

$$\Rightarrow\ \frac{d}{dt}\langle I(t)\rangle = \lambda q - \alpha\langle I(t)\rangle. \tag{2}$$

Current fluctuations from (1) and (2):[2]

$$dI^2 \doteq (I+dI)^2 - I^2 = 2IdI + (dI)^2,$$

$$\langle dI^2\rangle = 2\big\langle I\big([\lambda q - \alpha I]dt + qd\eta\big)\big\rangle + \Big\langle \big([\lambda q - \alpha I]dt + qd\eta\big)^2\Big\rangle$$
$$= \big(2\lambda q\langle I\rangle - 2\alpha\langle I^2\rangle + \lambda q^2\big)dt + \mathrm{O}\big([dt]^2\big)$$

$$\Rightarrow\ \frac{1}{2}\frac{d}{dt}\langle I^2\rangle = \lambda q\langle I\rangle - \alpha\langle I^2\rangle + \frac{1}{2}\lambda q^2. \tag{3}$$

Steady state: $\dfrac{d}{dt}\langle I\rangle_S = 0, \quad \dfrac{d}{dt}\langle I^2\rangle_S = 0$:

$$\Rightarrow\ \langle I\rangle_S = \frac{\lambda q}{\alpha}, \quad \langle\langle I^2\rangle\rangle_S \doteq \langle I^2\rangle_S - \langle I\rangle_S^2 = \frac{q^2\lambda}{2\alpha}. \tag{4}$$

Applications:

▷ Campbell processes [nex37]

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[1] Use $q\mu(t)dt = qdN(t) = qd\eta(t) + q\lambda dt$.
[2] Use $\langle I(t)d\eta(t)\rangle = 0$.

[nex37] Campbell processes.

Consider a stationary stochastic process of the general form $Y(t) = \sum_k F(t - t_k)$, where the times t_k are distributed randomly with an average rate λ of occurrences. Campbell's theorem then yields the following expressions for the mean value and the autocorrelation function of Y:

$$\langle Y \rangle = \lambda \int_{-\infty}^{\infty} d\tau \, F(\tau), \quad \langle\langle Y(t)Y(0) \rangle\rangle \equiv \langle Y(t)Y(0) \rangle - \langle Y(t) \rangle\langle Y(0) \rangle = \lambda \int_{-\infty}^{\infty} d\tau \, F(\tau)F(\tau + t).$$

Apply Campbell's theorem to calculate the average current $\langle I \rangle$ and the current autocorrelation function $\langle\langle I(t)I(0) \rangle\rangle$ for a shot noise process with $F(t) = qe^{-\alpha t}\theta(t)$, where $\theta(t)$ is the step function. Compare the results with those derived in [nln70] along a somewhat different route.

Solution:

[nex70] Critically damped ballistic galvanometer.

The response of a critically damped ballistic galvanometer to a current pulse at $t = 0$ is $\Psi(t) = cte^{-\gamma t}$. Consider the situation where the galvanometer experiences a steady stream of independent random current pulses, $X(t) = \sum_k \Psi(t - t_k)$, where the t_k are distributed randomly with an average rate n of occurrences.

(a) Use Campbell's theorem [nex37] to calculate the average displacement $\langle X \rangle$ and the autocorrelation function $\langle\langle X(t)X(0)\rangle\rangle$.

(b) Show that the associated spectral density reads

$$S_{XX}(\omega) \doteq \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle\langle X(t)X(0)\rangle\rangle = \frac{nc^2}{(\gamma^2 + \omega^2)^2}.$$

Solution:

Langevin's Theory [nln71]

Langevin's theory of Brownian motion operates on a less contracted level of description than Einstein's theory [nln65]. The operational time scale is small compared to the relaxation time: $dt \ll \Delta\tau_R$. [nln64]. On this time scale inertia matters, implying that velocity cannot change abruptly. Velocity and position variables are kinematically coupled.

The Langevin equation,

$$m\ddot{x} = -\gamma\dot{x} + f(t), \tag{1}$$

is constructed from Newton's second law with two forces acting:

- drag force: $-\gamma\dot{x}$ (parametrized by mobility γ^{-1}),
- random force: $f(t)$ (Gaussian white noise/Wiener process).

Since we do not know $f(t)$ explicitly we cannot solve (1) for $x(t)$. However, we know enough about $f(t)$ to solve (1) for $\langle x^2 \rangle$ as a function of time [nex118].

First step: derive the linear, 2nd-order ODE for $\langle x^2 \rangle$,

$$m\frac{d^2}{dt^2}\langle x^2 \rangle + \gamma\frac{d}{dt}\langle x^2 \rangle = 2k_BT, \tag{2}$$

using

- the white-noise implication that the random force and the position are uncorrelated, $\langle xf(t)\rangle$,
- the equilibrium implication that the average kinetic energy of the Brownian particle satisfies equipartition, $\langle\dot{x}^2\rangle = k_BT/m$.

Second step: Integrate (2) twice using

- initial conditions $\langle x^2 \rangle_0 = 0$ and $d\langle x^2 \rangle_0/dt = 0$,
- Einstein's fluctuation-dissipation relation $D = k_BT/\gamma$,
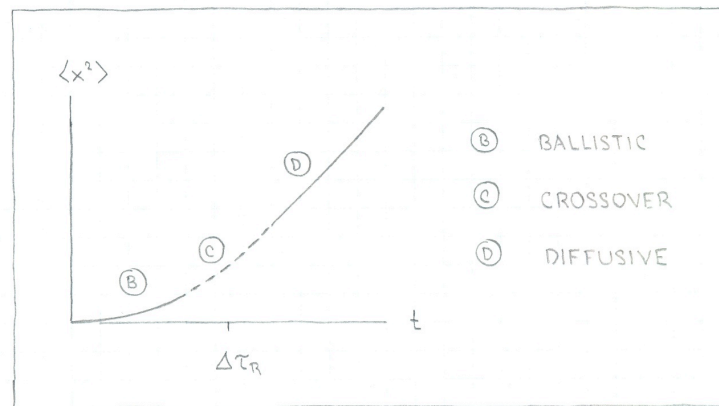- the fact that (2) is a 1st-order ODE for $d\langle x^2 \rangle/dt$.

The result reads

$$\langle x^2 \rangle = 2D\left[t - \frac{m}{\gamma}\left(1 - e^{-\gamma t/m}\right)\right]. \tag{3}$$

Within the framework of Langevin's theory, the relaxation time previously identified [nln64] is

$$\Delta\tau_R = \frac{m}{\gamma}.$$

This relaxation time separates short-time *ballistic* regime from a long-time *diffusive* regime:

- $t \ll \dfrac{m}{\gamma}:$ $\langle x^2 \rangle \sim \dfrac{D\gamma}{m}t^2 = \dfrac{k_B T}{m}t^2 = \langle v^2 \rangle t^2,$

- $t \gg \dfrac{m}{\gamma}:$ $\langle x^2 \rangle \sim 2Dt.$

Applications and variations:

    ▷ Mean-square displacement of Brownian particle [nex56] [nex57] [nex118]

    ▷ Formal solution of Langevin equation [nex53]

    ▷ Velocity correlation function of Brownian particle [nex55] [nex119] [nex120]

2

Brownian motion and Gaussian white noise

Gaussian white noise: completely factorizing stationary process.

- $P_w(y_1, t_1; y_2, t_2) = P_w(y_1)P_w(y_2)$ if $t_2 \neq t_1$ (factorizability)
- $P_w(y) = \dfrac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\dfrac{y^2}{2\sigma^2}\right)$ (Gaussian nature)
- $\langle y(t) \rangle = 0$ (no bias)
- $\langle y(t_1)y(t_2) \rangle = I_w \delta(t_1 - t_2)$ (whiteness)
- $I_w = \langle y^2 \rangle = \sigma^2$ (intensity)

Brownian motion: Markov process.

- Discrete time scale: $t_n = n\, dt$.
- Position of Brownian particle at time t_n: z_n.
- $P(z_n, t_n) = \underbrace{P(z_n, t_n | z_{n-1}, t_{n-1})}_{P_w(y_n)\delta(y_n - [z_n - z_{n-1}])} P(z_{n-1}, t_{n-1})$ (white-noise transition rate).
- Specification of white-noise intensity: $I_w = 2D\,dt$.
- Sample path of Brownian particle: $z(t_n) = \displaystyle\sum_{i=1}^{n} y(t_i)$.
- Position of Brownian particle:

  - mean value: $\langle z(t_n) \rangle = \displaystyle\sum_{i=1}^{n} \langle y(t_i) \rangle = 0$.

  - variance: $\langle z^2(t_n) \rangle = \displaystyle\sum_{i,j=1}^{n} \langle y(t_i)y(t_j) \rangle = 2Dn\,dt = 2Dt_n$.

Gaussian white noise with intensity $I_w = 2D\,dt$ is used here to generate the diffusion process discussed previously [nex26], [nex27], [nex97]:

$$P(z, t + dt | z_0, t) = \frac{1}{\sqrt{4\pi D\,dt}} \exp\left(-\frac{(z - z_0)^2}{4D\,dt}\right).$$

Sample paths of the diffusion process become continuous in the limit $dt \to 0$ (Lindeberg condition). However, in the present context, we must use $dt \gg \tau_R$, where τ_R is the relaxation time for the velocity of the Brownian particle.

On this level of contraction, the velocity of the Brownian particle is nowhere defined in agreement with the result of [nex99] that the diffusion process is nowhere differentiable.

Wiener process [nls4]

Specifications:

1. For $t_0 < t_1 < \cdots$, the position increments $\Delta x(t_n, t_{n-1}), n = 1, 2, \ldots$ are independent random variables.

2. The increments depend only on time differences: $\Delta x(t_n, t_{n-1}) = \Delta x(dt_n)$, where $dt_n = t_n - t_{n-1}$.
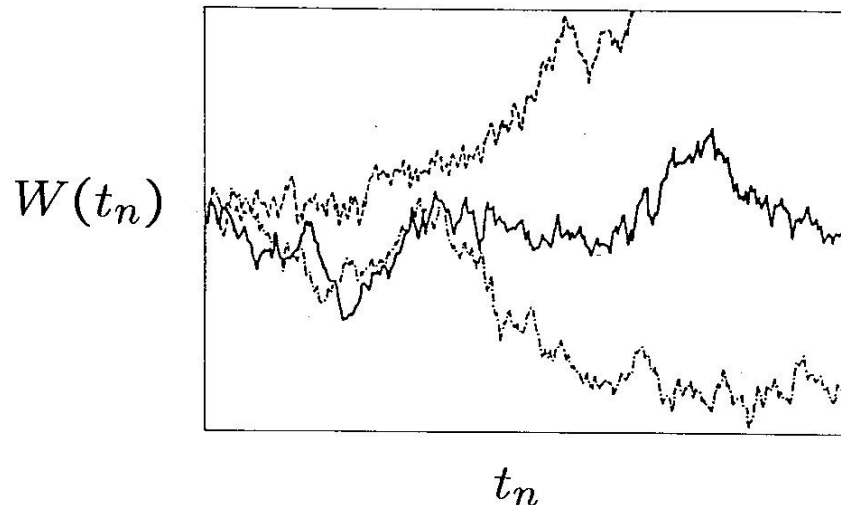
3. The increments satisfy the Lindeberg condition:

$$\lim_{dt \to 0} \frac{1}{dt} \mathcal{P}[\Delta x(dt) \geq \epsilon] = 0 \text{ for all } \epsilon > 0$$

The diffusion process discussed previously [nex26], [nex27], [nex97],

$$P(x, t + dt | x_0, t) = \frac{1}{\sqrt{4\pi D dt}} \exp\left(-\frac{(x - x_0)^2}{4D dt}\right),$$

is, for $dt \to 0$, a realization of the Wiener process. Sample paths of the Wiener process thus realized are everywhere continuous and nowhere differentiable.

$$W(t_n) = \sum_{i=1}^{n} \Delta x(dt_i), \qquad t_n = \sum_{i=1}^{n} dt_i.$$

[adapted from Gardiner 1985]

[nex54] Autocorrelation function of Wiener process.

The conditional probability distribution,

$$P(x + \Delta x, t + dt | x, t) = \frac{1}{\sqrt{4\pi D\, dt}} \exp\left(-\frac{(\Delta x)^2}{4D\, dt}\right),$$

which characterizes the realization of a Wiener process, depends on ly on dt but not on t. Use the regression theorem,

$$\langle x(t)x(t + dt) | [0, 0]\rangle = \int dx_1 \int dx_2\, x_1 x_2 P(x_2, t + dt | x_1, t) P(x_1, t | 0, 0),$$

to show that the autocorrelation function only depends on t but not on dt. Find that dependence.
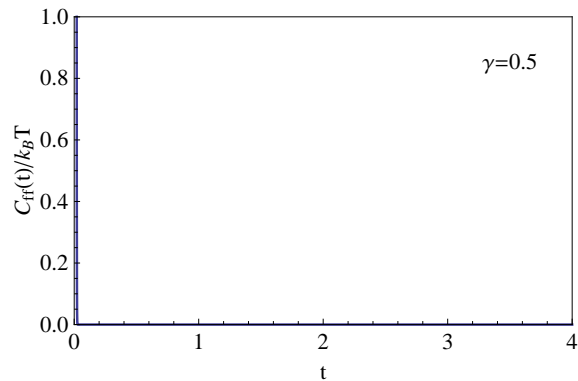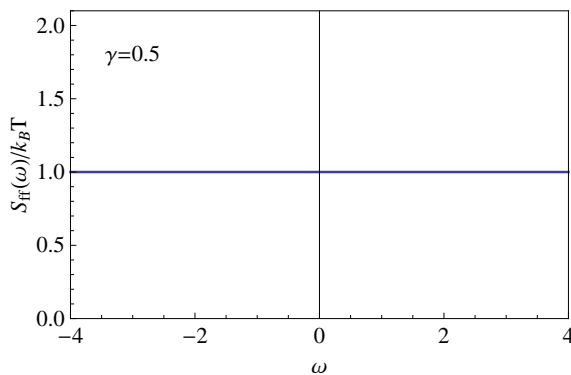
Solution:

Attenuation without memory [nln21]

Langevin equation for Brownian motion:

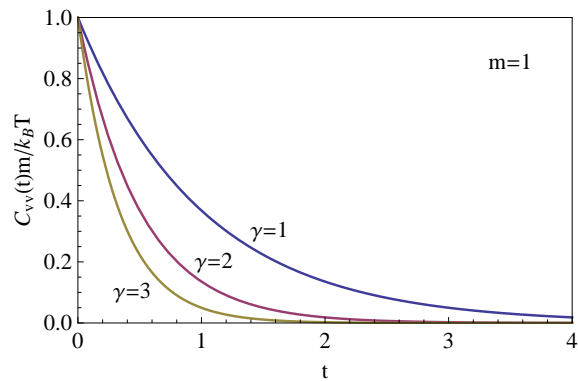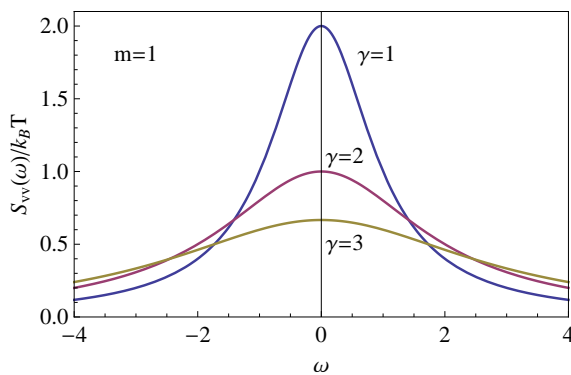$$m\frac{dv}{dt} + \gamma v = f(t).$$

Random force (uncorrelated noise):

$$S_{ff}(\omega) = 2\gamma k_B T, \qquad C_{ff}(t) = 2\gamma k_B T \delta(t).$$

Stochastic variable (velocity):

$$S_{vv}(\omega) = \frac{2\gamma k_B T}{\gamma^2 + m^2\omega^2}, \qquad C_{vv}(t) = \frac{k_B T}{m} e^{-(\gamma/m)t}.$$

[nex53] Formal solution of Langevin equation

Consider a Brownian particle of mass m constrained to move along a straight line. The particle experiences two forces: a drag force $-\gamma\dot{x}$ and a white-noise random force $f(t)$. The Langevin equation, which governs its motion, is expressed as follows:

$$\frac{dx}{dt} = v, \quad \frac{dv}{dt} = -\frac{\gamma}{m}v + \frac{1}{m}f(t).$$

Calculate, via formal integration, the functional dependence of (a) the velocity $v(t)$ and (b) the position $x(t)$ on the random force $f(t)$ for initial conditions $x(0) = 0$ and $v(0) = v_0$. For part (a) use the standard solution for the initial-value problem:

$$\frac{dy}{dt} = -ay + b(t) \quad \Rightarrow \quad y(t) = y_0 e^{-at} + \int_0^t dt' e^{-a(t-t')}b(t').$$

For part (b) integrate by parts to arrive at the result

$$x(t) = v_0 \frac{m}{\gamma}\left(1 - e^{-\gamma t/m}\right) + \frac{1}{\gamma}\int_0^t dt'\left(1 - e^{-\gamma(t-t')/m}\right)f(t').$$

Solution:

[nex55] Velocity correlation function of Brownian particle I

Consider a Brownian particle of mass m constrained to move along a straight line. The particle experiences two forces: a drag force $-\gamma\dot{x}$ and an uncorrelated (white-noise type) random force $f(t)$. Calculate the velocity autocorrelation function $\langle v(t_1)v(t_2)\rangle_0$ of a Brownian particle for $t_1 > t_2$ as a conditional average from the formal solution (see [nex53])

$$v(t) = v_0 e^{-\gamma t/m} + \frac{1}{m}\int_0^t dt'\, e^{-(\gamma/m)(t-t')} f(t')$$

of the Langevin equation with a random force of intensity I_f. Show that for $t_1 > t_2 \gg \gamma/m$ the result only depends on the time difference $t_1 - t_2$. Use equipartition, $\frac{1}{2}m\langle v^2\rangle = \frac{1}{2}k_{\mathrm{B}}T$, to determine the temperature dependence of the random-force intensity I_f.

Comment: By conditional average we mean that the initial velocity has the value v_0. For $t_1 > t_2 \gg \gamma/m$ the memory of that initial condition fades away.

Solution:

[nex56] Mean-square displacement of Brownian particle I

Consider a Brownian particle of mass m constrained to move along a straight line. The particle experiences two forces: a drag force $-\gamma v$ and a white-noise random force $f(t)$. In [nex118] we inferred from the Langevin equation an ODE for the mean-square displacement and solved it to obtain

$$\langle x^2(t)\rangle = 2D\left[t - \frac{m}{\gamma}\left(1 - e^{-(\gamma/m)t}\right)\right].$$

Here the task is to calculate $\langle x^2(t)\rangle$ from the (steady-state) velocity autocorrelation function,

$$\langle v(t_1)v(t_2)\rangle = \frac{k_B T}{m}e^{-(\gamma/m)|t_1 - t_2|}$$

determined in [nex55], via integration with initial condition $x(0) = 0$.

Solution:

[nex57] Mean-square displacement of Brownian particle II

Consider a Brownian particle of mass m constrained to move along a straight line. The particle experiences two forces: a drag force $-\gamma v$ and a white-noise random force $f(t)$. In [nex118] and [nex56] we have taken two different routes to calculate the mean-square displacement,

$$\langle x^2(t) \rangle = 2D \left[t - \frac{m}{\gamma} \left(1 - e^{-(\gamma/m)t} \right) \right], \tag{1}$$

from the Langevin equation. The task here is to derive (1) directly from the formal solution (obtained in [nex53]),

$$x(t) = v_0 \frac{m}{\gamma} \left(1 - e^{-(\gamma/m)t} \right) + \frac{1}{\gamma} \int_0^t ds \left(1 - e^{-(\gamma/m)(t-s)} \right) f(s), \tag{2}$$

of the Langevin equation with a white-noise random force. That random force is uncorrelated, $\langle f(t)f(t') \rangle = I_f \delta(t - t')$ and has intensity $I_f = 2k_B T \gamma$. Use equipartition, $\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$, when taking the thermal average $\langle v_0^2 \rangle$ of initial velocities v_0.

Solution:

[nex118] Mean-square displacement of Brownian particle III

Consider a Brownian particle of mass m constrained to move along a straight line. The particle experiences two forces: a drag force $-\gamma\dot{x}$ and a white-noise random force $f(t)$. Its motion is governed by the Langevin equation,

$$m\ddot{x} = -\gamma\dot{x} + f(t). \tag{1}$$

(a) Construct from (1) the linear ODE for the mean-square displacement,

$$m\frac{d^2}{dt^2}\langle x^2\rangle + \gamma\frac{d}{dt}\langle x^2\rangle = 2k_BT, \tag{2}$$

by using equipartition, $\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{1}{2}k_BT$ and the fact that position and random force at the same instant are uncorrelated, $\langle xf(t)\rangle = 0$.
(b) Solve this ODE for initial conditions $d\langle x^2\rangle/dt|_0 = 0$ and $\langle x^2\rangle|_0 = 0$. Note that (2) is a first-order ODE for the variable $d\langle x^2\rangle/dt$.
(c) Identify the quadratic time-dependence of $\langle x^2\rangle$ in the ballistic regime, $t \ll m/\gamma$, and the linear time dependence in the diffusive regime, $t \gg m/\gamma$. Express the last result in terms of the diffusion constant by invoking Einstein's fluctuation-dissipation relation from [nln67].

Solution:

Ergodicity [nln13]

Consider a stationary process $x(t)$.
Quantities of interest are expectation values related to $x(t)$.

- Theoretically, we determine *ensemble* averages:
  $\langle x(t) \rangle$, $\langle x^2(t) \rangle$, $\langle x(t)x(t+\tau) \rangle$ are independent of t.
- Experimentally, we determine *time* averages:
  $\overline{x(t)}$, $\overline{x^2(t)}$, $\overline{x(t)x(t+\tau)}$ are independent of t.

Ergodicity: time averages are equal to ensemble averages.

Implication: the ensemble average of a time average has zero variance.
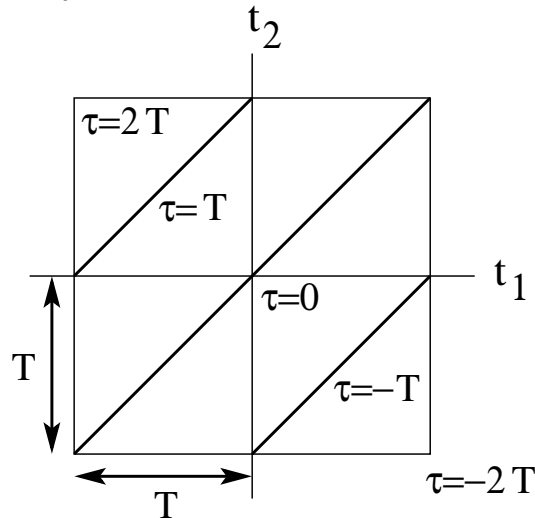
The consequences for the correlation function

$$C(t_1 - t_2) \doteq \langle x(t_1)x(t_2) \rangle - \langle x(t_1) \rangle \langle x(t_2) \rangle$$

are as follows (set $\tau = t_2 - t_1$ and $t = t_1$):

$$
\begin{aligned}
\langle \overline{x^2} \rangle - \langle \overline{x} \rangle^2 &= \lim_{T \to \infty} \frac{1}{4T^2} \int_{-T}^{+T} dt_1 \int_{-T}^{+T} dt_2 \left[\langle x(t_1)x(t_2) \rangle - \langle x(t_1) \rangle \langle x(t_2) \rangle \right] \\
&= \lim_{T \to \infty} \frac{1}{4T^2} \int_{-2T}^{+2T} d\tau \, C(\tau)(2T - |\tau|) \\
&= \lim_{T \to \infty} \frac{1}{2T} \int_{-2T}^{+2T} d\tau \, C(\tau) \left(1 - \frac{|\tau|}{2T} \right) = 0.
\end{aligned}
$$

Necessary condition: $\lim_{\tau \to \infty} C(\tau) = 0$.

Sufficient condition: $\displaystyle\int_0^\infty d\tau \, C(\tau) < \infty$.

Intensity spectrum and spectral density

Consider an ergodic process $x(t)$ with $\langle x \rangle = 0$.

Fourier amplitude: $\tilde{x}(\omega, T) \doteq \int_0^T dt\, e^{i\omega t} x(t) \quad \Rightarrow \quad \tilde{x}(-\omega, T) = \tilde{x}^*(\omega, T)$.

Intensity spectrum (power spectrum): $I_{xx}(\omega) \doteq \lim_{T \to \infty} \dfrac{1}{T} |\tilde{x}(\omega, T)|^2$.
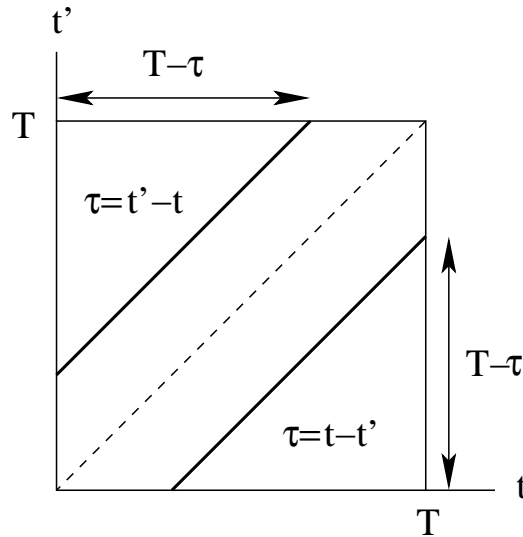
Correlation function: $C_{xx}(\tau) \doteq \langle x(t)x(t+\tau) \rangle = \lim_{T \to \infty} \dfrac{1}{T} \int_0^T dt\, x(t)x(t+\tau)$.

Spectral density: $S_{xx}(\omega) \doteq \displaystyle\int_{-\infty}^{+\infty} d\tau\, e^{i\omega\tau} C_{xx}(\tau)$.

Wiener-Khintchine theorem: $I_{xx}(\omega) = S_{xx}(\omega)$.

Proof:

$$
\begin{aligned}
I_{xx}(\omega) &= \lim_{T \to \infty} \frac{1}{T} \int_0^T dt' e^{-i\omega t'} x(t') \int_0^T dt\, e^{i\omega t} x(t) \\
&= \lim_{T \to \infty} \frac{1}{T} \int_0^T d\tau \left[e^{i\omega\tau} \int_0^{T-\tau} dt'\, x(t')x(t'+\tau) + e^{-i\omega\tau} \int_0^{T-\tau} dt\, x(t)x(t+\tau) \right] \\
&= \lim_{T \to \infty} 2 \int_0^T d\tau \, \cos\omega\tau \, \frac{1}{T} \int_0^{T-\tau} dt\, x(t)x(t+\tau) \\
&= 2 \int_0^\infty d\tau \, \cos\omega\tau \, C_{xx}(\tau) = \int_{-\infty}^{+\infty} d\tau\, e^{i\omega\tau} C_{xx}(\tau) = S_{xx}(\omega).
\end{aligned}
$$

[nex119] Velocity correlation function of Brownian particle II

Consider the Langevin equation for the velocity of a Brownian particle of mass m constrained to move along a straight line,

$$m\frac{dv}{dt} = -\gamma v + f(t), \tag{1}$$

where γ is the damping constant and $f(t)$ is a white-noise random force, $\langle f(t)f(t')\rangle = I_f\delta(t - t')$, with intensity $I_f = 2k_BT\gamma$ in thermal equilibrium (see [nex55]).

(a) Convert the differential equation (1) into the algebraic relation,

$$-i\omega m\tilde{v}(\omega) = -\gamma\tilde{v}(\omega) + \tilde{f}(\omega), \tag{2}$$

between the Fourier amplitudes,

$$\tilde{v}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}v(t), \quad \tilde{f}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}f(t), \tag{3}$$

of the velocity and the random force, respectively.

(b) Apply the Wiener-Khintchine theorem (see [nln14]) to calculate from (2) and the above specifications of the random force the velocity spectral density and, via inverse Fourier transform, the velocity correlation function in thermal equilibrium:

$$S_{vv}(\omega) = \frac{2k_BT\gamma}{\gamma^2 + \omega^2 m^2}, \quad \langle v(t)v(t+\tau)\rangle = \frac{k_BT}{m}e^{-\gamma\tau/m}. \tag{4}$$

Solution:

Generalized Langevin Equation

The Langevin equation,

$$m\frac{dv}{dt} = -\gamma v + f_{\mathrm{w}}(t),\tag{1}$$

was designed to describe Brownian motion [nln71]. The two forces on the rhs represent an instantaneous attenuation, specified by a damping constant γ and a white-noise random force $f_{\mathrm{w}}(t)$.

The generalized Langevin equation,

$$m\frac{dv}{dt} = -\int_{-\infty}^{t} dt'\alpha(t-t')v(t') + f_{\mathrm{c}}(t),\tag{2}$$

is constructed to describe fluctuations of any mode in a many-body system. A consistent generalization requires synchronized modifications of both forces:

- The instantaneous attenuation is replaced by attenuation with memory (retarded attenuation) represented by some attenuation function $\alpha(t)$.
- The white-noise random force is replaced by a random force $f_{\mathrm{c}}(t)$ representing correlated noise.

Fluctuation-dissipation relation:

- Instantaneous attenuation:

$$\langle f_{\mathrm{w}}(t)f_{\mathrm{w}}(t')\rangle = 2k_{\mathrm{B}}T\gamma\delta(t-t').\tag{3}$$

- Retarded attenuation:

$$\langle f_{\mathrm{c}}(t)f_{\mathrm{c}}(t')\rangle = k_{\mathrm{B}}T\alpha_{\mathrm{s}}(t-t')\tag{4}$$

  where $\alpha_{\mathrm{s}}(t) \doteq \alpha(t)\theta(t) + \alpha(-t)\theta(-t)$ is the symmetrized attenuation function.

A justification of relations (3) and (4) is based on the fluctuation-dissipation theorem derived from microscopic dynamics [nln39]. The special case (3) of instantaneous attenuation is a consequence of Einstein's relation [nln67].

The width of the (symmetrized) attenuation function $\alpha_{\mathrm{s}}(t)$ is a measure for the memory that governs the time evolution of the stochastic variable. In the limit of short memory (instantaneous attenuation) we have

$$\alpha_{\mathrm{s}}(t-t') \to 2\gamma\,\delta(t-t').$$

Fourier analysis:

Definitions:

$$\tilde{v}(\omega) \doteq \int_{-\infty}^{+\infty} dt\, e^{i\omega t} v(t), \quad \tilde{f}_c(\omega) \doteq \int_{-\infty}^{+\infty} dt\, e^{i\omega t} f_c(t), \quad \hat{\alpha}(\omega) \doteq \int_0^{\infty} dt\, e^{i\omega t} \alpha(t).$$

$$\Rightarrow\ v(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \tilde{v}(\omega), \quad f_c(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \tilde{f}_c(\omega).$$

Substitution of definitions in (2) yields (with $t'' = -t', \tau = t + t''$)

$$m \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t}(-i\omega)\tilde{v}(\omega) = \underbrace{- \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \int_{-\infty}^{t} dt'\, \alpha(t - t')\, e^{-i\omega t'}\, \tilde{v}(\omega)}_{(a)}$$

$$+ \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \tilde{f}_c(\omega).$$

$$\overbrace{- \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \int_{-t}^{\infty} dt''\, \alpha(t + t'')\, e^{i\omega t''}\, \tilde{v}(\omega)}^{(a)} = - \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \underbrace{\int_0^{\infty} d\tau\, \alpha(\tau)\, e^{i\omega \tau}}_{\hat{\alpha}(\omega)}\, e^{-i\omega t}\, \tilde{v}(\omega).$$

$$\Rightarrow\ -i\omega m \tilde{v}(\omega) = -\hat{\alpha}(\omega)\tilde{v}(\omega) + \tilde{f}_c(\omega).$$

Relation between Fourier amplitudes:

$$\tilde{v}(\omega) = \frac{\tilde{f}_c(\omega)}{\hat{\alpha}(\omega) - i\omega m}.$$

Spectral densities:

$$S_{vv}(\omega) \doteq \int_{-\infty}^{+\infty} d\tau\, e^{i\omega \tau} \langle v(t)v(t + \tau) \rangle, \quad S_{ff}(\omega) \doteq \int_{-\infty}^{+\infty} d\tau\, e^{i\omega \tau} \langle f_c(t)f_c(t + \tau) \rangle.$$

Correlations of Fourier amplitudes [nex119]:

$$\langle \tilde{v}(\omega)\tilde{v}^*(\omega') \rangle = 2\pi S_{vv}(\omega)\delta(\omega - \omega'), \quad \langle \tilde{f}_c(\omega)\tilde{f}_c^*(\omega') \rangle = 2\pi S_{ff}(\omega)\delta(\omega - \omega').$$

Relation between spectral densities:

$$S_{vv}(\omega) = \frac{S_{ff}(\omega)}{|\hat{\alpha}(\omega) - i\omega m|^2}. \tag{5}$$

Fluctuation-dissipation relation (4) in frequency domain:

$$\langle \tilde{f}_{\mathrm{c}}(\omega)\tilde{f}_{\mathrm{c}}^*(\omega')\rangle = 2\pi k_{\mathrm{B}}T \overbrace{\int_{-\infty}^{+\infty} d\tau\, e^{i\omega\tau}\alpha_{\mathrm{s}}(\tau)}^{\tilde{\alpha}_{\mathrm{s}}(\omega) = \hat{\alpha}(\omega) + \hat{\alpha}^*(\omega)}\, \delta(\omega - \omega')$$

$$= 4\pi k_{\mathrm{B}}T\mathrm{Re}\{\hat{\alpha}(\omega)\}\delta(\omega - \omega').$$

$$\Rightarrow\ S_{ff}(\omega) = 2k_{\mathrm{B}}T\mathrm{Re}\{\hat{\alpha}(\omega)\}. \tag{6}$$

Note: If $S_{ff}(\omega) \geq 0$ then $\alpha(t)$ has a global maximum at $t = 0$.

Solution of generalized Langevin equation (2) expressed by the spectral density of the stochastic variable assembled from (5) and (6):

$$S_{vv}(\omega) = \frac{2k_{\mathrm{B}}T\mathrm{Re}\{\hat{\alpha}(\omega)\}}{|\hat{\alpha}(\omega) - i\omega m|^2}. \tag{7}$$

Limit of instantaneous attenuation: $\hat{\alpha}(\omega) \to \gamma$

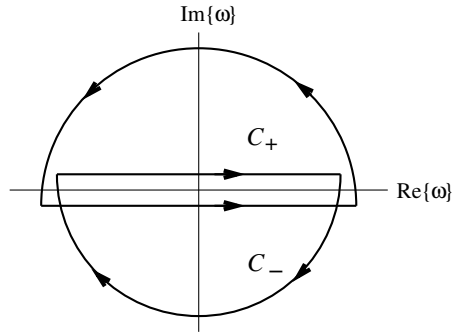$$S_{vv}(\omega) \to \frac{2k_{\mathrm{B}}T\gamma}{\gamma^2 + \omega^2 m^2}. \tag{8}$$

3

Velocity autocorrelation function:

Stationary state. Use $\hat{\alpha}(-\omega) = \hat{\alpha}^*(\omega)$.

$$
\langle v(t)v(0)\rangle = k_B T \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{\pm i\omega t} \overbrace{\frac{2\mathrm{Re}\{\hat{\alpha}(\omega)\}}{|\hat{\alpha}(\omega) - i\omega m|^2}}^{\text{symmetric in } \omega}
$$

$$
= \frac{k_B T}{2\pi} \int_{-\infty}^{+\infty} d\omega\, e^{\pm i\omega t} \frac{\hat{\alpha}(\omega) + \hat{\alpha}^*(\omega)}{[\hat{\alpha}(\omega) - i\omega m][\hat{\alpha}^*(\omega) + i\omega m]}
$$

$$
= \frac{k_B T}{2\pi} \int_{-\infty}^{+\infty} d\omega\, e^{\pm i\omega t} \left[\underbrace{\frac{1}{\hat{\alpha}(\omega) - i\omega m}}_{(a)} + \underbrace{\frac{1}{\hat{\alpha}^*(\omega) + i\omega m}}_{(b)} \right].
$$

(a) analytic for $\mathrm{Im}\{\omega\} > 0$,

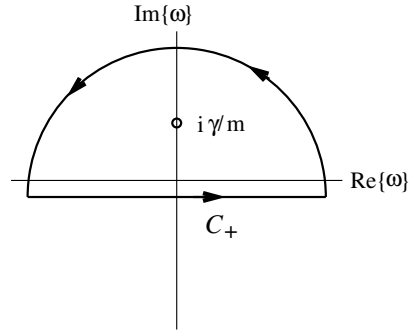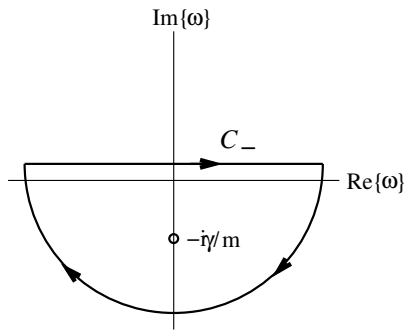(b) analytic for $\mathrm{Im}\{\omega\} < 0$.

$$
\langle v(t)v(0)\rangle = \frac{k_B T}{2\pi} \oint_{\mathcal{C}_-} d\omega\, \frac{e^{-i\omega t}}{\hat{\alpha}(\omega) - i\omega m} = \frac{k_B T}{2\pi} \oint_{\mathcal{C}_+} d\omega\, \frac{e^{i\omega t}}{\hat{\alpha}^*(\omega) + i\omega m}.
$$

Limit of instantaneous attenuation: $\hat{\alpha}(\omega) \to \gamma$ [nex120]

$$
\langle v(t)v(0)\rangle = \frac{k_B T}{2\pi} \oint_{\mathcal{C}_-} d\omega\, \frac{e^{-i\omega t}}{\gamma - i\omega m} = \frac{k_B T}{2\pi} \oint_{\mathcal{C}_+} d\omega\, \frac{e^{i\omega t}}{\gamma + i\omega m} = \frac{k_B T}{m} e^{-\gamma t/m}.
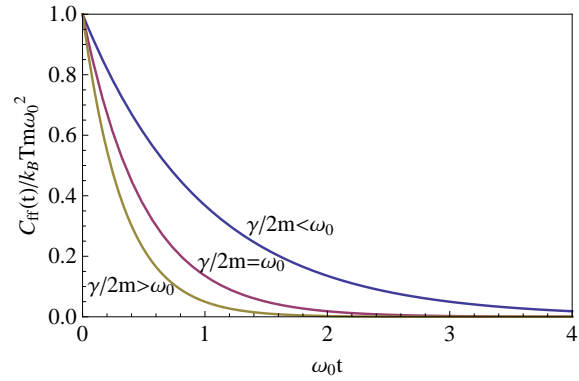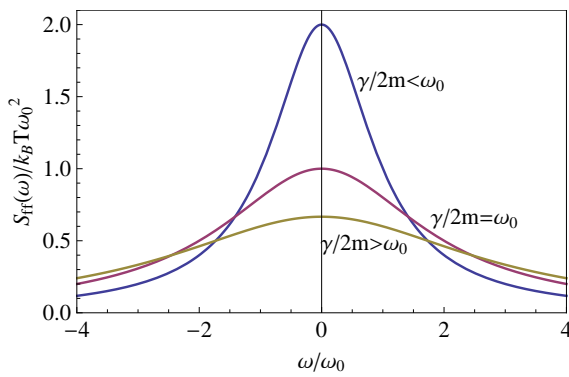$$

4

Attenuation with memory [nln22]

Generalized Langevin equation for Brownian harmonic oscillator:

$$m\frac{dx}{dt} + \int_{-\infty}^{t} dt' \alpha(t-t')x(t') = \frac{1}{\omega_0}f(t), \quad \alpha(t) = m\omega_0^2 e^{-(\gamma/m)t}.$$

Random force (correlated noise):

$$S_{ff}(\omega) = \frac{2k_BT\gamma m^2\omega_0^2}{\gamma^2 + m^2\omega^2}, \qquad C_{ff}(t) = k_BTm\omega_0^2 e^{-(\gamma/m)t}.$$

Stochastic variable (position):

$$S_{xx}(\omega) = \frac{2k_BT\gamma}{m^2(\omega_0^2-\omega^2)^2 + \gamma^2\omega^2},$$

$$C_{xx}(t) = \begin{cases} \frac{k_BT}{m\omega_0^2} e^{-\frac{\gamma}{2m}t}\left[\cos\omega_1 t + \frac{\gamma}{2m\omega_1}\sin\omega_1 t\right], & \omega_1 = \sqrt{\omega_0^2 - \gamma^2/4m^2} > 0 \\ \frac{k_BT}{m\omega_0^2} e^{-\frac{\gamma}{2m}t}\left[1 + \frac{\gamma}{2m}t\right], & \omega_0 = \gamma/2m \\ \frac{k_BT}{m\omega_0^2} e^{-\frac{\gamma}{2m}t}\left[\cosh\Omega_1 t + \frac{\gamma}{2m\Omega_1}\sinh\Omega_1 t\right], & \Omega_1 = \sqrt{\gamma^2/4m^2 - \omega_0^2} > 0 \end{cases}$$
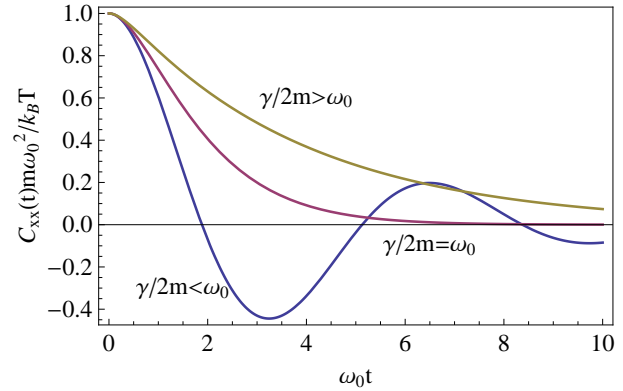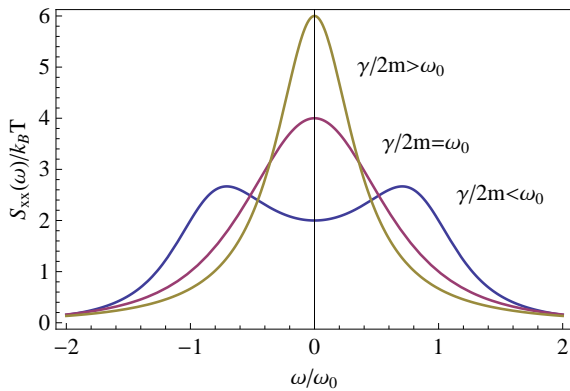
[nex120] Velocity correlation function of Brownian particle III

The generalized Langevin equation for a particle of mass m constrained to move along a straight line,

$$m\frac{dv}{dt} = -\int_{-\infty}^{t} dt'\alpha(t-t')v(t') + f(t),$$

is known to produce the following expression for the spectral density of the velocity:

$$S_{vv}(\omega) = \frac{S_{ff}(\omega)}{|\hat{\alpha}(\omega) - i\omega m|^2}, \quad \hat{\alpha}(\omega) \doteq \int_0^{\infty} dt\, e^{i\omega t}\alpha(t), \quad S_{ff}(\omega) = 2k_BT\,\Re[\hat{\alpha}(\omega)],$$

where the relation between the random-force spectral density, $S_{ff}(\omega)$, and the Laplace-transformed attenuation function, $\hat{\alpha}(\omega)$, is dictated by the fluctuation-dissipation theorem.

The special case of Brownian motion (see [nex55], [nex119]) uses attenuation without memory: $\alpha(t-t') = 2\gamma\delta(t-t')\theta(t-t')$. Calculate the velocity correlation function, $\langle v(t)v(t')\rangle$, of the Brownian particle in thermal equilibrium from the above expression for $S_{vv}(\omega)$ via contour integration in the plane of complex ω.

Solution:

Brownian Harmonic Oscillator [nln75]

A Brownian particle of mass m, immersed in a fluid, is constrained to move along the x-axis and subject to a restoring force. The motion is simultaneously propelled and attenuated by the fluid particles. We analyze this system in several different ways with consistent results.

Two equivalent specifications of the system by Langevin-type equations:

- Attenuation without memory and white-noise:

$$m\ddot{x} + \gamma\dot{x} + kx = f_{\mathrm{w}}(t), \tag{1}$$

   γ: damping constant representing instantaneous attenuation,

   $k = m\omega_0^2$: stiffness of the restoring force,

   $f_{\mathrm{w}}(t)$: white-noise random force.

- Attenuation with memory and correlated-noise:

$$m\frac{dx}{dt} + \int_{-\infty}^{t} dt'\alpha(t - t')x(t') = \frac{1}{\omega_0}f_{\mathrm{c}}(t), \tag{2}$$

   $\alpha(t) = m\omega_0^2 e^{-(\gamma/m)t}$: attenuation function,

   $f_{\mathrm{c}}(t)$: correlated-noise random force.

The random forces and their associated types of attenuation must satisfy the the fluctuation-dissipation relation of [nln72].

Tasks carried out in a series of exercises:

- Equivalence of (1) and (2) shown via derivation of (1) from (2) [nex129].
- Fourier analysis of (1) yields spectral density $S_{xx}(\omega)$ for position variable of Brownian particle [nex121].
- Position correlation function $\langle x(t)x(0)\rangle$ via inverse Fourier transform. Cases of underdamping, critical damping, and overdamping [nex122].
- Calculation of $S_{xx}(\omega)$ from (2) and $\langle x(t)x(0)\rangle$ via contour integrals [nex123]. Physical significance of pole structure in $S_{xx}(\omega)$.
- Spectral density $S_{vv}(\omega)$ and correlation function $\langle v(t)v(0)\rangle$ for velocity variable of Brownian particle [nex58].
- Langevin-type equation for velocity variable $v(t)$ and formal solution of that equation [nex59].
- Nonequilibrium velocity correlation function $\langle v(t_2)v(t_1)\rangle$ and stationarity limit $t_1, t_2 \to \infty$ with $0 < t_2 - t_1 < \infty$ [nex60].

[nex129] Brownian harmonic oscillator VII: equivalent specifications

In [nln75] we have introduced two alternative specifications for the Brownian harmonic oscillator:

$$m\ddot{x} + \gamma\dot{x} + kx = f_{\mathrm{w}}(t), \tag{1}$$

$$m\frac{dx}{dt} + \int_{-\infty}^{t} dt'\,\alpha(t - t')x(t') = \frac{1}{\omega_0}f_{\mathrm{c}}(t), \quad \alpha(t) = m\omega_0^2 e^{-(\gamma/m)t}, \tag{2}$$

where the white-noise random force $f_{\mathrm{w}}(t)$ and the correlated-noise random force $f_{\mathrm{c}}(t)$ each satisfy the fluctuation-dissipation relation introduced in [nln72]. Derive specification (1) from specification (2) including the change in random force.

Solution:

[nex121] Brownian harmonic oscillator I: Fourier analysis

The Brownian harmonic oscillator is specified by the Langevin-type equation,

$$m\ddot{x} + \gamma\dot{x} + kx = f(t), \tag{1}$$

where m is the mass of the particle, γ represents attenuation without memory, $k = m\omega_0^2$ is the spring constant, and $f(t)$ is a white-noise random force. Convert the ODE (1) into a an algebraic equation for the Fourier amplitude $\tilde{x}(\omega)$ of the position and the Fourier amplitude $\tilde{f}(\omega)$ of the random force. Proceed as in [nex119] to infer the spectral density

$$S_{xx}(\omega) = \frac{2\gamma k_B T}{m^2(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}.$$

of the position coordinate. In the process use the result $S_{ff}(\omega) = 2k_B T\gamma$ for the random-force spectral density as dictated by the fluctuation-dissipation theorem.

Solution:

[nex122] Brownian harmonic oscillator II: position correlation function

The Brownian harmonic oscillator is specified by the Langevin-type equation, $m\ddot{x} + \gamma\dot{x} + kx = f(t)$, where m is the mass of the particle, γ represents attenuation without memory, $k = m\omega_0^2$ is the spring constant, and $f(t)$ is a white-noise random force.

(a) Start from the result $S_{xx}(\omega) = 2\gamma k_B T/[m^2(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2]$ for the spectral density of the position coordinate as calculated in [nex121] to derive the position correlation function

$$\langle x(t)x(0)\rangle \doteq \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega t} S_{xx}(\omega) = \begin{cases} \frac{k_B T}{m\omega_0^2} e^{-\frac{\gamma}{2m}t} \left[\cos\omega_1 t + \frac{\gamma}{2m\omega_1}\sin\omega_1 t\right] \\[2mm] \frac{k_B T}{m\omega_0^2} e^{-\frac{\gamma}{2m}t} \left[1 + \frac{\gamma}{2m}t\right] \\[2mm] \frac{k_B T}{m\omega_0^2} e^{-\frac{\gamma}{2m}t} \left[\cosh\Omega_1 t + \frac{\gamma}{2m\Omega_1}\sinh\Omega_1 t\right] \end{cases}$$

for the cases $\omega_1 = \sqrt{\omega_0^2 - \gamma^2/4m^2} > 0$ (underdamped), $\omega_0^2 = \gamma^2/4m^2$ (critically damped), and $\Omega_1 = \sqrt{\gamma^2/4m^2 - \omega_0^2} > 0$ (overdamped), respectively.

(b) Plot $S_{xx}(w)$ versus ω/ω_0 and $\langle x(t)x(0)\rangle m\omega_0^2/k_B T$ versus $\omega_0 t$ with three curves in each frame, one for each case. Use Mathematica for both parts and supply a copy of the notebook.

Solution:

[nex123] Brownian harmonic oscillator III: contour integrals

The generalized Langevin equation for the Brownian harmonic oscillator,

$$m\frac{dx}{dt} + \int_{-\infty}^{t} dt' \alpha(t-t')x(t') = \frac{1}{\omega_0}f(t), \quad \alpha(t) = m\omega_0^2 e^{-(\gamma/m)t}, \tag{1}$$

where $\alpha(t)$ is the attenuation function, $m\omega_0^2$ the spring constant, and $f(t)$ a correlated-noise random force, is known to produce the following expression for the spectral density of the position coordinate:

$$S_{xx}(\omega) = \frac{S_{ff}(\omega)/\omega_0^2}{|\hat{\alpha}(\omega) - i\omega m|^2}, \quad \hat{\alpha}(\omega) = \int_0^\infty dt\, e^{i\omega t}\alpha(t), \quad S_{ff}(\omega) = 2k_B T\Re[\hat{\alpha}(\omega)], \tag{2}$$

where the relation between the random-force spectral density, $S_{ff}(\omega)$, and the Laplace-transformed attenuation function, $\hat{\alpha}(\omega)$, is dictated by the fluctuation-dissipation relation introduced in [nln72].
(a) Calculate $S_{ff}(\omega)$ or restate the result used in [nex129] and determine its singularity structure.
(b) Evaluat $S_{xx}(\omega)$ and identify its singularity structure for the cases (i) $\gamma/2m < \omega_0$ (underdamped), (ii) $\gamma/2m = \omega_0$ (critically damped), and (iii) $\gamma/2m > \omega_0$ (overdamped).
(c) Calculate

$$\langle x(t)x(0)\rangle \doteq \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega t} S_{xx}(\omega) \tag{3}$$

via contour integration for the cases (i)-(iii) and check the results against those obtained in [nex122].

Solution:

[nex58] Brownian harmonic oscillator IV: velocity correlations

The Brownian harmonic oscillator is specified by the Langevin-type equation,

$$m\ddot{x} + \gamma\dot{x} + kx = f(t), \tag{1}$$

where m is the mass of the particle, γ represents attenuation without memory, $k = m\omega_0^2$ is the spring constant, and $f(t)$ is a white-noise random force.

(a) Find the velocity spectral density by proving the relation

$$S_{vv}(\omega) = \omega^2 S_{xx}(\omega) \tag{2}$$

and using the result from [nex121] for the position spectral density $S_{xx}(\omega)$.

(b) Find the velocity correlation function by proving the relation

$$\langle v(t)v(0)\rangle = -\frac{d^2}{dt^2}\langle x(t)x(0)\rangle \tag{3}$$

and using the result from [nex122] for the position correlation function. Distinguish the cases (i) $\omega_1 = \sqrt{\omega_0^2 - \gamma^2/4m^2} > 0$ for underdamped motion, (ii) $\omega_0^2 = \gamma^2/4m^2$ for critically damped motion, and (iii) $\Omega_1 = \sqrt{\gamma^2/4m^2 - \omega_0^2} > 0$ for overdamped motion.

(c) Plot $S_{vv}(\omega)$ versus ω/ω_0 and $\langle v(t)v(0)\rangle m/k_B T$ versus $\omega_0 t$ with three curves in each frame, one for each case.

Solution:

[nex59] Brownian harmonic oscillator V: formal solution for velocity

Convert the Langevin-type equation, $m\ddot{x} + \gamma\dot{x} + kx = f(t)$, for the overdamped Brownian harmonic oscillator with mass m, damping constant γ, spring constant $k = m\omega_0^2$, and white-noise random force $f(t)$ into a second-order ODE for the stochastic variable $v(t)$. Then show that

$$v(t) = v_0 e^{-\Gamma t} c(t) - \frac{\omega_0^2}{\Omega_1} x_0 e^{-\Gamma t} \sinh \Omega_1 t + \frac{1}{m} \int_0^t dt' f(t') e^{-\Gamma(t-t')} c(t-t')$$

with $\Gamma = \gamma/2m$, $\Omega_1 = \sqrt{\Gamma^2 - \omega_0^2}$, $c(t) = \cosh \Omega_1 t - (\Gamma/\Omega_1) \sinh \Omega_1 t$ is a formal solution for initial conditions $x(0) = x_0$ and $v(0) = v_0$.

Solution:

[nex60] Brownian harmonic oscillator VI: nonequilibrium correlations

Use the formal solution for the velocity from [nex59],

$$v(t) = v_0 e^{-\Gamma t} c(t) - \frac{\omega_0^2}{\Omega_1} x_0 e^{-\Gamma t} \sinh \Omega_1 t + \frac{1}{m} \int_0^t dt' f(t') e^{-\Gamma(t-t')} c(t-t'),$$

with $\Gamma = \gamma/2m$, $\Omega_1 = \sqrt{\Gamma^2 - \omega_0^2}$, $c(t) = \cosh \Omega_1 t - (\Gamma/\Omega_1) \sinh \Omega_1 t$ of the Langevin-type equation, $m\ddot{x} + \gamma \dot{x} + kx = f(t)$, for the overdamped Brownian harmonic oscillator with mass m, damping constant γ, spring constant $k = m\omega_0^2$, initial conditions $x(0) = x_0$ and $v(0) = v_0$, and white-noise random force $f(t)$ with intensity I_f to calculate the velocity correlation function $\langle v(t_2) v(t_1) \rangle$ for the nonequilibrium state. Then take the limit $t_1, t_2 \to \infty$ with $0 < t_2 - t_1 < \infty$ to recover the result of [nex58] for the stationary state.

Solution:

Langevin Dynamics from Microscopic Model [nln74]

Brownian particle harmonically coupled to N otherwise free particles that serve as a primitive form of heat bath. [Wilde and Singh 1998]

Classical Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2m} + \sum_{i=1}^{N} \left(\frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 \bar{x}_i^2 \right), \quad \bar{x}_i \doteq x_i - \frac{c_i x}{m_i \omega_i^2}, \tag{1}$$

where $m_i \omega_i^2$ is the stiffness of the harmonic coupling between the Brownian particle and one of the heat-bath particles. The c_i are conveniently scaled coupling constants.

Canonical equations:

$$\frac{dx}{dt} = \frac{\partial \mathcal{H}}{\partial p} = \frac{p}{m}, \quad \frac{dp}{dt} = -\frac{\partial \mathcal{H}}{\partial x} = \sum_{i=1}^{N} c_i \bar{x}_i, \tag{2a}$$

$$\frac{dx_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i} = \frac{p_i}{m_i}, \quad \frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial x_i} = -m_i \omega_i^2 \bar{x}_i; \quad i = 1, \ldots, N. \tag{2b}$$

Elimination of momenta yields 2nd-order ODEs:

$$m \frac{d^2 x}{dt^2} = m \frac{d\dot{x}}{dt} = F(t), \quad F(t) \doteq \sum_{i=1}^{N} c_i \bar{x}_i, \tag{3a}$$

$$m_i \frac{d^2 x_i}{dt^2} = -m_i \omega_i^2 x_i + c_i x, \quad i = 1, \ldots, N. \tag{3b}$$

Formal solution of (3b):

$$x_i(t) = x_i(0) \cos(\omega_i t) + \frac{\dot{x}_i(0)}{\omega_i} \sin(\omega_i t) + \frac{c_i}{m_i \omega_i} \underbrace{\int_0^t dt' x(t') \sin\left(\omega_i(t - t') \right)}_{A(t)}. \tag{4}$$

Integrate by parts:

$$A(t) = \frac{1}{\omega_i} \left[x(t) - x(0) \cos(\omega_i t) - \int_0^t dt' \dot{x}(t') \cos\left(\omega_i(t - t') \right) \right]. \tag{5}$$

Assemble parts, then use (1) and (3a):

$$x_i(t) = \left(x_i(0) - \frac{c_i}{m_i \omega_i^2} x(0) \right) \cos(\omega_i t) + \frac{\dot{x}_i(0)}{\omega_i} \sin(\omega_i t)$$
$$+ \frac{c_i}{m_i \omega_i^2} \left[x(t) - \int_0^t dt' \dot{x}(t') \cos\left(\omega_i(t - t') \right) \right], \tag{6}$$

$$\bar{x}_i(t) = \bar{x}_i(0)\cos(\omega_i t) + \frac{\dot{x}_i(0)}{\omega_i}\sin(\omega_i t) - \frac{c_i}{m_i\omega_i^2}\int_0^t dt' \dot{x}(t')\cos\left(\omega_i(t-t')\right),$$

$$F(t) = \sum_{i=1}^{N}\left[c_i\bar{x}_i(0)\cos(\omega_i t) + \frac{c_i}{\omega_i}\dot{x}_i(0)\sin(\omega_i t)\right.$$
$$\left. - \frac{c_i^2}{m_i\omega_i^2}\int_0^t dt' \dot{x}(t')\cos\left(\omega_i(t-t')\right)\right]. \tag{7}$$

Expectation values at thermal equilibrium:

$$\langle\bar{x}_i(0)\rangle = 0, \quad \langle\dot{x}_i(0)\rangle = 0, \quad \omega_i^2\langle\bar{x}_i(0)\bar{x}_j(0)\rangle = \langle\dot{x}_i(0)\dot{x}_j(0)\rangle = \frac{k_B T}{m_i}\delta_{ij}.$$

$$\langle F(t)\rangle = -\int_0^t dt' \dot{x}(t')\alpha_s(t-t'), \quad \alpha_s(t-t') = \underbrace{\sum_{i=1}^{N}\frac{c_i^2}{m_i\omega_i^2}\cos\left(\omega_i(t-t')\right)}_{\text{attenuation function}}.$$

Random force:

$$f(t) \doteq F(t) - \langle F(t)\rangle = \sum_{i=1}^{N}\left[c_i\bar{x}_i(0)\cos(\omega_i t) + \frac{c_i}{\omega_i}\dot{x}_i(0)\sin(\omega_i t)\right]. \tag{8}$$

Generalized Langevin equation:

$$m\frac{d\dot{x}}{dt} = -\int_0^t dt' \dot{x}(t')\alpha_s(t-t') + f(t). \tag{9}$$

Fluctuation-dissipation relation:

$$\langle f(t)f(t')\rangle = \sum_{i=1}^{N}\left[c_i^2\cos(\omega_i t)\cos(\omega_i t')\underbrace{\langle\bar{x}_i(0)\bar{x}_i(0)\rangle}_{k_B T/m_i\omega_i^2}\right.$$
$$\left. + \frac{c_i^2}{\omega_i^2}\sin(\omega_i t)\sin(\omega_i t')\underbrace{\langle\dot{x}_i(0)\dot{x}_i(0)\rangle}_{k_B T/m_i}\right]$$
$$= k_B T\sum_{i=1}^{N}\frac{c_i^2}{m_i\omega_i^2}\cos\left(\omega_i(t-t')\right) = k_B T\alpha_s(t-t'). \tag{10}$$

Brownian motion: panoramic view [nln23]

- Levels of contraction (horizontal)
- Modes of description (vertical)

$$\longrightarrow \quad \text{contraction} \quad \longrightarrow$$

	N-particle phase space	1-particle phase space	configuration space
relevant space	N-particle phase space	1-particle phase space	configuration space
dynamical variables	$\{\mathbf{x}_i,\ \mathbf{p}_i\}$	$\mathbf{x},\ \mathbf{p}$	$\mathbf{x}$
theoretical framework	Hamiltonian mechanics	Langevin theory	Einstein theory
... for dynamical variables	generalized Langevin equation	Langevin equation (for $dt \ll \tau_R$)	Langevin equation (for $dt \gg \tau_R$)
... for probability distribution	quant./class. Liouville equation	Fokker-Planck equation (Ornstein-Uhlenbeck process)	Fokker-Planck equation (diffusion process)

- Here dt is the time step used in the theory and τ_R is the relaxation time associated with the drag force the Brownian particle experiences.
- The generalized Langevin equation is equivalent to the Hamiltonian equation of motion for a generic classical many-body system and equivalent to the Heisenberg equation of motion for a generic quantum many-body system.