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Statistical Physics

Lecture Notes
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General Literature

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Contents

1 Introduction

Our everyday experience is determined by classical mechanics and statistical physics. The physical processes, which we are witnessing consciously or unconsciously involve a huge number of interacting atoms and molecules. The air of the earth's atmosphere, for example, is comprised of simple gas molecules which can display complex patterns, turbulence, and chaotic behavior with severe consequences on our lives. Similarly, biological processes such as DNA replication, cell division, and the transport of blood through our body is determined by a multitude of particles and interactions. The understanding of the diversity of phenomena over the broad spectrum of length and time scales calls for specific description—statistical physics.

The well-known basic dynamical equations of classical mechanics are Newton's equations of motion

$$m\frac{d^2\boldsymbol{r}}{dt^2} = \boldsymbol{F},$$

which relate the acceleration of a point particle of mass m to the forces $\boldsymbol{F}$ it is exposed to. The solution of these equations provides the complete information of the time evolution of the particle's position and velocity for a given initial condition, i.e., its dynamics is deterministic. Thus, a Newtonian system is more in the spirit of Laplace than a quantum mechanical system described by the Schrödinger equation, where position and momentum cannot be determined exactly at the same time. A numerical solution of Newton's equations of motion is obtained in molecular dynamics simulations (MD) [1, 2]. The necessary discretization of the time derivatives for such an integration algorithm, however, destroys Laplace's dream. As it turns out, the trajectories of systems through phase space depend sensitively on the initial conditions.[1] This means that two trajectories, which are initially close, will diverge exponentially as time progresses. The integration error caused by the algorithm can be considered as the source of the initial small difference between the 'true' trajectory of the system and the trajectory generated in a simulation. Any small integration error, no matter how small, will always cause the simulated trajectory to diverge exponentially from the true trajectory compatible with the initial conditions. The system then exhibits deterministic chaos. This so-called Lyapunov instability does not render molecular dynamics simulations useless. First of all, the aim of a molecular dynamics simulation is not to predict precisely a particular trajectory, rather the statistical properties are of interest. We wish to determine the average behavior of a system, which is achieved when the trajectory covers an appropriate fraction of the energy surface in phase space. Still, this would not justify the use of inaccurate trajectories unless the trajectories obtained numerically, in some sense, are close to true trajectories.

The microscopic insight provided by molecular dynamics simulations is very helpful in understanding the system behavior on that length scale: *A picture is worth a thousand words.* However, the macroscopic world, in which we are living in, requires the translation of the microscopic information (positions and velocities) into macroscopic quantities like pressure, energy, etc.; quantities which are accessible by experiments. The link is provided by statistical mechanics. In statistical mechanics, no longer an individual system

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[1]The number of degrees of freedom has to exceed the number of conserved quantities for a conservative system.

is considered, but rather an ensemble of identical systems possessing the same macroscopic properties, like the same number of particles, volume, and mean energy. Then a probability (or probability density) can be given that the system is in a particular state $\mathbf{\Gamma} = (\boldsymbol{r}_i, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_i, \ldots, \boldsymbol{p}_N)^T$ – where $\boldsymbol{p}_i$ is the momentum of particle i – in phase space with energy $H(\mathbf{\Gamma})$, namely the Boltzmann distribution

$$P(\mathbf{\Gamma}) = \frac{1}{Z} \exp\left(-H/k_B T\right),$$

where k_B is the Boltzmann factor and Z the partition function, which ensures normalization.

Objects such as polymers or colloids in solution can be considered as stochastic systems. Their size is typically much larger than that of the surrounding fluid particles, i.e., there is a significant length- and time-scales difference between such objects and the fluid particles. The interaction of the solute with the solvent can then be described in an effective way. In its simplest form, the solvent is a frictional background and exerts a random force (thermal noise) on the solute particles. A more advanced description of the solute-solvent interactions takes into account solute-induced fluid motion and its influence on the solute itself. This type of interactions are denoted as hydrodynamic interactions. They govern the dynamical behavior of polymers in a dilute solution.

In this lecture, mainly dynamical aspects of stochastic systems are discussed, exploiting both, stochastic differential equations (Langevin equation) and partial differential equations for probability densities (Fokker-Planck equation).

2 Statistical Mechanics: Basics

Newtons' equations of a system of N (identical) particles

$$m_i \frac{d^2 \boldsymbol{r}_i}{dt^2} = \boldsymbol{F}_i,$$

provide the trajectories of all particles in a system. Hence, we know everything possible of such as system. However, these information cannot be handled in general for a system of 10^{23} particles. For the (macroscopic) characterization of a system, typically only a few variables are necessary, such as particle number, temperature, volume or pressure, or for the time dependence some correlations functions. Statistical physics provides a relation between the microscopic dynamics and the macroscopic equation of state of a system.

2.1 Phase Space

In statistical physics, the dynamics of a system is described in *phase space* of generalized coordinates and momenta. A system of f degrees of freedom, with the generalized coordinates $q_1, \ldots, q_f$ and adjoined momenta $p_1, \ldots, p_f$, phase space is $2f$ dimensional. A point in this Γ-space characterizes the total system. In statistics, many "points" in Γ-space are considered, where the various systems differ in their microscopic states, but have the same macroscopic state characterized by a few variables only, e.g., energy, volume, or particle number. This assembly of points is denoted as *ensemble*. A point in phase space can be expressed by the $2f$-dimensional vector

$$\boldsymbol{\Gamma}(t) = (q_1, q_2, \ldots, q_f, p_1, p_2, \ldots, p_f)^T . \tag{1}$$

The velocity follows as time derivative of $\boldsymbol{\Gamma}$.

2.2 Distribution Function, Liouville's Theorem

The distribution of points in phase space can be described by the distribution function $\rho(\boldsymbol{\Gamma})$. More precisely, ρ is the phase-space density , i.e., $\rho(\boldsymbol{\Gamma})d^f q d^f p = \rho(\{q\}, \{p\})d^f q d^f p$ is the probability to find a system of N particles with f degrees of freedom in the volume $\{q_i, q_i + dq_i\}, \{p_i, p_i + dp_i\}$. Since the system is certainly somewhere in the whole phase space (normalization)

$$\int \rho(\{q\}, \{p\}, t) \, d^f q d^f p = 1 . \tag{2}$$

Individual points move independently in phase space, because different systems don't interact. Hence, ρ changes in time. Conservation of the total number of systems implies (*Liouville's theorem*)

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{f} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = 0 . \tag{3}$$

H is Hamilton's function. Often, this equation is written as

$$\frac{\partial \rho}{\partial t} = -[\rho, H] = -i\mathcal{L}\rho \tag{4}$$

with the Liouville operator

$$\mathcal{L}\rho = i[H, \rho] \tag{5}$$

and the Poisson bracket of two quantities $A(\{q\}, \{p\})$, $B(\{q\}, \{p\})$

$$[A, B] = \sum_{i=1}^{f} \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right). \tag{6}$$

The equation of motion (3) is equivalent to the derivative

$$\frac{d\rho}{dt} = 0, \tag{7}$$

i.e., the total change of ρ with time is zero. The formal solution of equation (3) is

$$\rho(\{q\}, \{p\}, t) = \exp\left(-i\mathcal{L}t\right) \rho(\{q\}, \{p\}, 0). \tag{8}$$

The equation of motion of a function $A(\mathbf{\Gamma}) = A(\{q\}, \{p\})$, which does not explicitly depend on time, is of conjugated form

$$\dot{A}(\mathbf{\Gamma}(t)) = \frac{dA}{dt} = i\mathcal{L}A(\mathbf{\Gamma}(t)), \tag{9}$$

or

$$A(\mathbf{\Gamma}(t)) = \exp\left(i\mathcal{L}t\right) A(\mathbf{\Gamma}(0)). \tag{10}$$

In particular, these equations apply for $\mathbf{\Gamma}$ itself and are identical with Hamilton's equations.

In the stationary state, the condition applies $[H, \rho] = 0$. Hence, equilibrium distribution functions which depend on H only, i.e., $\rho = \rho(H)$ are solutions of the stationary state equation. This is the basis for the various distribution function of equilibrium statistical mechanics.

2.3 Maximum Entropy Principle

The maximum entropy principle offers a systematic way to derive distribution and partition functions in statistical physics [3–5].

The entropy of a system of f degrees of freedom is defined as [3–5]

$$S = -k_B \int \Psi \ln \Psi \, d^f q \, d^f p, \tag{11}$$

where $\Psi = \Psi(\mathbf{q}, \mathbf{p})$ is the distribution function of the generalized coordinates and momenta $\mathbf{q}$, $\mathbf{p}$. Since entropy assumes an extremum at equilibrium, the distribution function can be obtained by a variational calculation [3]. Usually, the extremum has to be calculated under macroscopic constraints. One of the constraints is the normalization condition

$$\int \Psi \, d^f q \, d^f p = 1. \tag{12}$$

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Furthermore, we assume that the system of interest is constrained by expectation values a_k of certain quantities $h_k(\boldsymbol{q}, \boldsymbol{p})$, $k = 1, \ldots, M$ ($f \gg M$)

$$\int h_k(\boldsymbol{q}, \boldsymbol{p})\, \Psi(\boldsymbol{q}, \boldsymbol{p})\, d^f q\, d^f p = \langle h_k \rangle = a_k. \tag{13}$$

The constraints (12) and (13) are taken into account in the calculate the extremum of S by Lagrangian multipliers λ_k, i.e., the extremum is sought after of the expression

$$S' = -k_B \int \Psi \ln \Psi\, d^f q\, d^f p - k_B \sum_{k=1}^{M} \lambda_k \left\{ \int h_k(\boldsymbol{q}, \boldsymbol{p})\, \Psi(\boldsymbol{q}, \boldsymbol{p})\, d^f q\, d^f p - a_k \right\}$$

$$- k_B \lambda_0 \left\{ \int \Psi\, d^f q\, d^f p - 1 \right\}.$$

For $\delta S' = 0$ follows with arbitrary $\delta \Psi$

$$\ln \Psi + 1 + \lambda_0 + \sum_{k=1}^{M} \lambda_k h_k = 0,$$

and the distribution function is given by

$$\Psi = \frac{1}{Z} \exp\left(-\sum_{k=1}^{M} \lambda_k h_k \right), \tag{14}$$

with the partition function

$$Z = e^{\lambda_0 + 1} = \int \exp\left(-\sum_{k=1}^{M} \lambda_k h_k \right) d^f q\, d^f p. \tag{15}$$

The constraints (13) lead to the equations

$$a_k = -\frac{\partial \ln Z}{\partial \lambda_k} \tag{16}$$

to determine the Lagrangian multipliers. The extremum of the entropy is given by

$$S = k_B \left(\ln Z + \sum_{k=1}^{M} \lambda_k a_k \right). \tag{17}$$

Example: Canonical distribution

Constraint: Mean of Hamiltonian is given, $\langle H \rangle = E$

$$\Rightarrow \Psi = \frac{1}{Z} \exp\left(-\lambda H \right).$$

Equipartition of kinetic energy: $\langle E_{kin} \rangle = f k_B T / 2 \Rightarrow \beta = \lambda = 1/(k_B T)$.

Entropy: $S = k_B \left(\ln Z + \beta E \right) \Rightarrow F = -k_B T \ln Z = E - TS$.

3 Langevin Equation

3.1 Classical Mechanics

In classical mechanics, the dynamics of a system of N mass points is described by Newton's equations of motion

$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i , \qquad i = 1, \ldots, N , \tag{18}$$

where m_i is the mass of particle i, $\boldsymbol{r}_i$ its position and $\boldsymbol{F}_i$ the total force on the particle. The force follows from the potential energy $U(\{\boldsymbol{r}\})$ via

$$\boldsymbol{F}_i = -\frac{\partial U}{\partial \boldsymbol{r}_i} . \tag{19}$$

$\{\boldsymbol{r}\} = \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$ refers to all particle positions. Together with the initial conditions, the solution of the equations of motion provides the full information on the time dependence of the system.

3.2 Stochastic System

Often, only a subset of degrees of freedom is of interest, e.g., the dynamics of a colloid, a polymer, or a bacterium in a solvent (water). Then the surrounding of the particle and its interaction with the considered system of interest can be described in a stochastic manner. An (simple) example is the Langevin equation

$$m\ddot{\boldsymbol{r}} + m\gamma\dot{\boldsymbol{r}} = \boldsymbol{F} + m\boldsymbol{\Gamma}, \quad \text{or} \tag{20}$$

$$\dot{\boldsymbol{v}} + \gamma\boldsymbol{v} = \frac{1}{m}\boldsymbol{F} + \boldsymbol{\Gamma}. \tag{21}$$

Here, the frictional force $m\gamma\dot{\boldsymbol{r}}$ and the stochastic force $m\boldsymbol{\Gamma}$ describe the influence of the surrounding on the dynamics of the particle at $\boldsymbol{r}$ and velocity $\boldsymbol{v}$. γ is the friction coefficient.

The time dependence of $\boldsymbol{\Gamma}$ is unknown. Rather, $\boldsymbol{\Gamma}$ is considered a stochastic quantity with a certain (plausible) distribution. For a complete characterization of the stochastic process, all correlations of the stochastic force are necessary. Typically, a Gaussian-Markovian process is assumed, i.e., the correlation functions are δ correlated in time and all higher correlations follow from that of the first and second moment. Explicitly (1D),

$$\langle \Gamma(t) \rangle = 0, \tag{22}$$

$$\langle \Gamma(t)\Gamma(t') \rangle = q\delta(t - t'), \tag{23}$$

$$\langle \Gamma(t_1)\Gamma(t_2)\ldots\Gamma(t_{2n-1}) \rangle = 0; \text{ odd}, \tag{24}$$

$$\langle \Gamma(t_1)\Gamma(t_2)\ldots\Gamma(t_{2n}) \rangle = q^n \sum_P \delta(t_{i_1} - t_{i_2})\ldots\delta(t_{i_{2n-1}} - t_{i_{2n}}); \text{ even}, \tag{25}$$

where $\sum_P$ indicates summation over all permutations of the indices. For $N = 2$, the correlation reads

$$\langle \Gamma(t_1)\Gamma(t_2)\Gamma(t_3)\Gamma(t_4) \rangle \tag{26}$$
$$= q^2 \left[\delta(t_1 - t_2)\delta(t_3 - t_4) + \delta(t_1 - t_3)\delta(t_2 - t_4) + \delta(t_1 - t_4)\delta(t_2 - t_3) \right].$$

Note, $\boldsymbol{\Gamma}$ itself is not a function, because it is not differentiable, it is denoted as *distribution*.

3.3 Solution of Langevin Equation

Here, a system is considered without external force and in one dimension only, then

$$\dot{v}(t) = -\gamma v(t) + \Gamma(t), \tag{27}$$

which is a lineare differential equation. Solution of the equation:

- Velocity

$$v(t) = v(t_0)e^{-\gamma(t-t_0)} + \int_{t_0}^{t} e^{-\gamma(t-t')}\Gamma(t')dt', \tag{28}$$

or, for $t_0 \to -\infty$

$$v(t) = \int_{-\infty}^{t} e^{-\gamma(t-t')}\Gamma(t')dt'. \tag{29}$$

- Position, for $t_0 = 0$, $v(0) = v_0$

$$x(t) = x(0) + \int_{0}^{t} v(t')dt' \tag{30}$$

$$= x(0) + \frac{v_0}{\gamma}\left(1 - e^{-\gamma t}\right) + \frac{1}{\gamma}\int_{0}^{t}\left(1 - e^{-\gamma(t-t')}\right)\Gamma(t')dt'. \tag{31}$$

3.3.1 Averages

Velocity correlation function

$$\langle v(t_1)v(t_2)\rangle = v_0^2 e^{-\gamma(t_1+t_2)}$$

$$+ v_0 e^{-\gamma t_1}\int_{0}^{t_2} e^{-\gamma(t_2-t')}\underbrace{\langle\Gamma(t')\rangle}_{=0} dt'$$

$$+ v_0 e^{-\gamma t_2}\int_{0}^{t_1} e^{-\gamma(t_1-t')}\underbrace{\langle\Gamma(t')\rangle}_{=0} dt'$$

$$+ \int_{0}^{t_1}\int_{0}^{t_2} e^{-\gamma(t_1+t_2-t_1'-t_2')}\underbrace{\langle\Gamma(t_1')\Gamma(t_2')\rangle}_{q\delta(t_1'-t_2')} dt_1' dt_2' \tag{32}$$

$$= v_0^2 e^{-\gamma(t_1+t_2)} + \frac{q}{2\gamma}\left(e^{-\gamma|t_1-t_2|} - e^{-\gamma(t_1+t_2)}\right). \tag{33}$$

Asymptotic behavior: $\gamma t_1, \gamma t_2 \gg 1$

$$\langle v(t_1)v(t_2)\rangle = \frac{q}{2\gamma}e^{-\gamma|t_1-t_2|}, \tag{34}$$

i.e., the correlation function decays exponentially.
Stationary state

$$\langle v(t)v(t)\rangle = \langle v(t)^2\rangle = v_0^2 e^{-2\gamma t} + \frac{q}{2\gamma}\left(1 - e^{-2\gamma t}\right) \overset{t\to\infty}{\longrightarrow} \frac{q}{2\gamma}. \tag{35}$$

Equipartition theorem: kinetic energy E of particle

$$\langle E \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \frac{q}{2\gamma} = \frac{1}{2} k_B T, \tag{36}$$

k_B Boltzmann constant, T temperature

$$\Rightarrow q = \frac{2\gamma k_B T}{m} \ ,$$

$$\Rightarrow \langle \Gamma(t_1) \Gamma(t_2) \rangle = \frac{2\gamma k_B T}{m} \delta(t_1 - t_2) \ .$$

Mean square displacement

1. Moment: Average position

$$\langle x \rangle = x_0 + \frac{v_0}{\gamma} \left(1 - e^{-\gamma t} \right) . \tag{37}$$

For $x_0 = 0$, $v_0 = 0 \Rightarrow \langle x \rangle = 0$.

2. Moment: Mean square displacement

$$\langle (x(t) - x_0)^2 \rangle = \int_0^t \int_0^t \langle v(t_1) v(t_2) \rangle \, dt_1 dt_2$$
$$= \frac{1}{\gamma^2} \left(v_0^2 - \frac{q}{2\gamma} \right) \left(1 - e^{-\gamma t} \right)^2 + \frac{q}{\gamma^2} t - \frac{q}{\gamma^3} \left(1 - e^{-\gamma t} \right) . \tag{38}$$

The average $\langle \ldots \rangle$ means that (infinitely) many realizations of the stochastic force are considered, i.e., an ensemble is considered or infinitely many (different) realizations of the same system. Since v_0 is not a stochastic variable, this realizations could all start out with the same velocity v_0. Alternatively, and this approach is adopted here, an ensemble can be considered, where the initial velocity is taken from the stationary state distribution, i.e., every realization starts from a stationary (equilibrium) state. Then

$$v_0^2 \longrightarrow \langle v_0^2 \rangle = \frac{q}{2\gamma} = \frac{k_B T}{m} \tag{39}$$

and

$$\langle (x(t) - x(0))^2 \rangle = \frac{q}{\gamma^2} t - \frac{q}{\gamma^3} \left(1 - e^{-\gamma t} \right) . \tag{40}$$

Asymptotic behavior:

- Ballistic motion: $\gamma t \ll 1$

$$\langle (x(t) - x(0))^2 \rangle = \frac{q}{\gamma^2} t - \frac{q}{\gamma^3} \left(1 - 1 + \gamma t - \frac{\gamma^3}{2} t^2 \pm \ldots \right) = \frac{q}{2\gamma} t^2 = \langle v_0^2 \rangle t^2. \tag{41}$$

- Diffusive motion: $\gamma t \gg 1$

$$\langle (x(t) - x(0))^2 \rangle = \frac{q}{\gamma^2} t = \frac{2 k_B T}{\gamma m} t = 2 D t, \tag{42}$$

with the diffusion coefficient $D = k_B T / (\gamma m)$.

3.3.2 Diffusion coefficient

Definition of diffusion coefficient via

- Einstein relation: mean square displacement

$$\left\langle (x(t) - x(0))^2 \right\rangle = 2Dt, \ D = \frac{k_B T}{m\gamma}; \qquad t \to \infty. \tag{43}$$

- Green-Kubo relation: velocity correlation function

$$D = \int_0^\infty \left\langle v(t)v(0) \right\rangle dt = \frac{q}{2\gamma} \int_0^\infty e^{-\gamma t} dt = \frac{q}{2\gamma^2} = \frac{k_B T}{m\gamma}, $$

with stationary state correlation function $\left\langle v(t)v(0) \right\rangle = qe^{-\gamma t}/(2\gamma)$.

3.3.3 Over-damped motion

Over-damped motion refers to the limit, where $m\dot{v} \ll m\gamma v$. Then,

$$v = \dot{x} = \frac{1}{\gamma}\Gamma. \tag{44}$$

Solution of the equation

$$x(t) = x(0) + \frac{1}{\gamma} \int_0^t \Gamma(t')dt'. \tag{45}$$

- Velocity correlation function

$$\left\langle v(t_1)v(t_2) \right\rangle = \frac{1}{\gamma^2} \left\langle \Gamma(t_1)\Gamma(t_2) \right\rangle = \frac{q}{\gamma^2} \delta(t_1 - t_2) = 2D\delta(t_1 - t_2), \tag{46}$$

i.e., velocities are uncorrelated. The distribution of velocities is decoupled from the distribution of positions. The velocities are always in thermal equilibrium (canonical ensemble).

- Mean square displacement

$$\left\langle (x(t - x(0))^2 \right\rangle = \int_0^t \int_0^t \left\langle v(t_1)v(t_2) \right\rangle dt_1 dt_2 = \frac{qt}{\gamma^2} = 2Dt. \tag{47}$$

3.4 Solution of Langevin Equation: Three Dimensions

Equations of motion

$$\dot{v}_\alpha = -\gamma v_\alpha + \Gamma_\alpha; \qquad \alpha \in \{x, y, z\}. \tag{48}$$

Stochastic force

$$\left\langle \boldsymbol{\Gamma}(t) \right\rangle = 0,$$
$$\left\langle \Gamma_\alpha(t)\Gamma_\beta(t') \right\rangle = q\delta_{\alpha\beta}\delta(t - t'). \tag{49}$$

Mean square displacement

$$\left\langle (\boldsymbol{r}(t) - \boldsymbol{r}(0))^2 \right\rangle = \sum_{\alpha=1}^3 \left\langle (x_\alpha(t) - x_\alpha(0))^2 \right\rangle \overset{t \to \infty}{\longrightarrow} \frac{6k_B T}{m\gamma}t. \tag{50}$$

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3.5 Many Variables: Ornstein-Uhlenbeck Process

Consider the set of Langevin equations for N stochastic variables x_i

$$\dot{x}_i + \sum_{j=1}^{N} \gamma_{ij} x_j = \Gamma_i(t). \tag{51}$$

γ_{ij} are time independent coefficients. Hence, Eq. (51) is the most general linear equation with constant coefficients. The variables can be positions or velocities, i.e., some of the stochastic forces Γ_i can be zero.

The stochastic forces read

$$\langle \Gamma_i \rangle = 0,$$

$$\langle \Gamma_i(t) \Gamma_j(t') \rangle = q_{ij} \delta(t - t'); \qquad q_{ij} = q_{ji}. \tag{52}$$

Again, a Gaussian and Markovian process is assumed (white noise).

Solution of the equations of motion

- Homogeneous equation: $\dot{x}_i^h = - \sum_{j=1}^{N} \gamma_{ij} x_j^h$
  or, with the vector $\boldsymbol{x} = (x_1, \ldots, x_N)^T$ and the matrix

$$\boldsymbol{\gamma} = \begin{pmatrix} \gamma_{11} & \cdots & \gamma_{1N} \\ \vdots & \vdots & \vdots \\ \gamma_{N1} & \cdots & \gamma_{NN} \end{pmatrix},$$

$$\dot{\boldsymbol{x}}^h = -\boldsymbol{\gamma} \boldsymbol{x}^h. \tag{53}$$

  Solution

$$\boldsymbol{x}^h(t) = \exp\left(-\boldsymbol{\gamma} t\right) \boldsymbol{x}(0) = \mathbf{G}(t) \boldsymbol{x}(0), \tag{54}$$

  withe the initial condition $G_{ij}(0) = \delta_{ij}$. Evidently, the Green's function G_{ij} satisfies the differential equation

$$\dot{G}_{ij}(t) + \sum_{k=1}^{N} \gamma_{ik} G_{kj} = 0. \tag{55}$$

- Inhomogeneous equation (variation of constant): $\boldsymbol{x}(t) = \boldsymbol{x}^h(t) + \boldsymbol{x}^{ih}(t)$

$$\boldsymbol{x}(t) = \mathbf{G}(t) \boldsymbol{x}(0) + \int_0^t \mathbf{G}(t) \mathbf{G}(t')^{-1} \boldsymbol{\Gamma}(t') dt'$$

$$= \mathbf{G}(t) \boldsymbol{x}(0) + \int_0^t \mathbf{G}(t - t') \boldsymbol{\Gamma}(t') dt'. \tag{56}$$

  In components

$$x_i(t) = \sum_{j}^{N} G_{ij} x_j(t) + \sum_{j=1}^{N} \int_0^t G_{ij}(t - t') \Gamma_j(t') dt'. \tag{57}$$

3.5.1 Calculation of Moments

With Eq. (52), the first moment and the variance are obtained as

$$M_i = \langle x_i(t) \rangle = \sum_{j=1}^{N} G_{ij} x_j(0) \tag{58}$$

$$\sigma_{ij} = \sigma_{ji} = \langle (x_i(t) - \langle x_i(t) \rangle)(x_j(t) - \langle x_j(t) \rangle) \rangle \tag{59}$$

$$= \int_0^t \int_0^t \sum_{k=1}^{N} \sum_{k'=1}^{N} G_{ik}(t_1') G_{jk'}(t_2') q_{kk'} \delta(t_1' - t_2') dt_1' dt_2'$$

$$= \sum_{k=1}^{N} \sum_{k'=1}^{N} \int_0^t G_{ik}(t') G_{jk'}(t') dt' q_{kk'} .$$

The σ_{ij} obey the differential equation

$$\dot{\sigma}_{ij} = -\sum_{k=1}^{N} \gamma_{ik} \sigma_{kj} - \sum_{k=1}^{N} \gamma_{jk} \sigma_{ki} + q_{ij} , \tag{60}$$

which follows from differentation of Eq. (59) and the equation for G_{ij} (55):

$$\dot{\sigma}_{ij} = \sum_{k=1}^{N} \sum_{k'=1}^{N} G_{ik}(t) G_{jk'}(t) q_{kk'} , \tag{61}$$

$$\ddot{\sigma}_{ij} = \sum_{k=1}^{N} \sum_{k'=1}^{N} \dot{G}_{ik}(t) G_{jk'}(t) q_{kk'} + \sum_{k=1}^{N} \sum_{k'=1}^{N} G_{ik}(t) \dot{G}_{jk'}(t) q_{kk'} \tag{62}$$

$$= -\sum_{k=1}^{N} \sum_{k'=1}^{N} \sum_{k''=1}^{N} \gamma_{ik''} G_{k''k}(t) G_{jk'}(t) q_{kk'} - \sum_{k=1}^{N} \sum_{k'=1}^{N} \sum_{k''=1}^{N} G_{ik}(t) \gamma_{jk''} G_{k''k'}(t) q_{kk'} , \tag{63}$$

or

$$\ddot{\sigma}_{ij} = -\sum_{k=1}^{N} \gamma_{ik} \dot{\sigma}_{kj} - \sum_{k=1}^{N} \gamma_{jk} \dot{\sigma}_{ki} . \tag{64}$$

With $\dot{\sigma}_{ij}(0) = q_{ij}$ and $\sigma_{ij}(0) = 0$ follows Eq. (60).

If the real parts of the eigenvalues of γ_{ij} are larger than zero, the Green's function vanishes in the asymptotic limit $t \to \infty$, i.e.,

$$\sigma_{ij} = \sum_{k=1}^{N} \sum_{k'=1}^{N} \int_0^{\infty} G_{ik}(t) G_{jk'} \, dt \, q_{kk'} . \tag{65}$$

At short times, Taylor expansion yields ($t \geq 0$)

$$\mathbf{G} = \mathbf{I} - \boldsymbol{\gamma} t + \frac{1}{2} \boldsymbol{\gamma}^2 t^2 + \dots \tag{66}$$

$$\mathbf{M} = \boldsymbol{x}(0) - \boldsymbol{\gamma} \boldsymbol{x}(0) t + O(t^2) \tag{67}$$

$$\boldsymbol{\sigma}(t) = \boldsymbol{q} t - \frac{1}{2} (\boldsymbol{\gamma} \boldsymbol{q} + (\boldsymbol{\gamma} \boldsymbol{q})^T) t^2 + \dots \tag{68}$$

Hence, the matrix $\boldsymbol{\gamma}$ determines the first moment, whereas the matrix $\boldsymbol{q}$ (noise) determines the variance.

3.6 Nonlinear Langevin Equation

Only the one-variable case will be considered. Equation of motion

$$\dot{x}(t) = h(x,t) + g(x,t)\Gamma(t). \tag{69}$$

Stochastic force

$$\langle \Gamma(t) \rangle = 0; \qquad \langle \Gamma(t)\Gamma(t') \rangle = 2\delta(t-t'). \tag{70}$$

The factor q is set to unity, because $g(x,t)$ appears in the equation of motion. For $g = const.$, the noise is denoted as *additive noise*, whereas for $g = g(x)$, the noise is called *multiplicative noise*.

For a single variable, the transformation $\dot{y} = \dot{x}/g(x)$, $g(x) \neq 0$, leads to

$$\dot{y}(t) = \frac{h(x,t)}{g(x)} + \Gamma(t),$$

$$y = f(x) = \int^x \frac{dx'}{g(x')}, \qquad \Rightarrow x = f(y)^{-1} = x(y),$$

i.e., multiplicative noise turns into additive noise.

The problem of multiplicative noise is the appearance of correlations $\langle g(x,t)\Gamma(t) \rangle$, $x = x(\Gamma)$. Which posses the question, which x value should be chosen for $g(x,t)$? Here, further assumptions are necessary. One solution is to use the representation of the δ function

$$\delta_\epsilon = \begin{cases} \frac{1}{\epsilon}, & -\frac{\epsilon}{2} < t < \frac{\epsilon}{2} \\ 0, & \text{elsewhere} \end{cases}. \tag{71}$$

As a consequence $\langle g(x,t)\Gamma(t) \rangle \neq 0$, if $g = g(x)$ and a noise-induced drift appears.

Example

$$\dot{x} = ax\Gamma(t). \tag{72}$$

(Formal) solution of equation of motion

$$x(t) = x(0) \exp\left(a \int_0^t \Gamma(t')dt' \right).$$

Average (Gaussian process)

$$\langle x(t) \rangle = x(0) \left\langle \exp\left(a \int_0^t \Gamma(t')dt' \right) \right\rangle = x(0) \exp\left(\frac{1}{2}a^2 \int_0^t \int_0^t \langle \Gamma(t_1)\Gamma(t_2) \rangle dt_1 dt_2 \right)$$

$$= x(0) \exp(a^2 t).$$

Note,

$$\frac{d}{dt} \langle x(t) \rangle = \langle \dot{x}(t) \rangle = a^2 \langle x(t) \rangle \overset{(72)}{=} a \langle x\Gamma(t) \rangle.$$

3.6.1 Ito and Stratonovich Definitions

Solution of Eq. (69)

$$x(t + \Delta t) = x(t) + \int_t^{t+\Delta t} h(x(t'), t')dt' + \int_t^{t+\Delta t} g(x(t'), t')\Gamma(t')dt'$$

$$= x(t) + \int_t^{t+\Delta t} h(x(t'), t')dt' + \int_t^{t+\Delta t} g(x(t'), t')dW(t'), \qquad (73)$$

with $dW(t) = \Gamma(t)dt$ (siehe Öttinger). Assumption: $\Delta W = W(t + \Delta t) - W(t) = \int_t^{t+\Delta t} \Gamma(t')dt'$ exists.

Consider integral $I = \int_0^t g(x(t'), t')dW(t') = \int_0^t g(W(t'), t')dW(t')$.

Definition of integrals

- Riemann integration

$$\int_0^t f(t')dt = \lim_{N \to \infty} \sum_{j=1}^N f(\tau_j)(t_{j+1} - t_j),$$

$t_{j+1} = t_j + \Delta t$, $\tau_j \in [t_j, t_{j+1}]$.

- Riemann-Stieltjes integration:

$$\int_0^t f(t')dg(t') = \lim_{N \to \infty} \sum_{j=1}^N f(\tau_j)[g(t_{j+1}) - g(t_j)].$$

For any smooth function (continuous and infinitely often differentiable), there is convergence for arbitrary $\tau_j \in [t_j, t_{j+1}]$. However, $W(t)$ is not smooth, i.e., asymptotic value depends on choice of τ_j.

Definitions for stochastic quantities:

- Ito: $\tau_j = t_j$, $W(\tau_j) = W(t_j)$,

- Stratonovich: $\tau_j = (t_j + t_{j+1})/2$, $W(\tau_j) = (W(t_j) + W(t_{j+1}))/2$.

That implies

$$\int_0^t g(W(t'), t')dW(t') = \begin{cases} \lim_{N \to \infty} \sum_{j=1}^N g(W(t_j), t_j)[W(t_{j+1}) - W(t_j)], & \text{Ito} \\ \lim_{N \to \infty} \sum_{j=1}^N g([W(t_j) + W(t_{j+1})]/2, [t_{j+1} + t_j]/2)[W(t_{j+1}) - W(t_j)], & \text{Str.} \end{cases}$$

$$(74)$$

Example:

$$I = \left\langle \int_0^t W(t')dW(t') \right\rangle,$$

with $\langle W(t_i)W(t_k) \rangle = \left\langle \int_0^{t_i} \Gamma(t')dt' \int_0^{t_k} \Gamma(t'')dt'' \right\rangle = 2 \int_0^{t_i} dt' = 2t_i$, for $t_k \geq t_i$.

- Ito

$$I = \lim_{N\to\infty} \sum_{j=1}^{N} \langle W(t_j)[W(t_{j+1}) - W(t_j)] \rangle = \lim_{N\to\infty} \sum_{j=1}^{N} (2t_i - 2t_i) = 0.$$

- Stratonovich

$$I = \frac{1}{2} \lim_{N\to\infty} \sum_{j=1}^{N} \langle [W(t_j) + W(t_{j+1})] [W(t_{j+1}) - W(t_j)] \rangle$$

$$= \frac{1}{2} \lim_{N\to\infty} \sum_{j=1}^{N} \langle [W(t_j)W(t_{j+1}) + W(t_{j+1})W(t_{j+1}) - W(t_j)W(t_{j+1}) - W(t_j)W(t_j)] \rangle$$

$$= \frac{1}{2} \lim_{N\to\infty} \sum_{j=1}^{N} [2t_j + 2t_{j+1} - 2t_j - 2t_j]$$

$$= \frac{1}{2} \lim_{N\to\infty} \sum_{j=1}^{N} 2[t_{j+1} - t_j] = N\Delta t = t.$$

$$\Rightarrow \left\langle \int_0^t W(t')dW(t') \right\rangle = \frac{1}{2} \left[\langle W(t)^2 \rangle - \langle W(0)^2 \rangle \right] = t$$

This is consistent with normal calculus! Ito formalism requires new rules for calculus.

3.7   Integration of Langevin Equation

Based on the integration scheme proposed in Ref. [6], the Langevin equation can be simulated by the following algorithm, which reduces to the velocity Verlet algorithm in the limit $\gamma \to 0$:

$$\boldsymbol{r}(t + h) = \boldsymbol{r}(t) + \Delta \boldsymbol{r}(t, h), \tag{75}$$

$$\Delta \boldsymbol{r}(t, h) = \frac{1}{\gamma} \left[1 - e^{-\gamma h} \right] \boldsymbol{v}(t) + \frac{1}{\gamma^2 m} \left[\gamma h - 1 + e^{-\gamma h} \right] \boldsymbol{F}(t) + \Delta \boldsymbol{\Gamma}(t, h), \tag{76}$$

$$\boldsymbol{v}(t + h) = \frac{\gamma}{e^{\gamma h} - 1} \left\{ \Delta \boldsymbol{r}(t, h) + \frac{1}{\gamma^2 m} \left[e^{\gamma h} - \gamma h - 1 \right] \boldsymbol{F}(t + h) + \Delta \boldsymbol{\Gamma}(t + h, -h) \right\}, \tag{77}$$

$$\Delta \boldsymbol{\Gamma}(t, h) = \frac{1}{\gamma m} \int_t^{t+h} \left[1 - e^{-\gamma(t+h-t')} \right] \boldsymbol{\Gamma}(t')dt'. \tag{78}$$

$\boldsymbol{\Gamma}(t)$ is Gaussian, hence $\Delta \boldsymbol{\Gamma}(t, h)$ is Gaussian.

Calculation of stochastic forces:

- Take $\Delta \boldsymbol{\Gamma}$ from Gaussian distribution of width σ_1

$$W(\Delta \Gamma_\alpha) = \frac{1}{\sqrt{2\pi\sigma_1^2}} \exp\left(-\frac{\Delta \Gamma_\alpha^2}{2\sigma_1^2} \right) \tag{79}$$

$\Delta \boldsymbol{\Gamma}(t + h, -h)$, $\Delta \boldsymbol{\Gamma}(t, h)$ are integrals over the same time interval of $\boldsymbol{\Gamma}(t)$, hence they are dependent.

- Take $\Delta \boldsymbol{\Gamma}(t+h, -h)$ from conditional probability distribution

$$W(\Delta \Gamma_\alpha(t,h) \Delta \Gamma_\beta(t+h,-h)) = \frac{1}{\sqrt{4\pi^2 \sigma_1^2 \sigma_2^2 (1-\eta^2)}} \tag{80}$$

$$\times \exp\left(-\frac{\sigma_2^2 \Delta \Gamma_\alpha^2(t,h) - 2\sigma_1\sigma_2\eta \Delta \Gamma_\alpha(t,h) \Delta \Gamma_\beta^2(t+h,-h) + \sigma_1^2 \Delta \Gamma_\beta^2(t+h,-h)}{2\sigma_1^2 \sigma_2^2 (1-\eta^2)}\right)$$

In practice, $\Delta \boldsymbol{\Gamma}(t,h)$ and $\Delta \boldsymbol{\Gamma}(t+h,-h)$ are calculated according as:

- Calculate Gaussian distributed random vectors $\boldsymbol{g}_1 = (g_{1x}, g_{1y}, g_{1z})^T$ and $\boldsymbol{g}_2$ of unit width.

- Stochastic forces

$$\Delta \boldsymbol{\Gamma}(t,h) = \boldsymbol{g}_1 \sqrt{\frac{k_B T}{m\gamma^2} C(\gamma h)}, \tag{81}$$

$$\Delta \boldsymbol{\Gamma}(t+h,-h) = \boldsymbol{g}_2 \sqrt{\frac{k_B T}{m\gamma^2} \frac{E(\gamma h)}{C(\gamma h)}} + \frac{G(\gamma h)}{C(\gamma h)} \Delta \boldsymbol{\Gamma}(t,h), \tag{82}$$

with

$$C(x) = 2x - 3 + 4e^{-x} - e^{-2x}, \tag{83}$$
$$G(x) = e^x - 2x - e^{-x}, \tag{84}$$
$$E(x) = -C(x)C(-x) - G(x)^2. \tag{85}$$

Algorithm

(i) Calculate $\Delta \boldsymbol{\Gamma}(t,h)$, $\Delta \boldsymbol{\Gamma}(t+h,-h)$

(ii) Calculate $\Delta \boldsymbol{r}(t,h)$

(iii) Calculate $\boldsymbol{r}(t+h)$ and $\boldsymbol{v}'(t+h) = \gamma[\Delta \boldsymbol{r}(t,h) + \Delta \boldsymbol{\Gamma}(t+h,-h)]/(e^{\gamma h} - 1)$

(iv) Calculate force $\boldsymbol{F}(t+h)$

(v) Calculate $\boldsymbol{v}(t+h) = \boldsymbol{v}'(t+h) + (e^{\gamma h} - 1 - \gamma h)\boldsymbol{F}(t+h)/[m\gamma(e^{\gamma h} - 1)]$

4 Probability Theory

4.1 Random Variable and Probability Density

A random variable or stochastic variable ξ is a variable whose value results from a measurement on some random process. A random variable is a function, which maps events or outcomes. Examples are

- tossing a coin and collecting the outcome (head or tail),

- measuring the length of a rod.

ξ can assume discrete or continuous values. By repeating the experiment N times, a set of values $\xi_1, \ldots, \xi_N$ is obtained. Alternatively, N identical systems can be considered (ensemble). By the obtained values, an average can be calculated according to

$$\langle \xi \rangle = \lim_{N \to \infty} \frac{1}{N} \left(\xi_1 + \ldots + \xi_N \right). \tag{86}$$

A general average is

$$\langle f(\xi) \rangle = \lim_{N \to \infty} \frac{1}{N} \left(f(\xi_1) + \ldots + f(\xi_N) \right). \tag{87}$$

Probability density

The probability $P(x)$ to find the value ξ of a continuous stochastic variable in the interval $x \leq \xi \leq x + dx$ is defined as

$$dP = P(x + dx) - P(x) = \Psi(x)dx. \tag{88}$$

$\Psi(x)$ is denoted as probability density. The average of a function $f(\xi)$ is the defined as

$$\langle f(\xi) \rangle = \int f(x)\Psi(x)dx. \tag{89}$$

With $f(\xi) = \int f(x)\delta(x - \xi)dx$, the average can be written as

$$\langle f(\xi) \rangle = \left\langle \int f(x)\delta(x - \xi)dx \right\rangle = \int f(x) \langle \delta(x - \xi) \rangle \, dx, \tag{90}$$

which implies

$$\Psi(x) = \langle \delta(x - \xi) \rangle. \tag{91}$$

Normalization: $\int \Psi(x)dx = 1 = \left\langle \int \delta(x - \xi)dx \right\rangle$.

For a discrete variable, the probability density is given by $\Psi(x) = \sum_n p_n \delta(x - x_n)$.

Several variables

Consider r variables $\xi_1, \xi_2, \ldots, \xi_r$. The average of a function $f(\xi_1, \ldots, \xi_r)$ is defined as

$$\langle f(\xi_1, \ldots, \xi_r) \rangle = \lim_{N \to \infty} \frac{1}{N} \left[f(\xi_{1_1}, \ldots, \xi_{r_1}) + \ldots + f(\xi_{1_N}, \ldots, \xi_{r_N}) \right]. \tag{92}$$

Similar to Eq. (91), an r-dimensional distribution function can be defined via

$$\Psi_r(x_1, \ldots, x_r) = \langle \delta(x_1 - \xi_1) \ldots \delta(x_r - \xi_r) \rangle. \tag{93}$$

Then, the average of $\langle f(\xi_1, \ldots, \xi_r) \rangle$ is given by

$$\langle f(\xi_1, \ldots, \xi_r) \rangle = \int \ldots \int f(x_1, \ldots, x_r) \Psi_r(x_1, \ldots, x_r) dx_1 \ldots dx_r. \tag{94}$$

As an additional quantity, the probability density can be calculated of the first $n < r$ random variables by integration over the other variables

$$\Psi_n(x_1, \ldots, x_n) = \int \Psi_r(x_1, \ldots, x_r) dx_{n+1} \ldots dx_r. \tag{95}$$

4.2   Conditional Probability Density

We now consider realizations of the r random variables, where the last $r - 1$ assume fixed values $\xi_2 = x_2, \ldots, \xi_r = x_r$. This probability density is called *conditional probability density* $P(x_1|x_2, \ldots, x_r)$. Then, $\Psi_r(x_1, \ldots, x_r)$ is given by

$$\Psi_r(x_1, \ldots, x_r) = P(x_1|x_2, \ldots, x_r) \Psi_{r-1}(x_2, \ldots, x_r), \tag{96}$$

or

$$P(x_1|x_2, \ldots, x_r) = \frac{\Psi_r(x_1, \ldots, x_r)}{\Psi_{r-1}(x_2, \ldots, x_r)} = \frac{\Psi_r(x_1, \ldots, x_r)}{\int \Psi_r(x_1, x_2, \ldots, x_r) dx_1}. \tag{97}$$

For two variables

$$P(x_1|x_2) = \frac{\Psi_2(x_1, x_2)}{\int \Psi_2(x_1, x_2) dx_1}. \tag{98}$$

4.3   Time-dependent Random Variables

Now, a random variable is considered, which depends on time, i.e., $\xi = \xi(t)$. Assuming that the ensemble average exists and can be calculated, one obtains the probability density

$$\Psi(x_1, t_1) = \langle \delta(x_1 - \xi(t_1)) \rangle. \tag{99}$$

For n different times $t_1, \ldots, t_n$, the probability density is given by

$$\Psi_n(x_1, t_1; x_2, t_2; \ldots; x_n, t_n) = \langle \delta(x_1 - \xi(t_1)) \ldots \delta(x_n - \xi(t_n)) \rangle. \tag{100}$$

If the infinite hierarchy of probability densities

$$\Psi_1(x_1, t_1), \tag{101}$$
$$\Psi_2(x_1, t_1; x_2, t_2),$$
$$\Psi_3(x_1, t_1; x_2, t_2; x_3, t_3)$$

is known for every t_i in the interval $t_0 \leq t_i \leq t_0 + T$, the complete time dependence of the random process $\xi(t)$ is known in the interval $[t_0, t_0 + T]$. As an example, the correlation function $\langle \xi(t)\xi(t') \rangle$ is given by

$$\langle \xi(t_1)\xi(t_2) \rangle = \int x_1 x_2 \Psi_2(x_1, t_1; x_2, t_2) dx_1 dx_2. \tag{102}$$

Stationary process

If the probabilities (101) do not change by replacing t_i by $t_i + \tau$, τ arbitrary, the process is denoted as a stationary process. As a consequence, Ψ_1 is independent of time and Ψ_2 depends on the time difference $t_2 - t_1$ only.

4.4 Classification of Stochastic Processes

As for a single random variable, we can introduce a conditional probability density for the time dependent variable ξ at the time t_n under the condition that random variable at the time $t_{n-1} < t_n$ assumes the sharp value x_{n-1}, at the time $t_{n-2} < t_{n-1}$ the sharp value x_{n-2}, etc, and at the time $t1 < t_2$ the sharp value x_1

$$P(x_n, t_n | x_{n-1}, t_{n-1}; \ldots; x_1, t_1) = \langle \delta(x_n - \xi(t_n)) \rangle |_{\xi(t_{n-1})=x_{n-1}, \ldots, \xi(t_1)=x_1}, \tag{103}$$

with $t_n > t_{n-1} > \ldots > t_1$. In analogy to Eq. (97) follows

$$
\begin{aligned}
P(x_n, t_n | x_{n-1}, t_{n-1}; \ldots; x_1, t_1) &= \frac{\Psi_n(x_n, t_n; x_{n-1}, t_{n-1}; \ldots; x_1, t_1)}{\Psi_{n-1}(x_{n-1}, t_{n-1}; \ldots; x_1, t_1)} \\
&= \frac{\Psi_n(x_n, t_n; x_{n-1}, t_{n-1}; \ldots; x_1, t_1)}{\int \Psi_n(x_n, t_n; x_{n-1}, t_{n-1}; \ldots; x_1, t_1) dx_n}.
\end{aligned}
$$

4.4.1 Purely Random Process

A process is called a *purely random* process, when the conditional probability density P_n ($n \geq 2$ arbitrary) does not depend on the values $x_i = \xi(t_i)$ ($i < n$) of the random variable at earlier times ($t_i < t_n$), i.e.,

$$P(x_n, t_n | x_{n-1}, t_{n-1}; \ldots; x_1, t_1) = P(x_n, t_n).$$

This implies

$$\Psi_n(x_n, t_n; \ldots; x_1, t_1) = P(x_n, t_n)\Psi_{n-1}(x_{n-1}, t_{n-1}; \ldots; x_1, t_1) = P(x_n, t_n) \ldots P(x_1, t_1)$$

Hence, the complete information of the process is captured in $P(x_1, t_1) = \Psi_1(x_1, t_1)$.

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4.4.2 Markov Process

For a Markov process, the conditional probability density depends on the value $\xi(t_{n-1}) = x_{n-1}$ at the next earlier time only, i.e.,

$$P(x_n, t_n | x_{n-1}, t_{n-1}; \ldots; x_1, t_1) = P(x_n, t_n | x_{n-1}, t_{n-1}).$$

Then,

$$\begin{aligned}
\Psi_n(x_n, t_n; \ldots; x_1, t_1) &= P(x_n, t_n | x_{n-1}, t_{n-1}) \Psi_{n-1}(x_{n-1}, t_{n-1}; \ldots; x_1, t_1) \\
&= P(x_n, t_n | x_{n-1}, t_{n-1}) P(x_{n-1}, t_{n-1} | x_{n-2}, t_{n-2}) \ldots P(x_2, t_2 | x_1, t_1) \Psi_1(x_1, t_1).
\end{aligned}$$

For $n = 2$, the conditional probability density (transition probability) reads

$$P(x_2, t_2 | x_1, t_1) = \frac{\Psi_2(x_2, t_2; x_1, t_1)}{\Psi_1(x_1, t_1)} = \frac{\Psi_2(x_2, t_2; x_1, t_1)}{\int \Psi_2(x_2, t_2; x_1, t_1) dx_2}.$$

Thus, for a Markovian process the complete information about the process is captured in $\Psi_2(x_2, t_2; x_1, t_1)$. In the limit $t_2 \to t_1$, the conditional probability density reduces to

$$\lim_{t_2 \to t_1} P(x_2, t_2; x_1, t_1) = \delta(x_1 - x_2).$$

4.4.3 Chapman-Kolmogorov Equation

For a Markov process, the general relation

$$\Psi_2(x_3, t_3; x_1, t_1) = \int \Psi_3(x_3, t_3; x_2, t_2; x_1, t_1) dx_2$$

implies ($t_3 \geq t_2 \geq t_1$)

$$P(x_3, t_3 | x_1, t_1) \Psi_1(x_1, t_1) = \int P(x_3, t_3 | x_2, t_2) P(x_2, t_2 | x_1, t_1) \Psi_1(x_1, t_1) dx_2,$$

which leads the the Chapman-Kolmogorov equation

$$P(x_3, t_3 | x_1, t_1) = \int P(x_3, t_3 | x_2, t_2) P(x_2, t_2 | x_1, t_1) dx_2, \tag{104}$$

because $\Psi_1(x_1, t_1)$ is arbitrary.

4.5 Several Time-dependent Random Variables

For r time-dependent random variables $\xi_1(t), \ldots, \xi_r(t)$ the probability density at the n times $t_n, \ldots, t_1$ is defined as

$$\begin{aligned}
&\Psi_n(x_1^n, \ldots, x_r^n, t_n; \ldots, x_1^1, \ldots, x_r^1, t_1) \\
&= \left\langle \delta(x_1^n - \xi_1(t_n)) \ldots \delta(x_r^n - \xi_r(t_n)) \ldots \delta(x_1^1 - \xi_1(t_1)) \ldots \delta(x_r^1 - \xi_r(t_1)) \right\rangle.
\end{aligned}$$

For a Markov process, the complete information is contained in $\Psi_2(x_1, \ldots, x_r, t | x_1', \ldots, x_r', t')$.

Example: Combining the random variables in a vector $\boldsymbol{\xi}(t)$

$$\Psi_n(\boldsymbol{r}_n, t_n; \ldots; \boldsymbol{r}_1, t_1) = \left\langle \delta(\boldsymbol{r}_n - \boldsymbol{\xi}_n(t_n)) \ldots \delta(\boldsymbol{r}_1 - \boldsymbol{\xi}_1(t_1)) \right\rangle.$$

5 Fokker-Planck Equation

For stochastic systems, expectation values have to be calculated. In the Langevin approach, this involves averaging over different realizations of the stochastic force $\Gamma(t)$. Alternatively, averages can be calculated with the help of a distribution function, which follows as solution of a partial differential equation—the *Fokker-Planck equation*. The equation itself can be obtained by the *Kramers-Moyal* (forward) expansion (cf. Risken).

5.1 Smoluchowski Equation: Single Variable

Starting point is the relation

$$\Psi(x, t + \Delta t) = \int P(x, t + \Delta t | x', t) \Psi(x', t) dx', \tag{105}$$

with

$$P(x, t | x', t') = \langle \delta(x - \xi(t)) \rangle |_{\xi(t') = x'}.$$

Hence,

$$\Psi(x, t + \Delta t) = \int \langle \delta(x - \xi(t + \Delta t)) \rangle |_{\xi(t) = x'} \Psi(x', t) dx'. \tag{106}$$

The replacement $\xi(t + \Delta t) = x'(t) + \Delta\xi(t) = x'(t) + \Delta\xi(x'(t))$ and Taylor expansion of the δ-function for $\Delta\xi \ll 1$, i.e., $\Delta t \to 0$,

$$\delta(x - x' - \Delta\xi) = \delta(x - x') - \frac{d\delta(x - x')}{d(x - x')}\Delta\xi + \frac{1}{2}\frac{d^2\delta(x - x')}{d(x - x')^2}\Delta\xi^2 + \dots$$

$$= \delta(x - x') + \frac{d\delta(x - x')}{dx'}\Delta\xi + \frac{1}{2}\frac{d^2\delta(x - x')}{dx'^2}\Delta\xi^2 + \dots ,$$

leads to

$$\Psi(x, t + \Delta t) = \Psi(x, t) \tag{107}$$

$$+ \int \left[\left(\frac{d\delta(x - x')}{dx'} \right) \langle\Delta\xi\rangle + \frac{1}{2} \left(\frac{d^2\delta(x - x')}{dx'^2} \right) \langle\Delta\xi^2\rangle \right] \Psi(x', t) dx'$$

$$\stackrel{PI}{=} \Psi(x, t)$$

$$- \int \frac{\partial}{\partial x'} \left[\langle\Delta\xi\rangle \Psi(x', t) \right] \delta(x - x') dx' + \frac{1}{2} \int \frac{\partial^2}{\partial x'^2} \left[\langle\Delta\xi^2\rangle \Psi(x', t) \right] \delta(x - x') dx'.$$

The averages over ξ can be obtained from the Langevin equation.

5.1.1 Linear Langevin Equation

$$\gamma\dot{\xi} = \frac{1}{m}F(\xi) + \Gamma(t).$$

$$\langle \Gamma(t) \rangle = 0,$$

$$\langle \Gamma(t)\Gamma(t') \rangle = \frac{2\gamma k_B T}{m}\delta(t - t').$$

Integration yields

$$\xi(t + \Delta t) = \xi(t) + \frac{1}{\gamma}\int_t^{t+\Delta t}\left[\frac{1}{m}F(t') + \Gamma(t')\right]dt' = \xi(t) + \frac{\Delta t}{\gamma m}F + \frac{1}{\gamma}\Delta\Gamma + O(\Delta t^2),$$

(108)

where $\Delta\Gamma = \int_t^{t+\Delta t}\Gamma(t')dt'$. Averaging yields

$$\langle \Delta\xi \rangle = \frac{\Delta t}{\gamma m}F + \frac{1}{\gamma}\langle \Delta\Gamma \rangle = \frac{\Delta t}{\gamma m}F(t) + O(\Delta t^2),$$

$$\langle \Delta\xi^2 \rangle = \left\langle \left(\frac{\Delta t}{\gamma m}F(t) + \frac{1}{\gamma}\Delta\Gamma\right)^2 \right\rangle = \frac{1}{\gamma^2}\int_t^{t+\Delta t}\int_t^{t+\Delta t}\langle \Gamma(t')\Gamma(t'') \rangle\, dt'dt'' + O(\Delta t^2)$$

$$= \frac{2k_B T}{m\gamma}\Delta t + O(\Delta t^2).$$

Hence,

$$\Psi(x, t + \Delta t) = \Psi(x, t) - \frac{\partial}{\partial x}\left(\frac{F}{\gamma m}\Psi(x, t)\right)\Delta t + \frac{k_B T}{\gamma m}\frac{\partial^2}{\partial x^2}\Psi(x, t)\Delta t + O(\Delta t^2),$$

or, with $F = -\partial U/\partial x$ and

$$\frac{\partial\Psi(x, t)}{\partial t} = \lim_{\Delta t \to 0}\frac{\Psi(x, t + \Delta t) - \Psi(x, t)}{\Delta t},$$

$$\boxed{\frac{\partial\Psi(x, t)}{\partial t} = \frac{1}{\gamma m}\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial x}\Psi(x, t)\right) + D\frac{\partial^2\Psi(x, t)}{\partial x^2}}$$

(109)

Fokker-Planck or Smoluchowski equation

with $D = k_B T/(\gamma m)$

Stationary solution

The stationary solution follows for $\partial\Psi/\partial t = 0$, i.e.,

$$\frac{1}{\gamma}\frac{\partial}{\partial x}\left[\frac{\partial U}{\partial x}\Psi(x) + k_B T\frac{\partial\Psi(x)}{\partial x}\right] = 0$$

The boundary condition of a vanishing probability flux at infinity implies (cf. Sec. 6.4)

$$\frac{\partial\Psi(x)}{\partial x} = -\frac{1}{k_B T}\frac{\partial U}{\partial x}\Psi(x),$$

or

$$\Psi(x) = \frac{1}{Z}\exp\left(-\beta U\right),$$

(110)

with $\beta = 1/(k_B T)$ and the normalization constant (partition function) $Z = \int \Psi(x)dx$. This is the Boltzmann distribution. The momentum part $\Psi(p) \sim \exp(-\beta p^2/(2m))$ (kinetic energy) is missing, since the over-damped dynamics is considered. The momenta are in thermal equilibrium.

5.1.2 Non-linear Langevin Equation

$$\dot{\xi} = h(\xi, t) + g(\xi, t)\Gamma(t). \tag{111}$$

$$\langle \Gamma(t) \rangle = 0,$$
$$\langle \Gamma(t)\Gamma(t') \rangle = 2\delta(t - t').$$

The correlation functions of the stochastic force are given in Eq. (70). Solution

$$\Delta\xi = \xi(t + \Delta t) - x = \int_t^{t+\Delta t} \left[h(\xi(t'), t') + g(\xi(t'), t')\Gamma(t') \right] dt'$$

With the Taylor expansion of $h(\xi, t)$ and $g(\xi, t)$ around x

$$h(\xi, t) = h(x, t) + h'(x, t)\left[\xi(t) - x\right] + \ldots,$$
$$g(\xi, t) = g(x, t) + g'(x, t)\left[\xi(t) - x\right] + \ldots$$

($h' = \partial h(x, t)/\partial x$, $g' = \partial g(x, t)/\partial x$) follows

$$\Delta\xi = \int_t^{t+\Delta t} h(x, t')dt' + \int_t^{t+\Delta t} h'(x, t')[\xi(t') - x]dt' \tag{112}$$

$$+ \int_t^{t+\Delta t} g(x, t')\Gamma(t')dt' + \int_t^{t+\Delta t} g'(x, t')[\xi(t') - x]\Gamma(t')dt' + \ldots,.$$

The expression $\xi(t') - x$ can be eliminated iteratively by repeated application of Eq. (112). Note, only terms up to linear order in Δt are relevant. One more iteration yields

$$\Delta\xi = h(x, t)\Delta t + \int_t^{t+\Delta t} h'(x, t') \int_t^{t'} h(x, t'')dt''dt' + \int_t^{t+\Delta t} h'(x, t') \int_t^{t'} g(x, t'')\Gamma(t'')dt''dt'$$

$$+ \int_t^{t+\Delta t} g(x, t')\Gamma(t')dt' + \int_t^{t+\Delta t} g'(x, t')\Gamma(t') \int_t^{t'} h(x, t'')dt''dt'$$

$$+ \int_t^{t+\Delta t} g'(x, t') \int_t^{t'} g(x, t'')\Gamma(t')\Gamma(t'')dt''dt' + \ldots$$

Averaging yields ($\int_{t_0}^t \delta(t - t')dt' = 1/2$)

$$\langle \Delta\xi(t) \rangle = h(x, t)\Delta t + \frac{\Delta t^2}{2}h'(x, t)h(x, t) + \int_t^{t+\Delta t} g'(x, t') \int_t^{t'} g(x, t'')2\delta(t' - t'')dt''dt'$$

$$= h(x, t)\Delta t + g(x, t)g'(x, t)\Delta t + O(\Delta t^2) = D^{(1)}(x, t)\Delta t + O(\Delta t^2)$$

Similarly, for $\langle \Delta\xi^2 \rangle$ follows

$$(\xi(t + \Delta t) - x)^2 = \left(\int_t^{t+\Delta t} h(x, t')dt' \right)^2 + \left(\int_t^{t+\Delta t} g(x, t')\Gamma(t')dt' \right)^2 + O(\Delta t^{3/2})$$

$$= \int_t^{t+\Delta t} \int_t^{t+\Delta t} g(x, t')g(x, t'')\Gamma(t')\Gamma(t'')dt'dt'' + O(\Delta t^{3/2}),$$

$$\langle (\xi(t + \Delta t) - x)^2 \rangle = \int_t^{t+\Delta t} \int_t^{t+\Delta t} g(x, t')g(x, t'')2\delta(t' - t'')dt'dt'' + O(\Delta t^2)$$

$$= 2g(x, t)^2\Delta t + O(\Delta t^2) = 2D^{(2)}(x, t)\Delta t + O(\Delta t^2).$$

Hence,

$$\boxed{\frac{\partial \Psi(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[D^{(1)}(x,t)\Psi(x,t)\right] + \frac{\partial^2}{\partial x^2}\left[D^{(2)}(x,t)\Psi(x,t)\right] = L_{FP}\Psi(x,t)},\quad (113)$$

with the Fokker-Planck operator

$$L_{FP} = -\frac{\partial}{\partial x}D^{(1)}(x,t) + \frac{\partial^2}{\partial x^2}D^{(2)}(x,t). \qquad (114)$$

As can be shown, all higher order correlations $\langle \Delta\xi^n \rangle$, $n \geq 3$, vanish. Hence,

$$D^{(1)}(x,t) = h(x,t) + g(x,t)\frac{\partial g(x,t)}{\partial x} \qquad \text{drift coefficient}, \qquad (115)$$

$$D^{(2)}(x,t) = g(x,t)^2 \qquad\qquad\qquad \text{diffusion coefficient}, \qquad (116)$$

$$D^{(n)}(x,t) = 0 \qquad\qquad\qquad\qquad\qquad n \geq 3. \qquad (117)$$

$D^{(1)}$ includes aside from the deterministic drift $h(x,t)$ the so called spurious drift or noise-induced drift

$$D^{(1)}_{\text{nois}} = g(x,t)\frac{\partial g(x,t)}{\partial x} = \frac{1}{2}\frac{\partial}{\partial x}D^{(2)}(x,t).$$

Probability Current

Equation (113) can be written as

$$\frac{\partial \Psi}{\partial t} + \frac{\partial S}{\partial x} = 0, \qquad (118)$$

with

$$S(x,t) = \left[D^{(1)}(x,t) - \frac{\partial}{\partial x}D^{(2)}(x,t)\right]\Psi(x,t) . \qquad (119)$$

Since (118) is a continuity equation for a probability distribution, S can be interpreted as a probability current. When this current vanishes at the boundaries $x = x_{\min}$ and $x = x_{\max}$, the normalization is preserved, i.e.,

$$\int_{x_{\min}}^{x_{\max}} \Psi(x,t)dx = const. = 1$$

The considered case $D^{(1)} = -\gamma v$, $D^{(2)} = \gamma k_B T/m$ of the previous section is a special case.

Equation (111) is a first order differential equation and its solution is uniquely determined by the initial value x_0. Hence, the process described by the Langevin equations is a *Markov process*. This implies that the Fokker-Planck equation also describes a Markov process. Since for such a system the relation

$$\Psi(x,t) = \int P(x,t|x',t')\Psi(x',t')dx' \qquad (120)$$

applies, the conditional probability density $P(x,t|x',t')$ obeys the same Fokker-Planck equation as $\Psi(x,t)$.

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5.1.3 Path Integral Solution

The solution of the Fokker-Planck equation can be represented in path integral form. Such a representation is obtained by a repeated application of the Chapman-Kolmogorov equation (104). With

$$\Psi(x,t) = \int P(x,t|x_0,t_0)\Psi(x_0,t_0)dx_0, \tag{121}$$

the division of the time interval $t - t_0$ in N small intervals of length $\tau = (t - t_0)/N$ leads to

$$\Psi(x,t) = \int P(x,t|x_{N-1},t_{N-1})P(x_{N-1},t_{N-1}|x_{N-2},t_{N-2}) \tag{122}$$
$$\ldots P(x_1,t_1|x_0,t_0)\Psi(x_0,t_0)dx_{N-1}\ldots dx_0.$$

In the limit $N \to \infty$, or $\tau \to 0$, an expression for the conditional probability $P(x,t+\tau|x',t)$ follows from the Fokker-Planck equation.

Conditional probability density for small times

Taylor expansion of $P(x,t+\tau|x',t)$ yields

$$P(x,t+\tau|x',t) = P(x,t|x',t) + \frac{\partial}{\partial t}P(x,t|x',t)\tau + O(\tau^2)$$
$$= \left[1 + \tau\left(-\frac{\partial}{\partial x}D^{(1)}(x,t) + \frac{\partial^2}{\partial x^2}D^{(2)}(x,t)\right)\right]P(x,t|x',t) + O(\tau^2), \tag{123}$$

with $P(x,t|x',t) = \delta(x-x')$. To evaluate the expression, we use the Fourier representation of the δ-function

$$\delta(x-x') = \frac{1}{2\pi}\int_{-\infty}^{\infty}e^{ik(x-x')}dk. \tag{124}$$

Moreover, we are allowed to replace x by x' in Eq. (123) due to the δ-function. Hence, we obtain

$$P(x,t+\tau|x',t) = \frac{1}{2\pi}\int\left(1 - \tau\left[ikD^{(1)}(x',t) + k^2D^{(2)}(x',t)\right]\right)e^{ik(x-x')}dk$$
$$= \frac{1}{2\pi}\int \exp\left(-ik\tau D^{(1)}(x',t) - k^2\tau D^{(2)}(x',t) + ik(x-x')\right)dk. \tag{125}$$

Thus,

$$P(x,t+\tau|x',t) = \frac{1}{2\sqrt{\pi D^{(2)}(x',t)\tau}}\exp\left(-\frac{(x-x'-D^{(1)}(x',t)\tau)^2}{4D^{(2)}(x',t)\tau}\right). \tag{126}$$

With this expression Eq. (122) becomes

$$\Psi(x,t) = \lim_{N\to\infty}\int\prod_{i=0}^{N-1}\left(4\pi D^{(2)}(x_i,t)\tau\right)^{-1/2}$$
$$\times \exp\left(-\sum_{i=0}^{N-1}\frac{(x_{i+1}-x_i-D^{(1)}(x_i,t_i)\tau)^2}{4D^{(2)}(x_i,t_i)\tau}\right)\Psi(x_0,t_0)dx_0\ldots dx_{N-1}, \tag{127}$$

or, with $x_{i+1} - x_i = \dot{x}(t_i)\tau$

$$\Psi(x, t) = \lim_{N \to \infty} \int \prod_{i=0}^{N=1} \left(4\pi D^{(2)}(x_i, t)\tau\right)^{-1/2} dx_i \tag{128}$$

$$\times \exp\left(-\int_{t_0}^{t} \frac{[\dot{x}(t') - D^{(1)}(x(t'), t')]^2}{4D^{(2)}(x(t'), t')} dt'\right) \Psi(x_0, t_0). \tag{129}$$

Evidently, for small $D^{(2)}$, only paths close to the deterministic solution of $\dot{x} = D^{(1)}$ contribute to Ψ.

5.2 General Case

5.2.1 Non-linear Langevin Equation

For the general case, the non-linear Langevin equation is considered for N variables and white noise

$$\dot{\xi}_i = h_i(\boldsymbol{\xi}, t) + \sum_{j=1}^{N} g_{ij}(\boldsymbol{\xi}(t), t)\Gamma_j(t), \tag{130}$$

$$\langle \Gamma_i(t) \rangle = 0, \tag{131}$$

$$\langle \Gamma_i(t)\Gamma_j(t') \rangle = 2\delta_{ij}\delta(t - t'). \tag{132}$$

Solution for $\Delta t \ll 1$

$$\xi_i(t + \Delta t) - x_i = \int_{t}^{t+\Delta t} \left[h_i(\boldsymbol{\xi}, t') + \sum_j g_{ij}(\boldsymbol{\xi}, t')\Gamma_j(t')\right] dt'$$

$$= \int_{t}^{t+\Delta t} \left[h_i(\boldsymbol{x}, t') + \sum_k \frac{\partial}{\partial x_k} h_i(\boldsymbol{x}, t')[\xi_k(t') - x_k]\right.$$

$$\left. + \sum_j g_{ij}(\boldsymbol{x}, t')\Gamma_j(t') + \sum_k \sum_j \frac{\partial}{\partial x_k} g_{ij}(\boldsymbol{x}, t')[\xi_k(t') - x_k]\Gamma_j(t') + \dots\right] dt'$$

Iteration yields

$$\langle \xi_i(t + \Delta t) - x_i \rangle = h_i(\boldsymbol{\xi}, t)\Delta t + \sum_k \sum_j \sum_l \int_{t}^{t+\Delta t} \int_{t}^{t'} \frac{\partial g_{ij}}{\partial x_k} g_{kl} \underbrace{\langle \Gamma_j(t')\Gamma_l(t'') \rangle}_{2\delta_{jl}\delta(t'-t'')} dt' dt''$$

$$= h_i(\boldsymbol{\xi}, t)\Delta t + \sum_k \sum_j g_{kj}\frac{\partial g_{ij}}{\partial x_k}\Delta t = D_i^{(1)}(\boldsymbol{x}, t)\Delta t. \tag{133}$$

Similar

$$\langle (\xi_i(t + \Delta t) - x_i)(\xi_j(t + \Delta t) - x_j) \rangle = 2D_{ij}^{(2)}(\boldsymbol{x}, t)\Delta t. \tag{134}$$

Where

$$D_i^{(1)}(\boldsymbol{x}, t) = h_i(\boldsymbol{x}, t) + \sum_k \sum_j g_{kj}(\boldsymbol{x}, t) \frac{\partial g_{ij}(\boldsymbol{x}, t)}{\partial x_k} \qquad \text{drift coefficient,} \qquad (135)$$

$$D_{ij}^{(2)}(\boldsymbol{x}, t) = \sum_k g_{jk}(\boldsymbol{x}, t) g_{ik}(\boldsymbol{x}, t) \qquad \text{diffusion coefficient,} \qquad (136)$$

$$D_{i,j,\ldots}^{(n)}(\boldsymbol{x}, t) = 0 \qquad n \geq 3. \qquad (137)$$

5.2.2 N Variable Fokker-Planck Equation

$$\Psi(\boldsymbol{x}, t + \Delta t) = \int \left\langle \prod_{i=1}^{N} \delta(x_i - \xi_i(t + \Delta t)) \right\rangle |_{\xi_i(t) = x'} \Psi(\boldsymbol{x}', t) d^N x' \qquad (138)$$

$$= \int \langle \delta(\boldsymbol{x} - \boldsymbol{\xi}(t + \Delta t)) \rangle |_{\boldsymbol{\xi}(t) = \boldsymbol{x}'} \Psi(\boldsymbol{x}', t) d^N x' \qquad (139)$$

Taylor expansion of δ-function ($\xi_i(t + \Delta t) = x_i'(t) + \Delta \xi_i(t)$) yields

$$\delta(\boldsymbol{x} - \boldsymbol{\xi}(t + \Delta t)) = \delta(\boldsymbol{x} - \boldsymbol{x}' - \Delta \boldsymbol{\xi}(t))$$

$$= \delta(\boldsymbol{x} - \boldsymbol{x}') + \sum_k \frac{\partial}{\partial x_k'} \delta(\boldsymbol{x} - \boldsymbol{x}') \Delta \xi_k + \frac{1}{2} \sum_k \sum_l \frac{\partial}{\partial x_k'} \frac{\partial}{\partial x_l'} \delta(\boldsymbol{x} - \boldsymbol{x}') \Delta \xi_k \Delta \xi_l$$

and

$$\Psi(\boldsymbol{x}, t + \Delta t) = \Psi(\boldsymbol{x}, t) + \sum_k \int \frac{\partial}{\partial x_k'} \delta(\boldsymbol{x} - \boldsymbol{x}') \langle \Delta \xi_k \rangle \Psi(\boldsymbol{x}', t) d^N x' \qquad (140)$$

$$+ \frac{1}{2} \sum_k \sum_l \int \frac{\partial}{\partial x_k'} \frac{\partial}{\partial x_l'} \delta(\boldsymbol{x} - \boldsymbol{x}') \langle \Delta \xi_k \Delta \xi_l \rangle \Psi(\boldsymbol{x}', t) d^N x'$$

$$\overset{PI}{=} \Psi(\boldsymbol{x}, t) - \sum_k \frac{\partial}{\partial x_k} [\langle \Delta \xi_k \rangle \Psi(\boldsymbol{x}, t)] + \frac{1}{2} \sum_k \sum_l \frac{\partial}{\partial x_k} \frac{\partial}{\partial x_l} [\langle \Delta \xi_k \Delta \xi_l \rangle \Psi(\boldsymbol{x}, t)].$$

Hence, in the limit $\Delta t \to 0$ and with Eqs. (133), (134)

$$\boxed{\begin{aligned} \frac{\partial}{\partial t} \Psi(\boldsymbol{x}, t) &= -\sum_{k=1}^{N} \frac{\partial}{\partial x_k} \left[D_k^{(1)} \Psi(\boldsymbol{x}, t) \right] + \sum_{k=1}^{N} \sum_{l=1}^{N} \frac{\partial^2}{\partial x_k \partial x_l} \left[D_{kl}^{(2)} \Psi(\boldsymbol{x}, t) \right] = L_{FP} \Psi(\boldsymbol{x}, t) \\ L_{FP} &= -\sum_{k=1}^{N} \frac{\partial}{\partial x_k} D_k^{(1)} + \sum_{k=1}^{N} \sum_{l=1}^{N} \frac{\partial^2}{\partial x_k \partial x_l} D_{kl}^{(2)} \end{aligned}}$$
$$(141)$$

5.2.3 Klein-Kramers Equation

As a example, the Klein-Kramers or Kramers equation can be derived, which is the Fokker-Planck equation for a particle with inertia.

Equations of motion in 1 dimension

$$\dot{x} = v,$$
$$m\dot{v} = -\gamma' v + \Gamma(t) + F(x),$$
$$\langle \Gamma(t) \rangle = 0,$$
$$\langle \Gamma(t)\Gamma(t') \rangle = 2\gamma' k_B T \delta(t - t') , \qquad \text{white noise.}$$

Notice the change in notation for the friction coefficient: $\gamma' = m\gamma$!

Setting $x_1 = x$, $x_2 = v$ implies $h_1 = v$, $g_{11} = g_{12} = g_{21} = 0$, $h_2 = -\gamma' v/m + F(x)$, and $g_{22} = \sqrt{\gamma' k_B T}/m$, or $D_1 = v$, $D_{11} = D_{12} = D_{21} = 0$, $D_2 = -\gamma' v/m + F(x)/m$, and $D_{22} = \gamma' k_B T/m^2$. Hence,

$$\boxed{\frac{\partial}{\partial t}\Psi(x,v,t) = \left[-v\frac{\partial}{\partial x} + \frac{\partial}{\partial v}\left(\frac{\gamma'}{m}v - \frac{F(x)}{m} \right) + \frac{\gamma' k_B T}{m^2}\frac{\partial^2}{\partial v^2} \right] \Psi(x,v,t)}. \qquad (142)$$

Stationary Solution

The stationary solution follows from $\partial \Psi/\partial t = 0$ and reads

$$\Psi(x,v) = \frac{1}{Z}\exp\left(-\beta\frac{1}{2}mv^2 - \beta U(x) \right) = \frac{1}{Z}\exp\left(-\beta H \right),$$

where $F(x) = -dU(x)/dx$ and $H = mv^2/2 + U(x)$. I.e, the Maxwell-Boltzmann distribution is obtained, which can easily be demonstrated by inserting $\Psi(x,v)$ in Eq. (142), with the partition function $Z = \int \exp\left(-\beta\frac{1}{2}mv^2 - \beta U(x) \right) dx dv$.

In contrast to Eq. (110), the distribution function also comprises the kinetic energy part.

5.3   Markov Property

As pointed out before, Eq. (130) are a set of N non-linear first order differential equations and their solution is uniquely determined by the N initial values. Hence, the process described by the Langevin equations is a *Markov process*. This implies that the Fokker-Planck equation also describes a Markov process. Since for such as system the relation

$$\Psi(\boldsymbol{x},t) = \int P(\boldsymbol{x},t|\boldsymbol{x}',t')\Psi(\boldsymbol{x}',t')d^N x' \qquad (143)$$

applies, the conditional probability density $P(\boldsymbol{x},t|\boldsymbol{x}',t')$ obeys the same Fokker-Planck equation as $\Psi(\boldsymbol{x},t)$.

6 Solution of Fokker-Planck Equation: Single Variable

In the following, solutions are discussed of the one-variable Fokker-Planck equation with time-independent drift and diffusion coefficients and the assumption $D^{(2)}(x) > 0$, i.e,

$$\frac{\partial}{\partial t}\Psi(x,t) = L_{FP}\Psi(x,t) = -\frac{\partial}{\partial x}S(x,t), \tag{144}$$

$$L_{FP} = -\frac{\partial}{\partial x}D^{(1)}(x) + \frac{\partial^2}{\partial x^2}D^{(2)}(x). \tag{145}$$

6.1 Stationary Solution

For the stationary state solution, the equation $S = const$ applies. We will here consider boundary conditions with a vanishing probability current, i.e., $S = 0$. Hence,

$$D^{(1)}(x)\Psi(x) = \frac{\partial}{\partial x}D^{(2)}(x)\Psi(x),$$

or

$$\frac{D^{(1)}(x)D^{(2)}(x)}{D^{(2)}(x)}\Psi(x) = \frac{\partial}{\partial x}D^{(2)}(x)\Psi(x). \tag{146}$$

Integration for the variable $D^{(2)}(x)\Psi(x)$ yields

$$\Psi(x) = \frac{N}{D^{(2)}}\exp\left(\int^x \frac{D^{(1)}(x')}{D^{(2)}(x')}dx'\right) = Ne^{-\Phi(x)} \tag{147}$$

with

$$\Phi(x) = \ln D^{(2)}(x) - \int^x \frac{D^{(1)}(x')}{D^{(2)}(x')}dx'. \tag{148}$$

The constant N follows from the normalization condition $\int \Psi(x)dx = 1$.

6.2 Wiener Process

Without an external force ($dU/dx = 0$) the Smoluchowski equation (109) for the conditional probability distribution $P(x,t|x',t')$ reads (cf. Sec. 5.3)

$$\frac{\partial}{\partial t}P(x,t|x',t') = D\frac{\partial^2}{\partial x^2}P(x,t|x',t'), \tag{149}$$

i.e., the diffusion equation is obtained with $D = k_BT/(\gamma m)$. A solution is obtained, with the initial condition $P(x,t'|x',t') = \delta(x-x')$ and the boundary condition $\lim_{x\to\pm\infty} P(x,t|x',t') = 0$, by Fourier transformation of the partial differential equation (149).
Fourier transformation gives

$$P(x,t|x',t') = \frac{1}{2\pi}\int P(k,t|x',t')e^{ikx}dk,$$

with the initial condition

$$P(k, t'|x', t') = \int P(x, t'|x', t')e^{-ikx}dx = \int \delta(x - x')e^{-ikx}dx = e^{-ikx'}. \qquad (150)$$

Equation (149) yields then

$$\frac{d}{dt}P(k, t|x', t') = -Dk^2 P(k, t|x', t'),$$

with the solution

$$P(k, t|x', t') = e^{-Dk^2(t-t')}P(k, t'|x't') = e^{-Dk^2(t-t')}e^{-ikx'}.$$

Fourier transformation gives

$$\boxed{P(x, t|x', t') = \frac{1}{2\pi}\sqrt{\frac{\pi}{D(t-t')}}\exp\left(-\frac{(x-x')^2)}{4D(t-t')}\right).} \qquad (151)$$

Probability density

$$\Psi(x, t) = \int P(x, t|x't')\Psi(x', t')dx'.$$

P is Green's function of diffusion equation

$$\frac{\partial}{\partial}P(x, t|x', t') - D\frac{\partial^2}{\partial x^2}P(x, t|x', t') = \delta(x - x')\delta(t - t').$$

6.3 Ornstein-Uhlenbeck Process

For the Ornstein-Uhlenbeck process, the drift coefficients depend linearly on the coordinates and the diffusion coefficients are constant, i.e.,

$$D_i = -\gamma_{ij}x_j; \qquad \gamma_{ij}, \ D_{ij} = D_{ji} = const. \ . \qquad (152)$$

Naturally, the above Wiener process is also an Ornstein-Uhlenbeck process.

6.3.1 Harmonic Oscillator

Langevin equation: overdamped motion

$$m\gamma\dot{x} = -m\omega^2 x + \sqrt{\gamma k_B T m}\Gamma(t),$$
$$\dot{x} = -\frac{\omega^2}{\gamma}x + \sqrt{D}\Gamma(t) = -\zeta x + \sqrt{D}\Gamma(t),$$

with $\zeta = \omega^2/\gamma$.

Fokker-Planck equation

$D^{(1)} = h = -\zeta x,\ D^{(2)} = D = k_B T/(\gamma m)$

$$\frac{\partial}{\partial t} P(x,t|x',t') = \zeta \frac{\partial}{\partial x}\left[x P(x,t|x't')\right] + D \frac{\partial^2}{\partial x^2} P(x,t|x',t'). \tag{153}$$

Fourier transformation

$$\frac{\partial}{\partial t} P(k,t|x',t') = -\zeta k \frac{\partial}{\partial k} P(k,t|x',t') - Dk^2 P(k,t|x',t'). \tag{154}$$

Solution: $P(k,t|x',t')$ is Gaussian, because stochastic force is Gaussian.
Ansatz

$$P(k,t|x',t') = \exp\left(-ikM(t-t') - \frac{1}{2}k^2\sigma(t-t')\right)$$

With the initial condition (150) follows $M(t',t') = x'$ and $\sigma(t',t') = 0$. Hence,

$$\frac{\partial}{\partial t} P(k,t|x',t') = \left(-ik\dot{M}(t,t') - \frac{1}{2}k^2\dot{\sigma}\right) P(k,t|k',t'),$$

$$\frac{\partial}{\partial k} P(k,t|x',t') = (-iM - k\sigma)\, P(k,t|x',t').$$

In Eq. (154)

$$\left[-ik\dot{M} - \frac{1}{2}k^2\dot{\sigma} - ik\zeta M - k^2\zeta\sigma + Dk^2\right] P(k,t|x',t') = 0$$

or

$$\dot{M} + \zeta M = 0 \qquad \wedge \qquad -\frac{1}{2}\dot{\sigma} - \zeta\sigma + D = 0.$$

Solution

$$M(t,t') = x' \exp\left(-\zeta(t-t')\right),$$

$$\sigma(t) = \frac{D}{\zeta}\left[1 - \exp\left(-2\zeta(t-t')\right)\right],$$

i.e.,

$$P(k,t|x',t') = \exp\left(-ikx'e^{-\zeta(t-t')} - \frac{Dk^2}{2\zeta}\left[1 - e^{-2\zeta(t-t')}\right]\right).$$

Fourier transformation

$$\boxed{P(x,t|x',t') = \sqrt{\frac{\zeta}{2\pi D\left[1 - e^{-2\zeta(t-t')}\right]}}\, \exp\left(-\frac{\zeta\left[x - x'e^{-\zeta(t-t')}\right]^2}{2D\left[1 - e^{-2\zeta(t-t')}\right]}\right).} \tag{155}$$

Limes $\zeta \to 0$, i.e, $1 - e^{-2\zeta(t-t')} = 2\zeta(t - t')$ yields

$$P(x,t|x',t') = \sqrt{\frac{1}{4\pi D(t-t')}}\, \exp\left(-\frac{(x-x')^2}{4D(t-t')}\right),$$

i.e., the result of the Wiener process. The stationary state solution follows for $t \to \infty$:

$$\Psi_0(x) = \sqrt{\frac{\zeta}{2\pi D}} \exp\left(-\frac{\zeta x^2}{2D}\right).$$

Joint probability density: $\Psi(x, t; x', t') = P(x, t | x', t')\Psi_0(x')$, $t > t'$

$$\boxed{\Psi(x, t; x', t') = \frac{\zeta}{2\pi D \sqrt{1 - \exp(-2\gamma(t - t'))}} \exp\left(-\zeta \frac{x^2 + x'^2 - 2xx' \exp(-\zeta(t - t'))}{2D\left[1 - \exp(-2\zeta(t - t'))\right]}\right).}$$
(156)

$t \to \infty$: $\Psi(x, t; x't') = \Psi(x, t)\Psi(x', t')$.

Expectation values

$$\langle x \rangle = \int x \Psi(x, t; x', t') dx dx' = 0,$$

$$\langle x^2 \rangle = \frac{D}{\zeta}.$$

Fixed initial value x'

$$\langle x \rangle = \int x P(x, t | x', t') dx = x' e^{-\zeta(t-t')},$$

$$\langle x^2 \rangle = \frac{D}{\zeta}\left(1 - e^{-2\zeta(t-t')}\right) + x'^2 e^{-2\zeta(t-t')}.$$

Asymptotic behavior

$$\langle x^2 \rangle = \begin{cases} 2D(t - t') + x'^2[1 - 2\zeta(t - t')], & \zeta|t - t'| \ll 1 \\ \dfrac{D}{\zeta} & \zeta|t - t'| \gg 1 \end{cases}.$$

6.4   Boundary Conditions

The Fokker-Planck equation for a single variable can be formulated as

$$\frac{\partial}{\partial t}\Psi(x, t) + \frac{\partial}{\partial x}S(x, t) = 0,$$
(157)

where S is the probability current

$$S(x, t) = \left[D^{(1)}(x, t) - \frac{\partial}{\partial x}D^{(2)}(x, t)\right]\Psi(x, t).$$
(158)

The following boundary conditions can then be considered

- Natural boundary conditions: $S = 0$ for $x \to \pm\infty$.

- Periodic boundary conditions: $\Psi(x, t) = \Psi(x + L, t)$, $S(x, t) = S(x + L, t)$.

- Reflecting boundary (wall): $S = 0$ at the position of the boundary.

- Absorbing boundary (wall): $\Psi = 0$ at the position of the boundary.

6.5 Eigenfunction Expansion

The Fokker-Planck equation can be solved by an eigenfunction expansion, similar to the Schrödinger equation. With the separation ansatz

$$\Psi(x,t) = \varphi(x)e^{-\lambda t}$$

follows

$$L_{FP}\varphi(x) = -\lambda\varphi(x), \tag{159}$$

where the eigenfunctions φ obey the appropriate boundary conditions.

The Fokker-Planck operator L_{FP} is not a Hermitian operator, but a Hermitian operator can be defined with the function $\phi(x)$ (148) of the stationary solution. The Fokker-Planck operator can be expressed as

$$L_{FP} = \frac{\partial}{\partial x}D^{(2)}(x)e^{-\phi(x)}\frac{\partial}{\partial x}e^{\phi(x)} \tag{160}$$

as is easily seen by application of the differential operators. However,

$$\boldsymbol{L} = e^{\phi}L_{FP} \qquad \text{or} \tag{161}$$

$$\boldsymbol{L} = e^{\phi/2}L_{FP}e^{-\phi/2} \tag{162}$$

are Hermitian operators. Proof for expression (161): $\Psi_1(x)$ and $\Psi_2(x)$ are solutions of the Fokker-Planck equation satisfying the same boundary condition

$$\int \Psi_1 e^{\phi}L_{FP}\Psi_2 dx = \int \Psi_1 e^{\phi}\frac{\partial}{\partial x}D^{(2)}e^{-\phi}\frac{\partial}{\partial x}e^{\phi}\Psi_2 dx = -\int \left[\frac{\partial}{\partial x}\Psi_1 e^{\phi}\right]D^{(2)}e^{-\phi}\left[\frac{\partial}{\partial x}e^{\phi}\Psi_2\right]dx$$

$$= \int \Psi_2 e^{\phi}\frac{\partial}{\partial x}D^{(2)}e^{-\phi}\frac{\partial}{\partial x}e^{\phi}\Psi_1 dx = \int \psi_2 e^{\phi}L_{FP}\Psi_1 dx \tag{163}$$

Hence, $\left(e^{\phi}L_{FP}\right)^{\dagger} = L_{FP}^{\dagger}e^{\phi} = e^{\phi}L_{FP}$ is a Hermitian operator.

Orthogonality of Eigenfunctions

Eigenvalues can be discrete, continuous, or both. In the following the notation for discrete eigenvalues will be used. The case of continuous eigenvalue is analogoues to quantum mechanics, where the Kronecker δ_{nm} is replaced by a δ function.

Multiplication of the eigenvalue equation (159) with $e^{\phi(x)/2}$ from left gives

$$e^{\phi(x)/2}L_{FP}\varphi_n(x) = -\lambda_n e^{\phi(x)/2}\varphi_n(x)$$

$$\Leftrightarrow e^{\phi(x)/2}L_{FP}\underbrace{e^{-\phi(x)/2}e^{\phi(x)/2}}_{=1}\varphi_n(x) = -\lambda_n e^{\phi(x)/2}\varphi_n(x).$$

Hence, we have

$$\boldsymbol{L}\psi_n(x) = -\lambda_n\psi_n(x),$$

where $\boldsymbol{L}$ is given by Eq. (162) and

$$\psi_n(x) = e^{\phi(x)/2}\varphi_n(x). \tag{164}$$

Since $\boldsymbol{L}$ is a Hermitian operator, its eigenvalues are real and two eigenfunctions ψ_1 and ψ_2 with different eigenvalues $\lambda_1 \neq \lambda_2$ are orthogonal. For normalized eigenfunctions, we thus find the orthonormality relation

$$\int \psi_n(x)\psi_m(x)dx = \int e^{\phi(x)}\varphi_n(x)\varphi_m(x)dx = \delta_{nm}. \tag{165}$$

Positivity of Eigenvalues

From Eq. (163)—first and third term—follows for $\psi_1 = \psi_2 = \varphi_n$

$$\int \varphi_n(x)e^\phi L_{FP}\varphi_n(x)dx = \int \psi_n(x)\boldsymbol{L}\psi_n(x)dx = -\lambda_n \tag{166}$$

$$= -\int \left(\frac{\partial}{\partial x}\psi_n(x)e^{\phi/2}\right)^2 D^{(2)}e^{-\phi}dx \leq 0 . \tag{167}$$

The equal sign applies for the stationary state $\lambda_0 = 0$ only, i.e.,

$$\frac{\partial}{\partial x}\psi_0(x)e^{\phi/2} = 0 \quad \Rightarrow \psi_0(x) = \sqrt{N}e^{-\phi/2} . \tag{168}$$

All other eigenvalues λ_n $(n > 0)$ are larger than zero.

Completeness Relation

For a complete set of eigenfunctions of a Hermitian operator follows

$$\sum_n \psi_n(x)\psi_n(x') = \delta(x - x')$$

$$= e^{\phi(x)/2+\phi(x')/2} \sum_n \varphi_n(x)\varphi_m(x')$$

$$= e^{\phi(x)} \sum_n \varphi_n(x)\varphi_m(x') = e^{\phi(x')} \sum_n \varphi_n(x)\varphi_m(x') \tag{169}$$

Conditional Probability Density

The formal solution of the Fokker-Planck equation $\partial/\partial t P(x,t|x',t') = L_{FP}P(x,t|x',t')$ is given by

$$P(x,t|x',t') = e^{L_{FP}(x)(t-t')}\delta(x - x'). \tag{170}$$

With the representation (169) of the δ function follows

$$P(x,t|x',t') = e^{\phi(x')} \sum_n e^{L_{FP}(t-t')}\varphi_n(x)\varphi_n(x') = e^{\phi(x')} \sum_n e^{-\lambda_n(t-t')}\varphi_n(x)\varphi_n(x')$$

$$= e^{\phi(x')/2-\phi(x)/2} \sum_n e^{-\lambda_n(t-t')}\psi_n(x)\psi_n(x'). \tag{171}$$

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Joint Probability Density

In the stationary state, the joint probability density is given by

$$\Psi(x, t; x', t') = P(x, t|x', t')\Psi_0(x'), \tag{172}$$

with $\Psi_0(x) = \psi_0(x)^2 = N\exp(-\phi(x))$ (cf. Eqs. (147), (168)). Since Eq. (171) yields in the stationary state

$$\lim_{t \to \infty} P(x, t|x', t') = \psi_0(x)\psi_0(x') \ ,$$

the joint probability distribution is

$$\Psi(x, t; x', t') = \psi_0(x)\psi_0(x') \sum_{n=0}^{N_{\max}} e^{-\lambda_n(t-t')}\psi_n(x)\psi_n(x'), \tag{173}$$

if $\psi_0(x)$ exists. In the asymptotic limit $|t - t'| \to \infty$, $\Psi(x, t; x', t')$ becomes

$$\lim_{|t-t'| \to \infty} \Psi(x, t; x', t') = \psi_0(x)^2\psi_0(x')^2. \tag{174}$$

6.6 Transformation to Schrödinger Equation

By a suitable transformation, the one-variable Fokker-Planck equation, with an x-dependent factor $D^{(2)}(x)$, can be transformed into a Fokker-Planck equation with a constant factor $D = D^{(2)}$. Consider the Langevin equation with time-independent factors $h(\xi)$ and $g(\xi)$ ($\langle \Gamma(t)\Gamma(t') \rangle = 2\delta(t - t')$)

$$\dot{\xi}(t) = h(\xi) + g(\xi)\Gamma(t) \ .$$

Multiplication with $\sqrt{D}/g(\xi)$, or $\hat{g}^2 = D = const.$ yields

$$\frac{\hat{g}}{g(\xi)}\dot{\xi}(t) = \frac{h(\xi)\hat{g}}{g(\xi)} + \hat{g}\Gamma(t) = \hat{h}(\xi) + \hat{g}\Gamma(t) \ .$$

Substitution $\eta = \eta(\xi)$ yields the new Langevin equation

$$\dot{\eta}(t) = \hat{h}(\xi(\eta)) + \hat{g}\Gamma(t), \tag{175}$$

with

- $\dot{\eta} = (\hat{g}/g(\xi))\,\dot{\xi} \ \Rightarrow \ d\eta = (\hat{g}/g(\xi))\,d\xi \ \Rightarrow \ \eta = \int^{\xi} (\hat{g}/g(\xi'))\,d\xi'$

- $\hat{h}(\eta) = h(\xi(\eta))\hat{g}/g(\xi(\eta)) \ .$

Fokker-Planck equation for variable y corresponding to stochastic variable η

$$\frac{\partial}{\partial t}\hat{\Psi}(y, t) = \left[-\frac{\partial}{\partial y}\hat{D}^{(1)}(y) + D\frac{\partial^2}{\partial y^2}\right]\hat{\Psi}(y, t).$$

Relation between $\hat{\Psi}(y)$ and $\Psi(x)$

- transformation of coordinates $\Psi(x,t)dx = \hat{\Psi}(y,t)dy = \hat{\Psi}(y,t)(dy/dx)dx$

$$\hat{\Psi}(y) = \left(\frac{dy}{dx}\right)^{-1} \Psi(x(y),t)$$

- $\hat{D}^{(2)} = \hat{g}^2 = D \;\Rightarrow\; dy/dx = \sqrt{D/D^{(2)}(x)}$ (see relation between ξ and η)

- $\hat{D}^{(1)}(y) = \hat{h}(y) = h(x)\hat{g}/g(x)$ or $(x = x(y))$

$$\hat{D}^{(1)}(y) = \sqrt{\frac{D}{D^{(2)}(x)}}\left[D^{(1)}(x) - \frac{dg(x)}{dx}g(x)\right] = \sqrt{\frac{D}{D^{(2)}(x)}}\left[D^{(1)}(x) - \frac{1}{2}\frac{dD^{(2)}(x)}{dx}\right]$$

Replacing y by x and defining $f'(x) = -D^{(1)}(x)$, i.e., $f(x) = -\int D^{(1)}(x)dx$ we find

$$\boxed{\frac{\partial}{\partial t}\Psi(x,t) = \left[\frac{\partial}{\partial x}f'(x) + D\frac{\partial^2}{\partial x^2}\right]\Psi(x,t) = -\frac{\partial}{\partial x}S(x,t) = L_{FP}\Psi(x,t).} \qquad (176)$$

Representation of operator $\boldsymbol{L}$:

$$\boldsymbol{L} = e^{\phi/2}L_{FP}e^{-\phi/2} \overset{Eq.\ (160)}{=} De^{\phi/2}\frac{\partial}{\partial x}e^{-\phi(x)}\frac{\partial}{\partial x}e^{\phi(x)/2}$$

$$= De^{\phi/2}\frac{\partial}{\partial x}\left(e^{-\phi(x)}\left[\frac{\phi'}{2}e^{\phi(x)/2} + e^{\phi(x)/2}\frac{\partial}{\partial x}\right]\right)$$

$$= De^{\phi/2}\left(\frac{\phi''}{2}e^{-\phi(x)/2} - \frac{\phi'^2}{4}e^{-\phi(x)/2} + \frac{\phi'}{2}e^{-\phi(x)/2}\frac{\partial}{\partial x} - \frac{\phi'}{2}e^{-\phi(x)/2}\frac{\partial}{\partial x} + e^{-\phi(x)/2}\frac{\partial^2}{\partial x^2}\right)$$

$$= D\left(\frac{\phi''}{2} - \frac{\phi'^2}{4} + \frac{\partial^2}{\partial x^2}\right)$$

$$= D\frac{\partial^2}{\partial x^2} - V_s(x).$$

Hence,

$$\boldsymbol{L} = D\frac{\partial^2}{\partial x^2} - V_s(x). \qquad (177)$$

This is the negative one-particle Hamiltonian

$$\boldsymbol{H} = -D\frac{\partial^2}{\partial x^2} + V_s(x), \qquad (178)$$

where

$$V_s = -D\frac{\phi''}{2} + D\frac{\phi'^2}{4}.$$

The stationary solution of Eq. (176) yields $\phi(x) = f(x)/D$, hence

$$V_s(x) = \frac{1}{4D}\left(f'(x)\right)^2 - \frac{1}{2}f''(x).$$

$f'(x)$ is negative force of Fokker-Planck equation.

Solutions of Schrödinger equation $\boldsymbol{H}\Psi = E\Psi$ with potential V_s are solutions of Fokker-Planck equation with potential $f(x)$.

Parabolic Potential: Harmonic Oscillator

As an example of the prescript procedure, we will discuss the harmonic oscillator. The potential is

$$f(x) = \frac{\zeta}{2}x^2 \; ; \; \zeta > 0 \; ,$$

hence, the potential V_s is

$$V_s(x) = \frac{1}{4D}\left(f'(x)\right)^2 - \frac{1}{2}f''(x) = \frac{\zeta^2}{4D}x^2 - \frac{\zeta}{2}. \tag{179}$$

We have to solve the equation

$$\frac{\partial}{\partial t}\Psi(x,t) = \left[D\frac{\partial^2}{\partial x^2} - V_s(x)\right]\Psi(x,t),$$

which leads, by an eigenfunction expansion, to the eigenvalue equation

$$\left[D\frac{\partial^2}{\partial x^2} - V_s(x)\right]\psi_n(x) = -\lambda_n\psi_n(x) \; .$$

With the potential V_s follows

$$\left[-D\frac{\partial^2}{\partial x^2} + \frac{\zeta^2}{4D}x^2\right]\psi_n(x) = \left(\lambda_n + \frac{\zeta}{2}\right)\psi_n(x) \; . \tag{180}$$

The Schrödinger equation of a harmonic oscillator is given by

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right]\psi_n(x) = E_n\psi_n(x) \; ,$$

with the solution

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \; ,$$

$$\psi_n(x) = \sqrt[4]{\frac{m\omega}{\pi\hbar}}\frac{1}{\sqrt{2^n n!}}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\exp\left(-\frac{m\omega}{\hbar}x^2\right) \; ,$$

$$\psi_0(x) = \sqrt[4]{\frac{m\omega}{\pi\hbar}}\exp\left(-\frac{m\omega}{\hbar}x^2\right) \; .$$

The H_n are Hermite polynomials.

With the mapping $D = \hbar^2/(2m)$, $\zeta^2/(2D) = m\omega^2$, or $\hbar = \sqrt{2mD}$ and $\omega = \sqrt{\zeta^2/(2mD)}$, and comparison with the Schrödinger equation yields the solution of Eq. (180)

$$\lambda_n = n\zeta \; ; n = 1,\ldots,\infty \tag{181}$$

$$\psi_0(x) = \sqrt[4]{\frac{\zeta}{2\pi D}}\exp\left(-\frac{\zeta}{4D}x^2\right), \tag{182}$$

$$\psi_n(x) = \sqrt[4]{\frac{\zeta}{2\pi D}}\frac{1}{\sqrt{2^n n!}}H_n\left(\sqrt{\frac{\zeta}{2D}}x\right)\exp\left(-\frac{\zeta}{4D}x^2\right) \; . \tag{183}$$

Conditional probability distribution function

With the stationary state equation $\phi(x) = f(x)/D = \zeta x^2/(2D)$ follows the conditional probability distribution (155)

$$
\begin{aligned}
P(x,t|x',t') &= e^{\phi(x')/2 - \phi(x)/2} \sum_{n=0}^{\infty} e^{-\lambda_n(t-t')} \psi_n(x) \psi_n(x') \\
&= \sqrt{\frac{\zeta}{2\pi D}} \sum_{n=0}^{\infty} \frac{1}{2^n n!} H_n\left(\sqrt{\frac{\zeta}{2D}}x\right) H_n\left(\sqrt{\frac{\zeta}{2D}}x'\right) \\
&\quad \times \exp\left(-\frac{\zeta}{4D}x^2\right) \exp\left(-\frac{\zeta}{4D}x'^2\right) \exp\left(\frac{\zeta}{4D}x^2\right) \exp\left(\frac{\zeta}{4D}x'^2\right).
\end{aligned}
\tag{184}
$$

With $(|\alpha| < 1/2)$

$$
\sum_{n=0}^{\infty} \frac{\alpha^n}{n} H_n(x) H_n(y) = \frac{1}{\sqrt{1-4\alpha^2}} \exp\left(-\frac{4\alpha}{1-4\alpha^2}\left[\alpha x^2 + \alpha y^2 - xy\right]\right)
\tag{185}
$$

follows $(2\alpha = \exp(-\zeta(t-t')) = \exp(-\zeta\Delta t)\,)$

$$
\begin{aligned}
P(x,t|x',t') &= \sqrt{\frac{\zeta}{2\pi D\left[1 - e^{-2\zeta(t-t')}\right]}} \exp\left(-\frac{\zeta}{2D}x^2\right) \\
&\quad \times \exp\left(\frac{\zeta e^{\zeta\Delta t}}{D(1 - e^{-2\zeta\Delta t})}\left[xx' - e^{-\zeta\Delta t}x - e^{-\zeta\Delta t}x'\right]\right) \\
&= \sqrt{\frac{\zeta}{2\pi D\left[1 - e^{-2\zeta(t-t')}\right]}} \exp\left(-\frac{\zeta\left[x - x'e^{-\zeta(t-t')}\right]^2}{2D\left[1 - e^{-2\zeta(t-t')}\right]}\right)
\end{aligned}
\tag{186}
$$

7 Solution of Fokker-Planck Equation for Several Variables

Fokker-Planck equation

$$\frac{\partial \Psi(\{x\})}{\partial t} = L_{FP}\Psi(\{x\}) = -\sum_i \frac{\partial S_i}{\partial x_i} = -\boldsymbol{\nabla}\boldsymbol{S}, \tag{187}$$

$$L_{FP} = -\sum_i \frac{\partial}{\partial x_i}D_i(\{x\}) + \sum_{i,j}\frac{\partial^2}{\partial x_i \partial x_j}D_{ij}(\{x\}) = -\boldsymbol{\nabla}\boldsymbol{D} + \boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\mathbf{D}. \tag{188}$$

$\boldsymbol{S}$ is the probability current

$$S_i = D_i\Psi - \sum_j \frac{\partial}{\partial x_j}D_{ij}(\{x\})\Psi \ , \qquad \Rightarrow \qquad \boldsymbol{S} = \boldsymbol{D}\Psi - \boldsymbol{\nabla}(\mathbf{D}\Psi). \tag{189}$$

In a on-dimensional system, the probability current is constant in the stationary state. For natural boundary conditions is $\boldsymbol{S} = 0$. For a system with N variables, the probability current is not a constant in general in the stationary state and for natural boundary conditions no longer equal to zero. Only under particular conditions (**potential condition**) may the probability current vanish in the stationary state.

Lets consider the particular case $D_{ij} = D\delta_{ij}$, with $D = const.$. Then,

$$S_i = \Psi\left(D_i - D\frac{\partial}{\partial x_i}\ln\Psi\right) = D_i\Psi - D\frac{\partial}{\partial x_i}\Psi. \tag{190}$$

The condition $S_i = 0$ implies $D_i = D\partial\ln\Psi/\partial x_i$. Hence, $D_i dx_i = D\,d\ln\Psi$ and

$$\Psi(\{x\}) = N_c \exp\left(\frac{1}{D}\int^{\{x\}} D_i(\{x'\})\,dx_i'\right) = N_c \exp\left(-\phi(\{x\})\right). \tag{191}$$

Therefore, we can define a potential ϕ via

$$\phi(\{x\}) = -\frac{1}{D}\int^{\{x\}} D_i(\{x'\})\,dx_i'. \tag{192}$$

The potential exists, if $\partial D_i/\partial x_j = \partial D_j/\partial x_i$. These conditions are necessary and sufficient. The condition under which the probability current vanishes is denoted as **detailed balance**.

In case the potential condition applies and $D_{ij} = D\delta_{ij}$, the Fokker-Planck operator can be represented as

$$L_{FP} = \sum_i D\frac{\partial}{\partial x_i}e^{-\phi}\frac{\partial}{\partial x_i}e^{\phi}. \tag{193}$$

Hence,

$$L_{FP}^\dagger e^\phi = D\sum_i e^\phi \frac{\partial}{\partial x_i}e^{-\phi}\frac{\partial}{\partial x_i}e^\phi = e^\phi L_{FP}, \tag{194}$$

and

$$\boldsymbol{L} = e^{\phi/2} L_{FP} e^{-\phi/2} = e^{-\phi/2} L_{FP}^\dagger e^{\phi/2} = \boldsymbol{L}^\dagger \tag{195}$$

$$= e^{-\phi/2} e^\phi L_{FP} e^{-\phi/2} = e^{-\phi/2} L_{FP}^+ e^{-\phi/2} e^\phi = e^{-\phi/2} L_{FP}^\dagger e^{\phi/2}. \tag{196}$$

Thus, $\boldsymbol{L} = \boldsymbol{L}^\dagger$ is an Hermitian operator.

In general, the Fokker-Planck equation cannot be brought in a Hermitian form. As a consequence, the eigenvalues of the Fokker-Planck operator can be complex numbers.

7.1 Approach of the Asymptotic Solution: H-Theorem

Here, it will be shown that two time-dependent solutions of the Fokker-Planck equation will approach the same limiting value in the limit $t \to \infty$, i.e., the same stationary state distribution, at least under certain conditions.
Prerequisites:

- natural boundary conditions apply: $\Psi \to 0$ for $|x_i| \to \infty$

- $\int \Psi(\{x\}) d^N x = 1$, normalization

- $\Psi(\{x\}) \neq \delta(\boldsymbol{x})$, is not a δ function

- $|D_i|, |D_{ij}| < \infty$, no singularities

H-theorem: consider functional

$$H(t) = \int \Psi_1 \ln(\Psi_1/\Psi_2) \, d^N x = \int (\Psi_1 \ln \Psi_1 - \Psi_1 \ln \Psi_2) \, d^N x, \tag{197}$$

with two solutions Ψ_1 and Ψ_2 of the FP equation.
Assertion: $H(t) \geq 0$

Define $R = \Psi_1/\Psi_2 \geq 0$, since Ψ_1 and Ψ_2 are probability densities. Moreover,

$$R \ln R - R + 1 = \int_1^R \ln x \, dx \geq 0, \tag{198}$$

since $\ln x$ is strictly monotonic. With the normalization $\int \Psi_1 \, d^N x = \int \Psi_2 \, d^N x = 1$ follows

$$H(t) = \int \Psi_1 \ln R \, d^N x + 1 - 1 = \int (\Psi_1 \ln R - \Psi_1 + \Psi_2) \, d^N x$$

$$= \int \Psi_2 (R \ln R - R + 1) \, d^N x \geq 0. \tag{199}$$

Differential equation for $\dot{H} = dH(t)/dt$; Assertion: $\dot{H} \leq 0$

$$\dot{H}(t) = \int \left[\dot{\Psi}_1 \ln\left(\frac{\Psi_1}{\Psi_2}\right) + \frac{\Psi_1}{\Psi_1} \dot{\Psi}_1 - \frac{\Psi_1}{\Psi_2} \dot{\Psi}_2 \right] d^N x \tag{200}$$

$$= \int \dot{\Psi}_1 \ln R - R \dot{\Psi}_2 \, d^N x$$

$$= \int (L_{FP} \Psi_1) \ln R - R \dot{\Psi}_2 \, d^N x \overset{P.I.}{=} \int \Psi L_{FP}^\dagger \ln R - R \dot{\Psi}_2 \, d^N x.$$

With

$$L_{FP}^\dagger \ln R = \sum_i \left(D_i + \sum_j D_{ij} \frac{\partial}{\partial x_j} \right) \frac{\partial}{\partial x_i} \ln R = \sum_i \left(D_i + \sum_j D_{ij} \frac{\partial}{\partial x_j} \right) \frac{1}{R} \frac{\partial R}{\partial x_i} \quad (201)$$

$$= \frac{1}{R} L_{FP}^\dagger R - \sum_{ij} D_{ij} \frac{1}{R^2} \frac{\partial R}{\partial x_j} \frac{\partial R}{\partial x_i}$$

follows

$$\dot{H}(t) = \int \frac{\Psi_1}{R} L_{FP}^\dagger R - R \dot{\Psi}_2 \, d^N x - \int \Psi_1 \sum_{ij} D_{ij} \frac{1}{R^2} \frac{\partial R}{\partial x_j} \frac{\partial R}{\partial x_i} \, d^N x \quad (202)$$

$$\overset{R=\Psi_1/\Psi_2}{=} \int R L_{FP}^\dagger \Psi_2 - R \dot{\Psi}_2 \, d^N x - \int \Psi_1 \sum_{ij} D_{ij} \frac{1}{R^2} \frac{\partial R}{\partial x_j} \frac{\partial R}{\partial x_i} \, d^N x$$

$$\overset{P.I.}{=} \int \underbrace{R L_{FP} \Psi_2 - R \dot{\Psi}_2}_{=0} \, d^N x - \int \Psi_1 \sum_{ij} D_{ij} \frac{1}{R^2} \frac{\partial R}{\partial x_j} \frac{\partial R}{\partial x_i} \, d^N x.$$

Hence,

$$\dot{H}(t) = - \int \Psi_1 \sum_{ij} D_{ij} \frac{1}{R^2} \frac{\partial R}{\partial x_j} \frac{\partial R}{\partial x_i} \, d^N x \leq 0 \quad (203)$$

if D_{ij} positive definite. Thus, $\dot{H}$ decreases with time as long as $\partial \ln R / \partial x_i \neq 0$. Since $H(t) \geq 0$, it cannot decrease unlimited. As a consequence, it is assumed that $\ln R$ and R become independent of $\boldsymbol{x}$ for $t \to \infty$. Thus, $\dot{H}(t) \overset{t \to 0}{\to} 0$. Because of

$$1 = \int \Psi_1 \, d^N x = \int \frac{\Psi_1}{\Psi_2} \Psi_2 \, d^N x = \int R \Psi_2 \, d^N x \overset{t \to \infty}{=} R \int \Psi_2 \, d^N x = R, \quad (204)$$

i.e., $\Psi_1 = \Psi_2$ for $H \to 0$ in the limit $t \to 0$.w

As a consequence, all solutions of the Fokker-Planck equation are equal on sufficiently large time scales. For time-independent drift and diffusion coefficients can be a stationary state solution, with

$$L_{FP} \Psi_{st} = 0. \quad (205)$$

Application: Kramers equation

The above considerations do not apply for the Kramers equation, because the diffusion matrix (D_{ij}) is not positive definite (several of the matric elements are zero). From Eq. (203), we can only conclude that $\partial \ln R / \partial v = 0$. The other matrix elements are zero. Hence, we assume that for long times the relation applies

$$\Psi(x, v, t) = h(x, t) \exp\left(-\frac{1}{2} \frac{m v^2}{k_B T} \right). \quad (206)$$

Insertion in the Klein-Kramers equation (142) yields

$$\dot{h}(x, t) = \left(-\frac{\partial}{\partial x} + \frac{F(x)}{k_B T} \right) v h(x, t). \quad (207)$$

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Stationary state: $\dot{h} = 0$

$$h(x) = h_0 \exp\left(\frac{F(x)}{k_B T}\right) = h_0 \exp\left(-\beta U(x)\right). \tag{208}$$

Hence, also the stationary state of the Kramers equation is unique.

7.2   Representation by a Biorthogonal Basis

The probability density Ψ can be represented by eigenfunctions in the form

$$\Psi(\boldsymbol{x}, t) = \sum_n \varphi_n(\boldsymbol{x}) e^{-\lambda_n t} \tag{209}$$

and the Fokker-Planck equation becomes

$$L_{FP}\varphi_n = -\lambda_n \varphi_n. \tag{210}$$

Since L_{FP} is in general non-Hermitian, the eigenfunctions of the adjunct operator are also required:

$$L_{FP}^\dagger \varphi_m^\dagger = -\lambda_m \varphi_m^\dagger. \tag{211}$$

For the definition of the $\varphi_m^\dagger$ can either the conjugated complex eigenvalue in Eq. (211) be used, or the eigenvalue itself. With the latter choice, the scalar product of the eigenfunctions becomes

$$\left(\varphi_m^\dagger, \varphi_n\right) := \int \varphi_m^\dagger(\boldsymbol{x}) \varphi_n(\boldsymbol{x}) \, d^N x. \tag{212}$$

As a consequence, the eigenvalues in Eqs. (210) and (211) are equal:

$$\int \varphi_m^\dagger(\boldsymbol{x}) L_{FP}\varphi_m(\boldsymbol{x}) \, d^N x = -\lambda_m \int \varphi_m^\dagger(\boldsymbol{x})\varphi_m(\boldsymbol{x}) \, d^N x = -\lambda_m \left(\varphi_m^\dagger, \varphi_m\right) \tag{213}$$

$$= \int L_{FP}^\dagger \varphi_m^\dagger(\boldsymbol{x})\varphi_m(\boldsymbol{x}) \, d^N x = -\lambda_m^\dagger \left(\varphi_m^\dagger, \varphi_m\right);$$

$$\Rightarrow \qquad \lambda_n = \lambda_n^\dagger. \tag{214}$$

The eigenfunctions corresponding to different eigenvalues are orthogonal.

$$-\lambda_n \left(\varphi_m^\dagger, \varphi_n\right) = \left(\varphi_m^\dagger, L_{FP}\varphi_n\right) = \left(L_{FP}^\dagger \varphi_m^\dagger, \varphi_n\right) = -\lambda_m^\dagger \left(\varphi_m^\dagger, \varphi_n\right), \tag{215}$$

$$\Rightarrow \qquad \left(\varphi_m^\dagger, \varphi_n\right) = 0, \qquad \lambda_n \neq \lambda_m. \tag{216}$$

Hence, $\left(\varphi_m^\dagger, \varphi_n\right) = \delta_{nm}$.

For a non-Hermitian operator, there is not always a complete set of eigenfunctions. If such a set would exist, the non-Hermitian matrix could be diagonalized. If all eigenvalues would be different, the matrix could be transformed into a diagonal matrix. Otherwise,

only the Jordan normal form exists.

We will assume that a biorthogonal basis set exists and the completeness relation is given by

$$\sum_n \varphi_n(\boldsymbol{x})\varphi_n^\dagger(\boldsymbol{x}') = \delta(\boldsymbol{x} - \boldsymbol{x}'). \tag{217}$$

When a stationary solution of the Fokker-Planck equation exists, the following relations apply

$$\lambda_0 = 0\,, \qquad \varphi_0(\boldsymbol{x}) = \Psi_{st}(\boldsymbol{x})\,, \qquad \varphi_0^\dagger(\boldsymbol{x}) = 1. \tag{218}$$

The transition probability is then

$$P(\boldsymbol{x}, t | \boldsymbol{x}', t') = e^{L_{FP}(\boldsymbol{x})(t-t')}\delta(\boldsymbol{x} - \boldsymbol{x}') = e^{L_{FP}(\boldsymbol{x})(t-t')}\sum_n \varphi_n(\boldsymbol{x})\varphi_n^\dagger(\boldsymbol{x}') \tag{219}$$

$$= \sum_n \varphi_n(\boldsymbol{x})\varphi_n^\dagger(\boldsymbol{x}')e^{-\lambda_n(t-t')}.$$

7.3 Detailed Balance

For the illustration of the meaning of detailed balance, it is most convenient to consider a master equation.
Master equation

$$\frac{d}{dt}\Psi_n(t) = \sum_m \left[w(m \to n)\Psi_m - w(n \to m)\Psi_n\right]. \tag{220}$$

Here, $w(n \to m)$ denotes the transition rate from a (discrete) state n to m
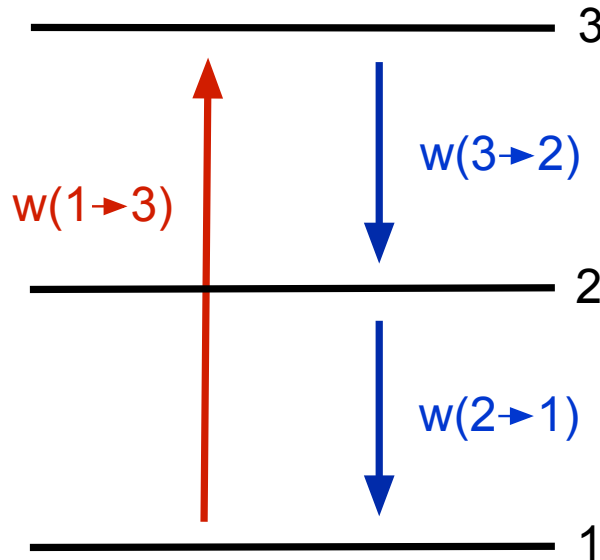

Illustration of the transitions from $1 \to 3$ and back from $3 \to 2$ and $2 \to 1$.

Stationary state, i.e., $\dot{\Psi}_n = 0$ implies

$$\sum_m [w(m \to n)\Psi_m - w(n \to m)\Psi_n] = 0. \tag{221}$$

Detailed balance yields

$$w(m \to n)\Psi_m = w(n \to m)\Psi_n. \tag{222}$$

This condition is sufficient, but not necessary. It is a rather strong condition on the transition between two levels. Stationary would be satisfied with a weaker relation.

Fokker-Planck equation

Fokker-Planck equation in master equation form

$$\frac{\partial}{\partial t}\Psi(\boldsymbol{x}, t) = \int [w(\boldsymbol{x}' \to \boldsymbol{x})\Psi(\boldsymbol{x}', t) - w(\boldsymbol{x} \to \boldsymbol{x}')\Psi(\boldsymbol{x}, t)]\, d^N x' , \tag{223}$$

where

$$w(\boldsymbol{x}' \to \boldsymbol{x}) = \frac{\partial}{\partial t} P(\boldsymbol{x}, t | \boldsymbol{x}', 0)|_{t=0} = L_{FP}(\boldsymbol{x})\delta(\boldsymbol{x} - \boldsymbol{x}') . \tag{224}$$

Detailed balance for even variables, i.e., variables which don't change sign during time inversion

$$\int w(\boldsymbol{x}' \to \boldsymbol{x})\Psi_{st}(\boldsymbol{x}')\, d^N x' = \int w(\boldsymbol{x} \to \boldsymbol{x}')\Psi_{st}(\boldsymbol{x})\, d^N x', \tag{225}$$

or

$$L_{FP}\Psi_{st}(\boldsymbol{x}) = L_{FP}(\boldsymbol{x}) \int \Psi_{st}(\boldsymbol{x}')\delta(\boldsymbol{x} - \boldsymbol{x}')\, d^N x' = \int L_{FP}(\boldsymbol{x}')\delta(\boldsymbol{x} - \boldsymbol{x}')\, d^N x' \Psi_{st}(\boldsymbol{x}) = 0 , \tag{226}$$

$(L_{FP}(\boldsymbol{x}')\Psi_{st}(\boldsymbol{x}) = 0)$ hence,

$$L_{FP}(\boldsymbol{x})\Psi_{st}(\boldsymbol{x}) = 0 \tag{227}$$

and the probability density function satisfies the Fokker-Planck equation.
If we require (detailed balance)

$$w(\boldsymbol{x}' \to \boldsymbol{x})\Psi_{st}(\boldsymbol{x}') = w(\boldsymbol{x} \to \boldsymbol{x}')\Psi_{st}(\boldsymbol{x}) \tag{228}$$

for the stationary state in Eq. (223), in analogy to Eq. (222), we obtain the condition

$$L_{FP}(\boldsymbol{x})\delta(\boldsymbol{x} - \boldsymbol{x}')\Psi_{st}(\boldsymbol{x}') = L_{FP}(\boldsymbol{x}')\delta(\boldsymbol{x} - \boldsymbol{x}')\Psi_{st}(\boldsymbol{x}) \tag{229}$$

or $(\boldsymbol{x}' \to \boldsymbol{x}$, left hand side)

$$L_{FP}(\boldsymbol{x})\Psi_{st}(\boldsymbol{x})\delta(\boldsymbol{x} - \boldsymbol{x}') = \Psi_{st}(\boldsymbol{x})L_{FP}^\dagger(\boldsymbol{x})\delta(\boldsymbol{x} - \boldsymbol{x}'). \tag{230}$$

Here, we used $A(\boldsymbol{x})\delta(\boldsymbol{x} - \boldsymbol{x}') = A^\dagger(\boldsymbol{x}')\delta(\boldsymbol{x} - \boldsymbol{x}')$. Hence,

$$L_{FP}(\boldsymbol{x})\Psi_{st}(\boldsymbol{x}) = \Psi_{st}(\boldsymbol{x})L^\dagger_{FP}(\boldsymbol{x}). \tag{231}$$

This is a relation for operators, i.e., it must be valid if it is applied to any arbitrary function. If we apply the relation to the function $f(\boldsymbol{x}) = 1$, we recover the Eq. (227), because $L^\dagger_{FP}(\boldsymbol{x}) \cdot 1 = 0$. Hence, $L_{FP}(\boldsymbol{x})\Psi_{st}(\boldsymbol{x}) = 0$.

The relation (231) can be generalized to odd functions. With the definition

$$\left. \begin{array}{ll} \tilde{x}_i & = x_i \\ \tilde{x}_i & = -x_i \end{array} \right\} \qquad \tilde{x}_i = \epsilon_i x_i \qquad \left\{ \begin{array}{ll} \tilde{\epsilon}_i & = 1, \quad \text{even} \quad \text{(position)} \\ \tilde{\epsilon}_i & = -1, \quad \text{odd} \quad \text{(velocity)} \end{array} \right. \tag{232}$$

Hence,

$$w(\boldsymbol{x}' \to \boldsymbol{x})\Psi_{st}(\boldsymbol{x}') = w(\epsilon\boldsymbol{x} \to (\epsilon\boldsymbol{x})')\Psi_{st}(\epsilon\boldsymbol{x}) \tag{233}$$

or

$$L_{FP}(\boldsymbol{x})\Psi_{st}(\boldsymbol{x}) = \Psi_{st}(\epsilon\boldsymbol{x})L^\dagger_{FP}(\epsilon\boldsymbol{x}). \tag{234}$$

7.4 Ornstein-Uhlenbeck Process

For the Ornstein-Uhlenbeck process, the drift and diffusion coefficients are constant, i.e.,

$$D_i = -\sum_j \gamma_{ij} x_j ; \qquad \gamma_{ij}, \ D_{ij} = D_{ji} \ \text{const.} . \tag{235}$$

We want to find the solution of the Fokker-Planck equation

$$\frac{\partial}{\partial t}P(\boldsymbol{x}, t|\boldsymbol{x}', t') = \sum_{i,j} \gamma_{ij} \frac{\partial}{\partial x_i}[x_j P(\boldsymbol{x}, t|\boldsymbol{x}', t')] + D_{ij} \frac{\partial^2}{\partial x_i \partial x_j}P(\boldsymbol{x}, t|\boldsymbol{x}', t') , \tag{236}$$

with the initial condition $P(\boldsymbol{x}, t'|\boldsymbol{x}', t') = \delta(\boldsymbol{x} - \boldsymbol{x}')$. Equation (236) is a linear equation, hence we solve it by Fourier transformation. Fourier representation of $P(\boldsymbol{x}, t|\boldsymbol{x}', t')$

$$P(\boldsymbol{x}, t|\boldsymbol{x}', t') = \frac{1}{(2\pi)^N} \int e^{i\boldsymbol{k}\cdot\boldsymbol{x}} P(\boldsymbol{k}, t|\boldsymbol{x}', t') \, d^N k . \tag{237}$$

Hence, Eq. (236) becomes

$$\frac{\partial}{\partial t}P(\boldsymbol{k}, t|\boldsymbol{x}', t') = -\sum_{i,j}\left(\gamma_{ij}k_i\frac{\partial}{\partial k_j}P(\boldsymbol{k}, t|\boldsymbol{x}', t') - D_{ij}k_ik_jP(\boldsymbol{k}, t|\boldsymbol{x}', t')\right) , \tag{238}$$

with the initial condition

$$P(\boldsymbol{k}, t'|\boldsymbol{x}', t') = e^{-i\boldsymbol{k}\boldsymbol{x}'} . \tag{239}$$

Ansatz

$$P(\boldsymbol{k}, t|\boldsymbol{x}', t') = \exp\left(-i\boldsymbol{k}\cdot\boldsymbol{M}(t, t') - \frac{1}{2}\boldsymbol{k}^T\boldsymbol{\sigma}(t, t')\boldsymbol{k}\right) . \tag{240}$$

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Hence,

$$\dot{P} + \sum_{i,j} \gamma_{ij} k_i \frac{\partial}{\partial k_j} P + \mathbf{k}^T \mathbf{D} \mathbf{k} P = \left(-i\mathbf{k} \cdot \dot{\mathbf{M}} - \frac{1}{2} \mathbf{k}^T \dot{\boldsymbol{\sigma}} \mathbf{k} - i\mathbf{k}^T \boldsymbol{\gamma} \mathbf{M} - \mathbf{k}^T \boldsymbol{\gamma} \boldsymbol{\sigma} \mathbf{k} + \mathbf{k}^T \mathbf{D} \mathbf{k} \right) P \tag{241}$$

$$= 0.$$

Separating time dependence for $\mathbf{M}$ and $\boldsymbol{\sigma}$:

$$\dot{\mathbf{M}} = -\boldsymbol{\gamma} \mathbf{M} \ , \tag{242}$$

$$\dot{\boldsymbol{\sigma}} = -\boldsymbol{\gamma} \boldsymbol{\sigma} - \boldsymbol{\sigma} \boldsymbol{\gamma} + 2\mathbf{D} \ . \tag{243}$$

Initial conditions: $\mathbf{M}(0) = \mathbf{x}'(0)$, $\boldsymbol{\sigma}(0) = 0$.

Solution of Eq. (242):

$$\mathbf{M}(t, t') = \exp\left(-\boldsymbol{\gamma}(t - t')\right) \mathbf{M}(t') \ , \tag{244}$$

or, with initial condition

$$\mathbf{M}(t) = e^{-\gamma t} \mathbf{x}' \ . \tag{245}$$

Solution of Eq. (243). First homogeneous equation, i.e. $\mathbf{D} = 0$

$$\boldsymbol{\sigma}^h(t) = e^{-\gamma t} \boldsymbol{\sigma}(0) e^{-\gamma t} \overset{\boldsymbol{\sigma}(0)=0}{=} 0 \ , \tag{246}$$

hence, solution of inhomogeneous equation

$$\boldsymbol{\sigma}(t) = \int_0^t e^{-\gamma t'} 2\mathbf{D} e^{-\gamma t'} \, dt' \ . \tag{247}$$

Or with $\mathbf{G}(t, t') = \mathbf{G}(t - t') = \exp\left(-\boldsymbol{\gamma}(t - t')\right)$:

$$\mathbf{M}(t) = \mathbf{G}(t)\mathbf{x}' \ , \qquad\qquad \boldsymbol{\sigma}(t) = 2 \int_0^t \mathbf{G}(t')\mathbf{D}\mathbf{G}(t') \, dt' \ , \tag{248}$$

$$M_i(t) = \sum_j G_{ij}(t) x'_j \ , \qquad\qquad \sigma_{ij} = 2 \sum_{kl} \int_0^t G_{ik}(t') D_{kl} G_{lj}(t') \, dt' \ . \tag{249}$$

Finally, conditional probability density

$$P(\mathbf{x}, t | \mathbf{x}', t') = \frac{1}{(2\pi)^N} \int e^{i\mathbf{k} \cdot \mathbf{x}} P(\mathbf{k}, t | \mathbf{x}', t') \, d^N k$$

$$= \frac{1}{(2\pi)^N} \int e^{i\mathbf{k} \cdot \mathbf{x}} \exp\left(-i\mathbf{k}^T \mathbf{G}(t)\mathbf{x}' - \frac{1}{2} \mathbf{k}^T \boldsymbol{\sigma}(t) \mathbf{k} \right) d^N k \ , \tag{250}$$

or

$$P(\mathbf{x}, t | \mathbf{x}', t') = \frac{1}{(2\pi)^{N/2}} \frac{1}{\sqrt{|\boldsymbol{\sigma}(t)|}} \exp\left(-\frac{1}{2} [\mathbf{x} - \mathbf{G}(t)\mathbf{x}']^T \boldsymbol{\sigma}^{-1}(t) [\mathbf{x} - \mathbf{G}(t)\mathbf{x}'] \right) \ . \tag{251}$$

Stationary state

If all the real parts of the eigenvalues of the matrix $\boldsymbol{\gamma}$ are larger than zero, there is a stationary state. This implies $\mathbf{G} \overset{t \to \infty}{\longrightarrow} 0$, and

$$\Psi(\mathbf{x}) = \frac{1}{(2\pi)^{N/2}} \frac{1}{\sqrt{|\boldsymbol{\sigma}(\infty)|}} \exp\left(-\frac{1}{2} \mathbf{x}^T \boldsymbol{\sigma}^{-1}(\infty) \mathbf{x} \right) \ , \tag{252}$$

where $\boldsymbol{\sigma}(\infty)$ obeys

$$\boldsymbol{\gamma} \boldsymbol{\sigma}(\infty) + \boldsymbol{\sigma}(\infty) \boldsymbol{\gamma} = 2\mathbf{D} \ . \tag{253}$$

8 Generalized Langevin Equation

So far, we discussed the Langevin equation as an empirical extension of Newton's equations of motion. However, the Langevin equations can be derived by a projection operator formalism. As an instructive and descriptive example, the dynamics of a particle of mass M (Brownian particle) embedded in a fluid of (N_s particles) will be considered. The particle mass obeys $M \gg m_i$, where m_i is the mass of the fluid particle i. The Hamiltonian of the whole system is then

$$H = \frac{\boldsymbol{p}}{2M} + \sum_{i=1}^{N_s} \frac{\boldsymbol{p}_i^2}{2m_i} + U_{fl}(\{\boldsymbol{r}_i\}) + U_{int} \, , \tag{254}$$

where
U_{fl} is the potential energy of the fluid particles, and
U_{int} the interaction energy between the fluid and the particle $U_{int} = \sum_{i=1}^{N_s} U_{int}(\boldsymbol{r}_i - \boldsymbol{r})$.

We are only interested in the dynamics of the "large" particle. The dynamics of the remaining degrees is not of interest. We will use a projection operator formalism to remove the undesired degrees of freedom.

8.1 Projection Operator Formalism

We divide the system in relevant and irrelevant variables

- relevant variables $\boldsymbol{r}$, $\boldsymbol{p}$, or, $\boldsymbol{v}$, $\boldsymbol{r}$

- irrelevant variables $\boldsymbol{p}_1, \ldots, \boldsymbol{p}_{N_s}, \boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_s}$

In general, we will now denote the relevant variables by A_i, $i = 1, \ldots N$. The equations of motion of the variables A_i are given by

$$\dot{A}_i = i\mathbf{L}A_i \, . \tag{255}$$

We introduce a projection operator $\mathbf{P}$ via

$$\mathbf{P} = \sum_{i,j=1}^{N} \langle \ldots A_i^* \rangle \langle A_i A_j^* \rangle \tag{256}$$

and the complementary operator $\mathbf{Q}$ by

$$\mathbf{Q} = \mathbf{I} - \mathbf{P} \, . \tag{257}$$

In the scaler product, $\langle \ldots \rangle$ means averaging over the equilibrium distribution function (ensemble average), i.e.,

$$\langle A_i A_j^* \rangle = \frac{1}{Z} \int A_i A_j^* e^{-\beta H} d\Gamma = \int A_i A_j^* \Psi_{st} d\Gamma \, . \tag{258}$$

The inverse $\langle \ldots \rangle^{-1}$ is defined as

$$\sum_{k=1}^{N} \langle A_i A_k^* \rangle \langle A_k A_j^* \rangle^{-1} = \delta_{ij} \ . \tag{259}$$

The equation of motion of A_j is then given by

$$\frac{dA_j}{dt} = i\mathbf{L}A_j(t) = e^{i\mathbf{L}t} i\mathbf{L}A_j(0) = e^{i\mathbf{L}t} \left(\mathbf{P} + \mathbf{Q} \right) i\mathbf{L}A_j(0) \ . \tag{260}$$

Using the identity

$$e^{i\mathbf{L}t} = e^{i\mathbf{Q}\mathbf{L}t} + \int_0^t e^{i\mathbf{L}(t-\tau)} i\mathbf{P}\mathbf{L}e^{i\mathbf{Q}\mathbf{L}\tau} \ d\tau \ , \tag{261}$$

we obtain

$$\frac{dA_j}{dt} = \sum_{k=1}^{N} \left(i\Omega_{jk} A_k(t) - \int_0^t K_{jk}(\tau) A_k(t-\tau) d\tau \right) + F_j(t) \ , \tag{262}$$

with the abbreviations

$$i\Omega_{kl} = \sum_{j=1}^{N} \langle (i\mathbf{L}A_k) A_j^* \rangle \langle A_j A_l^* \rangle^{-1} \ , \qquad \text{frequency function} \tag{263}$$

$$K_{kl} = \sum_{j=1}^{N} \langle F_k(\tau) F_j^* \rangle \langle A_j A_l^* \rangle^{-1} \ , \qquad \text{memory function} \tag{264}$$

$$F_k(t) = e^{i\mathbf{Q}\mathbf{L}t} i\mathbf{Q}\mathbf{L}A_k(0) \ , \qquad \text{stochastic forces} \ . \tag{265}$$

Brownian particle

Back to the dynamics of the Brownian particle. The relation between particle position and velocity is

$$\boldsymbol{r}(t) = (x_1, x_2, x_3)^T = (A_1, A_2, A_3)^T \ ; \quad \dot{\boldsymbol{r}}(t) = \boldsymbol{v}(t) = (v_1, v_2, v_3)^T = (A_4, A_5, A_6)^T \ . \tag{266}$$

The operator $\mathbf{L}$ is given by

$$\mathbf{L} = -i \sum_{\alpha=1}^{3} \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} + F_\alpha \frac{\partial}{\partial p_\alpha} \ , \tag{267}$$

which yields Hamilton's equations of motion

$$\dot{x}_\alpha = i\mathbf{L}x_\alpha = \frac{p_\alpha}{m} \ , \tag{268}$$

$$\dot{p}_\alpha = i\mathbf{L}p_\alpha = F_\alpha \ . \tag{269}$$

The operator $\mathbf{P}$ is

$$\mathbf{P} = \sum_{\alpha,\beta=1}^{3} \langle \ldots x_\alpha \rangle \langle x_\alpha x_\beta \rangle^{-1} x_\beta + \sum_{\alpha,\beta=1}^{3} \langle \ldots v_\alpha \rangle \langle v_\alpha v_\beta \rangle^{-1} v_\beta \ ; \tag{270}$$

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mixed terms vanish, because a canonical ensemble is considered.
Calculation of the correlation functions yields (distribution function $\Psi = Z^{-1} \exp(-\beta H)$)

$$\frac{d\boldsymbol{r}}{dt} = \boldsymbol{v} \ , \tag{271}$$

$$M\frac{d\boldsymbol{v}}{dt} = -\mathbf{O}\boldsymbol{r} - \frac{1}{k_B T} \int_0^t \langle \boldsymbol{f}(\tau) \cdot \boldsymbol{f}(0) \rangle \, \boldsymbol{v}(t-\tau) \, d\tau + \boldsymbol{f}(t) \tag{272}$$

with the definitions

$$\boldsymbol{f}(t) = M\boldsymbol{F}(t) \ ; \quad \langle \boldsymbol{F}(t) \cdot \boldsymbol{F}(0) \rangle = \frac{1}{M^2} \langle \boldsymbol{f}(t) \cdot \boldsymbol{f}(0) \rangle \ ; \quad \mathbf{O} \langle \boldsymbol{r} : \boldsymbol{r} \rangle = k_B T \mathbf{I} \ , \tag{273}$$

$\boldsymbol{r} : \boldsymbol{r}$: dyadic product; $\mathbf{O} \sim \langle AA \rangle^{-1}$.

We can compare Eq. (271) with the Langevin equation Eq. (130) of Sec. 5.2.1. Evidently, $\boldsymbol{f}(t)$ corresponds to the stochastic forces $\Gamma(t)$. Moreover, there are memory effects in general. In case $M \gg m_i$, the acceleration of the Brownian particle is negligible (overdamped dynamics). Then, we find

$$-\mathbf{O}\boldsymbol{r}(t) - \frac{1}{k_B T} \int_0^t \langle \boldsymbol{f}(\tau) \cdot \boldsymbol{f}(0) \rangle \, \dot{\boldsymbol{r}}(t-\tau) \, d\tau + \boldsymbol{f}(t) = 0 \ . \tag{274}$$

Multiplication by the inverse of $\langle \boldsymbol{f}(\tau) \cdot \boldsymbol{f}(0) \rangle$ and integration yields

$$\frac{d}{dt}\boldsymbol{r}(t) = \int_0^t \mathbf{M}(t-\tau) \left[-\mathbf{O}\boldsymbol{r}(\tau) + \boldsymbol{f}(\tau)\right] d\tau \ . \tag{275}$$

($\int_0^t \mathbf{M}(t-\tau) \langle \boldsymbol{f}(t'-\tau) \cdot \boldsymbol{f}(0) \rangle \, d\tau = 2k_B T \delta(t-t') \mathbf{I}$; 2. fluctuation dissipation theorem)

Assuming that the correlation function of the fluid-particle forces acting on the Brownian particles relax much faster than the correlations of the Brownian particles, we can write

$$\mathbf{M}(t-\tau) = \mathbf{M}\delta(t-\tau) \ . \tag{276}$$

Moreover, the stochastic forces can be described by a δ-correlated process, i.e., we obtain the equations

$$\dot{\boldsymbol{r}}(t) = \mathbf{M}\left(-\mathbf{O}\boldsymbol{r}(t) + \boldsymbol{\Gamma}(t)\right) \ , \tag{277}$$

$$\langle \boldsymbol{\Gamma}(t) \cdot \boldsymbol{\Gamma}(t') \rangle = 2k_B T \mathbf{M}^{-1}\delta(t-t') \ , \tag{278}$$

with $\mathbf{M}\mathbf{M}^{-1} = \mathbf{I}$.
For our original system, $\mathbf{M}$ is given by $\mathbf{M} = \mathbf{I}/\gamma$.

In case of a system with several degrees of freedom (polymer chain), the stochastic equation becomes

$$\frac{d}{dt}\boldsymbol{r}_i(t) = \sum_{k=1}^N \mathbf{M}_{ik} \left(-\sum_{j=1}^N \mathbf{O}_{kj}\boldsymbol{r}_j(t) + \boldsymbol{\Gamma}_k(t) \right) \ . \tag{279}$$

Naturally, for these general Langevin equations there exists a Fokker-Planck equation (Smoluchowski equation), namely

$$\frac{\partial}{\partial t}\Psi(t) = \sum_{i,j=1}^N \nabla_{\boldsymbol{r}_i}\mathbf{M}_{ij} \left(k_B T \nabla_{\boldsymbol{r}_j} - \sum_{k=1}^N O_{kj}\boldsymbol{r}_j \right) \Psi(t) \ . \tag{280}$$

Side remarks

Properties of projection operators

- $\mathbf{P}^2 = \mathbf{P}$

$$\mathbf{P} = \sum_{i,j} \langle \ldots A_i^* \rangle \langle A_i A_j^* \rangle^{-1} A_j$$

$$\mathbf{P^2} = \sum_{i,j} \sum_{i',j'} \left\langle \left[\langle \ldots A_{i'}^* \rangle \langle A_{i'} A_{j'}^* \rangle^{-1} A_{j'} \right] A_i^* \right\rangle \langle A_i A_j^* \rangle^{-1} A_j$$

$$= \sum_{i,j} \sum_{i',j'} \left[\langle \ldots A_{i'}^* \rangle \langle A_{i'} A_{j'}^* \rangle^{-1} \right] \langle A_{j'} A_i^* \rangle \langle A_i A_j^* \rangle^{-1} A_j$$

$$\stackrel{\sum_i \to \delta_{j,j'}}{=} \sum_{i',j'} \langle \ldots A_{i'}^* \rangle \langle A_{i'} A_{j'}^* \rangle^{-1} A_{j'} = \mathbf{P}$$

Identity

$$e^{i\mathbf{L}t} = e^{i\mathbf{QL}t} + \int_0^t e^{i\mathbf{L}(t-\tau)} i\mathbf{PL} e^{i\mathbf{QL}\tau} d\tau$$

Setting $f(t) = e^{i\mathbf{L}t}$; differential equation for $f(t)$

$$\frac{d}{dt} f(t) = i\mathbf{L} f(t) = i\mathbf{QL} e^{i\mathbf{QL}t} + i\mathbf{PL} e^{i\mathbf{QL}t} + i\mathbf{L} \int_0^t e^{i\mathbf{L}(t-\tau)} i\mathbf{PL} e^{i\mathbf{QL}\tau} d\tau$$

$$\stackrel{\mathbf{P+Q}=1}{=} i\mathbf{L} e^{i\mathbf{QL}t} + i\mathbf{L} \int_0^t e^{i\mathbf{L}(t-\tau)} i\mathbf{PL} e^{i\mathbf{QL}\tau} d\tau$$

$$= i\mathbf{L} f(t)$$

Hence, both sides of the equation satisfy the same differential equation. With the same initial condition, i.e., $f(0) = 1$ follows identical solution.

Derivatives

Identity

$$\frac{d}{dt} A_j = i\mathbf{L} A_j(t) = e^{i\mathbf{L}t} i\mathbf{L} A(0) = e^{i\mathbf{L}t} (\mathbf{P} + \mathbf{Q}) i\mathbf{L} A_j(0)$$

Moreover,

$$e^{i\mathbf{L}t} \mathbf{P} i\mathbf{L} A_j(0) = e^{i\mathbf{L}t} \sum_{k,l} \langle i\mathbf{L} A_j A_k^* \rangle \langle A_k A_l^* \rangle^{-1} A_l(0)$$

$$= \sum_{k,l} \langle i\mathbf{L} A_j A_k^* \rangle \langle A_k A_l^* \rangle^{-1} A_l(t)$$

$$= i \sum_l \Omega_{jl} A_l(t)$$

and

$$i\Omega_{jl} = \sum_k \langle i\mathbf{L}A_j A_k^* \rangle \langle A_k A_l^* \rangle^{-1}$$

Furthermore,

$$e^{i\mathbf{L}t}\mathbf{Q}i\mathbf{L}A_j(0) = \underbrace{e^{i\mathbf{QL}t}\mathbf{Q}i\mathbf{L}A_j(0)}_{F_j(t)} + \int_0^t e^{i\mathbf{L}(t-\tau)}i\mathbf{PL}e^{i\mathbf{QL}\tau}d\tau \; \mathbf{Q}i\mathbf{L}A_j(0)$$

$$= F_j(t) + \int_0^t e^{i\mathbf{L}(t-\tau)}i\mathbf{PL}\underbrace{e^{i\mathbf{QL}\tau}\mathbf{Q}i\mathbf{L}A_j(0)}_{F_j(\tau)} d\tau$$

$$= F_j(t) + \int_0^t e^{i\mathbf{L}(t-\tau)}i\mathbf{PL}F_j(\tau) \; d\tau$$

$$i\mathbf{PL}F_j(\tau) = i\mathbf{PL}(\mathbf{P} + \mathbf{Q})F_j(\tau) = i\mathbf{PLQ}F_j(\tau) \;, \quad \text{because } \mathbf{P}F_j(\tau) = 0$$

Consequently,

$$e^{i\mathbf{L}t}\mathbf{Q}i\mathbf{L}A_j(0) = F_j(t) + \int_0^t e^{i\mathbf{L}(t-\tau)}\sum_{k,l}\langle i\mathbf{LQ}F_j(\tau)A_k^*(0)\rangle \langle A_k A_l^*\rangle A_l(0) \; d\tau$$

$$\overset{(i\mathbf{LQ})^\dagger A_k^*(0)=-F_k^*(0)}{=} F_j(t) - \int_0^t e^{i\mathbf{L}(t-\tau)}\sum_{k,l}\langle F_j(\tau)F_k^*(0)\rangle \langle A_k A_l^*\rangle A_l(t-\tau) \; d\tau$$

And

$$\frac{d}{dt}A_j = i\sum_k \Omega_{jk}A_k(t) - \int_0^t \sum_k K_{jk}(\tau)A_k(t-\tau) \; d\tau + F_j(t)$$

with

$$i\Omega_{jk} = \sum_l \langle i\mathbf{L}A_j A_k^* \rangle \langle A_k A_j^* \rangle^{-1}$$

$$K_{jk} = \sum_l \langle F_j(\tau)F_l^*(0)\rangle \langle A_l A_k^* \rangle^{-1}$$

9 Hydrodynamic Interactions

Lets consider one or several objects composed of mass points in a fluid environment. The particles interact with each other by pair-wise forces, i.e, the potential reads

$$U = U_{ex}(\boldsymbol{r}) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}U_{ij}(\boldsymbol{r}_i - \boldsymbol{r}_j). \tag{281}$$

U_{ex} denotes an external potential, such as an electric field or gravitational force. The dynamics of the particles can be described by the Langevin equation

$$\dot{\boldsymbol{r}}_i = \frac{1}{\gamma}\left[\boldsymbol{F}_i + \boldsymbol{\Gamma}_i(t)\right], \tag{282}$$

$\boldsymbol{F}_i = \sum_j \boldsymbol{F}_{ij}$ (external force is dropped) and the stochastic force is considered a Gaussian-Markovian process (white noise)

$$\langle \boldsymbol{\Gamma}_i(t)\rangle = 0, \tag{283}$$
$$\langle \Gamma_{i,\alpha}(t)\Gamma_{j,\beta}(t')\rangle = 2k_BT\gamma\delta_{\alpha\beta}\delta_{ij}\delta(t - t'). \tag{284}$$

Here, correlations in the solvent are neglected. The motion of a fluid particle, however, implies fluid motion due to non-slip boundary conditions (Stokes law: $F = 3\pi\eta d$, where d is the particle diameter), i.e., the fluid at the position of the particle moves with the same velocity as the particle itself and vice versa. This fluid motion affects the dynamics of other particles and is denoted as hydrodynamic interactions. To determine the velocity of a particle i, the fluid velocity $\boldsymbol{v}(\boldsymbol{r})$ is needed, which is created by "external" forces on the fluid element at the particle position $\boldsymbol{r}_i$.

To tackle this problem analytically, the fluid is considered a continuum and its dynamics obeys the Navier-Stokes equation, more precisely, the Stokes equation, since the low Reynolds number limit is considered. The particle at $\boldsymbol{r}_i$ has then to be coupled to the solution of Stokes equation.

9.1 Stokes Equation

The Navier-Stokes equation of an incompressible, i.e., $\nabla\boldsymbol{v} = 0$, and isotropic fluid is given by

$$\rho\left(\frac{\partial}{\partial t}\boldsymbol{v} + (\boldsymbol{v}\nabla)\boldsymbol{v}\right) = \eta\Delta\boldsymbol{v} - \nabla p + \boldsymbol{f}, \tag{285}$$

where $\boldsymbol{v}(\boldsymbol{r}, t)$ is the fluid flow field, ρ the fluid density, η its viscosity, $p(\boldsymbol{r}, t)$ the pressure field, and $f(\boldsymbol{r}, t)$ an external volume force (force per volume). The various terms in this equation can significantly differ in magnitude, depending on the hydrodynamic problem under consideration. To get an estimate of the various terms, we scale the fluid velocity by a typical value u, the length scale by a a, and the time by the time M/γ (Brownian time), where M is the mass of a dissolved particle. I.e.,

$$\boldsymbol{v}' = \boldsymbol{v}/u ,$$
$$\boldsymbol{r}' = \boldsymbol{r}/a ,$$
$$t' = t/(M/\gamma) .$$

Then, the Navier-Stokes equation reads

$$\rho \frac{\gamma u}{M} \frac{\partial}{\partial t'} \boldsymbol{v}' + \frac{\rho u^2}{a} (\boldsymbol{v}'\nabla')\boldsymbol{v}' = \frac{\eta u}{a^2} \Delta' \boldsymbol{v}' - \frac{1}{a} \nabla' p + \boldsymbol{f}. \tag{286}$$

Introducing the dimensionless pressure and external force

$$p' = \frac{a}{\eta u} p \ ,$$

$$\boldsymbol{f}' = \frac{a^2}{\eta u} \boldsymbol{f} \ ,$$

hence,

$$\rho \frac{a^2 \gamma}{M\eta} \frac{\partial}{\partial t'} \boldsymbol{v}' + Re(\boldsymbol{v}'\nabla')\boldsymbol{v}' = \Delta' \boldsymbol{v}' - \nabla' p' + \boldsymbol{f}'. \tag{287}$$

The dimensionless number

$$Re = \frac{\rho a u}{\eta} \tag{288}$$

is denoted as Reynolds number.

By construction, we have $|(\boldsymbol{v}'\nabla')\boldsymbol{v}'| \approx |\Delta'\boldsymbol{v}'| \approx 1$. Hence, for small Reynolds numbers $Re \ll 1$, the non-linear term $(\boldsymbol{v}\nabla)\boldsymbol{v}$ in Eq. (285) can be neglected.

For a spherical particle of radius a in a fluid, the relation $\gamma = 6\pi\eta a$ (Stokes law) applies. Hence, $\rho a^2 \gamma/M\eta = 9\rho/2\rho_p$, where ρ_p is the mass density of the spherical particle. Since the Brownian particle swims in the fluid, $\rho \approx \rho_p$, and $\rho a^2 \gamma/M\eta = 9/2$. The time derivative in Eq. (287) should therefore kept in general, even for small Reynolds numbers. However, on diffusive time scales $\tau_D \gg M/\gamma$, the time derivative $\partial \boldsymbol{v}'/\partial t'$ has decayed to zero, since $\boldsymbol{v}$ decays to zero as a result of friction during the interval M/γ. The reaming time dependence is due to a possible time dependence of the external force.

On the diffusive (Brownian) time scale and at low Reynolds numbers, the original Navier-Stokes equation simplifies to

$$\boxed{\eta \Delta \boldsymbol{v} = \nabla p - \boldsymbol{f}}. \tag{289}$$

This equation is denoted as Stokes or creeping flow equation.

Typical values for a Brownian particle (colloid):

- velocity: equipartition of energy $M \langle \boldsymbol{v}^2 \rangle /2 = 3k_B T/2 \quad \Rightarrow v \approx \sqrt{\langle \boldsymbol{v}^2 \rangle}$

- mass: $m \approx 10^{-17} kg$

- size: $a \approx 100 nm$

- Reynolds number: $Re \approx 10^{-2}$

Note that the inertial term in the Navier-Stokes equation can only be neglected on the Brownian time scale $\tau_D \gg M/\gamma$. Hence, solutions of Eq. (289) can only be combined with the Smoluchowski equation, but not the Fokker-Planck equation. On the Fokker-Planck time scale, the non-linear term can be neglected for small Reynolds numbers, but the time derivative $\partial/\partial t$ has to be kept. Hydrodynamic friction on the Fokker-Planck time scale follows from the equation

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla p + \eta \Delta \boldsymbol{v} + \boldsymbol{f}. \tag{290}$$

In the following, we will consider the solution of the Stokes equation (289).

9.2 Oseen Tensor

Equation (289) is a linear, inhomogeneous differential equation and can be solved by Fourier transformation

$$\boldsymbol{v}_k = \int \boldsymbol{v}(\boldsymbol{r}) e^{i\boldsymbol{kr}} d^3 r.$$

In (289) yields

$$\eta \boldsymbol{k}^2 \boldsymbol{v}_k - i\boldsymbol{k} p_k = \boldsymbol{f}_k. \tag{291}$$

Incompressibility: $\nabla \boldsymbol{v} = 0 \implies \boldsymbol{k}\boldsymbol{v}_k = 0$, i.e., $\boldsymbol{v}_k \perp \boldsymbol{k}$. Multiplication of Eq. (291) with $\boldsymbol{k}$ yields

$$\boldsymbol{v}_k = \frac{1}{\eta \boldsymbol{k}^2} \left(\mathbf{I} - \frac{\boldsymbol{k}:\boldsymbol{k}}{\boldsymbol{k}^2} \right) \boldsymbol{f}_k = \Omega(\boldsymbol{k}) \boldsymbol{f}_k,$$

where $\boldsymbol{k}:\boldsymbol{k}$ denotes the tensor product. Fourier transformation gives

$$\boldsymbol{v}(\boldsymbol{r}) = \int \Omega(\boldsymbol{r} - \boldsymbol{r}') \boldsymbol{f}(\boldsymbol{r}') d^3 r', \tag{292}$$

with the *Oseen* tensor

$$\boldsymbol{\Omega}(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \int \frac{1}{\eta \boldsymbol{k}^2} \left(\mathbf{I} - \frac{\boldsymbol{k}:\boldsymbol{k}}{\boldsymbol{k}^2} \right) e^{-i\boldsymbol{kr}} d^3 k.$$

Since the tensor $\boldsymbol{\Omega}$ depends on the vector $\boldsymbol{r}$ only, it can be written in terms of two scalars A and B and the unit vector $\boldsymbol{r}/|\boldsymbol{r}|$ as

$$\Omega_{\alpha\beta} = A\delta_{\alpha\beta} + B\frac{r_\alpha r_\beta}{r^2}.$$

A and B follow from the conditions

$$\Omega_{\alpha\alpha} = 3A + B , \quad \Omega_{\alpha\beta}\frac{r_\alpha r_\beta}{r^2} = A + B.$$

Evaluation of the integrals yields $A = B = 1/(8\pi\eta r)$, with $r = |\boldsymbol{r}|$, and hence, the Oseen tensor is given by

$$\boldsymbol{\Omega}(\boldsymbol{r}) = \frac{1}{8\pi\eta r} \left(\mathbf{I} + \frac{\boldsymbol{r}:\boldsymbol{r}}{r^2} \right) \tag{293}$$

or, in components

$$\Omega_{\alpha\beta}(\boldsymbol{r}) = \frac{1}{8\pi\eta r} \left(\delta_{\alpha\beta} + \frac{r_\alpha r_\beta}{r^2} \right). \tag{294}$$

This tensor applies for point-like particles and diverges at $\boldsymbol{r} = 0$. For finite size particles of diameter d the positive definite Rotne-Prager tensor can be used ($r > d$)

$$\boldsymbol{\Omega}(\boldsymbol{r}) = \frac{1}{8\pi\eta r} \left(\mathbf{I} + \frac{\boldsymbol{r}:\boldsymbol{r}}{r^2} + \frac{d}{2r^2} \left[\frac{1}{3}\mathbf{I} - \frac{\boldsymbol{r}:\boldsymbol{r}}{r^2} \right] \right). \tag{295}$$

9.3 Equation of Motion of Solute

The flow field $\boldsymbol{v}(\boldsymbol{r})$ is created by the motion of the particles $\boldsymbol{r}_i$. Hence, with the force density

$$\boldsymbol{f}(\boldsymbol{r}) = \sum_{i=1}^{N} [\boldsymbol{F}_i + \boldsymbol{\Gamma}_i] \, \delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

$\boldsymbol{v}(\boldsymbol{r})$ becomes

$$\boldsymbol{v}(\boldsymbol{r}) = \sum_{i=1}^{N} \boldsymbol{\Omega}(\boldsymbol{r} - \boldsymbol{r}_i) [\boldsymbol{F}_i + \boldsymbol{\Gamma}_i]. \tag{296}$$

In the presence of a solvent, the friction between a particle at $\boldsymbol{r}_i$ and the fluid background is described by

$$\gamma \, [\dot{\boldsymbol{r}}_i - \boldsymbol{v}(\boldsymbol{r}_i(t))] = \boldsymbol{F}_i + \boldsymbol{\Gamma}_i,$$

or, with Eq. (296)

$$\dot{\boldsymbol{r}}_i = \boldsymbol{v}(\boldsymbol{r}_i) + \frac{1}{\gamma}[\boldsymbol{F}_i + \boldsymbol{\Gamma}_i] = \sum_{j=1}^{N} \left(\boldsymbol{\Omega}(\boldsymbol{r}_i - \boldsymbol{r}_j) + \frac{\delta_{ij}}{\gamma} \right) [\boldsymbol{F}_j + \boldsymbol{\Gamma}_j] = \sum_{j=1}^{N} \mathbf{H}(\boldsymbol{r}_i - \boldsymbol{r}_j) [\boldsymbol{F}_j + \boldsymbol{\Gamma}_j], \tag{297}$$

where $\mathbf{H}$ is the hydrodynamic tensor

$$\mathbf{H}(\boldsymbol{r}_i - \boldsymbol{r}_j) = \begin{cases} \boldsymbol{\Omega}(\boldsymbol{r}_i - \boldsymbol{r}_j) \, , & i \neq j, \text{ i.e. } |\boldsymbol{r}_i - \boldsymbol{r}_j| \neq 0 \\ \dfrac{\mathbf{I}}{\gamma} \, , & i = j \end{cases}. \tag{298}$$

Alternatively,

$$\mathbf{H}(\boldsymbol{r}_i - \boldsymbol{r}_j) = \frac{\delta_{ij}}{\gamma} \mathbf{I} + (1 - \delta_{ij}) \boldsymbol{\Omega}(\boldsymbol{r}_i - \boldsymbol{r}_j). \tag{299}$$

For an one-dimensional *continuous* object embedded in 3-dimensional space, the equation of motion (297) turns into

$$\boxed{\frac{\partial \boldsymbol{r}(s,t)}{\partial t} = \int \mathbf{H}(\boldsymbol{r}(s) - \boldsymbol{r}(s')) \, [\boldsymbol{F}(s') + \boldsymbol{\Gamma}(s')] \, ds',} \tag{300}$$

with

$$\mathbf{H}(\boldsymbol{r}(s) - \boldsymbol{r}(s')) = \frac{\delta(s - s')}{\gamma} \mathbf{I} + \Theta(|\boldsymbol{r}(s) - \boldsymbol{r}(s')| - d) \boldsymbol{\Omega}(\boldsymbol{r}(s) - \boldsymbol{r}(s')). \tag{301}$$

Note, the forces in Eq. (300) are force densities, i.e., forces per length; s is the contour coordinate along the 1-dimensional object. Similar, γ in Eq. (301) is a friction density, i.e., friction per length. To exclude self-interactions, the parameter d is introduced in Eq. (301), i.e., a lower cut-off is introduced for hydrodynamic interactions. d can be the excluded volume of the considered particles. For a polymer model, e.g., DNA, d will be the thickness of the molecule.

10 Polymer Models

Before diving into the dynamics of polymers, a suitable polymer model has to be chosen. There are a number models, which describe polymer properties. However, not all of them are suitable for an analytical treatment.

10.1 Flexible Polymer

10.1.1 Polymer of Finite-Length Bonds
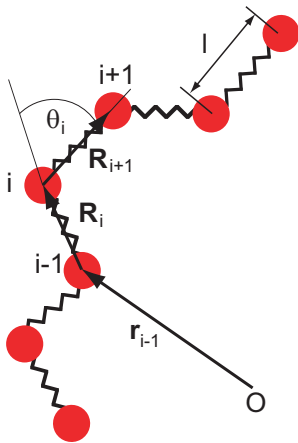
Model:

$N + 1$ mass points at positions $\boldsymbol{r}_i$, $i = 0, \ldots, N$

Bond vectors: $\boldsymbol{R}_i = \boldsymbol{r}_i - \boldsymbol{r}_{i-1}$

Bond potential

$$U_l = \frac{\kappa_l}{2} \sum_{i=1}^{N} (|\boldsymbol{R}_i| - l)^2 \qquad (302)$$

Remove translational degrees of freedom: $\boldsymbol{r}_0 = 0$, $\boldsymbol{p}_0 = 0$

The partition function (15) of this model reads ($H = E_{kin} + U_l$)

$$Z_{tot} = \int \exp\left(-\beta H\right) d^{3N}r\, d^{3N}p = Z_{kin} \int \exp\left(-\beta U\right) d^{3N}r,$$

or

$$Z = \int \exp\left(-\frac{\beta \kappa_l}{2} \sum_{i=1}^{N} (|\boldsymbol{R}_i| - l)^2\right) d^{3N}R.$$

Expanding Z by $(2\pi/(\beta\kappa_l))^{N/2}$ yields with $\hat{\sigma}^2 = 1/(\beta\kappa_l)$

$$Z = \left(\frac{2\pi}{\beta\kappa_l}\right)^{N/2} \int \prod_{i=1}^{N} \left[\left(\frac{1}{2\pi\hat{\sigma}^2}\right)^{1/2} \exp\left(-\frac{1}{2\hat{\sigma}^2} (|\boldsymbol{R}_i| - l)^2\right)\right] d^{3N}R.$$

Using the representation of a δ-function

$$\delta(x) = \lim_{\hat{\sigma} \to \infty} \sqrt{\frac{1}{2\pi\hat{\sigma}^2}} \exp\left(-\frac{x^2}{2\hat{\sigma}^2}\right)$$

yields in the limit $\kappa_l \to \infty$

$$Z = \int \prod_{i=1}^{N} \delta(|\boldsymbol{R}_i| - l) d^{3N}R. \qquad (303)$$

Note, constant factors have been neglected.

This is the partition function of a random walk of step length l. In the simplest case, a polymer can be considered a random walk. Now, we formally consider a chain of segments of length l. However, this segments are flexible segments and not rigid rods. The partition function of a chain of rigid rods is very different. The partition function (303) is very often used to describe flexible polymers.

For a random walk, successive steps are independent. Of course, this also applies for the considered polymer, as can easily be shown. Hence, $\langle \boldsymbol{R}_i \boldsymbol{R}_j \rangle = l^2 \delta_{ij}$. With this property, certain averages can easily be calculated, e.g., the

- mean square end-to-end distance

$$
r_e^2 = \left\langle (\boldsymbol{r}_N - \boldsymbol{r}_0)^2 \right\rangle = N l^2, \tag{304}
$$

- radius of gyration

$$
r_g^2 = \frac{1}{2(N+1)^2} \sum_{i=0}^{N} \sum_{j=0}^{N} \left\langle (\boldsymbol{r}_i - \boldsymbol{r}_j)^2 \right\rangle = l^2 \frac{N(N+2)}{6(N+1)}, \tag{305}
$$

which leads to $r_g^2 = r_e^2/6$ in the limit $N \to \infty$ (self-similarity of random walk).

Various other quantities can only be obtained with a major analytical effort or by numerical methods, with the corresponding limitation of the number of polymer segments.

10.1.2 Gaussian polymer

The generic aspects of a polymer can be described and captured by a Gaussian polymer. Typically, this model yields the correct qualitative properties of flexible polymers, often it is even quantitatively correct. There are various ways to derive the Gaussian polymer model. Here, the maximum entropy principle is exploited.

The constraints

$$
\left\langle \boldsymbol{R}_i^2 \right\rangle = l^2 \ , \tag{306}
$$

yield the partition function

$$
Z = \int \exp\left(-\sum_{i=1}^{N} \lambda_i \boldsymbol{R}_i^2 \right) d^{3N} R = \prod_{i=1}^{N} \int \exp\left(-\lambda_i \boldsymbol{R}_i^2 \right) d^3 R = \prod_{i=1}^{N} \left(\frac{\pi}{\lambda_i} \right)^{3/2}. \tag{307}
$$

The independent Gaussian integrals can evidently easily be calculated. The λ_i follow from the equation [cf. Eq. (16)]

$$
\frac{\partial \ln Z}{\partial \lambda_i} = -l^2, \qquad \Rightarrow \lambda_i = \frac{3}{2l^2}.
$$

Hence,

$$\Psi(\{\boldsymbol{r}\}) = \frac{1}{Z} \exp\left(-\frac{3}{2l^2}\sum_{i=1}^{N}\boldsymbol{R}_i^2\right), \tag{308}$$

$$Z = \int \exp\left(-\frac{3}{2l^2}\sum_{i=1}^{N}\boldsymbol{R}_i^2\right) d^{3N}R. \tag{309}$$

The model yields the same mean square end-to-end distance and radius of gyration as the polymer model of Sec. 10.1.1, i.e., Eqs. (304), (305). In addition, the end-to-end vector distribution function can easily be calculated, which reads

$$\Psi(\boldsymbol{r}_N) = \int \Psi(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N) d^{3N-1}r = \left\langle \delta\left(\boldsymbol{r}_N - \sum_{i=1}^{N}\boldsymbol{R}_i\right)\right\rangle$$

$$= \frac{1}{Z}\int \exp\left(-\frac{3}{2l^2}\sum_{i=1}^{N}\boldsymbol{R}_i^2\right)\delta\left(\boldsymbol{r}_N - \sum_{i=1}^{N}\boldsymbol{R}_i\right)d^{3N}R$$

$$= \left(\frac{3}{2\pi Nl^2}\right)^{3/2}\exp\left(-\frac{3}{2Nl^2}r_N^2\right). \tag{310}$$

The end-to-end vector distribution function is again Gaussian, which reflects the self-similarity of that distribution function.

10.1.3 Continuous Polymer

For various calculations, a continuous polymer model is advantageous. Instead of sums, integrals appear, which can often be evaluated more easily. However, there are also drawbacks, as will be shown below. From a physical point of view, it does not matter whether a continuous or a discrete model is used. Because of the adopted abstraction of a real polymer, the chosen description applies on larger length scale only. For the above models only properties are described on length scales larger than the segment length l.

The continuum transition: $N \to \infty$, $l \to 0$, such that $L = Nl = const.$, where L is the length of the polymer, yields

$$Z = \int \exp\left(-\sum_{i=1}^{N}\lambda_i\boldsymbol{R}_i^2\right)d^{3N}r = \int \exp\left(-\sum_{i=1}^{N}\lambda_i\frac{\boldsymbol{R}_i^2}{l^2}l^2\right)d^{3N}r$$

$$\stackrel{l\to 0, N\to\infty}{\longrightarrow} \int \exp\left(-\int_0^L \lambda(s)l\left(\frac{\partial\boldsymbol{r}}{\partial s}\right)^2 ds\right)\mathcal{D}^3r,$$

i.e., a functional integral (path integral) is obtained. However, the limit of $\lambda(s)l = 3/(2l) \to \infty$ for $l \to 0$ and the partition function approaches 0 ($\lim_{l\to 0} Z = 0$). The polymer collapses into a point in this case. The reason is that the distribution function (308) corresponds to a Wiener process (cf. Sec. 6.2), which implies that the derivative of the 'trajectory', i.e., the polymer contour, does not exist! A meaningful continuum transition can only be performed for a semiflexible polymer, as shown in the next section.

Here, a continuum description can only be adopted on length scales $s \gg l$. Hence, the length l is assumed to be small, but finite and the distribution function reads

$$Z = \int \exp\left(-\frac{3}{2l} \int_0^L \left(\frac{\partial r}{\partial s}\right)^2 ds\right) \mathcal{D}^3 r. \tag{311}$$

l is sometimes denoted as Kuhn length l_K. As will be shown, it is related to the polymer persistence length l_p via $l_K = l = 2l_p$.

10.2 Semiflexible Polymer

Most biological polymers, e.g., DNA, actin filaments, or viruses, are rather semiflexible than flexibel. Semiflexible means that there are correlations between successive polymer segments.
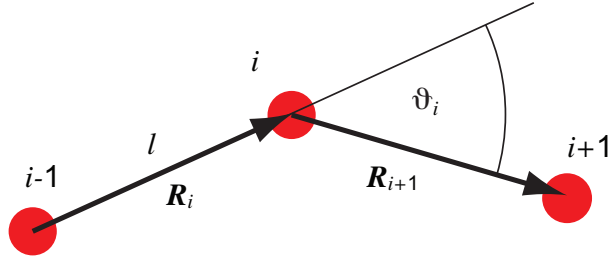
To account for the correlations, the constraints

$$\langle \boldsymbol{R}_i \boldsymbol{R}_{i+1} \rangle = l^2 t, \qquad i = 1, \dots, N-1 \tag{312}$$

are introduced for the orientation of successive bonds. The parameter t is a measure for the correlations. For rather rigid bonds with $R_i = |\boldsymbol{R}_i| = l$, the correlation function is $\langle \boldsymbol{R}_i \boldsymbol{R}_{i+1} \rangle = \langle R_i R_{i+1} \cos \vartheta_i \rangle = l^2 t$, i.e., $t = \langle \cos \vartheta_i \rangle$. The flexible polymer of the previous section follows for $t = 0$.

The constraints (312) can be combined with any bond potential or constraint.

10.2.1 Kratky-Porod Wormlike Chain

Using the bond potential (302) of Sec. 10.1.1, the maximum entropy principle yields in the limit $\kappa_l \to \infty$

$$Z = \int \exp\left(\sum_{j=1}^{N-1} \mu_i \boldsymbol{R}_i \boldsymbol{R}_{i+1}\right) \prod_{i=1}^{N} \delta(|\boldsymbol{R}_i| - l) d^{3N} r,$$

with the Lagrangian multipliers μ_i for the constraints (312). Introducing spherical coordinates, the partition function reads

$$Z = \int \exp\left(\sum_{j=1}^{N-1} \mu_i R_i R_{i+1} \cos \vartheta_i\right) \prod_{i=1}^{N} \delta(R_i - l) \prod_{j=1}^{N} \sin \vartheta_j R_j^2 dR_j d\varphi_j d\vartheta_j$$

$$= \left(4\pi l^2\right)^N \prod_{i=1}^{N-1} \frac{\sinh \mu_i l^2}{\mu_i l^2}.$$

With the condition $\partial \ln Z / \partial \mu_i = l^2 t$ follows

$$\coth \mu_i l^2 - \frac{1}{\mu_i l^2} = \mathcal{L}(\mu_i l^2) = t. \tag{313}$$

The Lagrangian multipliers are independent of i und are given by $\mu l^2 = \mathcal{L}^{-1}(t)$, where $\mathcal{L}(x) = \coth x - 1/x$ is the Langevin function.

There are only of few quantities, which can be obtained analytical for this model. One is the mean square end-to-end distance:

$$\langle \boldsymbol{r}_N^2 \rangle = \left\langle \sum_{i=1}^N \boldsymbol{R}_i^2 \right\rangle + 2 \left\langle \sum_{j=1}^N \sum_{i=1}^{j-1} \boldsymbol{R}_i \boldsymbol{R}_j \right\rangle = Nl^2 + 2l^2 \sum_{j=1}^N \sum_{i=1}^{j-1} t^{j-i},$$

or,

$$\langle \boldsymbol{r}_N^2 \rangle = Nl^2 \left(\frac{1+t}{1-t} + \frac{2t}{N} \frac{t^N - 1}{(t-1)^2} \right) \tag{314}$$

$$\langle \boldsymbol{r}_G^2 \rangle = \frac{Nl^2}{N+1} \left(\frac{(N+2)(1+t)}{6(1-t)} - \frac{t}{(1-t)^2} + \frac{2t^2}{(N+1)(1-t)^3} + \frac{2t^3(t^N-1)}{N(N+1)(t-1)^2} \right). \tag{315}$$

Continuum

To derive the continuum representation of the Kratky-Porod model, the identity $2\boldsymbol{R}_i \boldsymbol{R}_{i+1} = 2l^2 - (\boldsymbol{R}_{i+1} - \boldsymbol{R}_i)^2$ is considered. With the constraints (312) follows

$$\left\langle (\boldsymbol{R}_{i+1} - \boldsymbol{R}_i)^2 \right\rangle = 2l^2(1-t). \tag{316}$$

Taylor expansion in the vicinity of $\boldsymbol{r}_i$ yields up to second order in l

$$\boldsymbol{R}_{i+1} - \boldsymbol{R}_i = \boldsymbol{r}_{i+1} + \boldsymbol{r}_{i-1} - 2\boldsymbol{r}_i = \boldsymbol{r}_i + l\frac{\partial \boldsymbol{r}_i}{\partial s} + \frac{l^2}{2}\frac{\partial^2 \boldsymbol{r}_i}{\partial s^2} + \boldsymbol{r}_i - l\frac{\partial \boldsymbol{r}_i}{\partial s} + \frac{l^2}{2}\frac{\partial^2 \boldsymbol{r}_i}{\partial s^2} - 2\boldsymbol{r}_i = l^2\frac{\partial^2 \boldsymbol{r}_i}{\partial s^2}.$$

Hence, Eq. (316) yields

$$l^2 \left\langle \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2} \right)^2 \right\rangle = 2(1-t).$$

Limiting process: $l \to 0$, $t \to 1$ such that $p = \lim_{t \to 1, l \to 0} (1-t)/(2l)$ is finite. Hence,

$$\lim_{t \to 1, l \to 0, N \to \infty} l \left\langle \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2} \right)^2 \right\rangle = 4p, \tag{317}$$

where $l_p = 1/(2p)$ is denoted as persistence length. With the same replacement, the partition function turns into

$$Z = \int \exp \left(\sum_{j=1}^{N-1} \mu_i \boldsymbol{R}_i \boldsymbol{R}_{i+1} \right) \prod_{i=1}^N \delta(|\boldsymbol{R}_i| - l) d^{3N} r$$

$$\to \int \exp \left(2\mu l L - \frac{\mu l^3}{2} \int_0^L \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2} \right)^2 ds \right) \prod_s^\infty \delta(|\boldsymbol{u}| - 1) \mathcal{D}^3 r.$$

The limit is performed such that $\epsilon = \lim_{l\to 0} \mu l^3$ is finite. The equation (313) for the Lagrangian multiplier μ yields then ($\coth \mu l^2 = \coth \epsilon/l \to 1$ for $l \to 0$)

$$\epsilon = \frac{l}{1-t} \xrightarrow{l\to 0, t\to 1} \frac{1}{2p} = l_p. \tag{318}$$

Thus,

$$\boxed{Z = \int \exp\left(-\frac{\epsilon}{2}\int_0^L \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2}\right)^2 ds\right) \mathcal{D}^3 r}, \tag{319}$$

Kratky-Porod model

with the constraint $\boldsymbol{u}(s)^2 = (\partial \boldsymbol{r}(s)/\partial s)^2 = 1 \;\forall s$ and $\epsilon = l_p = 1/(2p)$.

Averages

$$\langle \boldsymbol{r}_L^2 \rangle = \frac{L}{p} - \frac{1}{2p^2}\left(1 - e^{-2pL}\right), \tag{320}$$

$$\langle \boldsymbol{r}_g^2 \rangle = \frac{L}{6p} - \frac{1}{4p^2} + \frac{1}{4p^3 L} - \frac{1}{8p^4 L^2}\left(1 - e^{-2pL}\right). \tag{321}$$

10.2.2 Gaussian Semiflexible Chain

For an analytical treatment, a Gaussian model is more suitable than the Kratky-Porod model. The constraints for auch a model are

$$\langle \boldsymbol{R}_i^2 \rangle = l^2 \,, \qquad i = 1, \ldots, N, \tag{322}$$
$$\langle \boldsymbol{R}_i \boldsymbol{R}_{i+1} \rangle = l^2 t \,, \qquad i = 1, \ldots, N-1. \tag{323}$$

The partition reads ($\boldsymbol{r}_0 = 0$)

$$Z = \int \exp\left(-\sum_{i=1}^{N} \lambda_i \boldsymbol{R}_i^2 + \sum_{i=1}^{N-1} \mu_i \boldsymbol{R}_i \boldsymbol{R}_{i+1}\right) d^{3N} r. \tag{324}$$

The term in the exponent is a quadratic form, hence, the integral is easily calculated and gives

$$Z = \pi^{3N/2} |\boldsymbol{A}|^{-3/2}.$$

$|\boldsymbol{A}|$ is the determinant of the matrix

$$\boldsymbol{A} = \begin{pmatrix} \lambda_1 & -\frac{\mu_1}{2} & 0 & \ldots & 0 \\ -\frac{\mu_1}{2} & \lambda_2 & -\frac{\mu_2}{2} & \ldots & 0 \\ 0 & \ddots & \ddots & \ddots & -\frac{\mu_{N-1}}{2} \\ 0 & \ldots & 0 & -\frac{\mu_{N-1}}{2} & \lambda_N \end{pmatrix}.$$

Unfortunately, no general expression can be given for $|\mathbf{A}|$ with arbitrary λ_i and μ_i. However, a solution can be derived for the constraints

$$\sum_{i=2}^{N-2} \langle \boldsymbol{R}_i^2 \rangle = (N-1)l^2, \tag{325}$$

$$\langle \boldsymbol{R}_1^2 \rangle = \langle \boldsymbol{R}_N^2 \rangle = l^2, \tag{326}$$

$$\sum_{i=1}^{N-1} \langle \boldsymbol{R}_i \boldsymbol{R}_{i+1} \rangle = (N-1)l^2 t. \tag{327}$$

Then, the distribution and partition function read

$$\Psi(\{\boldsymbol{r}\}) = \frac{1}{Z} \exp \left(-\lambda \sum_{i=2}^{N-1} \boldsymbol{R}_i^2 - \lambda_1 \boldsymbol{R}_1^2 - \lambda_N \boldsymbol{R}_N^2 + \mu \sum_{i=1}^{N-1} \boldsymbol{R}_i \boldsymbol{R}_{i+1} \right), \tag{328}$$

$$Z = \int \exp \left(-\lambda \sum_{i=2}^{N-1} \boldsymbol{R}_i^2 - \lambda_1 \boldsymbol{R}_1^2 - \lambda_N \boldsymbol{R}_N^2 + \mu \sum_{i=1}^{N-1} \boldsymbol{R}_i \boldsymbol{R}_{i+1} \right) d^{3N} r = \pi^{3N/2} |\mathbf{A}_0|^{-3/2}, \tag{329}$$

with

$$|\mathbf{A}_0| = \left(\frac{\mu}{2} \right)^N \left(4 \frac{\lambda_1^2}{\mu^2} \frac{\sinh(N-1)\theta}{\sinh \theta} - 4 \frac{\lambda_1}{\mu} \frac{\sinh(N-2)\theta}{\sinh \theta} + \frac{\sinh(N-3)\theta}{\sinh \theta} \right),$$

where, $\cosh \theta = \lambda/\mu$. For symmetry reasons $\lambda_1 = \lambda_N$. The solution of the equations for the Lagrangian multipliers is given by

$$\lambda = \frac{3}{2l^2} \frac{1+t^2}{1-t^2}, \qquad \lambda_1 = \frac{3}{2l^2} \frac{1}{1-t^2}, \qquad \mu = \frac{3}{l^2} \frac{t}{1-t^2}. \tag{330}$$

The multipliers are evidently independent of the polymer length. Hence, we found a solution of the original problem with the matrix $\mathbf{A}$. This is confirmed by the distribution function of bond vectors

$$\Psi(\boldsymbol{R}_i) = \left(\frac{3}{2\pi l^2} \right)^{3/2} \exp \left(-\frac{3}{2l^2} \boldsymbol{R}_i^2 \right),$$

which follows from Eq. (328).

The partition function itself is given by

$$Z = \left(\frac{2\pi l^2}{3} \right)^{3N/2} \left(1 - t^2 \right)^{3(N-1)/2}. \tag{331}$$

Calculation of the mean square end-to-end distance and the radius of gyration yields exactly the same expressions as the Kratky-Porod model Eqs. (314) and (315).

Continuum

In the continuum limit, the constraints (325) – (327) are given by

$$\left\langle \int_0^L \left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2 ds \right\rangle = L, \tag{332}$$

$$\left\langle \left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2_{s=0,L} \right\rangle = 1, \tag{333}$$

$$\lim_{l \to 0} l \left\langle \int_0^L \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2}\right)^2 ds \right\rangle = 4pL. \tag{334}$$

The partition function reads

$$\boxed{Z = \int \exp\left(-\nu \int_0^L \left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2 ds - \nu_0 \left[\left(\frac{\partial \boldsymbol{r}(0)}{\partial s}\right)^2 + \left(\frac{\partial \boldsymbol{r}(L)}{\partial s}\right)^2\right] - \frac{\epsilon}{2} \int_0^L \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2}\right)^2 ds\right) \mathcal{D}^3 x,}$$
$$\tag{335}$$

with the Lagrangian multipliers

$$\nu = \lim_{l,t,N \to 0,1,\infty} (\lambda - \mu)l = \frac{3p}{2}, \tag{336}$$

$$\nu_0 = \lim_{l,t,N \to 0,1,\infty} (\lambda_1 - \frac{\mu}{2})l^2 = \frac{3}{4}, \tag{337}$$

$$\epsilon = \lim_{l,t,N \to 0,1,\infty} \mu l^3 = \frac{3}{4p}, \tag{338}$$

such that $L = \lim_{l,N \to 0,\infty} lN$ and $l_p = 1/(2p) = \lim_{l,t \to 0,1} l/(1 - t)$. The mean square end-to-end distance and the radius of gyration are given by Eqs. (320) and (321).

In addition, the correlation function of the tangent vectors $\boldsymbol{u}(s) = \partial \boldsymbol{r}(s)/\partial s$ can be calculated

$$\langle \boldsymbol{u}(s)\boldsymbol{u}(s')\rangle = e^{-2p|s-s'|}, \tag{339}$$

which decays on the length scale $l_p = 1/(2p)$.

More importantly, at equilibrium, the distribution function for any distance $\Delta \boldsymbol{r} = \boldsymbol{r}(s) - \boldsymbol{r}(s')$ can be determined. Explicitly, the distribution reads

$$\Psi(\Delta \boldsymbol{r}) = \left(\frac{3}{2\pi\sigma^2(s,s')}\right)^{3/2} \exp\left(-\frac{3\Delta \boldsymbol{r}^2}{2\sigma^2}\right), \tag{340}$$

where

$$\sigma^2(s,s') = \left\langle (\boldsymbol{r}(s) - \boldsymbol{r}(s'))^2 \right\rangle = \frac{|s-s'|}{p} - \frac{1}{2p^2}\left[1 - \exp(-2p|s-s'|)\right]. \tag{341}$$

As follows from Eq. (332), the difference between the Gaussian semiflexible chain and the Kratky-Porod model is the constraint on the tangent vector. For the Gaussian polymer the average $\langle \boldsymbol{u}(s)^2 \rangle = 1$ is used, whereas the Kratky-Porod model requires $\boldsymbol{u}(s)^2 = 1$, i.e., in the Gaussian model the constraint is relaxed and fluctuations along the chain contour appear.

11 Stretching Polymers

There are various ways—corresponding to different ensemble—to stretch a polymer chain [5,7]. In an isometric ensemble, the end-to-end vector is fixed and the force is determined as function of that distance. In an isotensional ensemble, a force is applied at the free chain end and the mean extension of the polymer is determined. In the following, only the isotensional ensemble is considered.

Within the maximum entropy approach, the constraint ($\boldsymbol{r}_0 = 0$)

$$\langle \boldsymbol{r}_N \rangle = \boldsymbol{a} \tag{342}$$

is taken into account additionally for the (free) end point of the polymer.

11.1 Polymer of Finite Length Bonds (Kratky-Porod)

With the Lagrangian multiplier $\boldsymbol{\eta}$ accounting for the constraint (342), the partition function (303) turns into

$$Z = \int \exp\left(-\boldsymbol{\eta}\boldsymbol{r}_N\right) \prod_{i=1}^{N} \delta(|\boldsymbol{R}_i| - l) \; d^{3N}R \tag{343}$$

$$= \prod_{i=1}^{N} \int \exp\left(-\eta l \cos\vartheta_i\right) 2\pi l^2 \sin\vartheta_i d\vartheta_i = \left(4\pi l^2\right)^N \left(\frac{\sinh l\eta}{l\eta}\right)^N. \tag{344}$$

$\boldsymbol{\eta}$ follows from $\partial \ln Z/\partial \boldsymbol{\eta} = -\boldsymbol{a}$, which yields

$$\boldsymbol{a} = \frac{N}{\eta^2}\boldsymbol{\eta} - Nl \coth(\eta l)\frac{\boldsymbol{\eta}}{\eta}, \tag{345}$$

or, since $\boldsymbol{a} \parallel \boldsymbol{\eta}$,

$$\boldsymbol{F} = -k_B T \boldsymbol{\eta} = \frac{k_B T}{l}\mathcal{L}^{-1}\left(\frac{a}{L}\right)\frac{\boldsymbol{a}}{a}. \tag{346}$$

$\mathcal{L}$ is the Langevin function. This relation has been derived more than 50 years ago by Kuhn and Grün [8].

11.2 Gaussian Polymer

With the additional constraint (342), the partition function of the Gaussian flexible polymer [cf. Eq. (307)] is given by

$$Z = \int \exp\left(-\sum_{i=1}^{N} \lambda_i \boldsymbol{R}_i^2 - \boldsymbol{\eta}\sum_{i=1}^{N} \boldsymbol{R}_i\right) d^{3N}R = \prod_{i=1}^{N} \int \exp\left(-\lambda_i \boldsymbol{R}_i^2 - \boldsymbol{\eta}\boldsymbol{R}_i\right) d^3R$$

$$= \prod_{i=1}^{N} \left(\frac{\pi}{\lambda_i}\right)^{3/2} \exp\left(\frac{\boldsymbol{\eta}^2}{4\lambda_i}\right). \tag{347}$$

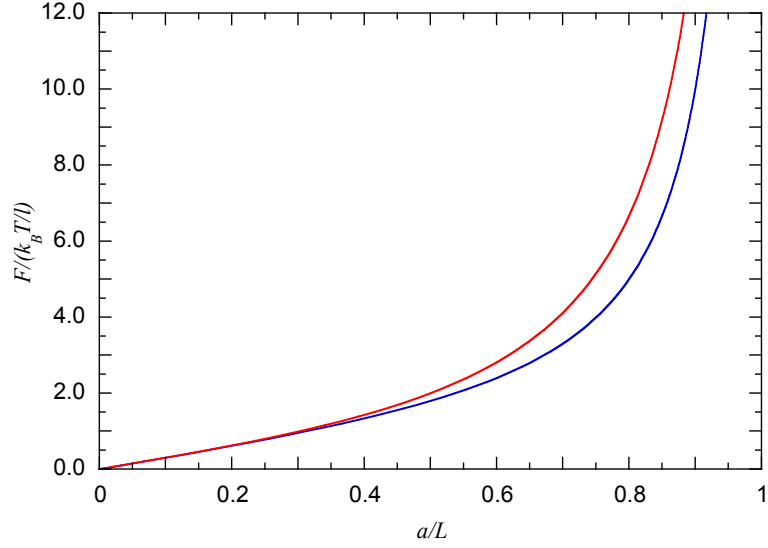Figure 1: Force extension relation for a polymer of "rigid" segments (blue) and Gaussian segments (red).

Lagrangian multipliers

$$\frac{\partial \ln Z}{\partial \lambda_i} = -\frac{3}{2\lambda_i} - \frac{\boldsymbol{\eta}}{4\lambda_i^2} = -l^2,$$

$$\frac{\partial \ln Z}{\partial \boldsymbol{\eta}} = \frac{1}{2}\boldsymbol{\eta} \sum_{i=1}^{N} \frac{1}{\lambda_i} = -\boldsymbol{a}, \qquad \Rightarrow \boldsymbol{a} \parallel \boldsymbol{\eta}.$$

For $\lambda_i = \lambda_j = \lambda$, $\forall i, j$, follows

$$\eta = -\frac{2a\lambda}{N},$$

$$\lambda = \frac{3}{2l^2 \left[1 - (a/L)^2\right]},$$

which yields the force-extension relation

$$\boldsymbol{F} = -k_B T \boldsymbol{\eta} = \frac{3k_B T}{l \left[1 - (a/L)^2\right]} \frac{\boldsymbol{a}}{L}. \tag{348}$$

As shown in Fig. 1, the two force-extension relations are identical for $a/L \ll 1$ and deviate from each other at large extensions. In the limit $a/L \to 1$, both functions exhibit the asymptotic dependence $F \sim 1/(1 - a/L)$; only the Gaussian function is by the factor 1.5 larger. The reason is the different number of relevant degrees of freedom. The fluctuations of the Gaussian model along the chain contour corresponds to 3 degrees of freedom per bond, whereas the for the potential (302), the degree of freedom along the polymer contour is suppressed, i.e., 2 degrees of freedom are left.

11.3 Gaussian Semiflexible Polymer

The partition function of a continuous Gaussian semiflexible polymer with the constraints

$$\left\langle \left(\frac{\partial \boldsymbol{r}}{\partial s} \right)^2 \right\rangle = 1, \tag{349}$$

$$\lim_{l,t,N \to 0,1,\infty} l \left\langle \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2} \right)^2 \right\rangle = 4p,$$

$$\langle \boldsymbol{r}(L) \rangle = \boldsymbol{a},$$

is given by

$$Z = \int \exp \left(-\int_0^L \nu(s) \left(\frac{\partial \boldsymbol{r}}{\partial s} \right)^2 ds - \frac{\epsilon}{2} \int_0^L \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2} \right)^2 ds - \boldsymbol{\eta} \int_0^L \frac{\partial \boldsymbol{r}}{\partial s} ds \right) \mathcal{D}^3 x.$$

Here, ν is no longer constant along the polymer contour, which makes it impossible to calculate the partition function in closed form. We will assume that $\nu(s) = \nu = const.$ is suitable approximation for most of the relevant cases and that useful expectation values are obtained, which only deviate slightly from the exact result with $\nu(s)$. As it turns out, the force-extension relation of the analytical model agrees very well with that of a discrete model, which accounts for every constraint individually in the appropriate continuum limit, for $pL \gtrsim 5$ [9]. Hence, a contour-independent parameter ν is an excellent approximation to capture the overall polymer response. However, the multiplier ϵ and ν_0 can be determined exactly for any external potential and are given by the equilibrium values Eqs. (337) and (338). The proof is outlined in Ref. [7]. With $\nu(s) = \nu$, the partition function becomes

$$Z = \int \exp \left(-\int_0^L \nu(s) \left(\frac{\partial \boldsymbol{r}}{\partial s} \right)^2 ds - \frac{\epsilon}{2} \int_0^L \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2} \right)^2 ds - \boldsymbol{\eta} \int_0^L \frac{\partial \boldsymbol{r}}{\partial s} ds \right.$$

$$\left. - \nu_0 \left[\left(\frac{\partial \boldsymbol{r}(0)}{\partial s} \right)^2 + \left(\frac{\partial \boldsymbol{r}(L)}{\partial s} \right)^2 \right] \right) \mathcal{D}^3 x.$$

The path integral can be evaluated by exploiting the analogy with the path integral of a harmonic oscillator in quantum mechanics, using the eigenfunction expansion for the operator $\mathcal{O} = \nu - (\epsilon/2)\partial^2/\partial s^2$ with the appropriate boundary conditions, or by a continuum transition of the discrete model [7]. The result is

$$Z = \lim_{l,N \to 0,\infty} |\mathbf{A}|^{3/2} \exp \left(\frac{1}{6} \boldsymbol{\eta}^2 \boldsymbol{R}^2 \right),$$

with

$$|\boldsymbol{A}| = \left(\frac{\pi \mu}{2} \right)^N l \sqrt{\frac{\epsilon}{2\nu}} \left[\left(\frac{2\nu_0^2}{\epsilon^2} + \frac{\nu}{\epsilon} \right) \sinh L \sqrt{\frac{2\nu}{\epsilon}} + \frac{2\nu_0}{\epsilon} \sqrt{\frac{2\nu}{\epsilon}} \cosh L \sqrt{\frac{2\nu}{\epsilon}} \right],$$

$$\boldsymbol{R}^2 = \frac{3}{2\nu} \left(L - \frac{2\nu_0}{\nu} \left[1 + \frac{2\nu_0}{\nu} \sqrt{\frac{\nu}{2\epsilon}} \coth L \sqrt{\frac{\nu}{2\epsilon}} \right]^{-1} \right).$$
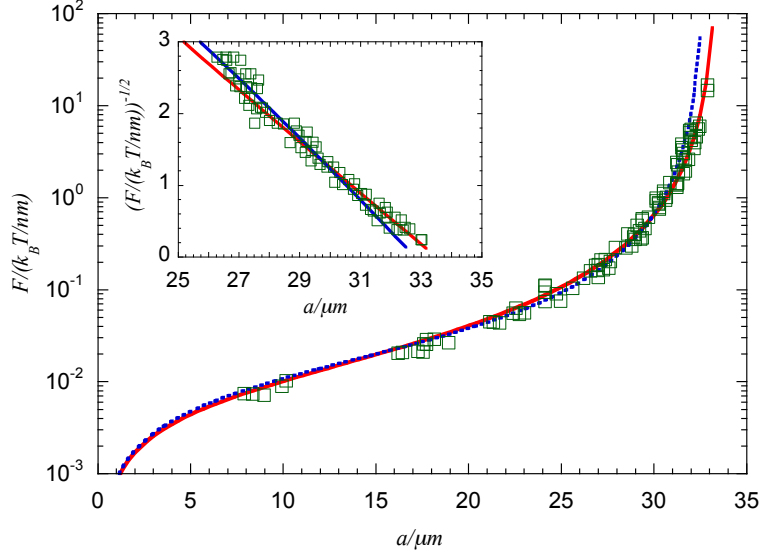
Figure 2: Fit of the force-extension curve of the Gaussian semiflexible chain model (red) to experimental data of Smith et al. [10] (squares). The fit parameters obtained from a logarithmic fit are $l_p = 53.5$ nm and $L = 33.5$ μm. The blue line is calculated using the interpolation formula derived by Marko and Siggia [11] for the Kratky-Porod model with the parameters $l_p = 53$ nm and $L = 32.8$ μm, respectively.

Calculation of the Lagrangian multiplier:

- $\boldsymbol{\eta}$: $\partial \ln Z / \partial \boldsymbol{\eta} = -\boldsymbol{a} \Rightarrow \boldsymbol{\eta} = -3\boldsymbol{a}/\boldsymbol{R}^2$ or $\boldsymbol{F} = -k_B T \boldsymbol{\eta} = 3k_B T \boldsymbol{a}/\boldsymbol{R}^2$.

- ν: $\partial \ln Z / \partial \nu = -L$

$$\Rightarrow \quad \nu = \begin{cases} \dfrac{3}{2}p \left(1 - \dfrac{a^2}{L^2}\right)^{-2} , & pL > 1 \\[3mm] \dfrac{3}{2}\left(p + \dfrac{a^2}{L^3}\right)\left(1 - \dfrac{a^2}{L^2}\right)^{-1} , & pL \ll 1 \end{cases} ,$$

or

$$F/k_B T = \begin{cases} 2\nu\dfrac{a}{L} = \dfrac{3pa}{L}\left(1 - \dfrac{a^2}{L^2}\right)^{-2} , & pL \gg 1 \\[3mm] \dfrac{3a}{L^2}\left(1 + \dfrac{2\nu L}{3}\right) = \dfrac{3(1+pL)a}{L^2}\left(1 - \dfrac{a^2}{L^2}\right)^{-1} , & pL \ll 1 . \end{cases}$$

Force-extension relation of Kratky-Porod model

The force-extension relation of the Kratky-Porod model can be approximated by

$$F/k_B T = \frac{1}{4l_p}\left[\left(1 - \frac{a}{L}\right)^{-2} - 1 + \frac{4a}{L}\right]$$

for $pL \gg 1$. Hence, the two relations are equal for $a/L \ll 1$, where $F/k_BT \approx 3a/(2l_pL) = 3a/(l_KL)$, with the Kuhn segment length $l_K = 2l_p$. In the limit $a \to L$ follows

$$\frac{a}{L} = \begin{cases} 1 - \sqrt{\dfrac{3}{8}}\sqrt{\dfrac{k_BT}{Fl_p}} & \text{Gauss} \\ 1 - \dfrac{1}{2}\sqrt{\dfrac{k_BT}{Fl_p}} & \text{Kratky} - \text{Porod} \end{cases}.$$

In this limit, the correction terms deviate by approximately 20%.

12 Dynamics of Semiflexible Polymers

The comparison of the polymer force-extension relation with experimental results shows that only the semiflexible polymer describes stretching correctly. Since we are interested in the dynamics of biological systems, we will therefore only discuss the dynamics of semiflexible polymer models and not that of flexible models. The latter corresponds to the Rouse or Zimm model, respectively, for systems with and without hydrodynamic interactions of classical polymer theory (cf. book of Doi and Edwards) and follows from the general result in the limit of flexible polymers ($pL \gg 1$).

The question, which model to use to investigate the dynamics of biopolymers is simply answered, since there is so far no analytical solution for the Kratky-Porod model due to the strict inextensibility constraint. Only in the limit of a nearly rigid rod or a very stiff polymer, an analytical solution of the Kratky-Porod model has been determined. Here, the dynamics along the polymer contour is suppressed and only fluctuations transverse to the contour are considered [12–14]. The fluctuations themselves are considered to be Gaussian, i.e., they are described in the same spirit as for the Gaussian semiflexible polymer [9].

Only the continuous polymer will be considered. To derive an equation of motion, the exponent of the partition function (335) is identified with the potential energy of the polymer. The Lagrangian is then given by

$$
\mathcal{L} = \int_{-L/2}^{L/2} \frac{1}{2}\rho \left(\frac{\partial \boldsymbol{r}}{\partial t}\right)^2 ds - \nu k_B T \int_{-L/2}^{L/2} \left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2 ds - \frac{\epsilon k_B T}{2} \int_{-L/2}^{L/2} \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2}\right)^2 ds \qquad (350)
$$
$$
- \nu_0 k_B T \left[\left(\frac{\partial \boldsymbol{r}(L/2)}{\partial s}\right)^2 + \left(\frac{\partial \boldsymbol{r}(-L/2)}{\partial s}\right)^2\right].
$$

The first term is the kinetic energy with the mass density ρ. Newton's equations of motion follow via the Lagrangian equations of the second kind

$$
\frac{\partial}{\partial t} \frac{\delta \mathcal{L}}{\delta \dot{\boldsymbol{r}}(s)} - \frac{\delta \mathcal{L}}{\delta \boldsymbol{r}(s)} = 0.
$$

12.1 Free-Draining Dynamics

For simplicity, the free-draining case will be considered first, i.e., hydrodynamic interactions are neglected. Taking the force from Newton's equations of motion, the following Langevin equation is obtained for the over-damped motion

$$
\gamma \frac{\partial \boldsymbol{r}(s,t)}{\partial t} = 2\nu k_B T \frac{\partial^2 \boldsymbol{r}(s,t)}{\partial s^2} - \epsilon k_B T \frac{\partial^4 \boldsymbol{r}(s,t)}{\partial s^4} + \boldsymbol{\Gamma}(s,t), \qquad (351)
$$

with the boundary conditions

$$
2\nu \frac{\partial \boldsymbol{r}(s,t)}{\partial s} - \epsilon \frac{\partial^3 \boldsymbol{r}(s,t)}{\partial s^3} \bigg|_{s=\pm L/2} = 0, \qquad (352)
$$

$$
2\nu_0 \frac{\partial \boldsymbol{r}(s,t)}{\partial s} \pm \epsilon \frac{\partial^2 \boldsymbol{r}(s,t)}{\partial s^2} \bigg|_{s=\pm L/2} = 0, \qquad (353)
$$

and the stochastic force (white noise)

$$\langle \boldsymbol{\Gamma}(s,t) \rangle = 0, \tag{354}$$

$$\langle \Gamma_\alpha(s,t) \Gamma_{\alpha'}(s',t') \rangle = 2\gamma k_B T \delta_{\alpha\alpha'} \delta(t-t') \delta(s-s'). \tag{355}$$

γ is here the friction per length. Equation (351) is a linear partial differential equation, which is easily solved by an eigenfunction expansion.

Eigenvalue equation

$$\epsilon k_B T \frac{\partial^4}{\partial s^4} \varphi_n(s) - 2\nu k_B T \frac{\partial^2}{\partial s^2} \varphi_n(s) - \xi_n \varphi_n(s) = 0 \; ; \tag{356}$$

or

$$\mathbf{O} \varphi_n(s) = \xi_n \varphi_n(s) \tag{357}$$

with

$$\mathbf{O} = \epsilon k_B T \frac{\partial^4}{\partial s^4} - 2\nu k_B T \frac{\partial^2}{\partial s^2} \; . \tag{358}$$

Boundary conditions

$$2\nu \frac{\partial \varphi_n(s)}{\partial s} - \epsilon \frac{\partial^3 \varphi_n(s)}{\partial s^3} \bigg|_{s=\pm L/2} = 0, \qquad 2\nu_0 \frac{\partial \varphi_n(s)}{\partial s} \pm \epsilon \frac{\partial^2 \varphi_n(s)}{\partial s^2} \bigg|_{s=\pm L/2} = 0. \tag{359}$$

There are even and odd eigenfunctions, which are combinations of the 4 basis functions $\sin x$, $\cos x$, $\sinh x$, and $\cosh x$ of the 4th order differential equation, namely

$$\varphi_0 = \sqrt{\frac{1}{L}},$$

$$\varphi_n(s) = \sqrt{\frac{c_n}{L}} \left(\zeta_n' \frac{\sinh \zeta_n' s}{\cosh \zeta_n' L/2} + \zeta_n \frac{\sin \zeta_n s}{\cos \zeta_n L/2} \right), \forall \, n \text{ odd},$$

$$\varphi_n(s) = \sqrt{\frac{c_n}{L}} \left(\zeta_n' \frac{\cosh \zeta_n' s}{\sinh \zeta_n' L/2} - \zeta_n \frac{\cos \zeta_n s}{\sin \zeta_n L/2} \right), \forall \, n \text{ even} \; . \tag{360}$$

φ_0 describes the translational motion of the whole molecule. The c_ns follow from the normalization condition. The wave numbers ζ_n and ζ_n', where $\zeta_n'^2 - \zeta_n^2 = 4p^2$, are determined by the boundary conditions (359), which read now as

$$\zeta_n^3 \sin \zeta_n \frac{L}{2} \cosh \zeta_n' \frac{L}{2} - \zeta_n'^3 \cos \zeta_n \frac{L}{2} \sinh \zeta_n' \frac{L}{2} - 2p(\zeta_n^2 + \zeta_n'^2) \cos \zeta_n \frac{L}{2} \cosh \zeta_n' \frac{L}{2} = 0, \; n \text{ odd}$$

$$\zeta_n^3 \cos \zeta_n \frac{L}{2} \sinh \zeta_n' \frac{L}{2} + \zeta_n'^3 \sin \zeta_n \frac{L}{2} \cosh \zeta_n' \frac{L}{2} + 2p(\zeta_n^2 + \zeta_n'^2) \sin \zeta_n \frac{L}{2} \sinh \zeta_n' \frac{L}{2} = 0, \; n \text{ even,} \tag{361}$$

and are related to the eigenvalues via $\xi_n = k_B T \left(\epsilon \zeta_n^4 + 2\nu \zeta_n^2 \right)$. The solutions of these equations are presented in Fig. 3.

Eigenfunction expansion

The solution of Eq. (351) is then obtained by the eigenfunction expansion

$$\boldsymbol{r}(s,t) = \sum_{n=0}^{\infty} \boldsymbol{\chi}_n(t)\varphi_n(s) , \qquad \boldsymbol{\Gamma}(s,t) = \sum_{n=0}^{\infty} \boldsymbol{\Gamma}_n(t)\varphi_n(s), \qquad (362)$$

which yields the Langevin equations for the amplitudes $\boldsymbol{\chi}_n(t)$

$$\frac{d}{dt}\boldsymbol{\chi}_n = -\frac{1}{\tau_n}\boldsymbol{\chi}_n + \frac{1}{\gamma}\boldsymbol{\Gamma}_n , \; n > 0 ; \qquad \frac{d}{dt}\boldsymbol{\chi}_0 = \frac{1}{\gamma}\boldsymbol{\Gamma}_0 , \qquad (363)$$

with the relaxation times

$$\tau_n = \frac{\gamma}{\xi_n} \quad ; \quad \tau_0 = \infty . \qquad (364)$$

The solution of the Langevin equation (Ornstein-Uhlenbeck process) is ($t_0 = -\infty$)

$$\boldsymbol{\chi}_n(t) = \frac{1}{\gamma}\int_{-\infty}^t \exp\left(-\frac{t-t'}{\tau_n}\right)\boldsymbol{\Gamma}_n(t')dt' ; \qquad \boldsymbol{\chi}_0(t) = \boldsymbol{\chi}_0(0) + \frac{1}{\gamma}\int_0^t \boldsymbol{\Gamma}_0(t')dt' . \quad (365)$$

Note: $\left\langle \Gamma_n^\alpha(t)\Gamma_m^{\alpha'}(t') \right\rangle = 2\gamma\delta_{\alpha\alpha'}\delta_{nm}\delta(t-t')$. Hence,

$$\boldsymbol{r}(s,t) = \boldsymbol{\chi}_0(t)\varphi_0 + \sum_{n=1}^{\infty}\frac{1}{\gamma}\int_{-\infty}^t \exp\left(-\frac{t-t'}{\tau_n}\right)\boldsymbol{\Gamma}_n(t')dt'\varphi_n(s). \qquad (366)$$

The relaxation times are presented in Fig. 4.

For the evaluation of time correlation functions, typically the correlations of the amplitudes $\boldsymbol{\chi}_n$ are required. By Eq. (365) follows ($n, m > 0$)

$$\langle\boldsymbol{\chi}_n(t)\boldsymbol{\chi}_m(0)\rangle = \frac{1}{\gamma^2}\int_{-\infty}^t\int_{-\infty}^0 \exp\left(-\frac{t-t'}{\tau_n}\right)\exp\left(\frac{t''}{\tau_m}\right)\langle\boldsymbol{\Gamma}_n(t')\boldsymbol{\Gamma}_m(t'')\rangle\, dt'dt'' \qquad (367)$$

$$= \frac{6k_BT}{\gamma}\delta_{nm}e^{-t/\tau_n}\int_{-\infty}^0 e^{2t'/\tau_n}dt' = \frac{3k_BT}{\gamma}\tau_n\delta_{nm}e^{-t/\tau_n} = \left\langle\boldsymbol{\chi}_n^2\right\rangle\delta_{nm}e^{-t/\tau_n}.$$

Moreover, $\langle\boldsymbol{\chi}_n(t)\boldsymbol{\chi}_0(t')\rangle = 0$ for $n > 0$, and $\langle\boldsymbol{\chi}_0(t)\boldsymbol{\chi}_0(t')\rangle = \langle\boldsymbol{\chi}_0(0)^2\rangle + 6k_BTt'/\gamma$ for $t' \leq t$.

Asymptotic behavior

- Flexible polymer (Rouse chain): $pL \to \infty$

$$\zeta_n = \frac{n\pi}{L}, \;\; \xi_n = 2\nu k_BT\zeta_n^2 = \frac{3\pi^2 pk_BTn^2}{L^2}, \;\; \tau_n = \frac{\gamma L^2}{3\pi^2 k_BTpn^2}$$

$$\varphi_0 = \sqrt{\frac{1}{L}},$$

$$\varphi_n(s) = \sqrt{\frac{2}{L}}\sin\frac{n\pi s}{L} , \; \forall\, n \text{ odd,}$$

$$\varphi_n(s) = \sqrt{\frac{2}{L}}\cos\frac{n\pi s}{L} , \; \forall\, n \text{ even .} \qquad (368)$$

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Alternatively,

$$\varphi_n(s) = \sqrt{\frac{2}{L}} \cos \frac{n\pi(s - L/2)}{L} \;,\; \forall\, n > 0 \;. \tag{369}$$

- Semiflexible polymer (weakly bending rod): $pL \to 0$

$$\zeta_n = \frac{(2n-1)\pi}{2L}, \; \xi_n = \epsilon k_B T \zeta_n^4 = \frac{3\pi^4(2n-1)^4 k_B T}{64 p L^4}, \; \tau_n = \frac{64\gamma p L^4}{3\pi^4(2n-1)^4 k_B T}$$

$$\varphi_0 = \sqrt{\frac{1}{L}},$$

$$\varphi_n(s) = \sqrt{\frac{1}{L}} \left(\frac{\sinh \zeta_n s}{\sinh \zeta_n L/2} + \frac{\sin \zeta_n s}{\sin \zeta_n L/2} \right), \forall\, n \text{ odd},$$

$$\varphi_n(s) = \sqrt{\frac{1}{L}} \left(\frac{\cosh \zeta_n s}{\cosh \zeta_n L/2} + \frac{\cos \zeta_n s}{\cos \zeta_n L/2} \right), \forall\, n \text{ even} \;. \tag{370}$$

- Rod: $pL = 0 \Rightarrow \zeta_1 \to (48pL)^{1/4}/L \to 0$

$$\xi_1 = \frac{36 k_B T}{L^3}, \qquad\qquad \tau_1 = \frac{\gamma L^3}{36 k_B T}$$

$$\varphi_0 = \sqrt{\frac{1}{L}}, \qquad\qquad \varphi_1(s) = \sqrt{\frac{12}{L^3}} s.$$

12.1.1 Center-of-Mass Mean Square Displacement

Center-of-mass: $\boldsymbol{r}_{cm}(t) = \boldsymbol{r}_0(t) = \int_{-L/2}^{L/2} \boldsymbol{r}(s) ds / L = \boldsymbol{\chi}_0(t)\varphi_0$. Hence,

$$\left\langle \Delta \boldsymbol{r}_{cm}(t)^2 \right\rangle = \left\langle (\boldsymbol{r}_0(t) - \boldsymbol{r}_0(0))^2 \right\rangle = \frac{1}{L} \left\langle (\boldsymbol{\chi}_0(t) - \boldsymbol{\chi}_0(0))^2 \right\rangle$$

$$= \frac{1}{\gamma^2 L} \int_0^t \int_0^t \left\langle \boldsymbol{\Gamma}_0(t') \boldsymbol{\Gamma}_0(t'') \right\rangle dt' dt'' = \frac{6 k_B T}{\gamma L} t,$$

or $\left\langle (\boldsymbol{r}_0(t) - \boldsymbol{r}_0(0))^2 \right\rangle = 6 D_0 t$, with $D_0 = k_B T / (\gamma L)$.

12.1.2 Segmental Mean Square Displacement

With Eq. (367) follows

$$\left\langle \Delta \boldsymbol{r}(s,t)^2 \right\rangle = \left\langle [\boldsymbol{r}(s,t) - \boldsymbol{r}(s,0)]^2 \right\rangle = \left\langle \left[\sum_{n=0}^{\infty} \varphi_n \left(\boldsymbol{\chi}_n(t) - \boldsymbol{\chi}_n(0) \right) \right]^2 \right\rangle$$

$$= \left\langle \Delta \boldsymbol{r}_{cm}(t)^2 \right\rangle + \sum_{n=1}^{\infty} 2\varphi_n(s)^2 \left\langle \boldsymbol{\chi}_n^2 \right\rangle \left(1 - e^{-t/\tau_n} \right)$$

$$= \left\langle \Delta \boldsymbol{r}_{cm}(t)^2 \right\rangle + \frac{6 k_B T}{\gamma} \sum_{n=1}^{\infty} \varphi_n(s)^2 \tau_n \left(1 - e^{-t/\tau_n} \right)$$
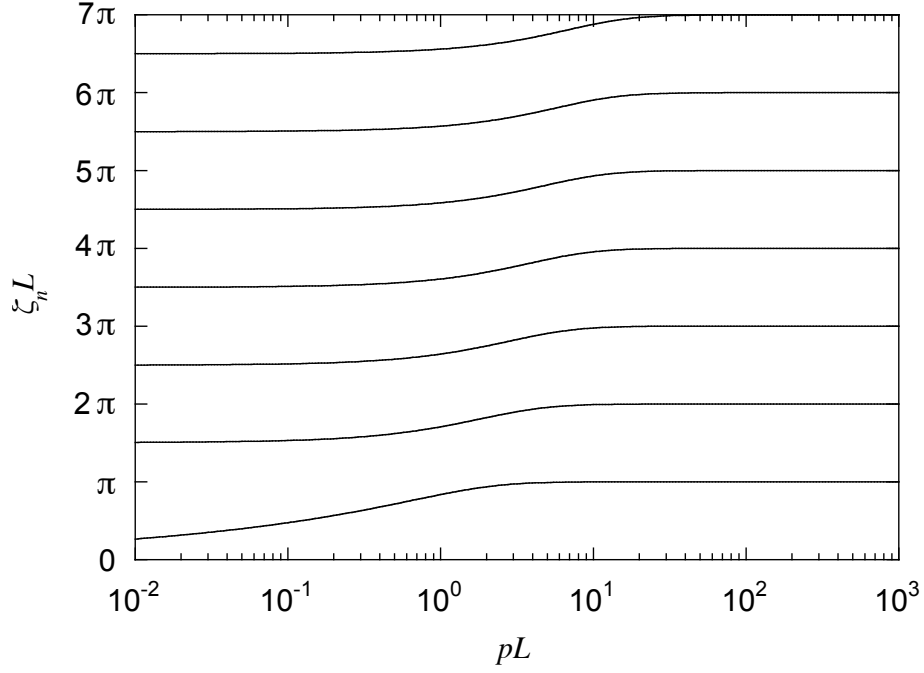
Figure 3: The first seven wave numbers ζ_n as a function of pL, numerically determined from Eqs. (361). For $pL \gg 1$, $\zeta_n L$ approaches the value $n\pi$ ($n \geq 1$) (Rouse chain), and for $pL \to 0$ $(2n-1)\pi/2$ ($n > 1$) (slightly bending chain). ζ_1 approaches zero in the rodlimit ($pL \to 0$) according to $\zeta_1 L = (48pL)^{1/4}$.

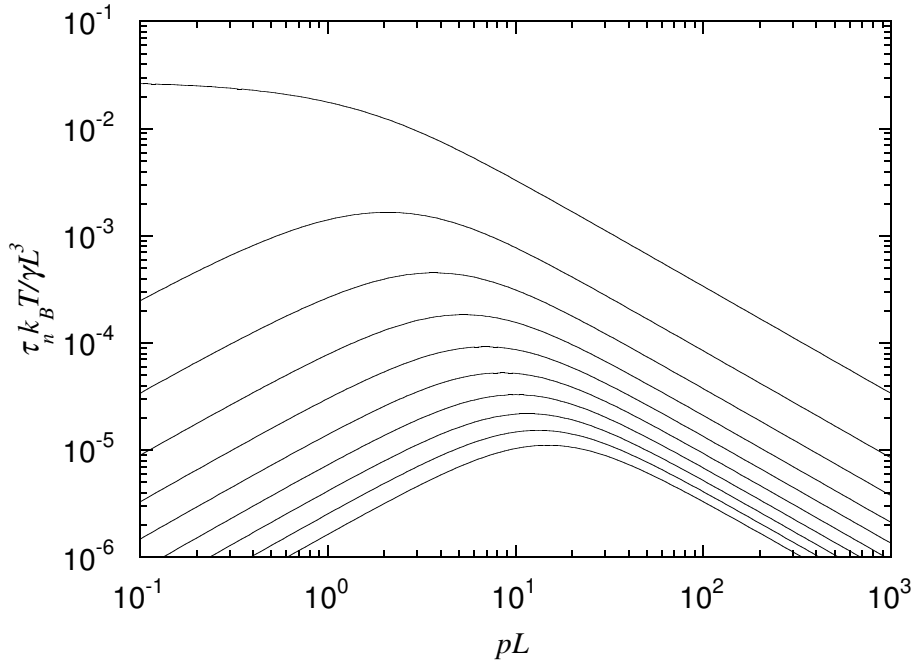Figure 4: First ten relaxation times τ_n as a function of pL. For the flexible chain $\tau_n \sim L^2/n^2$ ($n \geq 1$, $pL \to \infty$), whereas for the rodlike chain $\tau_n \sim L^4/(2n-1)^4$ ($n > 1$, $pL \to 0$) and $\tau_1 \sim L^3$.

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To arrive at a s-independent term, $\langle \Delta \boldsymbol{r}(s,t)^2 \rangle$ is averaged over s, i.e., $\langle \Delta \boldsymbol{r}(t)^2 \rangle = \int \langle \Delta \boldsymbol{r}(s,t)^2 \rangle \, ds/L$. Alternatively, a chain end or the chain center could be considered. Averaging yields ($\int_{-L/2}^{L/2} \varphi_n^2 ds = 1$)

$$\langle \Delta \boldsymbol{r}(t)^2 \rangle = \langle \Delta \boldsymbol{r}_{cm}(t)^2 \rangle + \frac{6k_BT}{\gamma L} \sum_{n=1}^{\infty} \tau_n \left(1 - e^{-t/\tau_n} \right) \tag{371}$$

For $t \gg \tau_1$, the terms $e^{-t/\tau_n} \ll 1 \; \forall n$ and the mean square displacement is dominated by the center-of-mass mean square displacement, thus, $\langle \Delta \boldsymbol{r}(t)^2 \rangle = \langle \Delta \boldsymbol{r}_{cm}(t)^2 \rangle$. In the opposite case $t \ll \tau_1$, the sum is dominated by contributions from large n values. Therefore, the mean square displacement depends on the stiffness of the polymer—probing large n corresponds to probing small length scales. Therefore, the behavior of flexible and semiflexible polymers will be considered separately.

Flexible Polymer

Here, the relaxation times are given by $\tau_n = \tau_R/n^2$, with the Rouse relaxation time $\tau_R = \gamma L^2/(3\pi^2 pk_BT)$. For $t/\tau_R \ll 1$, the difference between $x_{n+1} = (n+1)\sqrt{t/\tau_R}$ and $x_n = n\sqrt{t/\tau_R}$ is very small and the sum can be replaced by an integral over $x^2 = n^2 t/\tau_R$, i.e.,

$$\sum_{n=1}^{\infty} \frac{\tau_R}{n^2} \left[1 - e^{-tn^2/\tau_R} \right] = \sqrt{t\tau_R} \sum_{n=1}^{\infty} \frac{\tau_R}{n^2 t} \left[1 - e^{-tn^2/\tau_R} \right] \Delta n \sqrt{\frac{t}{\tau_R}}$$

$$\longrightarrow \sqrt{t\tau_R} \int_0^{\infty} \frac{1}{x^2}(1 - e^{-x^2}) dx = \sqrt{t\tau_R}\sqrt{\pi}.$$

Hence,

$$\langle \Delta \boldsymbol{r}(t)^2 \rangle = \langle \Delta \boldsymbol{r}_{cm}(t)^2 \rangle + \frac{6k_BT}{\gamma L} \sqrt{\pi t \tau_R} \stackrel{t/\tau_R \ll 1}{\longrightarrow} \frac{2L}{p\sqrt{\pi^3}} \sqrt{\frac{t}{\tau_R}}, \tag{372}$$

i.e. the segments display an anomalous (fractal) diffusion behavior.
Asymptotic limit $t \to \infty$:

$$\langle \Delta \boldsymbol{r}(t)^2 \rangle - \langle \Delta \boldsymbol{r}_{cm}(t)^2 \rangle = \frac{6k_BT}{\gamma L} \sum_{n=1}^{\infty} \tau_n = \frac{2L}{\pi^2 p} \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{L}{3p} = 2\langle r_G^2 \rangle. \tag{373}$$

Semiflexible Polymer

Similarly, $x^4 = (2n-1)^4 t/\tau_1$, with $\tau_1 = 64\gamma pL^4/(3\pi^4 k_BT)$ yields

$$\sum_{n=1}^{\infty} \frac{\tau_1}{(2n-1)^4} \left[1 - e^{-t(2n-1)^4/\tau_1} \right] \longrightarrow \frac{1}{2} \sqrt[4]{t^3\tau_1} \int_0^{\infty} \frac{1}{x^4}(1 - e^{-x^4}) dx \approx \frac{1.21}{2} \sqrt[4]{t^3\tau_1}.$$

Hence,

$$\langle \Delta \boldsymbol{r}(t)^2 \rangle \sim t^{3/4}. \tag{374}$$
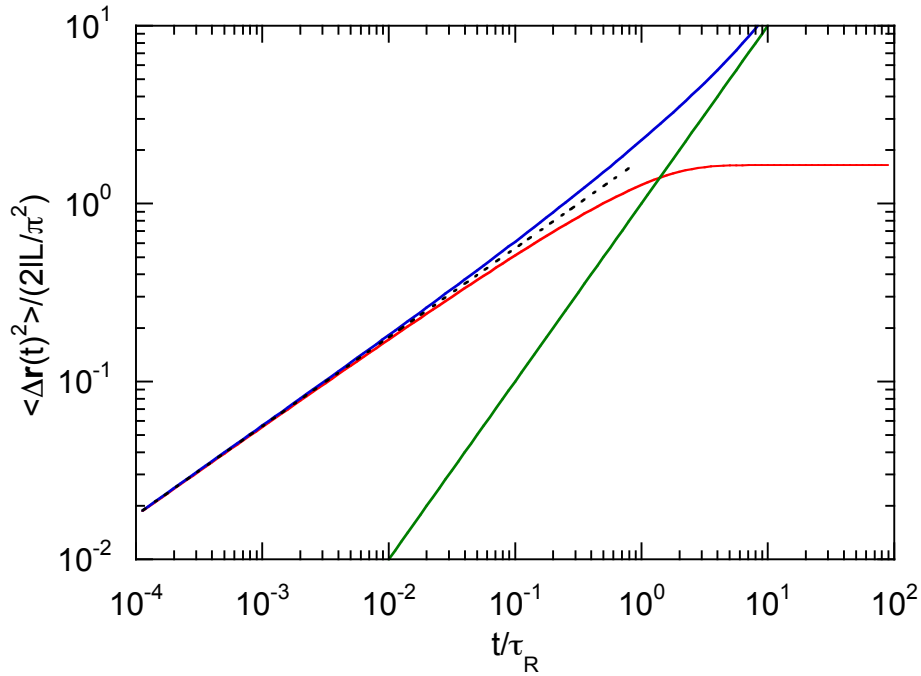
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Figure 5: Mean square displacements of a free-draining polymer. The green line indicates $\langle \Delta \boldsymbol{r}_{cm}(t)^2 \rangle$, the blue line the total MSD $\langle \Delta \boldsymbol{r}(t)^2 \rangle$, and the red line the segmental MSD in the center-of-mass reference frame: $\langle \Delta \boldsymbol{r}(t)^2 \rangle - \langle \Delta \boldsymbol{r}_{cm}(t)^2 \rangle$. The red line approaches the asymptotic value $2R_G^2$ in the limit $t \to \infty$. The dotted line represents the analytical approximation (372).

12.1.3 End-to-End Vector Correlation Function

The correlation function of the end-to-end vector $\boldsymbol{r}_e(t) = \boldsymbol{r}(L/2, t) - \boldsymbol{r}(-L/2, t)$ is given by

$$\langle \boldsymbol{r}_e(t)\boldsymbol{r}_e(0) \rangle = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \langle \boldsymbol{\chi}_n(t)\boldsymbol{\chi}_m(0) \rangle \, (\varphi_n(L/2) - \varphi_n(-L/2))(\varphi_m(L/2) - \varphi_m(-L/2))$$

$$= \sum_{n,\mathrm{odd}} \langle \boldsymbol{\chi}_n(t)\boldsymbol{\chi}_n(0) \rangle \, 4\varphi_n(L/2)^2 = \frac{12k_BT}{\gamma} \sum_{n,\mathrm{odd}} \tau_n e^{-t/\tau_n}\varphi_n(L/2)^2.$$

For $t \gtrsim \tau_1$ follows

$$\langle \boldsymbol{r}_e(t)\boldsymbol{r}_e(0) \rangle = \frac{12k_BT}{\gamma}\tau_1 e^{-t/\tau_1}\varphi_1(L/2)^2.$$

At $t = 0$, $\langle \boldsymbol{r}_e(0)\boldsymbol{r}_e(0) \rangle = \boldsymbol{r}_e^2$, hence

$$\langle \boldsymbol{r}_e(t)\boldsymbol{r}_e(0) \rangle \approx \boldsymbol{r}_e^2 e^{-t/\tau_1}.$$

The model discussed so for applies to systems without hydrodynamic interactions. Strictly speaking, it applies for systems without excluded volume interactions. This is (approximately) realized in polymer melts, as long as the polymer length is not exceeding a certain value denoted as entanglement length.

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12.2 Non-Draining Dynamics: Hydrodynamic Interactions

In dilute solution, the polymer dynamics is governed by hydrodynamic interactions. As a consequence, the diffusion and relaxation behavior is significantly different from that of a free-draining system.

As outlined in Sec. 9.3 [Eq. (300)], the equation of motion of the continuous polymer is given by

$$\frac{\partial \boldsymbol{r}(s,t)}{\partial t} = \int_{-L/2}^{L/2} \mathbf{H}(\boldsymbol{r}(s) - \boldsymbol{r}(s')) \left[2\nu k_B T \frac{\partial^2 \boldsymbol{r}(s',t)}{\partial s'^2} - \epsilon k_B T \frac{\partial^4 \boldsymbol{r}(s',t)}{\partial s'^4} + \boldsymbol{\Gamma}(s',t) \right] ds',$$

(375)

with the force from Eq. (351) and the boundary conditions (352), (353). Note, the correlations of the stochastic forces changed now. The corresponding Fokker-Planck equation (Smoluchowski equation) reads

$$\frac{\partial \Psi}{\partial t} = \int_{-L/2}^{L/2} \frac{\delta}{\delta \boldsymbol{r}(s)} \mathbf{H}(\boldsymbol{r}(s) - \boldsymbol{r}(s')) \left[\frac{\delta U}{\delta \boldsymbol{r}(s')} \Psi + k_B T \frac{\delta}{\delta \boldsymbol{r}(s')} \Psi \right] ds' ds.$$

(376)

The stationary state solution of this equation is

$$\Psi([\boldsymbol{r}(s)]) = \frac{1}{Z} \exp\left(-\beta U\right),$$

since $\delta\Psi/\delta\boldsymbol{r}(s) + \Psi\delta U/\delta\boldsymbol{r}(s)/k_B T = 0$. ($Z$ is given in Eq. (335).) Thus, the stationary state solution is independent of $\mathbf{H}$. As a consequence, hydrodynamic interactions affect dynamical properties only.

To solve the non-linear equation (375) the following approaches are typically adopted.

Preaveraging Approximation

Here, the hydrodynamic tensor is replaced by its spatial isotropic averaged expression (cf. Doi and Edwards). Utilizing the Gaussian joint probability density (340), $\boldsymbol{\Omega}(\Delta\boldsymbol{r})$ becomes

$$\boldsymbol{\Omega}(s - s') = \langle \boldsymbol{\Omega}(\Delta\boldsymbol{r}) \rangle = \frac{\Theta(|s - s'| - d)}{3\pi\eta} \sqrt{\frac{3}{2\pi\sigma^2}} \mathbf{I} = \Omega(s - s')\mathbf{I}.$$

(377)

The expression is isotropic, because any non-diagonal part of $\boldsymbol{\Omega}$ vanishes (space is homogeneous and isotropic). Moreover, the averages of the various Cartesian components are equal, i.e.,

$$\left\langle \frac{1}{|\Delta\boldsymbol{r}|} \frac{\Delta r_\alpha \Delta r_\alpha}{\Delta\boldsymbol{r}^2} \right\rangle = \frac{1}{3} \left\langle \frac{1}{|\Delta\boldsymbol{r}|} \frac{\Delta\boldsymbol{r}^2}{\Delta\boldsymbol{r}^2} \right\rangle = \frac{1}{3} \left\langle \frac{1}{|\Delta\boldsymbol{r}|} \right\rangle.$$

Hence, $\mathbf{H}(s - s') = \mathbf{I}H(s - s') = \mathbf{I}\left[\delta(s - s')/3\pi\eta + \Omega(s - s')\right]$, where $\gamma = 3\pi\eta$ has be used. For the latter, it is assumed that every segment is a sphere of diameter l with the friction coefficient $\gamma = 3\pi\eta l$ (Stokes law). This leads to the friction density $\gamma \to \gamma/l \to 3\pi\eta$ in

the continuum limit $l \to 0$.

Within the preaveraging approximation, the equation of motion (375) is linear and the eigenfunction expansion (362) leads to the equation for the amplitudes

$$3\pi\eta\frac{\partial \boldsymbol{\chi}_k}{\partial t} = \sum_{n=0}^{\infty} \mathrm{H}_{kn}\left(-\frac{3\pi\eta}{\tau_n}\boldsymbol{\chi}_n + \boldsymbol{\Gamma}_n\right), \tag{378}$$

where $\mathrm{H}_{kn} = 3\pi\eta\Omega_{kn} + \delta_{kn}$ and (σ from Eq. (341)),

$$\Omega_{kn} = \frac{1}{\sqrt{6\pi^3}\eta} \int_{-L/2}^{L/2} \varphi_k(s')\frac{\Theta(|s-s'|-d)}{\sigma(s-s')}\varphi_n(s)dsds', \tag{379}$$

$$\langle \Gamma_{n\alpha}(t)\Gamma_{k\alpha'}(t')\rangle = 6\pi\eta k_B T\delta_{\alpha\alpha'}\delta(t-t')\mathrm{H}_{nk}^{-1}.$$

Eq. (378) is an infinite system of coupled linear differential equations, which can be solved (numerically) by diagonalization. For an analytical solution, the off-diagonal elements are neglected and an approximation for the eigenfunctions is used, i.e.,

$$\Omega_{kn} \approx \sqrt{\frac{2}{3\pi^3}}\frac{\delta_{kn}}{\eta L}\int_d^L \frac{L-s}{\sigma(s)}\cos(\zeta_n s)ds. \tag{380}$$

This is reasonable approximation, since a numerical calculation shows that the matrix H_{nk} is almost diagonal over the whole range of the flexibility parameter pL, except for the first few modes in the limit of large chain stiffness. As for the non-hydrodynamic case, we then obtain

$$\boldsymbol{\chi}_n(t) = \frac{\tau_n}{3\pi\eta\tilde{\tau}_n}\int_{-\infty}^{t}\exp\left(-\frac{t-t'}{\tilde{\tau}}\right)\boldsymbol{\Gamma}_n(t')dt', \tag{381}$$

$$\frac{1}{\tilde{\tau}_n} = \frac{1+3\pi\eta\Omega_{nn}}{\tau_n}, \tag{382}$$

$$\langle \boldsymbol{\chi}_k(t)\boldsymbol{\chi}_n(0)\rangle = \frac{k_B T}{\pi\eta}\tau_n\delta_{kn}e^{-t/\tilde{\tau}_n} \ , \ \forall k, n \neq 0. \tag{383}$$

The relaxation times τ_n are given in Eq. (364).

Asymptotic behavior

- Flexible polymer (Zimm model): $pL \to \infty$

$$\sigma(s)^2 = \frac{|s|}{p}, \quad \tilde{\tau}_n = \frac{\eta}{\sqrt{3\pi}k_B T}\left(\frac{L}{np}\right)^{3/2}. \tag{384}$$

- Semiflexible polymer: $pL \ll 1$

$$\sigma(s)^2 = s^2, \quad \tilde{\tau}_n = \frac{64\eta pL^4}{\pi^3 k_B T(2n-1)^4}\left[1 - \sqrt{\frac{6}{\pi}}\left(C + \ln\left(\frac{(2n-1)\pi d}{2L}\right)\right)\right]^{-1}, \tag{385}$$
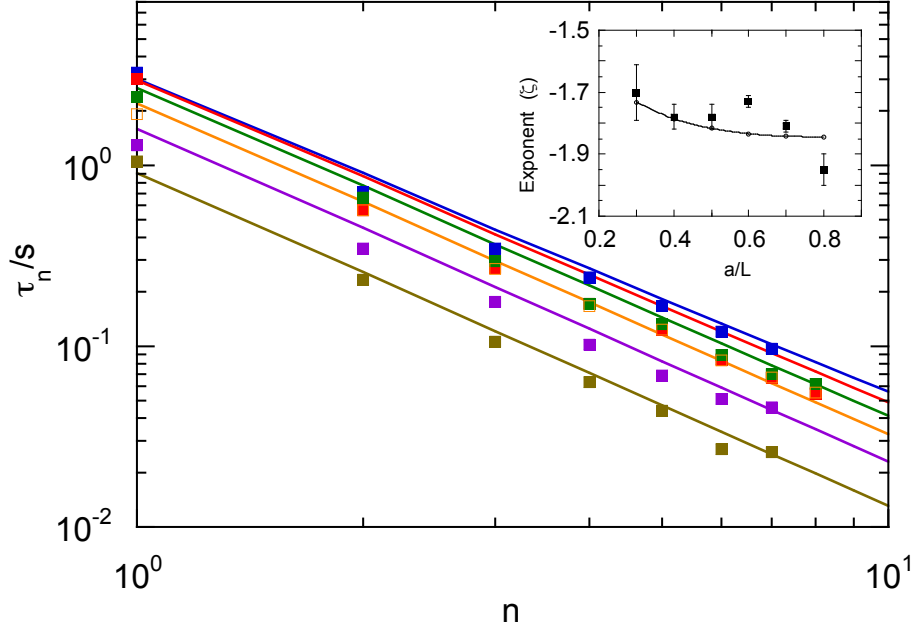
$C = 0.57721..$ is the Euler constant.

Figure 6: Relaxation times for the extensions $a/L = 0.3,\ 0.4,\ 0.5,\ 0.6,\ 0.7$, and 0.8 (from top to bottom) [15]. The experimental data (symbols) are taken from Ref. [16]. The inset shows the exponents (ζ) of the relation $\tau_n \sim n^\zeta$ corresponding to the various curves .

12.2.1 Center-of-Mass Mean Square Displacement

Equation (378) gives for $\boldsymbol{\chi}_0(t)$

$$\boldsymbol{\chi}_0(t) = \boldsymbol{\chi}_0(0) + \frac{\mathrm{H}_{00}}{3\pi\eta} \int_0^t \boldsymbol{\Gamma}_0(t')dt',$$

which yields the center-of-mass mean square displacement

$$\left\langle \Delta \boldsymbol{r}_{cm}(t)^2 \right\rangle = \frac{1}{L} \left\langle (\boldsymbol{\chi}_0(t) - \boldsymbol{\chi}_0(0))^2 \right\rangle = \frac{\mathrm{H}_{00}^2}{(3\pi\eta)^2} \int_0^t \left\langle \boldsymbol{\Gamma}_0(t')\boldsymbol{\Gamma}_0(t'') \right\rangle dt'dt'' = \frac{6k_B T}{3\pi\eta L}\mathrm{H}_{00}t.$$

Hence, the diffusion coefficient is

$$D = \frac{k_B T}{3\pi\eta L}\mathrm{H}_{00} = \frac{k_B T}{3\pi\eta L}\left[1 + \sqrt{\frac{6}{\pi}}\frac{1}{L}\int_d^L \frac{L-s}{\sigma(s)}ds\right]. \tag{386}$$

The asymptotic dependence on polymer length is

$$D = \begin{cases} \dfrac{8k_B T}{3\sqrt{6\pi^3}\eta}\sqrt{\dfrac{p}{L}}\,, & pL \gg 1 \\[3mm] \sqrt{\dfrac{6}{\pi}}\dfrac{k_B T}{3\pi\eta L}\ln(L/d)\,, & pL \ll 1 \end{cases}$$

to leading order in L/d. Note, the preaveraging approximation does not strictly apply in the rod limit. Hence, a more accurate calculation of the diffusion coefficient yields other front factors in that limit.
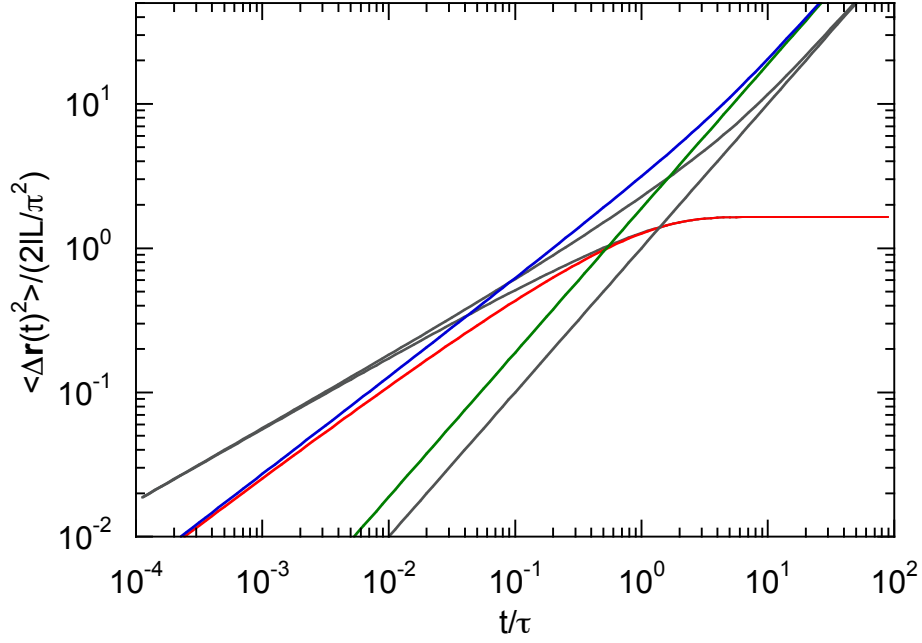
Figure 7: Mean square displacements of polymers in dilute solution. The gray lines correspond to the Rouse model (see Fig. 5) and the colored lines to the non-draining Zimm model (flexible polymer). The green line indicates $\langle \Delta \boldsymbol{r}_{cm}(t)^2 \rangle$, the blue line the total MSD $\langle \Delta \boldsymbol{r}(t)^2 \rangle$, and the red line the segmental MSD in the center-of-mass reference frame $\langle \Delta \boldsymbol{r}(t)^2 \rangle - \langle \Delta \boldsymbol{r}_{cm}(t)^2 \rangle$. The red line approaches the asymptotic value $2R_G^2$ in the limit $t \to \infty$.

12.2.2 Segmental Mean Square Displacement

Similar to the free-draining case, the averaged segmental mean square displacement is given by

$$\langle \Delta \boldsymbol{r}(t)^2 \rangle = 6Dt + \frac{2k_BT}{\pi \eta L} \sum_{n=1}^{\infty} \tau_n \left(1 - e^{-t/\tilde{\tau}_n} \right). \tag{387}$$

Flexible Polymer

With the Zimm relaxation time

$$\tau_z = \frac{\eta}{\sqrt{3\pi}k_BT} \left(\frac{L}{p} \right)^{3/2},$$

the sum is replaced by an integral as follows ($x = n(t/\tau_z)^{2/3}$)

$$\sum_{n=1}^{\infty} \frac{\tau_R}{n^2} \left[1 - e^{-tn^{3/2}/\tau_z} \right] \to \left(\frac{t}{\tau_z} \right)^{2/3} \tau_R \int_0^{\infty} \frac{1}{x^2} \left[1 - e^{-x^{3/2}} \right] dx = 2.6789 \left(\frac{t}{\tau_z} \right)^{2/3} \tau_R. \tag{388}$$

Hence, $\langle \Delta \boldsymbol{r}^2 \rangle \sim t^{2/3}$.

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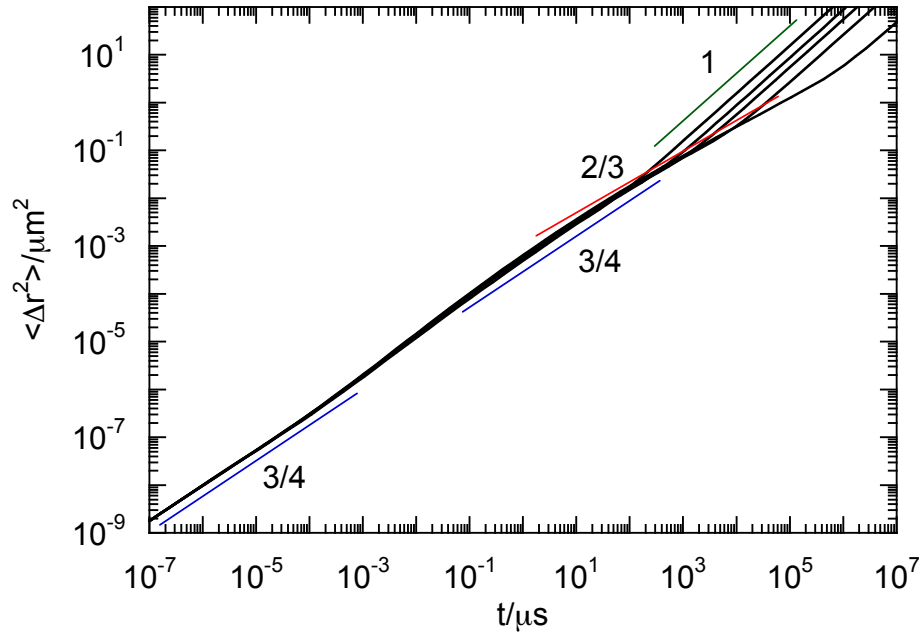
Figure 8: Mean square displacements of DNA molecules with $pL = 0.68,\ 1.7,\ 3.4,\ 10,\ 170$ (left to right). The thickness is $d = 2.5\,nm$ and persistence length $l_p = 50\,nm$.

Semiflexible Polymer

Hydrodynamic interactions yield a logarithmic correction in the relaxation times only [cf. Eq. (385)], compared to the free-draining case. Suppression of this extra dependence leads to the same time dependence of the segmental mean square displacement as for the free-draining case, namely

$$\left\langle \Delta \boldsymbol{r}(t)^2 \right\rangle \sim t^{3/4}.$$
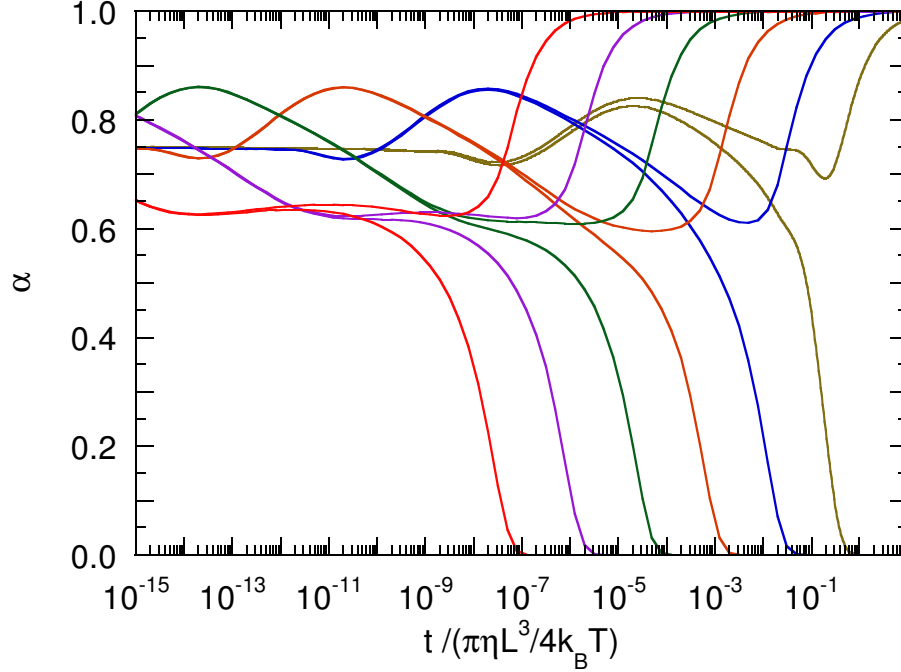
Figure 9: Local slope $\alpha(t) = d \ln \langle \Delta r(t)^2 \rangle / d \ln t$ for DNA-like molecules with $pL = 1, 10, 10^2, 10^3, 10^4, 10^5$ (right to left). The thickness is $d = 2.5\,nm$ and persistence length $l_p = 50\,nm$.
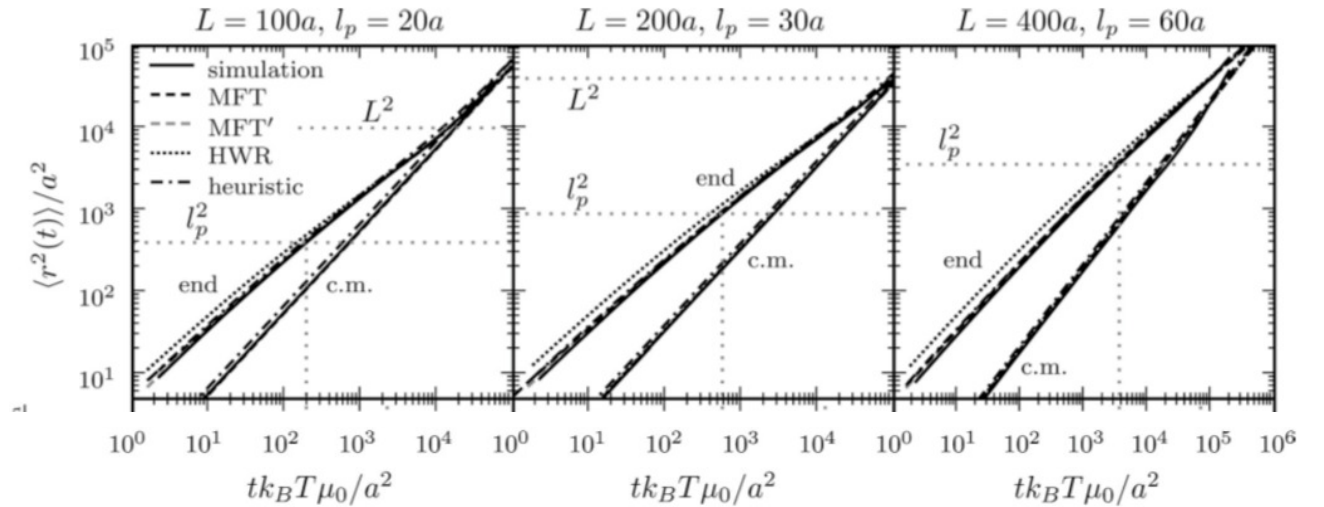
Figure 10: Mean square displacements of semiflexible polymers [17]. Comparison of Brownian dynamics simulations and various theoretical approaches.
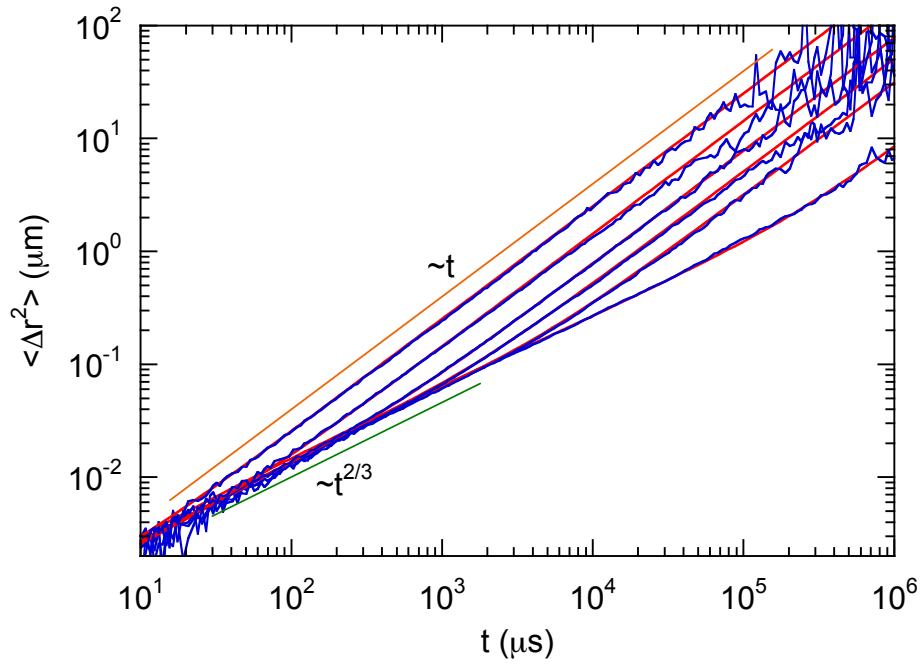
Figure 11: Mean square displacements of dsDNA ends of various lengths ($L = 100, 200, 500, 1000, 2000, 20000$ bp). The experimental values (blue) are from Ref. [18], and the red lines are calculated by the semiflexible polymer model, where the hydrodynamic tensor components H_{nn} are multiplied by the factor $\Lambda_D = 0.9$ for $n = 0$ and $\Lambda = 0.6$ otherwise.
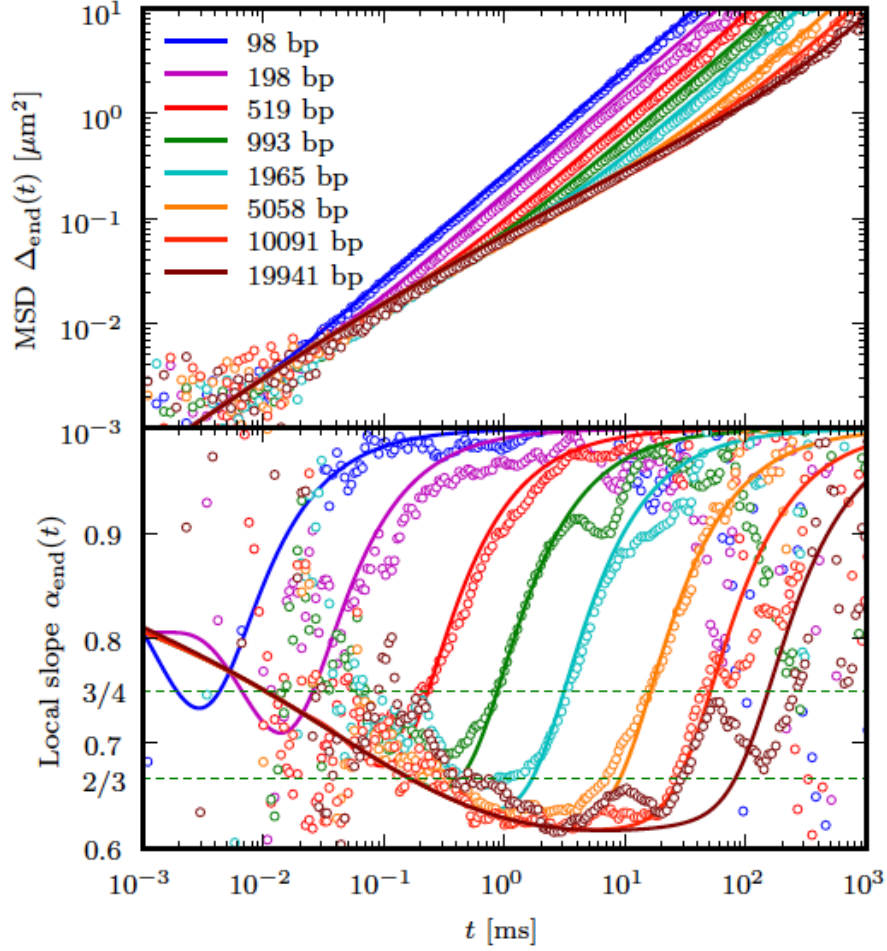
Figure 12: Top: $\Delta_{\mathrm{end}}(t)$, the mean square displacement of an end-monomer in a dsDNA strand, for various lengths $L = 98 - 19941$ bp. Bottom: the local slope $\alpha_{\mathrm{end}}(t) = d\ln_{\mathrm{end}}/d\ln t$ of the log-log curves in the top panel. In both panels the circles are from the experimental FCS measurements in Ref. [18]. The solid lines are MFT predictions, without any fitting parameters [19].
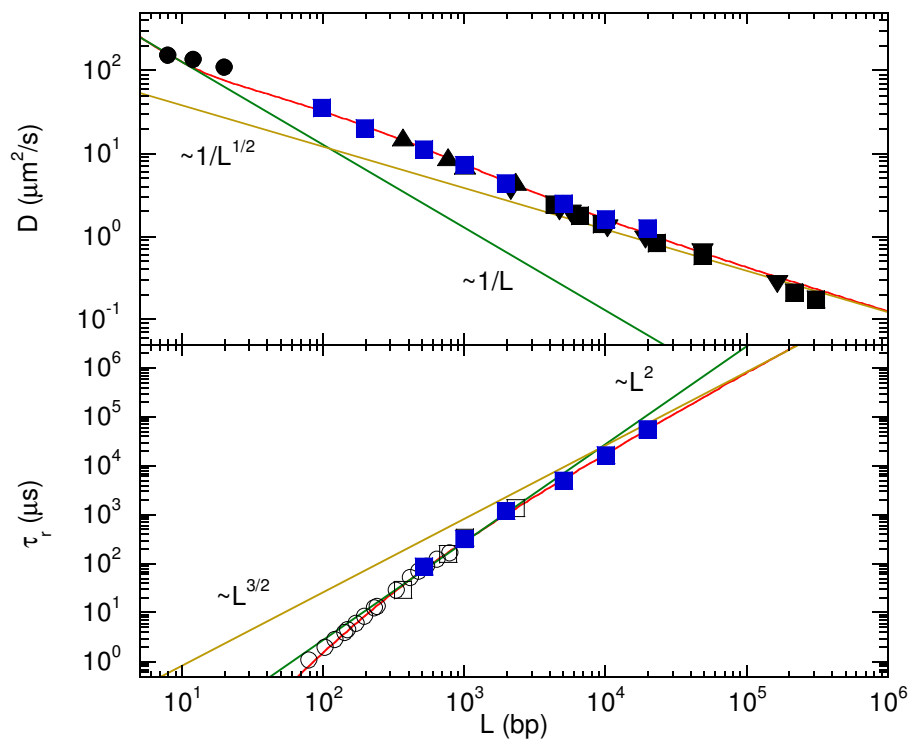
Figure 13: Diffusion coefficients (a) and longest relaxation times (b) of dsDNA [18]. Symbols represent various experimental results and the theoretical curve are obtained by the semiflexible polymer model.

12.2.3 Diffusion of Rod

The preaveraging approximation does not apply to rather stiff polymers or rods. Here, the anisotropy of the hydrodynamic interactions has to be taken into account (cf. Eq. (389)). For an infinitely thin rod, a position independent tensor is obtained. With $\Delta \boldsymbol{r} = \boldsymbol{r}(s) - \boldsymbol{r}(s') = (s - s')\hat{\boldsymbol{u}}$, where $\hat{\boldsymbol{u}}$ is the unit vector pointing along the rod axis, we obtain

$$\boldsymbol{\Omega}(s - s') = \frac{\Theta(|s - s'| - d)}{8\pi\eta|s - s'|} \left(\mathbf{I} + \hat{\boldsymbol{u}} : \hat{\boldsymbol{u}}\right).$$

Hence, the Oseen tensor components parallel and perpendicular to $\hat{\boldsymbol{u}}$ are

$$\Omega_\perp(s) = \Omega_\parallel(s)/2 = \frac{\Theta(|s| - d)}{8\pi\eta|s|}, \tag{389}$$

which is evident, when, e.g., $\hat{\boldsymbol{u}} = (1, 0, 0)^T$ is used.
Within the approximation $\boldsymbol{\Omega}_{kn} = \boldsymbol{\Omega}_{nn}\delta_{kn}$, the segmental mean square displacement (387) reduces to

$$\left\langle \Delta \boldsymbol{r}(t)^2 \right\rangle = 6Dt + \frac{L^2}{6} \left(1 - e^{-t/\tilde{\tau}_1}\right), \tag{390}$$

since all τ_n, with $n > 1$ are zero for $pL = 0$. The two terms describe the center-of-mass motion and the rotational diffusion of the rod. $\tilde{\tau}_1$ is the rotational relaxation time, which is related to the rotational diffusion coefficient via $D_r = 1/(2\tilde{\tau}_1)$.

D is given by the average $D = (2D_\perp + D_\parallel)/3$, where $D_\perp$ and $D_\parallel$ are the diffusion coefficients perpendicular and parallel to the rod axis.

The equation of motion for $\boldsymbol{r}_{cm} = \boldsymbol{\chi}_0\varphi_0$ reads

$$\dot{\boldsymbol{r}}_{cm} = \frac{1}{3\pi\eta\sqrt{L}}\mathbf{H}_{00}\boldsymbol{\Gamma}_0 \ ,$$

or, parallel and perpendicular to director $\hat{\boldsymbol{u}}$

$$\dot{\boldsymbol{r}}_{cm,\perp} = \frac{1}{3\pi\eta\sqrt{L}}\mathbf{H}_{00,\perp}\boldsymbol{\Gamma}_{0,\perp},$$

$$\dot{\boldsymbol{r}}_{cm,\parallel} = \frac{1}{3\pi\eta\sqrt{L}}\mathbf{H}_{00,\parallel}\boldsymbol{\Gamma}_{0,\parallel},$$

where $\mathbf{H}_{00,\parallel,\perp} = 3\pi\eta\Omega_{\parallel,\perp} + 1$ and $\Omega_{\parallel,\perp}$ is given in Eq. (389). The solution yields the mean square displacements $\left\langle \Delta \boldsymbol{r}_{cm,\perp,\parallel}^2 \right\rangle = 2D_{\perp,\parallel}t$, with

$$D_{\perp,\parallel} = \frac{k_BT}{3\pi\eta L} + \frac{k_BT}{L^2} \int_{-L/2}^{L/2} \Omega_{\perp,\parallel}(s - s)dsds'.$$

Evaluation yields for $L/d \gg 1$

$$D_\perp = D_\parallel/2 = \frac{k_BT}{4\pi\eta L} \ln(L/d). \tag{391}$$

More precise calculations yield correction terms ($O(d/L)$)

$$D_\parallel = \frac{k_B T}{2\pi\eta L} \left[\ln(L/d) - 0.2\right] \ ,$$

$$D_\perp = \frac{k_B T}{4\pi\eta L} \left[\ln(L/d) + 0.84\right] \ ,$$

$$D_r = \frac{3k_B T}{\pi\eta L^3} \left[\ln(L/d) - 0.66\right] \ .$$

(392)

Evidently, the rod diffuses faster parallel to its main axis than perpendicular to it.

13 Excluded-Volume Interactions

So far, polymers in a Θ solvent have been discussed, i.e., polymers, where the excluded-volume interactions between the various monomers are screened. Experimentally, it has been show that this is an adequate description of polymers in melts. In dilute solution under so-called good solvent conditions, excluded-volume interactions lead to a swelling of a polymer coil. The mean square end-to-end distance increases then with the power law $\langle (\boldsymbol{r}_N - \boldsymbol{r}_0)^2 \rangle \sim l^2 N^{2\nu}$ with polymer length, where mean field approaches predict $\nu = 0.6$ and more precise renormalization group calculations $\nu \approx 0.588$ [20, 21].

13.1 Model of the Excluded Volume Chain

The interaction between the polymer segment n and m is of short-range nature and can be expressed by the potential

$$u^{ex} = k_B T \tilde{u}(\boldsymbol{r}_n - \boldsymbol{r}_m).\tag{393}$$

It can even, for a theoretical study, be approximated by the delta function

$$u^{ex} = v k_B T \delta(\boldsymbol{r}_n - \boldsymbol{r}_m).\tag{394}$$

v is the excluded volume and has the dimension of a volume. The total energy of a continuous polymer is then

$$U^{ex} = \frac{1}{2} v k_B T \int \delta(\boldsymbol{r}(s) - \boldsymbol{r}(s')) ds ds'.\tag{395}$$

With the density of segments

$$\rho(\boldsymbol{r}) = \int \delta(\boldsymbol{r} - \boldsymbol{r}(s)) ds\tag{396}$$

the energy (395) can be written as

$$U^{ex} = \frac{1}{2} k_B T v \int \rho(\boldsymbol{r})^2 d^3 r.$$

Hence, U^{ex} can be considered as the first term in a density expansion of the excluded volume interaction, i.e., a virial expansion.

The partition function of a flexible polymer is then given by

$$Z = \int \exp\left(-\frac{3p}{2} \int_0^L \left(\frac{\partial \boldsymbol{r}(s)}{\partial s} \right)^2 ds - \frac{1}{2} v \int_0^L \int_0^L \delta(\boldsymbol{r}(s) - \boldsymbol{r}(s')) ds ds' \right) \mathcal{D}^3 r.\tag{397}$$

13.2 Mean-Field Estimation of Swelling Exponent

A estimation of the swelling exponent is obtained by a dimension analysis of the partition function. Alternative the free energy can be considered. For a Gaussian polymer with fixed ends at $\boldsymbol{r} = 0$ and $\boldsymbol{r}(L) = \boldsymbol{R}$, the partition function is ($l = 1/p$)

$$Z \sim \exp\left(-\frac{3\boldsymbol{R}^2}{2lL} \right).$$

Hence, the free energy of the Gaussian polymer reads

$$F_G = -k_B T \ln Z = k_B T \frac{3\mathbf{R}^2}{2lL} \tag{398}$$

To estimate the effect of the excluded volume interaction, the connectivity of the chain is disregarded, i.e, an 'segment gas' is considered confined in a volume $V = 4\pi R^3/3$, with $R = |\mathbf{R}|$. The concentration of the segment gas is

$$\bar{\rho} = \frac{1}{V} \int \rho(\mathbf{r}) d^3 r = \frac{L}{V} \tag{399}$$

(for a discrete system $\bar{\rho} = N/V$). Then, the energy U^{ex} becomes

$$U^{ex} = k_B T \frac{vL^2}{2V}. \tag{400}$$

With

$$Z = \int \exp\left(-\frac{3p}{2} \int_0^L \left(\frac{\partial \mathbf{r}(s)}{\partial s}\right)^2 ds\right) \mathcal{D}^3 r \exp\left(-\frac{vL^2}{2V}\right)$$

follows for the free energy

$$F \approx k_B T \left(\frac{3\mathbf{R}^2}{2lL} + \frac{vL^2}{8R^3}\right). \tag{401}$$

Minimization of F yields

$$R = \left(\frac{vl}{8}\right)^{1/5} L^{3/5} \sim L^{\nu}. \tag{402}$$

Hence, $\nu = 3/5 = 0.6$.

13.3   Dynamics

The swelling also affects the dynamics of a polymer. Qualitatively, this effect can be captured by the linearization approximation [21]. Here the distribution function $\Psi(\mathbf{r}(s) - \mathbf{r}(s')) = F(|\mathbf{r}(s) - \mathbf{r}(s')|/[|(s-s')/l|^{\nu}])$ is used, which gives

$$\left\langle \frac{1}{|\mathbf{r}(s) - \mathbf{r}(s')|} \right\rangle \approx \left(\frac{l}{|s-s'|}\right)^{\nu} \tag{403}$$

and leads to the relaxation times $(L/l \gg 1)$ [21]

$$\tilde{\tau}_n \approx \frac{\eta l^3}{k_B T} \left(\frac{L}{ln}\right)^{3\nu}. \tag{404}$$

With the exponent $\nu = 1/2$ for a Θ solvent, the dependencies (384) are recovered. Renormalization group theory calculations yield the diffusion coefficient $D_Z = 0.2 k_B T/(\sqrt{6}\eta R_G)$ in good solvent, with the radius of gyration $R_G \approx l(L/l)^{\nu}$ [21, 22].

14 Mesoscale Hydrodynamic Simulations

During the last two decades, varies mesoscale hydrodynamic simulation techniques have been developed to account for hydrodynamic interactions and to bridge the length- and time-scale gap between solvent and solute degrees of freedom. Popular approaches are the *Lattice Boltzmann (LB)* method, *Dissipative Particle Dynamics (DPD)* simulations, and recently the *Multiparticle Collision* Dynamics (*MPC*) method (the latter is often denoted as *Stochastic Rotation Dynamics (SRD)*) [23, 24]. Aside from these, simulation methods are used, which capture hydrodynamic interactions by a hydrodynamic tensor, e.g., the Oseen (293) or Rotne-Prager (295) tensor, or more elaborated ones, and solve a Langevin equation [cf. Eq. 297]. *Stokesian Dynamics* is applied for rather large objects, where Brownian motion, i.e., thermal motion, can be neglected—here, random forces are neglected. Simulations including thermal (random) force are denoted as *Brownian Dynamics* simulations with or without hydrodynamic interactions. All these approaches are essentially alternative ways of solving the NavierStokes equation and its generalizations. This is because the hydrodynamic equations are expressions for the local conservation laws of mass, momentum, and energy, complemented by constitutive relations which reflect some aspects of the microscopic details. Frisch et al. [25] demonstrated that discrete algorithms can be constructed which recover the NavierStokes equation in the continuum limit as long as these conservation laws are obeyed and space is discretized in a sufficiently symmetric manner.

14.1 Multiparticle Collision Dynamics (MPC)

As an example, I will briefly outline the MPC method and its coupling to the dynamics of polymers.

The common approach of all mesoscale methods is to *average out* irrelevant microscopic details in order to achieve high computational efficiency while keeping the essential features of the microscopic physics on the length scales of interest. Applying these ideas to suspensions leads to a simplified, coarse-grained description of the solvent degrees of freedom, in which embedded macromolecules such as polymers are treated by conventional molecular dynamics simulations. For MPC, this means that the fluid is represented by point particles, which interact with each other by a stochastic process, thereby preserving locally momentum and energy. It is momentum conservation, which leads to the build-up of a correlated fluid motion. Specifically, the solvent is composed of N_s pointlike particles of mass m and the algorithm consists of alternate streaming and collision steps. In the streaming step, the particles move ballistically and their positions are updated according to

$$\boldsymbol{r}_i(t + h) = \boldsymbol{r}_i(t) + h\boldsymbol{v}_i \ , \tag{405}$$

where h is the time interval between collisions and is denoted as collision time. In the collision step, the system is partitioned into cubic cells of side length a. The particles are sorted into this cells according to their position and their relative velocities $\Delta\boldsymbol{v}_i = \boldsymbol{v}_i - \boldsymbol{v}_{cm}$,

with respect to the center-of-mass velocity of the cell

$$\boldsymbol{v}_{cm} = \frac{1}{N_c} \sum_{j=1}^{N_c} \boldsymbol{v}_j,$$

are changed by a random process. N_c denotes the particles in the particular cell. There are various realizations of the stochastic process. Here, two examples are given:

(i) Stochastic rotation

A randomly oriented axis is selected for every collision cell and every collision step, and the relative velocities $\Delta \boldsymbol{v}_i$ are rotated around the corresponding axis by the fixed angle α, i.e.,

$$\boldsymbol{v}_i(t + h) = \boldsymbol{v}_i(t) + (\mathbf{R}(\alpha) - \mathbf{I})(\boldsymbol{v}_i - \boldsymbol{v}_{cm}) . \tag{406}$$

$\mathbf{R}(\alpha)$ is the rotation matrix

$$\mathbf{R}(\alpha) = \begin{pmatrix} l_x^2 + (1 - l_x^2)c & l_x l_y(1 - c) - l_z s & l_x l_z(1 - c) + l_y s \\ l_x l_y(1 - c) + l_z s & l_y^2 + (1 - l_y^2)c & l_y l_z(1 - c) - l_x s \\ l_x l_z(1 - c) - l_y s & l_y l_z(1 - c) + l_x s & l_z^2 + (1 - l_z^2)c \end{pmatrix},$$

with $l_x = \cos(\varphi)\sqrt{1 - \theta^2}$, $l_y = \sin(\varphi)\sqrt{1 - \theta^2}$, $l_z = \theta$, $c = \cos(\alpha)$, and $s = \sin(\alpha)$. φ and θ are uncorrelated random numbers, which are taken from uniform distributions in the intervals $[0, 2\pi]$ and $[-1, 1]$, respectively.

(ii) Maxwellian distributed random numbers

Velocities $\Delta \boldsymbol{v}_i$ are taken from the Maxwellian distribution $P(\Delta \boldsymbol{v}) = \exp(-m\Delta \boldsymbol{v}^2/(2k_B T))/Z$ and the velocity of a fluid particle is calculated according to

$$\boldsymbol{v}_i(t + h) = \boldsymbol{v}_{cm}(t) + \Delta \boldsymbol{v}_i - \frac{1}{N_c} \sum_{j=1}^{N_c} \Delta \boldsymbol{v}_i . \tag{407}$$

The last sum ensures conservation of momentum. The advantage of this method is that the system is always thermalized.

To establish Galilean invariance, a random shift is performed at every collision step. This means that a uniformly distributed random number $\xi \in [-0.5, 0.5]$ is taken for every spatial direction and every collision step, and the collision lattice is shifted by that amount. In practice, the particles are shifted and redistributed in the collision lattice.

The advantage of the method is that the viscosity and Schmidt number can be given. The viscosity $\eta = \eta_{\mathrm{kin}} + \eta_{\mathrm{col}}$ has two contributions, a kinetic one η_{kin} and a collisional one η_{col}, which read

$$\eta_{\mathrm{kin}} = \frac{N_s k_B T h}{V} \left[\frac{5 N_c}{(N_c - 1)(4 - 2\cos(\alpha) - 2\cos(2\alpha))} - \frac{1}{2} \right],$$

$$\eta_{\mathrm{col}} = \frac{N_s m a^2}{18 V h} (1 - \cos(\alpha)) \left(1 - \frac{1}{N_c} \right).$$
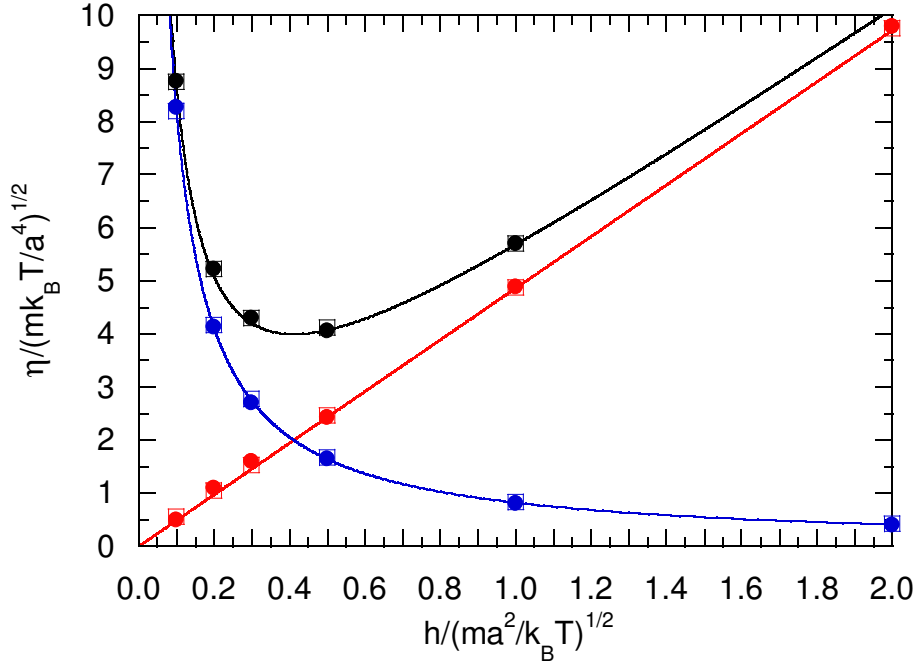
Figure 14: Viscosities determined via the internal (bullets) and external (open squares) stress tensors ($\alpha = 130^o$, $\langle N_c \rangle = 10$). The analytical results for the total (black), the kinetic (red, $\sim h$), and collisional (blue, $\sim 1/h$) contributions are presented by solid lines [26].

Figure 14 shows a comparison with simulation results.

The Schmidt is defined as $Sc = \nu/D$, where $\nu = \eta/\rho$ is the kinematic viscosity and D the diffusion coefficient. Thus, Sc is the ratio between momentum transport and mass transport. It is known that this number for gases is smaller than but on the order of unity, while in fluids like water it is on the order of 10^2 to 10^3. A prediction for the Schmidt number of a MPC fluid can be obtained from the theoretical expressions for the viscosity and the diffusion coefficient

$$D = \frac{1}{3} \left[\frac{1}{2} \left\langle \boldsymbol{v}^2(0) \right\rangle + \sum_{n=1}^{\infty} \left\langle \boldsymbol{v}(nh)\boldsymbol{v}(0) \right\rangle \right] h \approx \frac{k_B T}{m} h \left(\frac{1}{\gamma_\alpha} - \frac{1}{2} \right) ,$$

with $\gamma_\alpha = 2(1-\cos\alpha)(1-1/N_c)/3$. For $h \ll 1$, the Schmidt number increase as $Sc \sim 1/h^2$, i.e., large Schmidt numbers can be achieved.

Hydrodynamic interactions lead to long-time correlations, which is reflected in the decay of the fluid particle auto-correlation function and is denoted as long-time tail. Figure 15 gives a example of such a behavior.

14.2 Hybrid MPC-MD Simulations

There are various ways to couple the MPC solvent with another object in the solution, such as a colloid or a polymer.
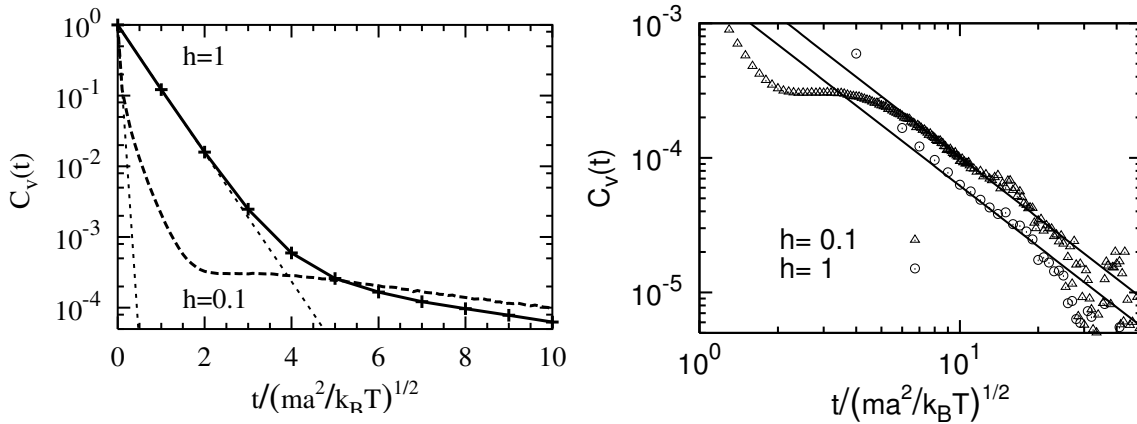
Figure 15: Time dependence of the normalized velocity autocorrelation function for $h = 1$ and $h = 0.1$. Dashed lines correspond to an exponential decay. In both cases the number density is $\langle N_c \rangle = 5$, the rotation angle $\alpha = 130^o$, and the system size $L/a = 20$. On the right, the data are compared with long-time the tail prediction $t^{-3/2}$.

(i) Hard sphere colloid

Two type of boundary conditions are typically applied for colloidal particles, namely slip or no-slip boundary conditions. In the first case, the interaction of the solvent particle with the colloid can be described by a Lennard-Jones potential, i.e., the particle is reflected by the colloid. Similarly, the elastic collision rule for reflection can be applied. In the no-slip case, the bounce-back rule is applied. This means that the relative velocity between the colloid and solvent particle is reverted.

(ii) Polymers

Objects composed of point particles, such as polymers (linear, branched) can very easily be coupled by incorporation of the monomers in the collision step. Since hydrodynamic interactions definitely appear only beyond one collision cell–the actual minimal distance depends on the collision step size—the monomer size is typically set equal to a collision cell. This implies that typically at most one monomer is in a collision cell. To achieve a sufficiently strong coupling, the monomer mass M is set equal to the average mass of fluid in a collision cell, i.e., $M = \langle N_c \rangle m$. The center-of-mass velocity is the given by

$$\boldsymbol{v}_{cm} = \frac{\sum_{j=1}^{N_c} m\boldsymbol{v}_j + \sum_{j=1}^{N_c^m} M\boldsymbol{V}_j}{mN_c + MN_c^m},$$

where N_c^m is the number of monomers in the considered collision cell and the $\boldsymbol{V}_j$ are their velocities. The collision is then either performed via the rule (406) or (407).

14.2.1 Gaussian Polymer in dilute solution

As an example, results are presented for the dynamics of a Gaussian polymer in dilute solution.

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- Center-of-mass mean square displacement neglecting fluid-fluid correlations (no HI)

$$\langle (\boldsymbol{r}_{cm}(nh) - \boldsymbol{r}_{cm}(0))^2 \rangle = \frac{6k_BTh^2}{MN_m} \left[\left(\frac{1}{\gamma} - \frac{1}{2} \right) n - \frac{(1-\gamma) - (1-\gamma)^{n+1}}{\gamma^2} \right] \quad (408)$$

$\gamma = \gamma_\alpha (e^{-\phi} + \phi - 1)/\phi^2$, ϕ: average number of monomers in collision cell.

- Kirkwood diffusion coefficient [27]

$$D^{(K)} = \frac{D_0}{N_m} + \frac{k_BT}{6\pi\eta} \frac{1}{R_H}, \quad (409)$$

where the hydrodynamic radius R_H is defined as

$$\frac{1}{R_H} = \frac{1}{N_m^2} \left\langle \sum_{i=1}^{N_m} \sum_{j=1}^{N_m}{}' \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right\rangle \quad (410)$$

and the prime indicates that the term with $j = i$ has to be left out in the summation. For a Gaussian chain, the hydrodynamic radius is found to be

$$R_H = \frac{3l}{8} \sqrt{\frac{\pi}{6}} N_m^{1/2} \left[1 - \frac{3}{4}\zeta(1/2)N_m^{-1/2} + \mathcal{O}(N_m^{-3/2}) \right] \quad (411)$$

where $\zeta(1/2) = -1.460\ldots$. Thus, $R_H \sim r_g$ to leading order in N_m, but corrections to scaling are different. D_0 is the diffusion coefficient of a single monomer in the same solvent. Equation (409) applies for a single chain in an infinitely large system only. In a system with periodic boundary conditions, interactions with periodic images appear. We are primarily interested in the scaling behavior of the diffusion coefficient with respect to the hydrodynamic radius and not in its absolute values for a finite system. Therefore, we discuss the diffusion coefficient as a function of the hydrodynamic radius of an infinite system, assuming that $D - D_0/N_m \sim g(r_g/L)/R_H$, where D is extracted from the center of mass mean-square displacement [27].
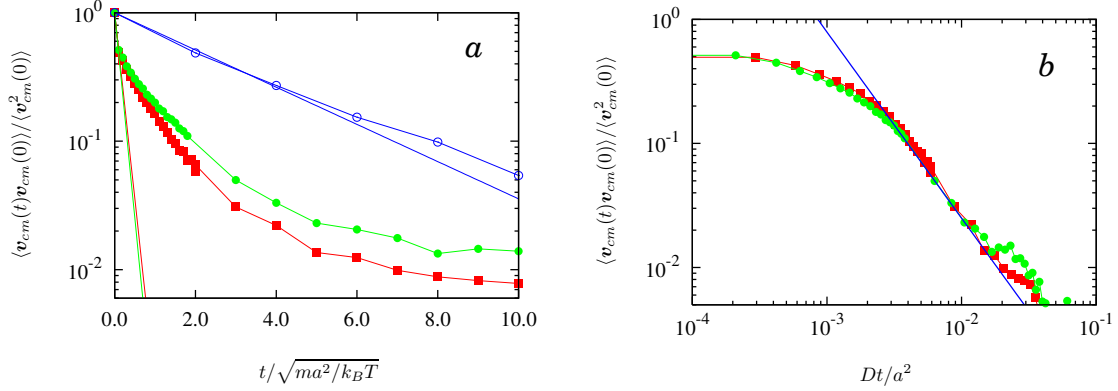
Figure 16: Center-of-mass velocity autocorrelation functions for Gaussian polymers of length $N_m = 20$, with $h = 0.1$ (■) and $h = 2$ (○) as well as for $N_m = 40$ and $h = 0.1$ (●). (a) The solid lines show the exponential decay. (b) Log-log representation of the correlation functions for $N_m = 20$, $N_m = 40$ and $h = 0.1$ as a function of Dt. The solid line is proportional to $(Dt)^{-3/2}$.
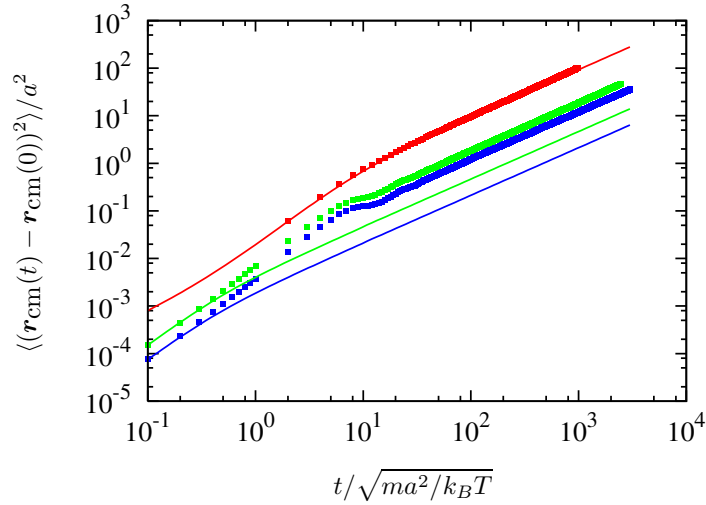

Figure 17: Center-of-mass mean square displacements for Gaussian polymers of lengths $N_m = 20$ and $N_m = 40$ (symbols). The data are for $N_m = 20$ and $h = 2$ (top), $N_m = 20$ and $h = 0.1$ (middle), and for $N_m = 40$ and $h = 0.1$ (bottom). The lines are calculated according to Eq. (408).
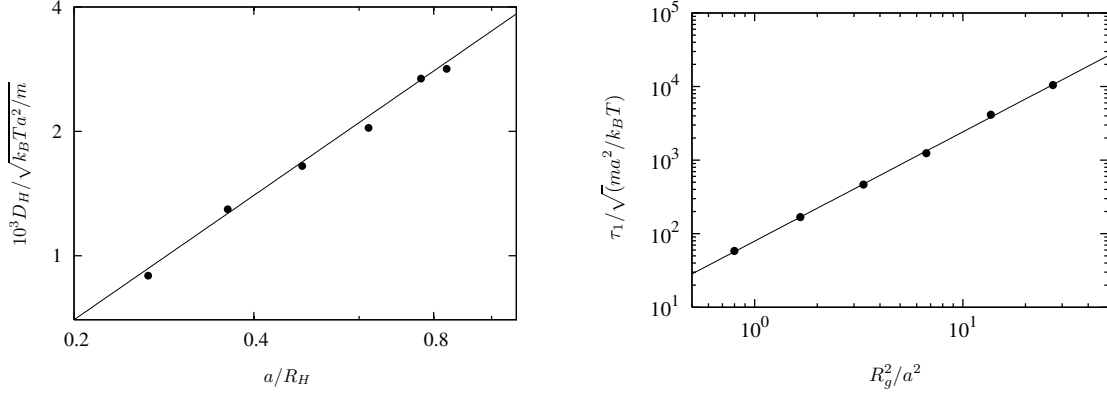
Figure 18: Dependence of the hydrodynamic part of the diffusion coefficient, $D_H = D - D_0/N_m$, on the hydrodynamic radius (left). Dependence of the longest relaxation time τ_1 on the radius of gyration (right). The lengths of the Gaussian chains are $N_m = 5$, 10, 20, 40, 80, and 160.
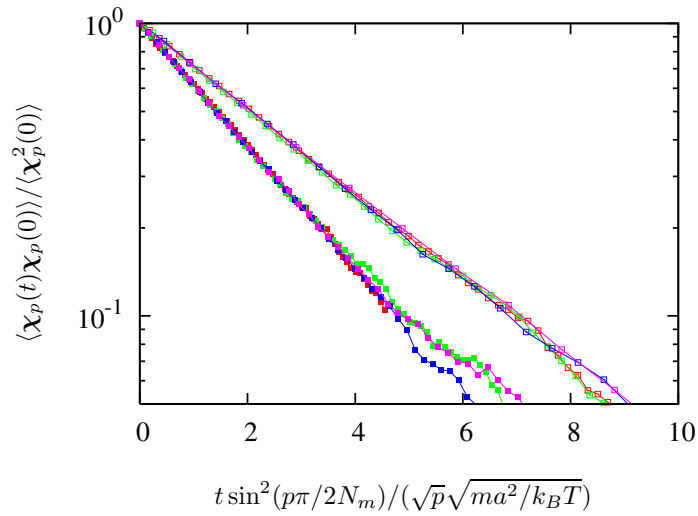
Figure 19: Correlation functions of the Rouse-mode amplitudes for the modes $p = 1 - 4$ of Gaussian polymers. The chain lengths are $N_m = 20$ (right) and $N_m = 40$ (left).

15 Microswimmers

Life at low Reynolds numbers is quit different from our everyday experience, as has already be recognized by Purcell [28] several decades ago. Low Reynolds numbers ($R_e = \rho v L / \eta$) can either be achieved by small objects or at very high viscosity. Hence, a microorganism experiences a similar dynamics as a human swimming in a very viscous honey. Since inertia effects are negligible, forward motion stops immediately when the motor driving the object forward stops. Therefore, a continuous action of a motor is necessary to maintain motion.

The time-reversal symmetry of the Stokes equation implies another fundamental consequence, which is denoted as 'scallop theorem' by Purcell: To achieve propulsion at low Reynolds number in simple fluids (i.e., Newtonian fluids), a swimmer must deform in a *none invariant* manner under time-reversal. It means that just by opening and closing its two shells, a mussel cannot move forward. A non-time reversal sequence of moves is required to generate motion.

15.1 Swimming of Bacteria

Some bacteria, such as Escherichia coli (E. coli) and Salmonella, swim by rotating helical filaments called flagella. Several of these flagella are attached to the cell body. By rotating the flagella, a bundle is formed, which drives the bacteria forward.

The bacteria swim in a 'run-and-tumble' motion as illustrated in Fig. 21. This is only possible by hydrodynamic interactions, which are essential, e.g., for bundle formation.

Essential for swimming by flagella is the anisotropy of the hydrodynamic friction of a *slender body* [29]. As pointed out in section 12.2.3, the friction of a rod is different parallel and perpendicular to its orientation. As illustrated in Fig. 22, by the motion in the direction of $\boldsymbol{u}$, a force is induced in the direction $\boldsymbol{f}_{\text{prop}}$. This can easily be demonstrate. According to Eqs. (391), (392), friction coefficients parallel and perpendicular to a rodlike segment can be defined: $\xi_{\perp,\|} = k_B T / D_{\perp,\|}$. The frictional force due to the velocity $\boldsymbol{u}$ is then

$$\boldsymbol{f} = -\xi_\| \boldsymbol{u}_\| - \xi_\perp \boldsymbol{u}_\perp.$$

Introducing polar coordinates, we find

$$\boldsymbol{u}_\perp = u_\perp \begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix}, \boldsymbol{u}_\| = u_\| \begin{pmatrix} -\sin\theta \\ \cos\theta \end{pmatrix}$$

Hence

$$\boldsymbol{f}_{\text{prop}} = \left(\xi_\| u_\| \sin\theta - \xi_\perp u_\perp \cos\theta \right) \boldsymbol{e}_x = \left(\xi_\| - \xi_\perp \right) u \sin\theta \cos\theta \boldsymbol{e}_x,$$
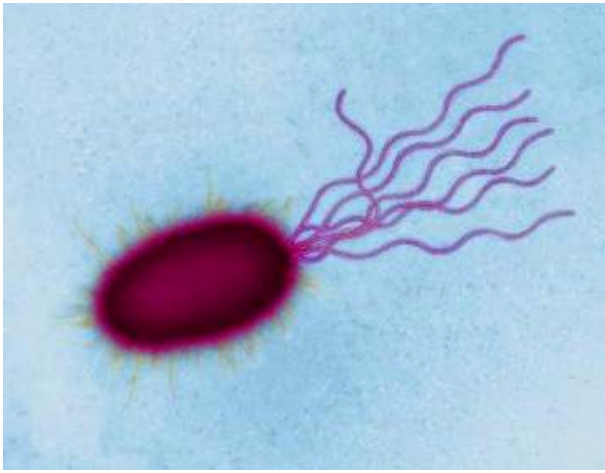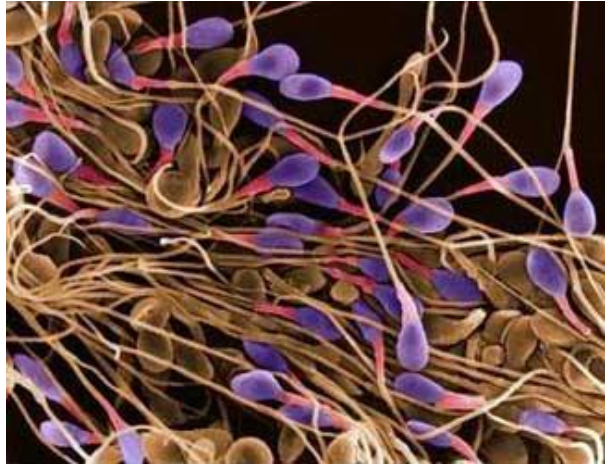
with $u_\perp = u \sin\theta$ and $u_\| = u \cos\theta$.

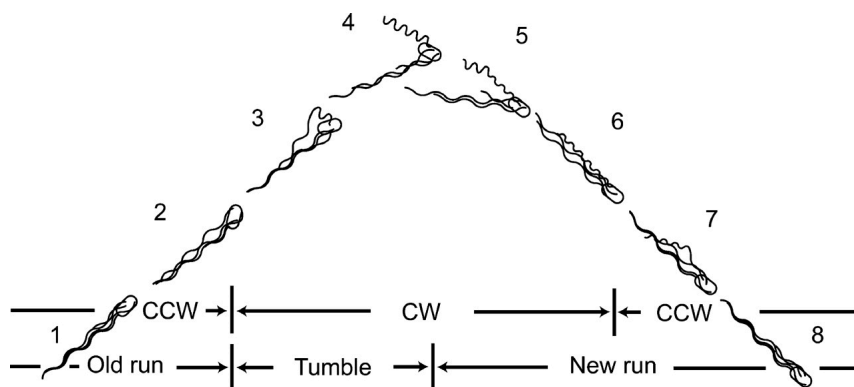Figure 20: Various microswimmers: (top) sperm, (middle) E. coli, (bottom) Clamydomonas.

Figure 21: Sequence of events in a tumble caused by the reversal of a single motor. From left to right: 1, a bacterium swimming along its original trajectory with all left-handed normal filaments; 2, a motor reversal (CCW (counter-clockwise) to CW (clockwise)) causing the filament to start unbundling and the cell body to deflect slightly; 3, initiation of the transformation of the filament from the left-handed normal form to the right-handed semicoiled form and the beginning of a large deflection of the cell body opposite the previous small deflection; 4, complete transformation of the filament to the semicoiled form and reorientation of the cell along a new trajectory; 5, movement of the cell along the new trajectory, propelled by a normal bundle turning CCW and a semicoiled filament turning CW which has partially transformed to the right-handed curly 1 form; 6, complete conversion of the filament to the curly 1 form, which is flexible enough to twist loosely around the bundle; 7, the motor reversing again (CW to CCW), causing the curly 1 form to revert to normal; and 8, after the filament has rejoined the bundle [30].
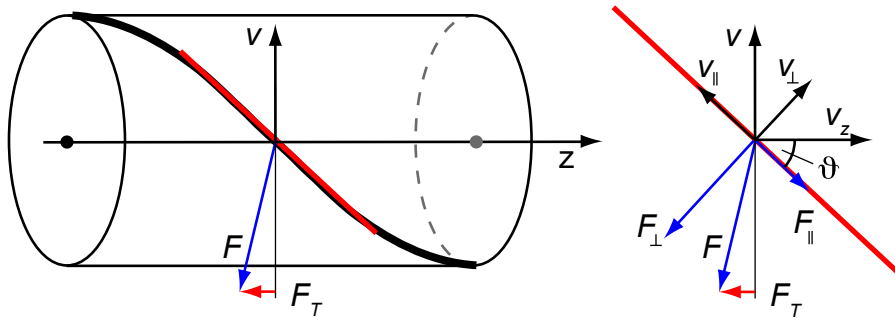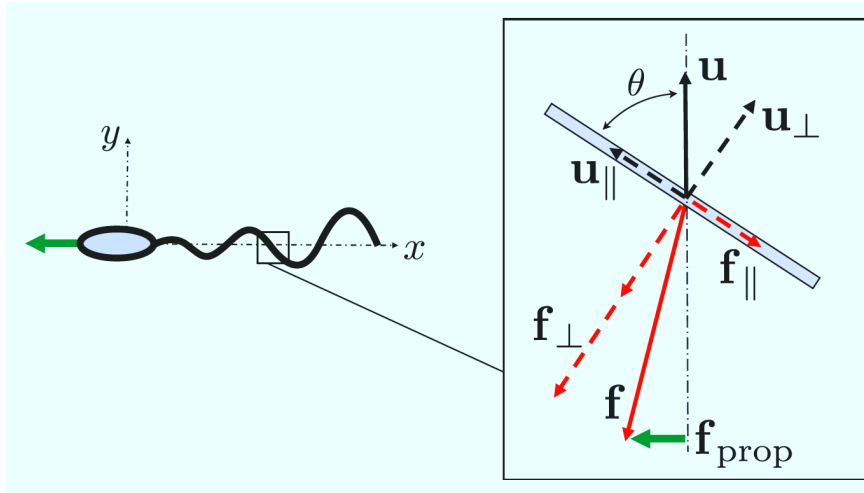
Figure 22: Drag-based thrust: drag anisotropy provides a means to generate forces perpendicular to local actuation [29].

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