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Lecture on

Dynamics of Soft-Matter Systems

Contact: klapp@physik.tu-berlin.de

Scope of this lecture:

Understanding theoretical concepts to describe the dynamical behavior of classical soft-matter (soft-condensed matter)

↳ - colloidal suspensions: (nano-micronsized particles in a solvent)
difference to atomic fluids!

- liquid crystals
- other anisotropic fluids such as ferrofluids
- polymers (more complicated, not in focus here)
- membranes, vesicles, ... (mesoscale objects)

„soft" $\hat{=}$ systems are mechanically deformable, i.e. very sensitive to mechanical forces and generally, to external fields!

„Condensed"

→ interactions between constituents are important!
→ phase transitions, structure formation in and out of equilibrium

difference to "hard condensed matter":

thermal fluctuations are important!
⟺ relevant energy scale ~ $k_B T$
interesting physics occurs at room temperature!

→ no quantum effects!

What kind of dynamics ??

- Equilibrium dynamics
  (relaxation into equilibrium, fluctuations around equilibrium states)

  examples:
  - Brownian motion 
  - Dynamics of phase separation
    (after quench into two-phase region

- Driven Systems

  → true non-equilibrium !

  e.g shear flow

<u>Theoretical concepts to be used</u> :

- a few concepts from the theory of stochastic processes
  (Markov, Master-eq...)

- Langevin- and Fokker-Planck equations
  (FP)

  ↳ Dynamics on the particle level, solvent is already "integrated out"!

  ↳ Dynamics on the level of a probability density for "relevant" degrees of freedom

- Dynamical Density Functional theory :

  special form of a FP equation

  → involves a one-particle density and a special closure relation for dynamical correlations

→

- Dynamical equations for order parameters
  (conserved and non-conserved)
  (classification after Hohenberg / Halperin)
  applications: magnetization in ferrofluids, order parameter of liquid crystals
- How to derive Langevin-like equations:

  Mori-Zwanzig formalism,
  memory effects

I. Elements from the theory of stochastic processes

Recall:
~~Why do~~ we need stochasticity at all ??

Remember: Consider systems at room temperature

→ thermal fluctuations of the molecules in the liquid are important !!

specifically in a colloidal system.

frequent collisions of solvent molecules with the colloidal particles ($\sim 10^{21}$ per second!)

→ irregular "Brownian" motion of colloidal particles!!

⇒ translational/rotational motion corresponds to a stochastic process!

general property of a stochastic process

Knowledge about the history of the system (e.g. particle positions at earlier times) does not determine its time evolution at future times

(different from Newton!!)

e.g. the position in D=1

Consider now system with 1 random variable x and discrete

To characterize the process, consider the joint probability density

$$P(x_1 t_1; x_2 t_2; \ldots\ldots)$$

Probability, that x has value x_1 at time t_1
x_2 " " t_2
⋮

and the conditional probability

$$P(\overbrace{x_{n+1}, t_{n+1}}^{\text{future}} | \overbrace{x_1 t_1; x_2 t_2; \ldots}^{\text{history}}; \overbrace{x_n t_n}^{\text{presence}})$$

Probability for the occurrence of x_{n+1} at time t_{n+1}, if $x = x_1$ at t_1, $x = x_2$ at t_2, ...)

The two probabilities are related by

$$P(x_{n+1}, t_{n+1} | x_1 t_1; \ldots, x_n t_n) = \frac{P(x_1 t_1; x_2 t_2; \ldots x_n t_n; x_{n+1} t_{n+1})}{P(x_1 t_1; \ldots; x_n t_n)}$$

The probabilities allow for a classification of stochastic processes!

a) Purely random process:

$$p(x_1t_1; \dots ; x_nt_n) = p(x_1t_1)\,p(x_2t_2) \dots p(x_nt_n)$$

$$\Rightarrow p(x_{n+1}t_{n+1} \mid x_1t_1; \dots, x_nt_n) = p(x_{n+1}, t_{n+1})$$

Complete decoupling, no correlations between the system's behavior at different times!

b) Markov-Process

$$p(x_{n+1}, t_{n+1} \mid x_1t_1; \dots ; x_nt_n)$$
$$= p(x_{n+1}, t_{n+1} \mid x_n, t_n)$$ ← often called "transition probability"

⇒ future is determined only by the presence, not by the (full) history !!

⇒ stochastic process "without memory"

Consequence for joint probability: decoupling into products of transition probabilities

⇒ "Markov chain"

special case: stationary Markov proc.

$p(x_{n+1}, t_{n+1} \mid x_n, t_n)$

c) Non-Markovian processes

— the history is important

$\Rightarrow$ Memory effects!!

Examples:

supercooled liquids, (systems close to a glass transition); anomalous transport of colloids (subdiffusion)

From now on we focus on <u>Markov processes</u> (justification later!!)

there are 2 important equations for such processes which we will briefly discuss:

- Chapman–Kolmogorov equation
- (Pauli–) Master equation

Chapman-Kolmogorov

Consider Markov process involving three time steps

joint probability:

general def. of conditional probabilities

$$P(x_1t_1; x_2t_2; x_3t_3) = p(x_3t_3 | x_1t_1; x_2t_2) \cdot p(x_1t_1; x_2t_2)$$

$$= p(x_3t_3 | x_1t_1; x_2t_2) \cdot p(x_2t_2 | x_1t_1) \cdot p(x_1t_1)$$

$$= p(x_3t_3 | x_2t_2) \cdot p(x_2t_2 | x_1t_1) \cdot p(x_1t_1) \quad (*)$$

Markov

Assume that the variable x is continuous and integrate over x_2 (otherwise, if x_2 is discrete, sum up)

$$\rightarrow P(x_1t_1; x_3t_3) \equiv \int dx_2 \, P(x_1t_1; x_2t_2; x_3t_3)$$

$$\overset{(*)}{=} \int dx_2 \, p(x_3t_3 | x_2t_2) \, p(x_2t_2 | x_1t_1) \cdot p(x_1t_1)$$

divide by $p(x_1t_1)$

$\longrightarrow$

Chapman–Kolmogorov

$$\Rightarrow \boxed{p(x_3 t_3 | x_1 t_1) = \int dx_2 \, p(x_3 t_3 | x_2 t_2) \cdot p(x_2 t_2 | x_1 t_1)}$$

the transition probability from the initial state x_1 (at t_1) to the final state x_2 (at t_2) is given by the product of the transition probabilities involving intermediate states, integrated over all these intermediate states!

Question:

How does the probability density evolve in time?

Use Taylor expansion of the transition probability in the time difference $\Delta t = t_{i+1} - t_i$

define:

$$\frac{\partial}{\partial t} p(x_3 t_3 | x_1 t_1) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \Big(p(x_3 t_3 | x_1 t_1) - p(x_3 t_3 - \Delta t | x_1 t_1) \Big)$$

$$\boxed{\frac{\partial}{\partial t_3} p(x_3 t_3 | x_1 t_1) = \int dx_2 \Big[\overbrace{W(x_3 ; x_2 t_3)}^{\text{transition rate (probability per unit of time)}} P(x_2 t_3 | x_1 t_1) - W(x_2 ; x_3 t_3) P(x_3 t_3 | x_1 t_1) \Big]}$$

final state, initial state

Pauli-Master equation

multiply both sides by $p(x_1 t_1)$ and integrate over x_1

(use: $\int dx_1 \, p(x_3 t_3 | x_1 t_1) \, p(x_1 t_1) = \int dx_1 \underbrace{p(x_1 t_1 ; x_3 t_3)}_{\text{joint probability}} = p(x_3 t_3)$

$$\Rightarrow \frac{\partial}{\partial t_3} p(x_3 t_3) = \int dx_2 \Big[W(x_3 ; x_2 t_3) p(x_2, t_3) - W(x_2 ; x_3 t_3) p(x_3, t_3) \Big]$$

$\longrightarrow$

simpler notation:

$$t_3 \to t \,, \quad x_3 \to x \,, \quad x_2 \to x'$$

$$\boxed{\frac{\partial}{\partial t} p(x,t) = \int dx' \left[W(x; x' t)\, p(x' ; t) - W(x'; x, t)\, p(x,t) \right]}$$

Master equation

First term on the rhs:

→ increase of probability due to transitions from states x' to x

Second term:

→ decrease of probability due to transitions away from x

Remarks

- Markovian character: reflected by the fact that only one time (t) occurs, no integral over many times !!
- How to calculate transition probabilities?
  E.g. Quantum mechanics (Fermi's golden rule)
  $W_{mn} = \frac{2\pi}{\hbar} |\langle m | \hat{V} | n \rangle|^2 \delta(E_m - E_n \pm \hbar\omega)$

  otherwise: E.g. Kramers rate

Stationary states :

$$\Longleftrightarrow \quad \frac{\partial}{\partial t} p(x,t) = 0$$

$$\underbrace{\int dx'}_{\text{or sum for discrete states}} \left[W(x;x' t)\, P(x',t) - W(x';x,t)\, P(x,t) \right] = 0$$

for $P(x',t) = P^{stat}(x')$
$P(x,t) = P^{stat}(x)$

Microreversibility / Detailed balance

not only the integral / sum vanishes but also the integrand → defines true equilibrium !

$$W(x;x' t)\, P^{eq}(x') = W(x';x,t)\, P^{eq}(x)$$

$$\rightarrow \frac{W(x;x' t)}{W(x';x,t)} = \frac{P^{eq}(x)}{P^{eq}(x')}$$

e.g. canonical ensemble

$$= e^{-(H(x)-H(x'))/k_B T}$$

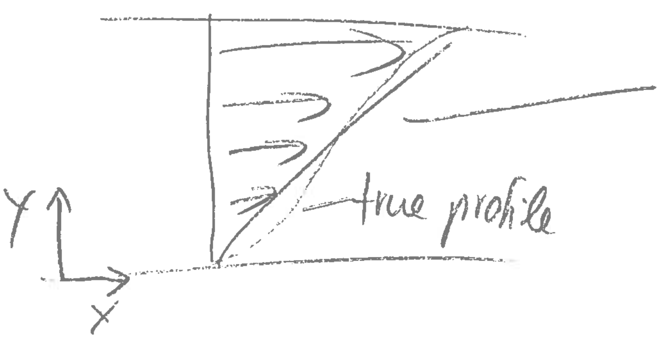
Basis of the metropolis algorithm !!

note:

microreversibility / detailed balance is more than stationarity !!

example of a stationary state out of equilibrium

shear flow (plane Couette flow)



$\underline{v}^{ext} = \gamma \cdot y \, \hat{\underline{e}}_x$

shear rate

- velocity profile leads to current $j^{ext}(\underline{r},t) = p(\underline{r},t)\underline{v}^{ext}$
  non-vanishing
- for not too large shear rate the system becomes stationary with constant velocity profile $\underline{v}^{true}(y)$

Another formulation of stationarity / equilibrium

$$\frac{\partial}{\partial t} p(\underline{r},t) = - \nabla j(\underline{r},t) \qquad \text{Fokker/Planck equation}$$

stationarity: $\nabla j = 0$

equilibrium: $j = 0$

II. Brownian motion

history: 1827 Robert Brown detects irregular motion (via microscope) of "pollen" in water

trajectory

one also says: "diffusive behavior" of the particle!

1905: Interpretation of the Brown discovery by A. Einstein

→ Pollen particles collide with solvent particles ($\sim 10^{21}$ times/second)

→ random walk!
→ differential equation for probability density

notice: time scale of solvent particles

$\sim 10^{-14}\,s$ ← typical relaxation time

$\ll \underbrace{10^{-9}\,s}_{\text{typical relaxation time of colloids}}$ $(= 1\,ns)$

1906: parallel theoretical description by Marian Smoluchowski

1908: alternative theoretical approach by Paul Langevin
→ stochastic differential equation

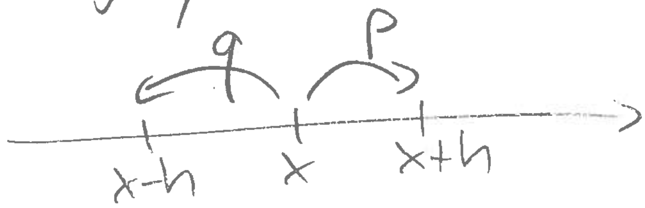
1923: Mathematical formulation by Norbert Wiener
→ "Wiener Process"

I.1.
Diffusion equation

– derived from a random-walk model

Consider motion in 1D (along x-axis), discrete positions! → jumps!

let p: probability to jump to the right
q: " " " " " left
h: distance of a jump



$\boxed{p+q=1}$

"random" walk: jumps are statistically independent!

Consider position at time t after n jumps

assume: particle has jumped m times to the right
$(n-m)$ " " " left

$$\Rightarrow x(t) = mh + (n-m)(-h) = h(2m-n)$$

Corresponding probability distribution: (binomial!)

$$P(x,t) = \binom{n}{m} p^m q^{n-m} = \frac{n!}{m!(n-m)!} p^m q^{n-m}$$

↑ probability (density) that particle is at x at time t

question: time evolution of this probability?

starting point:

$$P(x, \underbrace{t+\Delta t}_{\text{next timestep after present one}}) = p\, P(x-h, t) + q\, P(x+h, t)$$

„transition probability" left -> right

transition probability right -> left

(note: this is an application of the relation

$$p(x,t) = \int dx'\, \underbrace{P(x't'; xt)}_{\text{joint probability}}$$

$$= \underbrace{\int dx'}_{\text{here: sum over 2 discrete states}} P(xt \,|\, x't') \cdot p(x't'))$$

$$\Rightarrow P(x, t+\Delta t) - P(x,t) = p\, P(x-h, t) + q\, P(x+h, t) - \underbrace{P(x,t)}_{p+q=1}$$

$$= p\, P(x-h,t) - p\, P(x,t) + q\, P(x+h,t) - q\, P(x,t)$$

now assume that we can perform Taylor expansion of $P(x,t)$ in x and t!

($\Leftrightarrow$ Δt and h are small!)

define:

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

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

$$\Rightarrow \frac{\partial}{\partial t} P(x,t)\, \Delta t + O(\Delta t^2)$$

$$= -ph \frac{\partial}{\partial x} P(x,t) + qh \frac{\partial}{\partial x} P(x,t)$$

$$+ \frac{p}{2} h^2 \frac{\partial^2}{\partial x^2} P(x,t) + \frac{q}{2} h^2 \frac{\partial^2}{\partial x^2} P(x,t)$$

$$+ O(h^3)$$

$$\approx -(p-q)\, h \frac{\partial}{\partial x} P(x,t) + \frac{h^2}{2} \frac{\partial^2}{\partial x^2} P(x,t)$$

truncate after 2. Order

define: $v^D = \frac{(p-q) \cdot h}{\Delta t}$ "drift velocity"

and assume that $\frac{h^2}{2 \Delta t} \to \text{const} = D$ "diffusion constant"

$$\Rightarrow \boxed{\frac{\partial}{\partial t} P(x,t) = -v^D \frac{\partial}{\partial x} P(x,t) + D \frac{\partial^2}{\partial x^2} P(x,t)} \quad (*)$$

special case:

$p = q \implies$ no drift

$$\overset{(*)}{\implies} \quad \frac{\partial}{\partial t} P(x,t) = D \frac{\partial^2}{\partial x^2} P(x,t) \qquad (1D)$$

or
$$\boxed{\begin{aligned} \frac{\partial}{\partial t} P(\underline{r},t) &= D \nabla^2 P(\underline{r},t) \\ &= D \, \Delta P(\underline{r},t) \end{aligned}} \qquad (3D)$$

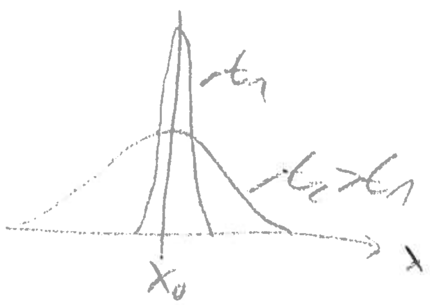
standard diffusion equation!

mathematically:
standard partial differential equation, linear

$\rightarrow$ solve by Fourier transformation

assume: $P(\underline{r}, t=0) = \delta(\underline{r} - r_0)$

$$\implies P(\underline{r},t / \underline{r}_0 0) = \frac{e^{-(r-r_0)^2/4Dt}}{(4\pi D t)^{3/2}}$$



normalized Gaussian distribution!!

Consequences:

$$\langle \underline{r}(t) \rangle \equiv \int d\underline{r}\ (\underline{r} - \underline{r}_0)\ P(\underline{r}, t \mid \underline{r}_0, 0)$$

$$= \underline{r}_0 = \text{const}$$

$\Rightarrow$ Center of mass of the "package" does not move

$$\langle (\underline{r}(t) - \underline{r}(0))^2 \rangle = \langle (\Delta \underline{r}(t))^2 \rangle$$

mean-squared displacement

$$= \underbrace{3}_{\text{in 3D}} \cdot 2Dt = \underline{\underline{6Dt}}$$

linear time dependence is characteristic feature of diffusive behavior!

Relation between diffusion and friction

background:

<u>phenomenological interpretation</u> of the diffusion equation

start with continuity equation

$$① \quad \frac{\partial}{\partial t} n(\underline{r},t) + \nabla \cdot \underline{j_N(\underline{r},t)} = 0$$

particle density (plays here the role of $P(\underline{r},t)$)

current density (through surface of the volume element $d\underline{r}$ around $\underline{r}$)

Combine with Fick's law

$$② \quad j_N(\underline{r},t) = -D \nabla n(\underline{r},t)$$

„macroscopic law": means that density gradient leads to a current

$$①+② \Rightarrow \boxed{\frac{\partial}{\partial t} n(\underline{r},t) = D \nabla^2 n(\underline{r},t)}$$

diffusion equation

now conside the case that there is an additional contribution to the current, that is, a "drift"

drift velocity

$$j^{total}(\underline{r},t) = \underbrace{-D\nabla n(\underline{r},t)}_{\text{Fick's law}} + \underbrace{n(\underline{r},t)\,\underline{v}^D(\underline{r},t)}_{j^{Drift}(\underline{r},t)}$$

relation to friction.

viscosity of the solvent

radius of (spherical) particle

force on a particles pulled through a viscous fluid, e.g. gravitation

$$\underline{F}^{Stokes} = -6\pi\eta R\underline{v}^D$$

$$\Leftrightarrow \underline{v}^D = -\frac{\underline{F}}{6\pi\eta R}$$

$$\Rightarrow j(\underline{r},t) = -D\nabla n(\underline{r},t) - n(\underline{r},t)\frac{\underline{F}}{6\pi\eta R}$$

Combine with continuity equation (1)

$$\Rightarrow \frac{\partial}{\partial t} n(\underline{r},t) + \nabla\left(\frac{\underline{F}}{6\pi\eta R} - D\nabla\right) n(\underline{r},t) = 0$$

now specialize to thermal equilibrium

$$j^{total}(\underline{r},t) = 0 \Leftrightarrow n(\underline{r},t) = \text{const}$$

also note:
Einstein relation is an example for the fluctuation-dissipation theorem

$$D = \frac{\langle (\Delta \underline{r}(t))^2 \rangle}{6t} \longleftrightarrow \eta$$

positional fluctuations

friction
→ dissipation !!

example of a transport coefficient: describes response to external perturbation

What about rod-like particles ?!

Diffusion equation for a system with rotational degrees of freedom:

introduce: $P(\underline{r}, \underline{u}, t)$ probability distribution to find a particle at position $\underline{r}$ with orientation $\underline{u}$ at time t

orientation of a particle (assumed to be uniaxial, e.g. ellipsoids, spherocylinders, ferromagnetic particles)

$$\Rightarrow \quad \frac{n(\underline{r})}{6\pi\eta R}\underline{F} - D\nabla n(\underline{r}) = 0 \qquad (*)$$

neglect time dependence since we are in equilibrium

also use

$$\underline{F} = -\nabla U(\underline{r}) \qquad \text{(e.g. gravitation)}$$

and $n(\underline{r}) \sim e^{-\beta U(\underline{r})}$ $\qquad (\beta = 1/k_B T)$

$\Rightarrow$ from $(*)$

$$\frac{-n(\underline{r})}{6\pi\eta R}\nabla U(\underline{r}) = D\, n(\underline{r})\left(-\beta\nabla U(\underline{r})\right)$$

$$\Rightarrow \quad \boxed{D = \frac{k_B T}{6\pi\eta R}}$$

Relation between diffusion and friction coefficients!!

often called "Einstein relation"

assume:

$$\underbrace{\rho(\underline{r},t)}_{\text{number density}} = \int \underbrace{d\underline{u}}_{\int d\omega = \int d\vartheta \sin\vartheta \int d\varphi} P(\underline{r},\underline{u},t)$$

similarly: $\psi(\underline{r},t) = \int d\underline{r}\, P(\underline{r},\underline{u},t)$ orientational distribution

normalization: $\int d\underline{u} \int d\underline{r}\, P(\underline{r},\underline{u},t) = \underbrace{\int d\underline{r}\, \rho(\underline{r},t)}_{= \int d\underline{u}\, \psi(\underline{r},t)} = N$

Diffusion equation (see, e.g. book of Dhont)

$$\boxed{\frac{\partial}{\partial t} P(\underline{r},\underline{u},t) = \nabla \cdot \Big(D_{\parallel} \overbrace{\underline{u}\cdot\underline{u}}^{\text{Tensor with components } u_\alpha u_\beta} + D_{\perp} (\hat{1} - \underline{u}\,\underline{u}) \Big) \cdot \nabla P(\underline{r},\underline{u},t) + D_{rot} \hat{R}^2 P(\underline{r},\underline{u},t)}$$

remarks:

- translational part: reflects the fact that diffusion along the axis of the particles can be different from diffusion perpendicular to the axis

∘ rotational part. Definition of operator $\hat{R}$:

$$\hat{R} = \underline{u} \times \nabla_{\underline{u}}$$

note: This generalized diffusion equation neglects the presence of so-called hydrodynamic interactions! (solvent-mediated) (HI)

HI's would lead to a coupling between translational and rotational motion!

Brownian motion on the particle level

a) spherical particle, pure translational motion

starting point.
Newton's equation of motion with friction (no noise)

$$m\ddot{\underline{r}} = m\dot{\underline{v}} = -6\pi R\eta \underline{v} \qquad \text{Stokes friction}$$

solution: $\underline{v}(t) = \underline{v}(t_0)\, e^{-\gamma(t-t_0)}$

where $\gamma := \dfrac{6\pi R\eta}{m}$

$\rightarrow$ velocity decays to zero exponentially!

but: this is not what one observes in a true colloidal suspension. Instead: irregular thermal motion!

Ansatz (Langevin)

$$\boxed{m\dot{\underline{v}}(t) = m\ddot{\underline{r}}(t) = -\gamma m \underline{v}(t) + \underline{f}(t)} \quad (*)$$

and $\boxed{\dot{\underline{r}}(t) = \underline{v}(t)}$

$-\gamma m \underline{v}(t)$: friction

$\underline{f}(t)$: stochastic force ("random force" or "noise")

where $\langle f_\alpha(t) \rangle = 0$, $\alpha = x, y, z$

average over the distribution of the random force: i.e. $\langle f \rangle = \int df\, f\, P(f,t)$ average over note:

- (*) is mathematically a stochastic differential equation $\Rightarrow$ both $\underline{r}(t)$ and $\underline{v}(t) = \dot{\underline{r}}(t)$ are random variables!

- there are (so far) no particle interactions (but these can be incorporated)

- (*) is often called "underdamped" Langevin equation
$\Rightarrow$ in contrast to "overdamped" $\Leftrightarrow$ $m\ddot{\underline{r}}$ is negligible

$$\Leftrightarrow \quad 0 = -\gamma m \underline{v} + \underline{f}(t)$$

$$\Leftrightarrow \quad \dot{\underline{r}}(t) = \frac{1}{\gamma m}\, \underline{f}(t)$$

we will come back to that point later!

- Langevin's crucial assumption regarding the stochastic force:

$$\langle f_\alpha(t)\, f_\beta(t') \rangle = \int d\underline{f} \int d\underline{f}'\, f_\alpha f_\beta'\, P_2(\underline{f}, t; \underline{f}', t')$$

$$\stackrel{!}{=} \Gamma\, \delta_{\alpha\beta}\, \delta(t-t')$$

White noise

$\rightarrow$ different force components are independent

<u>and</u>: forces at different times are independent!

physical background:

typical relaxation time in the solvent: $\tau_s \approx 10^{-14}\,s$
" " " of the particles $\tau_p \approx 10^{-9}\,s$

$\Rightarrow \tau_s \ll \tau_p$

note: τ_p can be identified with γ^{-1}

$\Rightarrow$ The random forces induced by collisions with solvent particles change so fast, that their values at different times are uncorrelated!!

(note: This neglects feedback effects due to momentum transfer on the colloids during the collisions)

Corresponding power spectrum:

$$S_{\alpha\beta}(\omega) \equiv \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau} \langle f_\alpha(0)\, f_\beta(\tau)\rangle$$

definition

$$= \Gamma\, \delta_{\alpha\beta} \int d\tau\, e^{-i\omega\tau}\, \delta(\tau)$$

$$= \Gamma\, \delta_{\alpha\beta} = \text{const}$$

independent of frequency!

$\Leftrightarrow$ typical for white noise

Solution of the Langevin equation (for a spherical particle)

$$m\dot{\underline{v}}(t) = -\gamma m \underline{v}(t) + \underline{f}(t)$$

$$\Rightarrow \dot{\underline{v}}(t) = -\gamma \underline{v}(t) + m^{-1}\underline{f}(t)$$

mathematically: inhomogeneous linear differential equation for $\underline{v}(t)$

Solution: general solution of the homogeneous problem (i.e., $\underline{f}=0$) plus special solution of inhomogeneous problem

$$\Rightarrow \underline{v}(t) = \underbrace{\underline{v}(t=t_0)}_{\underline{v}_0} e^{-\gamma(t-t_0)} + \underline{g}(t)$$

where $\dot{\underline{g}}(t) \overset{!}{=} -\gamma \underline{g} + m^{-1}\underline{f}$

ansatz: $\underline{g} = \underline{u}\, e^{-\gamma(t-t_0)}$

insert $\Rightarrow \dot{\underline{u}} = e^{+\gamma(t-t_0)}\underline{f}\cdot m^{-1}$

$$\Rightarrow \underline{u} = \frac{1}{m}\int_{t_0}^{t} dt'\, e^{+\gamma(t-t_0)}\underline{f}$$

$$\Rightarrow \underline{v}(t) = \underline{v}_0\, e^{-\gamma(t-t_0)} + e^{-\gamma(t-t_0)}\int_{t_0}^{t} dt'\, e^{\gamma(t-t_0)}\underline{f}(t')\, m^{-1}$$

Consequences

- $\langle \underline{v}(t) \rangle = \langle \underline{v}_0 \rangle e^{-\gamma(t-t_0)} + e^{-\gamma(t-t_0)} \int dt' e^{\gamma(t-t^0)} \underbrace{\langle f(t) \rangle}_{\text{zero!!}}$

average over stochastic force with the condition, that $\langle \underline{v}_0 \rangle \stackrel{!}{=} \underline{v}_0$

$\Rightarrow \langle \underline{v}(t) \rangle = \underline{v}_0 e^{-\gamma(t-t_0)}$ as in the case without noise!

note: For $t \to \infty$ we therefore find $\langle v \rangle \to 0$
(initial velocity disappears)

— consistent with our expectation for a system, where there are no external driving forces!!

Velocity autocorrelation function

- $\langle v_\alpha(t_1) v_\beta(t_2) \rangle$ (we skip the detailed calculation here)

$= v_{\alpha,0} v_{\beta,0} e^{-\gamma(t_1+t_2)}$

$+ \delta_{\alpha\beta} \frac{\Gamma}{2\gamma m^2} \left(e^{-\gamma|t_2-t_1|} - e^{-\gamma(t_1+t_2)} \right)$

special cases:

- $t_1 = t_2 = t$, $\alpha = \beta$

$$\langle v_\alpha^2(t) \rangle = v_{\alpha,0}^2 e^{-2\gamma t} + \frac{\Pi}{2\gamma}\left(1 - e^{-2\gamma t}\right)$$

$$\xrightarrow[t \to \infty]{} \frac{\Pi}{2\gamma m^2}$$

in this limit the initial velocity becomes irrelevant!

- $t_1 = t_2$, $\alpha \neq \beta$ $\quad \langle v_\alpha(t) v_\beta(t) \rangle \xrightarrow[t \to \infty]{} \delta_{\alpha\beta} \frac{\Pi}{2\gamma m^2}$ (**)

- $t_2 > t_1$ (or vice versa)
  $t_2 \to \infty$

e.g., $t_1 = 0$, $t_2 = t$

$$\langle v_\alpha(0) v_\beta(t) \rangle = v_{\alpha,0} v_{\beta,0} e^{-\gamma t} + \delta_{\alpha\beta} \frac{\Pi}{2\gamma m^2}\left(e^{-\gamma t} - e^{-\gamma t}\right)$$

$$= v_{\alpha,0} v_{\beta,0} e^{-\gamma t}$$

We see:
- the time scale for the decay of $\underbrace{\text{velocity correlations}}_{}$ (i.e., the relaxation time) is γ^{-1}
- In the limit $t \to \infty$ the velocity correlations decay to zero!

We now specialize to systems which approach for long time equilibrium!

here we know:

$$\frac{m}{2} \langle v_\alpha v_\beta \rangle_{eq} = \delta_{\alpha\beta} \frac{k_B T}{2}$$

time average or ensemble average, e.g. in the canonical ensemble

Combine that with (**)

$$\langle v_\alpha(t) v_\beta(t) \rangle \xrightarrow[t\to\infty]{} \langle v_\alpha v_\beta \rangle_{eq}$$

$$= \delta_{\alpha\beta} \frac{k_B T}{m}$$

$$\Rightarrow \quad \delta_{\alpha\beta} \frac{\Gamma}{2\gamma m^2} \overset{!}{=} \delta_{\alpha\beta} \frac{k_B T}{m}$$

friction

$$\Rightarrow \quad \boxed{\Gamma = 2\gamma k_B T m}$$

(squared) strength of random force

! "Einstein relation"

Interpretation:

- stochastic force (collisions with solvent) and friction are not independent – rather they must balance each other!

  (in an equilibrium system)

Consequences:

- random force-correlations:

$$\langle f_\alpha(t)\, f_\beta(t')\rangle = \Gamma' \delta_{\alpha\beta}\, \delta(t-t')$$

$$\stackrel{!}{=} 2\gamma k_B T m\, \delta_{\alpha\beta}\, \delta(t-t')$$

- Relation to diffusion coefficient:

we already had: $\gamma = \dfrac{6\pi R\eta}{m}$, $D = \dfrac{k_B T}{6\pi\eta R}$

$$\Rightarrow \gamma = \frac{k_B T}{Dm}$$

$$\Rightarrow \Gamma = 2\gamma k_B T m = \frac{2(k_B T)^2}{D}$$

- Positional correlations

Consider first: $\Delta \underline{r}(t) = \underline{r}(t) - \underline{r}_0 \leftarrow \underline{r}(t=0)$

$$= \int_0^t dt' \, \underline{v}(t')$$

general (follows from the relation $\dot{\underline{r}} = \underline{v}$)

from the Langevin equation it follows that:

$$\langle \Delta \underline{r}(t) \rangle = \int_0^t \langle \underline{v}(t) \rangle_0 \, dt = \frac{v_0}{\gamma}(1 - e^{-\gamma t}) \xrightarrow[t \to \infty]{} \frac{v_0}{\gamma} = \text{const}$$

average over noise at fixed $\underline{r}_0$ and $\underline{v}_0$

specialize to thermal equilibrium (and the case of no external drive)

$$\Rightarrow \langle \Delta \underline{r}(t) \rangle^{eq} \xrightarrow[t \to \infty]{} 0$$

mean-squared displacement:

$$\langle \Delta r_\alpha(t) \, \Delta r_\beta(t) \rangle^{eq}$$

$$= \dots = \delta_{\alpha\beta} \frac{2 k_B T}{m \gamma} \left(t - \frac{1}{\gamma}(1 - e^{-\gamma t}) \right)$$

skip calculation

(*)

long times:

$$t \gg \tau = \frac{1}{\gamma}$$

$$\Leftrightarrow \gamma t \gg 1$$

terms in ⊛:

$$\Rightarrow e^{-\gamma t} \approx 0$$

$$t - \frac{1}{\gamma} \approx t$$

$$\Rightarrow \langle \Delta r_\alpha(t) \Delta r_\beta(t) \rangle^{eq} \xrightarrow[t\to\infty]{} 2\, \delta_{\alpha\beta} \frac{k_B T}{m\gamma} t$$

linear time dependence!

use: $\gamma = \frac{k_B T}{D m}$

$$\Rightarrow \lim_{t\to\infty} \langle \Delta r_\alpha(t) \Delta r_\beta(t) \rangle^{eq} = 2\, \delta_{\alpha\beta} D t$$

and $\lim_{t\to\infty} \langle (\Delta \underline{r}(t))^2 \rangle^{eq} = \lim_{t\to\infty} \langle \sum_{\alpha=x,y,z} (\Delta r_\alpha(t))^2 \rangle$

$$= 6 D t$$

same as our old result from the diffusion equation!

short times:

use Taylor expansion of $e^{-\gamma t}$ in ⊛

$$\Rightarrow \langle (\Delta \underline{r}(t))^2 \rangle^{eq} = 3 \underbrace{\frac{k_B T}{m}}_{\langle v^2 \rangle^{eq}} t^2$$

„ballistic behavior"

question:

Formulation of the Langevin equation for rotational motion ??

II.2.b) Langevin equation for spheres with an internal degree of freedom, e.g. ferromagnetic colloid

σ  vector $\underline{\mu}(t)$ describing the permanent magnetic dipole moment

Diameter $\approx 10\,nm$

define: $\underline{u}(t) = \frac{\underline{\mu}(t)}{|\underline{\mu}|} = \underline{u}(t)$

Newton's equation for pure rotational motion:

$$\dot{\underline{u}}(t) = \frac{d}{dt}\underline{u}(t) = \underline{\omega} \times \underline{u}$$

angular velocity

$$I\,\dot{\underline{\omega}}(t) = \underline{T}(t)$$

momentum of inertia

torque

(note: for a non-spherical particle we had $\underline{\underline{I}}\,\dot{\underline{\omega}} = \underline{T}$

inertia tensor

introduce friction:

→ "frictional torque" (or "viscous torque") (instead of frictional force for translations)

$$\underline{T}^{visc} = -6\eta V \underline{\omega}$$

volume

plus (white) noise

$$\Rightarrow \boxed{I \frac{d}{dt} \underline{\omega}(t) = -6\eta V \underline{\omega} + \underline{T}^{rah}(t)} \quad (*)$$

where (as in the translational case)

$$\langle T_\alpha^{rah}(t) T_\beta^{rah}(t') \rangle = \Gamma^{rot} \delta_{\alpha\beta} \, \delta(t-t')$$

note: (*) looks fully equivalent to the corresponding translational equation!!

→ To fix Γ_{rot}, use the equipartition theorem for rotations.

Starting point is the kinetic energy

$$E^{kin} = \frac{1}{2} m \underline{v}_c^2 + \frac{1}{2} \underline{\omega} \, \underline{\underline{I}} \, \underline{\omega} \underset{\text{sphere!}}{=\!=} \frac{1}{2} m \underline{v}_c^2 + \frac{1}{2} I \underline{\omega}^2$$

$$\Rightarrow \frac{I}{2}\langle w_\alpha w_\beta \rangle_{eq} = \delta_{\alpha\beta}\frac{k_B T}{2}$$

From (*) one finds, in the long-time limit

$$\langle w_\alpha(t)\, w_\beta(t)\rangle \to \delta_{\alpha\beta}\frac{\Gamma^{rot}}{2\gamma_{rot} I^2}$$

where $\gamma_{rot} = \frac{6\eta V}{I}$

Combine:

$$\delta_{\alpha\beta}\frac{k_B T}{2}\frac{2}{I} \overset{!}{=} \delta_{\alpha\beta}\frac{\Gamma^{rot}}{2\gamma_{rot} I^2}$$

$$\Rightarrow \boxed{\Gamma^{rot} = 2\gamma^{rot} k_B T\, I}$$

From now on we focus on the overdamped limit

$\Leftrightarrow$ in (*) : $I\frac{d}{dt}\underline{w}(t) = 0$

$\Rightarrow$ (*) reduces to

$$\boxed{\underline{w} = \frac{1}{6\eta V}\underline{T}^{ran}(t) = \frac{I}{\gamma_{rot}}\underline{T}^{ran}(t)} \quad (**)$$

question: Dynamics of $\underline{u}(t) = \hat{\underline{\mu}}(t)$??

Recall:

$$\dot{\underline{u}} = \underline{\omega} \times \underline{u}$$

(this is equivalent to

$$\underline{\omega} = \underline{u} \times \frac{d\underline{u}}{dt}$$

since

$$\underline{u} \times \dot{\underline{u}} = \underline{u} \times (\underline{\omega} \times \underline{u}) = (\underline{u} \cdot \underline{u})\,\underline{\omega} - (\underline{u} \cdot \underline{\omega})\,\underline{u} = 1\,\underline{\omega} - 0 = \underline{\omega}$$)

⇒ from (**):

$$\boxed{\dot{\underline{u}} = \underline{\omega} \times \underline{u} = \frac{I}{\gamma_{rot}}\, \underline{\Gamma}^{ran}(t) \times \underline{u}}$$

note: Contrary to the (corresponding) translational equation, $\dot{\underline{r}} = \frac{m}{\gamma}\,\underline{f}(t)$,

the noise is now coupled to the dynamical variable itself! ⤳ „multiplicative noise" !

The above equation has been used, e.g, to study a ferrocolloid in an external time-dependent field

A. Engel, H. W. Müller, P. Reimann, A. Jung
Phys. Rev. Lett. 91, 060602 (2003)

$$\Rightarrow \quad \dot{\underline{u}} = \frac{1}{\gamma_{rot}}\, \underline{T}(t) \times \underline{u} + \underline{T}^{conservative} \times \underline{u}$$

where $\underline{T}^{conservative}(t) = -\underline{u} \times \nabla_{\underline{u}} U^{pot}(t)$

and $U^{pot} = -\mu\, \underline{u} \cdot \underline{H}(t)$

$$\Rightarrow \quad \underline{T}^{conservative} = \underline{u} \times \underline{H}(t)$$

external magnetic field

also note:

The vector equation can be simplified by introducing Euler angles

$$\underline{e} = (\sin\vartheta \cos\varphi,\ \sin\vartheta \sin\varphi,\ \cos\vartheta)$$

see A. Engel et al.

one finds:

$$\frac{\partial}{\partial t}\vartheta = \frac{1}{2\gamma_{rot}} \Gamma \cot\vartheta + \frac{1}{\gamma_{rot}} T_\vartheta(t)$$

$$\frac{\partial}{\partial t}\varphi = \frac{1}{\gamma_{rot}} \frac{1}{\sin\vartheta} T_\varphi(t)$$

where T_ϑ, T_φ are independent, δ-correlated variables

ote: In the second equation we have multiplicative noise. However, since the coupling term is independent on φ there is no Ito-Stratonovich dilemma when we go to the [illegible]

II.2.c) Langevin equations for a rod

consider first non-overdamped case

translations.

$$M\ddot{\underline{r}} = -\underline{\underline{G}}\cdot\dot{\underline{r}} + \underline{f}(t)$$

$$\dot{\underline{r}} = \underline{v}$$

where

unit vector!

$$\underline{\underline{G}} = \gamma_{\parallel} M \underline{u}\,\underline{u} + \gamma_{\perp} M (\underline{\underline{1}} - \underline{u}\,\underline{u})$$

note $\underline{v} \parallel \underline{u} \Rightarrow (\underline{u}\,\underline{u})\cdot\underline{v} = \underline{u}(\underline{u}\cdot\underline{v}) = \underline{v}$

$$\Rightarrow \underline{\underline{G}}\cdot\underline{v} = -\gamma_{\parallel} M \underline{v}$$

$\underline{v} \perp \underline{u} \Rightarrow \underline{\underline{G}}\cdot\underline{v} = -\gamma_{\perp} M \underline{v}$

rotations:

$$\underline{\underline{I}}\cdot\frac{d\underline{\omega}}{dt} = -6\eta V \underline{\omega} + \underline{T}(t)$$

(inertia tensor

$$\dot{\underline{u}} = \underline{\omega}\times\underline{u}$$

Solution

translational part:

$$\underline{v}(t) = \underline{v}_0\, e^{-\underline{\underline{\Gamma}}(t-t_0)} + \int_{t_0}^{t} dt'\, e^{\underline{\underline{\Gamma}}(t-t')}\, \underline{f}(t')$$

use: $$e^{\underline{\underline{A}}} = \sum_{n=0}^{\infty} \frac{1}{n!} \underline{\underline{A}}^n$$

and $$(\underline{\underline{\Gamma}})^n = \gamma_{\parallel}^n\, \underline{u}\underline{u} + \gamma_{\perp}^n\, (\underline{\underline{1}} - \underline{u}\underline{u})$$

$$\Rightarrow e^{-\underline{\underline{\Gamma}}(t-t_0)} = e^{-\gamma_{\parallel}(t-t_0)}\, \underline{u}\underline{u} + e^{-\gamma_{\perp}(t-t_0)}\, (\underline{\underline{1}} - \underline{u}\underline{u})$$

decoupling!
into parallel and perpendicular parts

$$\Rightarrow \underline{v}_{\parallel/\perp}(t) = \underline{v}_{0\,\parallel/\perp}\, e^{-\gamma_{\parallel/\perp} t} + \int_{t_0}^{t} dt'\, e^{\gamma_{\parallel/\perp}(t-t')}\, \underline{f}_{\parallel/\perp}(t')$$

where $\underline{f}_{\parallel} = \underline{u}\underline{u}\,\underline{f}$

$\underline{f}_{\perp} = (\underline{\underline{1}} - \underline{u}\underline{u})\,\underline{f}$

one then assumes that $\underline{f}_{\parallel}, \underline{f}_{\perp}$ are white noise
and $\langle \underline{f}_{\parallel} \cdot \underline{f}_{\perp} \rangle = 0$

$$\langle \underline{f}_{\parallel/\perp}(t) \cdot \underline{f}_{\parallel/\perp}(t') \rangle = \Gamma_{\parallel/\perp}\, \delta(t-t')$$

in thermal equilibrium (equipartition one obtains)

$$\Gamma_{\parallel} = 2\gamma_{\parallel} M k_B T \quad , \quad \Gamma_{\perp} = 2\gamma_{\perp} M k_B T$$

<u>rotational part</u>

see case b)

$$\Gamma^{rot} = 2 \cdot 6\eta V \, k_B T$$

$$(= 2\gamma_{rot} I \, k_B T \qquad \text{for a sphere, with } \gamma = \frac{6\eta V}{I}$$

<u>Note</u>:
so far, everything in the rotational motion seems to be analogous to rotations !!

but: consider the motion of $\underline{u}(t)$ (instead of $\underline{\omega}(t)$)

for simplicity, focus on overdamped state

$$\underset{\text{from II.2b)}}{\Longrightarrow} \quad \dot{\underline{u}} = \underline{\omega} \times \underline{u} = \frac{1}{6\eta V} \underline{T}^{ran}(t) \times \underline{u}$$

one finds (see book of Dhont!)

$$\langle \underline{u}(t) \rangle = \underline{u}(t_0)\, e^{-2 D_r t} \quad (*)$$

where $D_r = \dfrac{k_B T}{6 \eta V}$

and

$$\langle (\Delta \underline{u}(t))^2 \rangle = \langle (\underline{u}(t) - \underline{u}(0))^2 \rangle$$

$$= 2 (1 - e^{-2 D_r t})$$

- small times ($D_r t \ll 1$)

$$\langle (\Delta u(t))^2 \rangle = 4 D_r t$$

"diffusive behavior" on a two-dimensional surface (around a point on the unit sphere)

- long times: <u>no</u> linear time dependence!

To obtain ⊛ one starts by rewriting $\frac{d\underline{u}}{dt} = \frac{1}{6\eta V} \underline{T}^{ran} \times \underline{u}$

as $\dot{\underline{u}} = \underline{\underline{A}}\,\underline{u}$

$$\text{where } \underline{\underline{A}} = \frac{1}{6\eta V}\begin{pmatrix} 0 & -T_3 & T_2 \\ T_3 & 0 & -T_1 \\ -T_2 & T_1 & 0 \end{pmatrix}$$

Solution:

$$\Rightarrow \underline{u}(t) = \underline{u}(t_0) + \int_{t_0}^{t} dt' \underline{\underline{A}}(t')\underline{u}(t')$$

set $t_0 = 0$ in the following

solve by iteration:

$$\underline{u}(t) = \underline{u}(t_0) + \sum_{n=1}^{\infty} \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \; \underline{\underline{A}}(t_1)\underline{\underline{A}}(t_2)\ldots\underline{\underline{A}}(t_n)\underline{u}(0)$$

<u>ensemble average</u>??

lowest-order terms on the right-hand side

$$\int_0^t dt_1 \langle \underline{\underline{A}}(t_1)\rangle \underline{u}(0) = 0 \qquad \text{since } \underline{\underline{A}} \sim \underline{T}^{ran}$$

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \underbrace{\langle \underline{\underline{A}}(t_1)\underline{\underline{A}}(t_2)\rangle}_{\sim \delta(t_1 - t_2)} \underline{u}(0) = -2\frac{k_B T}{6\eta V} t\, \underline{u}(0)$$

$\vdots$

(note: this is already a non-trivial result due to the argument of the δ-function!)

also: terms with odd number of $\underline{\underline{A}}$-tensors are zero!

~~and generally:~~ $\cancel{\int_0^t dt_1 \ldots \int^{t_{n-1}} dt_n \langle A(t_1)\ldots A(t_n)\rangle}$

For the remaining calculation, see Dhont