Linear response theory for equilibrium and nonequilibrium systems perturbed by nonconservative forces: The role of symmetries

Von der Fakultät für Mathematik und Physik der Universität Stuttgart
zur Erlangung der Würde eines Doktors der Naturwissenschaften
(Dr. rer. nat.)
genehmigte Abhandlung

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Tag der Einreichung:	05.05.2020
Tag der mündlichen Prüfung:	06.07.2020

Institut für Theoretische Physik IV der Universität Stuttgart und
Max-Planck-Institut für Intelligente Systeme, Stuttgart

2020

Acknowledgments

Many people contributed to this thesis. First, I would like to thank Prof. Matthias Krüger for his supervision. A great expertise in the subject, an ability to easily generate interesting scientific ideas, and enthusiasm for solving unsolvable problems make Prof. Krüger an excellent supervisor, a supervisor who not just gives an advice, but who really fights a scientific problem together with his student. Many thanks go to Prof. Krüger also for his support regarding financing and organization of my research, and for discussing with me nonscientific topics of the project. He was always available when I needed help.

I am very grateful to Prof. Siegfried Dietrich for the opportunity to do the thesis in his group at the Max Planck Institute for Intelligent Systems, where excellent working conditions and a good atmosphere definitely make work pleasant. Prof. Dietrich gave me a big support in organizational and bureaucratic aspects of the project. His wise suggestions are also very appreciated.

I thank Prof. Udo Seifert and Prof. Sebastian Loth for being a part of the examination committee.

I would like to thank Dr. Christian M. Rohwer and Dr. Alexandre P. Solon for their collaboration. Many results of this dissertation would not be possible without the work of these two scientists with super powerful minds. I gained a lot of knowledge in physics from our productive discussions, and also learned how a good scientific collaboration should be done.

I greatly acknowledge financial support from the Studienstiftung des deutschen Volkes and from the Physics Department of the University of Stuttgart. The Studienstiftung also gave me the opportunity to participate in interesting seminars and workshops.

I thank Prof. Hans Peter Büchler, Dr. Bruno Gompf, and Dr. Artem Pronin for the opportunity to assist them in teaching. Many thanks also go to Simone Blümlein, Dr. Kathrin Gallmeister, and Mia Kumrić for their help in solving bureaucratic issues.

My colleagues in Stuttgart and in Göttingen enriched my daily life, for which I thank them. Special thanks go to Oleksii Maistrenko, Dr. Christian M. Rohwer, Dr. Grigorii Zarubin, and Dr. Boris Müller for interesting discussions. Oleksii Maistrenko is also acknowledged for a critical reading of the manuscript, and Boris Müller is acknowledged for a proofreading of the text written in German.

I cannot forget to thank the teachers of Moscow Institute of Physics and Technology and of the University of Stuttgart for giving me the essential knowledge in physics and many other subjects during my Bachelor's and Master's studies. I also thank the teachers in my homeland, Belarus, for giving me the basic knowledge during my school education.

Contents

1 Introduction

1.1 Preamble

The research presented in this thesis is the research in theoretical classical statistical physics. It is really a huge and crucial discipline, penetrating to many areas of science. The fundamentals of statistical physics are not discussed here in detail; this discussion can be found elsewhere [1–3]. Yet, we start the story with a short qualitative picture of these fundamentals.

Roughly speaking, statistical physics is about averaging (therefore, many formulas below contain average brackets $\langle \cdots \rangle$). This averaging can be done in different ways, e.g., over time or ensembles. As an everyday life example, consider that you want to see a person on some summer evening (maybe to make a surprise with a gift). In principle, this person can be anywhere in the universe, and, to be sure about her or his location, you should know each her or his step. But this is usually not possible, and, actually, not needed. What you need is to know where the person is on summer evenings *on average*. Making a statistical averaging (e.g., by considering previous meetings on summer evenings), you conclude that the person you want to meet will be. . . at home. Similarly in statistical physics: one is interested in the average, because the exact value either has less sense or is much more difficult to find.

Importantly, statistical approach allows to connect macroscopic properties of a considered system with its microscopic ones. For example, by averaging over the velocities of particles forming a gas, one finds the gas temperature. Similarly, the information about interactions between fluid molecules can be used to predict the viscosity of the fluid.

Since one uses statistics to find averages, the key element of statistical physics is the distribution, which tells probabilities of different states. Coming back to our example, a simple distribution W could be a discrete set of numbers, each corresponding to the probability to find the person in a particular place: say $W = \left\{\frac{1}{2}, \frac{1}{4}, \frac{1}{8}, \frac{1}{8}\right\}$, with the probabilities to be at home, in the university, in the cinema, and anywhere else, respectively. For many physical systems, the distribution is typically given as a continuum function of the degrees of freedom, telling how likely it is to find particles at certain positions and with certain velocities. However, it can be also a more complicated object, as, e.g., a path integral, discussed in detail in Chapter 3. But the sense is the same for any W: once it is known, then the statistics of the considered system is also known, and hence the desired average can be found.

Since the average is not the exact result, there must be something which describes the uncertainty of this result (the statistical error). This something is called the variance, and, alongside with the average, it is a crucial quantity in statistical physics. The variance is also found from the distribution, and it tells us the mean squared deviation of possible solutions from the average. In addition to the average and the variance, further details of the statistics are described by higher moments of the distribution.

In many physical systems, the quantity which is responsible for stochasticity is temperature. Thermal fluctuations lie at the heart of statistical physics and they are responsible for various phenomena, such as Brownian motion [2–4], solar radiation, and Casimir forces [5, 6].

A qualitative picture of statistical physics may appear clear now. You know nothing exactly: a system can evolve in different ways, particles can be in different places, and the person you want to meet on some summer evening can also be anywhere. But you know the statistics, and use it to find a single solution which gives the most probable result.

1.2 Brownian motion

One of the most important, popular, and elucidative system in statistical physics, is a system of Brownian particles. The discovery of Brownian motion was made nearly 200 years ago by R. Brown [7], who observed random motion of organic particles in water. Later, it became clear that the nature of this motion is due to collisions of these particles (today known as Brownian particles) with water molecules [4]. In his seminal work [8], A. Einstein provided a physical description of Brownian motion, finding that the mean square displacement (MSD) of a Brownian particle is linear in time t:

$$\left\langle [x(t) - x(0)]^2 \right\rangle = 2Dt, \tag{1.1}$$

where D is the diffusion coefficient. Several years later, J. Perrin experimentally confirmed Eq. (1.1) [4]. Note that MSD is an average quantity, indicating that Einstein used a statistical approach to describe Brownian motion. Indeed, due to a huge number of collisions and inability to know exactly all the forces from the molecules, deterministic approach is not reasonable, while statistical mechanics deals with this problem easily and quickly [9].

Brownian motion is not only a fundamental physical phenomenon, but also a key historical discovery which lead to an improvement of understanding of thermal fluctuations and atomic nature of matter, as well as to new methods in statistical physics and to the birth of stochastic calculus [10]. Since the beginning of the 20th century, a big progress has been made in the field of Brownian dynamics: new theoretical methods provided various modeling [9], computers allowed to study complex Brownian systems in numerical simulations [11], and the progress in micro- and nanotechnology allowed to improve experimental investigation of Brownian motion [12–17] as well as to design potential Brownian motors [18].

Most of explicit results and examples of this thesis are given for a system of Brownian particles. Therefore, we review key aspects of Brownian systems in the next three subsections.

1.2.1 Passive Brownian particles – an equilibrium stochastic system

Modeling Brownian motion: the Langevin equation

How to model Brownian motion? There are several ways to do this. Since the dynamics is random (stochastic), the model can be based on the distribution function. For example, to derive Eq. (1.1), Einstein found that the particle density (which plays the role of the distribution function) obeys the diffusion equation [8]. It is, however, more illustrative, and, probably, more general to write down the corresponding equation of motion.

As we mentioned before, an exact deterministic equation of motion for Brownian dynamics is not reasonable, because one should consider a huge number of degrees of freedom (a Brownian particle together with the molecules). To deal with this problem, one can combine all the forces acting from the molecules on the particle into a reasonable number of forces (this number is actually two as we will shortly see), concentrating only on the degrees of freedom corresponding to the particle[1]. Inability to know the exact dynamics then translates to the fact that the resulting forces are stochastic, and hence also the corresponding equation of motion, – statistical physics comes into play.

It was first Paul Langevin who came up with the idea of formulating Brownian dynamics via a stochastic generalization of Newton's equation [19]. Langevin described the collective effect of the molecules via two forces acting on Brownian particle i: (i) fluctuating (or random, or stochastic) force $\mathbf{f}_i$, modeling the collisions; (ii) friction force $-\frac{1}{\mu}\mathbf{v}_i$ (where $\mathbf{v}_i$ and μ are the particle velocity and mobility, respectively)[2], modeling the friction between the particle and the molecules. We further consider a general many-body system of interacting Brownian particles (see Fig. 1.1), where interaction forces $\mathbf{F}_i^{\text{int}}$ arise from the corresponding interaction potential, $\mathbf{F}_i^{\text{int}} = -\nabla_i U^{\text{int}}$. The system may be also subject to external potential forces $\mathbf{F}_i^{\text{ext}} = -\nabla_i U^{\text{ext}}$. The corresponding equation of motion (the celebrated Langevin equation) for particle i, with position $\mathbf{r}_i$, velocity $\mathbf{v}_i$, mass m, and mobility μ, then reads [3, 9, 19–21]

$$m\dot{\mathbf{v}}_i = -\frac{1}{\mu}\mathbf{v}_i + \mathbf{F}_i^{\text{int}} + \mathbf{F}_i^{\text{ext}} + \mathbf{f}_i, \qquad \dot{\mathbf{r}}_i = \mathbf{v}_i. \tag{1.2}$$

Equation (1.2) is incomplete without specifying statistical properties of random force $\mathbf{f}_i$. It is natural to model $\mathbf{f}_i$ in terms of Gaussian white noise [9, 20], such that

$$\langle \mathbf{f}_i(t)\rangle = 0, \qquad \langle \mathbf{f}_i(t) \otimes \mathbf{f}_j(t')\rangle = \frac{2k_\text{B}T}{\mu}\mathbb{I}\delta_{ij}\delta(t-t'), \tag{1.3}$$

where $\otimes$ denotes the tensor product, k_B is Boltzmann's constant, T is the temperature of the system, $\mathbb{I}$ is the identity matrix, and the average $\langle\cdots\rangle$ is over noise realizations, i.e., over ensemble of systems with different $\mathbf{f}_i$. The first part of Eq. (1.3), $\langle \mathbf{f}_i(t)\rangle = 0$,

[1] This procedure, when one integrates out many degrees of freedom to obtain a few collective variables, is usually called coarse-graining.

[2] It is probably more natural to define friction force via the friction coefficient γ as $-\gamma\mathbf{v}_i$. However, to avoid confusions with the shear rate $\dot{\gamma}$ introduced in Sec. 1.4, we choose the definition via the mobility μ. The relation $\mu = \frac{1}{\gamma}$ is assumed in this thesis.

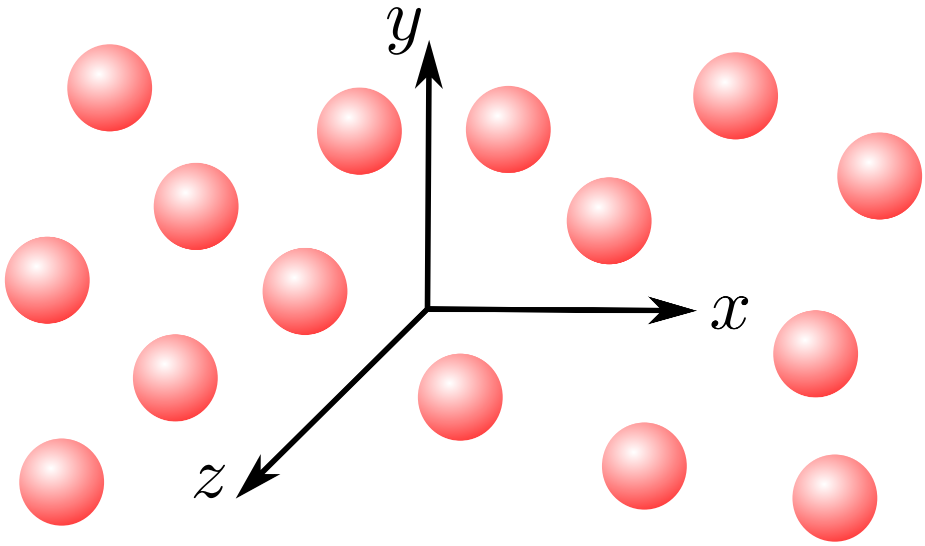

Figure 1.1. Interacting (Brownian) particles, an equilibrium system that we use to demonstrate general results of Chapter 2.

is clear from physical grounds: the collisions of the molecules with the particle have no preferred direction, i.e., the molecules hit the particle equally likely from all sides. The second part tells how the random forces are correlated, and it is much less obvious. First, via $\mathbb{I}$, one assumes no correlation between different directions. Second, it is assumed that random forces acting on different particles are also not correlated, which is encoded in δ_{ij}. Third, the collisions have no memory, i.e., random forces at two distinct times, t and t', are independent, which is modeled by $\delta(t-t')$. Finally, the prefactor $\frac{2k_{\mathrm{B}}T}{\mu} > 0$ corresponds to the strength, and also to the variance, of random forces. Since velocities of the molecules determine the temperature of the system (i.e., the faster the molecules move, the higher the temperature is), it is clear that this strength should grow with temperature[3]. However, it seems to be unconvincing to speculate about the exact expression for the prefactor; instead, we derive this expression in the example below.

We note that Eqs. (1.2) and (1.3) describe the simplest Brownian motion. There are many generalizations of Langevin equation (1.2), including space-dependent strength of the random force (multiplicative noise), retarded friction, colored noise[4] [9, 20, 21], as well as consideration of hydrodynamic effects (see Subsec. 1.2.3). In this thesis, we restrict to the model given by Eqs. (1.2) and (1.3).

[3]Although, typically, *thermal* fluctuations are considered for Brownian dynamics of physical systems, we note that, in general, fluctuations *of any nature* can lead to Brownian motion (see, e.g., Ref. [22] for application of Brownian motion in finance). Therefore, the random force strength in Eq. (1.3) does not necessarily have to be related to the temperature.

[4]The term "colored" means that the power spectrum of the random force is not constant, but depends on frequency (i.e., on "color"). This is the case, when $\langle \mathbf{f}_i(t) \otimes \mathbf{f}_j(t') \rangle$ is not delta correlated in time. In contrast, in the case $\langle \mathbf{f}_i(t) \otimes \mathbf{f}_j(t') \rangle \sim \delta(t-t')$, the power spectrum is constant, and the noise is hence called "white".

A remark about equilibrium

A crucial property of a Brownian system described by Eq. (1.2) is that, in steady state, the system has a uniform temperature T, and no heat flow or other flows are present. Therefore, the system obeys detailed balance, meaning that Brownian particles are in thermodynamic equilibrium. Equilibrium is ensured by two facts: first, friction force $-\frac{1}{\mu}\mathbf{v}_i$ and random force $\mathbf{f}_i$ balance each other (they, in fact, determine each other as we shall see in the example below), and second, external forces $\mathbf{F}_i^{\text{ext}}$ are conservative.

An equilibrium state is a special state, having certain fundamental properties [2, 3]. In particular, the equilibrium distribution function is known: it has the form of Maxwell-Boltzmann distribution and reads

$$W_{\text{eq}}(\Gamma) = \frac{e^{-\frac{H(\Gamma)}{k_B T}}}{\int d\Gamma e^{-\frac{H(\Gamma)}{k_B T}}}, \tag{1.4}$$

where $\Gamma = \{\{\mathbf{r}_i\}, \{\mathbf{v}_i\}\}$ is the phase space (notation $\{\mathbf{r}_i\}$ denotes the set of positions of all particles) and $H(\Gamma) = \sum_{i=1}^{N} \frac{m\mathbf{v}_i^2}{2} + U^{\text{int}}(\{\mathbf{r}_i\}) + U^{\text{ext}}(\{\mathbf{r}_i\})$ is the system Hamiltonian. In contrast, statistical physics of nonequilibrium states is much more complex, and the corresponding nonequilibrium distribution is typically unknown [3]. The difference between equilibrium and nonequilibrium systems in the context of linear response theory is discussed in detail throughout this thesis.

It is important to note that Brownian particles must not have internal driving forces in order to be in equilibrium, i.e., they must be passive. The physical picture of this passivity is such that the dynamics of any particle is fully determined by the surrounding system (random forces, interaction and external potentials), i.e., the particle does not try to move in a certain preferred direction. This motion would violate detailed balance, driving the system out of equilibrium. In reality, passive Brownian particles can be represented by any object with no internal energy, e.g., a simple colloidal particle. However, living organisms, such as bacteria, can move in a preferred direction, thereby violating detailed balance. Therefore, an equilibrium Brownian motion cannot be applied to model living systems and has to be modified to include nonequilibrium effects. This modified model is called "active Brownian particles", and it is discussed in Subsec. (1.2.2).

Underdamped versus overdamped

Often, to simplify the analysis, one takes certain limits of the system dynamics. Regarding Brownian particles described by Eq. (1.2), the most important and popular limit concerns particles' inertia $m\dot{\mathbf{v}}_i$. Indeed, if one thinks of a heavy particle suspended in a low-friction environment (large m and μ), the dynamics of this particle is far from a typical erratic Brownian motion. This is because such a particle almost does not respond to the collisions with the molecules (roughly speaking, the particle is so heavy and the effect of the molecules is so low, such that the particle almost does not feel them). In this case, the term $m\dot{\mathbf{v}}_i$ in Eq. (1.2) dominates over the random force $\mathbf{f}_i$, and one calls

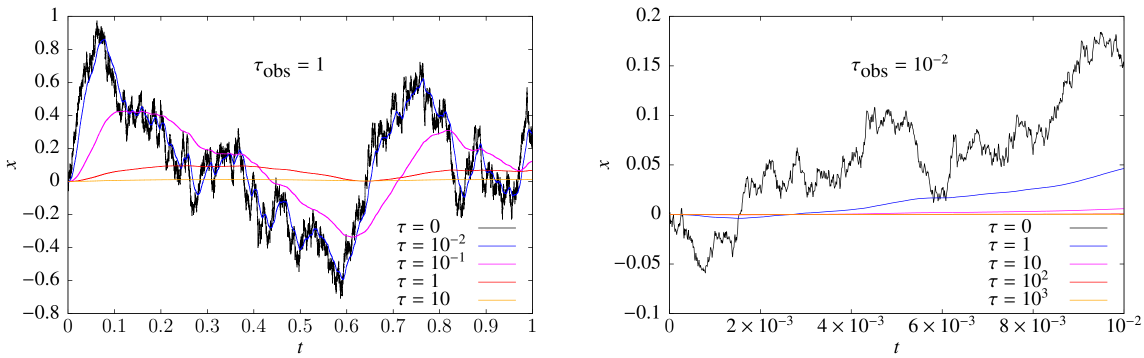

Figure 1.2. Trajectories of a free Brownian particle in one dimension for different ratio $\tau = \frac{\tau_m}{\tau_{\text{obs}}}$ between the inertia time $\tau_m = m\mu$ and the observation time τ_{obs} (noise realizations are the same for all cases). The particle obeys Langevin equation (1.2) with $k_{\text{B}}T = \mu = 1$ and initial conditions $x(0) = v(0) = 0$. The dynamics is simulated using the Euler method. The left panel shows the trajectories during time $\tau_{\text{obs}} = 1$, while the right panel considers $\tau_{\text{obs}} = 10^{-2}$ (i.e., the right panel shows zoomed region $t = [0, 10^{-2}]$ of the left one).

the dynamics "inertial" or "underdamped" (i.e., damping, related to random forces and friction, has a weak effect). In the opposite limit (small m and μ), the effect of the random force dominates over the inertia, the particle quickly responses to the collisions, and the dynamics is called "Brownian" or "overdamped".

Compared to what must m and μ be large or small to identify the type of dynamics? Since $m\mu$ has the unit of time, one might guess that the relevant parameter is the time of observation. Indeed, a heavy particle needs more time to response to random forces, while a light one needs less. Therefore, if the particle inertia time $\tau_m = m\mu$ is large compared to the observation time τ_{obs}, one sees underdamped dynamics. In the opposite case, $\tau_m \ll \tau_{\text{obs}}$, one observes erratic Brownian motion, – the dynamics is overdamped. In that respect, it is useful to introduce the ratio $\tau \equiv \frac{\tau_m}{\tau_{\text{obs}}}$ to distinguish between the two types of dynamics ($\tau \gtrsim 1$ for underdamped; $\tau \ll 1$ for overdamped).

Figure 1.2 compares trajectories of a free Brownian particle in one dimension (described by the x coordinate) starting at the origin and with zero velocity (i.e., $x(0) = v(0) = 0$) for different τ. The observation time for the left panel of Fig. 1.2 is $\tau_{\text{obs}} = 1$. Here, one can see that for $\tau = 0$ the trajectory is purely stochastic, i.e., the particle responses to the collisions immediately, erratically changing its direction, – it is what one typically calls Brownian motion. For finite but small τ ($\tau = \{10^{-2},\ 10^{-1}\}$), the trajectory acquires smoothness (now the particle is able to resist chaotic collisions), but still retains stochastic behavior. The trajectory for $\tau = 1$ shows weak fluctuations, which corresponds to similar contributions of the inertia and random forces. For $\tau = 10$, one can see that the particle hardly leaves its initial position, i.e., it does not feel the environment, – the motion is inertial (or underdamped). Similar behavior is observed for the same system when the observation time is reduced from $\tau_{\text{obs}} = 1$ to $\tau_{\text{obs}} = 10^{-2}$, as shown on the right panel of Fig. 1.2. This demonstrates that limiting cases of the dynamics have to be determined relative to the observation time scale.

Note that the particle velocity in the purely overdamped limit ($m = 0$) is not well-defined. Indeed, one can see that the curve corresponding to $\tau = 0$ in Fig. 1.2 is not differentiable. This issue was first pointed out by Einstein [23], whose simple arguments follow from his result for MSD (1.1)[5]. According to Eq. (1.1), one could define the mean absolute velocity measured over time interval t as $\overline{v} = \frac{\sqrt{\langle [x(t)-x(0)]^2\rangle}}{t} = \frac{\sqrt{2D}}{\sqrt{t}}$. But $\overline{v}$ diverges as t approaches zero – instantaneous velocity is thus not well defined. Therefore, only position-dependent observables can be measured in the overdamped case.

Finally, we would like to mention that many explicit results and examples of this dissertation are given for purely overdamped Brownian systems. Therefore, let us agree on the following convention for this thesis: if not stated otherwise, a system with any finite m is formally called underdamped, while a system with $m = 0$ is called overdamped. While the former is described by Eq. (1.2), the latter obeys overdamped Langevin equation:

$$\dot{\mathbf{r}}_i = \mu \mathbf{F}_i^{\text{int}} + \mu \mathbf{F}_i^{\text{ext}} + \mu \mathbf{f}_i, \tag{1.5}$$

where $\mathbf{f}_i$ is determined by Eq. (1.3). Physically, Eq. (1.5) is a good approximation of Eq. (1.2) whenever $\tau \ll 1$.

Example: the mean square displacement and the fluctuation-dissipation theorem

Let us close this subsection with a simple yet illustrative example [3, 24]. Consider a single free particle in one dimension following underdamped Langevin dynamics:

$$\begin{aligned} m\dot{v} &= -\frac{1}{\mu}v + f, \\ \dot{x} &= v, \end{aligned} \tag{1.6}$$

where random force properties read as

$$\langle f(t)\rangle = 0, \qquad \langle f(t)f(t')\rangle = c\delta(t-t'), \tag{1.7}$$

with $c > 0$ being an unknown parameter.

Our first goal is to find c in order to justify the random force variance in Eq. (1.3). Assuming initial condition $v(0) = 0$, the solution of Eq. (1.5) reads

$$v(t) = v(0)e^{-\frac{t}{m\mu}} + \frac{1}{m}e^{-\frac{t}{m\mu}}\int_0^t dt_1 e^{\frac{t_1}{m\mu}} f(t_1), \tag{1.8}$$

and the average square velocity is thus

$$\langle v^2(t)\rangle = v^2(0)e^{-\frac{2t}{m\mu}} + \frac{1}{m^2}e^{-\frac{2t}{m\mu}}\int_0^t dt_1 \int_0^t dt_2 e^{\frac{1}{m\mu}(t_1+t_2)}\langle f(t_1)f(t_2)\rangle. \tag{1.9}$$

[5] Recall that Einstein derived Eq. (1.1) by finding that the distribution function obeys the diffusion equation, which is equivalent to assuming the overdamped Langevin dynamics. Therefore, Eq. (1.1) can be applied in the overdamped case only. A more detailed discussion is given in the example below.

In the long time limit, $t \gg m\mu$, $\langle v^2(t)\rangle$ approaches its equilibrium value, $\langle v^2\rangle \equiv \lim_{t\gg m\mu}\langle v^2(t)\rangle$. The idea is to apply equipartition theorem,

$$\frac{m\langle v^2\rangle}{2} = \frac{k_\mathrm{B}T}{2}. \tag{1.10}$$

Using Eqs. (1.9), (1.7), and (1.10), we obtain

$$c \lim_{t\to\infty} e^{-\frac{2t}{m\mu}} \int_0^t dt_1 e^{\frac{2t_1}{m\mu}} = mk_\mathrm{B}T. \tag{1.11}$$

Performing the integration and taking the limit, one finally finds

$$c = \frac{2k_\mathrm{B}T}{\mu}, \tag{1.12}$$

in agreement with Eq. (1.3).

There is a deep physical sense in Eq. (1.12). It states that the strength of random force is proportional to the strength of friction force, and vice versa. This means that, in equilibrium, fluctuations (random force) and dissipation (friction force) determine each other. A particle moves due to the collisions with the molecules (thermal fluctuations), this motion results in friction between the particle and the molecules (dissipation), which in turn affects the molecules (dissipation turns into thermal fluctuations) and how they hit the particle again, – the process repeats. This simple observation is a manifestation of the fluctuation-dissipation theorem (FDT): fluctuations lead to dissipation, and vice versa.

Second, we aim to compute MSD using the solution for $x(t)$ [with the initial condition $x(0)$],

$$x(t) = x(0) + v(0)\int_0^t dt_1 e^{-\frac{t_1}{m\mu}} + \frac{1}{m}\int_0^t dt_1 e^{-\frac{t_1}{m\mu}} \int_0^{t_1} dt_2 e^{\frac{t_2}{m\mu}} f(t_2), \tag{1.13}$$

obtained by integrating Eq. (1.8). Using Eq. (1.13), we find

$$\begin{aligned}\left\langle [x(t)-x(0)]^2\right\rangle &= v^2(0)\left(\int_0^t dt_1 e^{-\frac{t_1}{m\mu}}\right)^2 \\ &\quad + \frac{1}{m^2}\int_0^t dt_1 \int_0^t dt_3 e^{-\frac{1}{m\mu}(t_1+t_3)} \int_0^{t_1} dt_2 \int_0^{t_3} dt_4 e^{\frac{1}{m\mu}(t_2+t_4)} \langle f(t_2) f(t_4)\rangle.\end{aligned} \tag{1.14}$$

The integrals in the second line of Eq. (1.14) can be computed using Eqs. (1.7) and (1.12). To perform integration of the delta-function, one should split one of the first two integrals into two: for example, $\int_0^t dt_3 = \int_0^{t_1} dt_3 + \int_{t_1}^t dt_3$. We obtain

$$\left\langle [x(t)-x(0)]^2\right\rangle = \left(mv^2(0) - k_\mathrm{B}T\right) m\mu^2 \left(1 - e^{-\frac{t}{m\mu}}\right)^2 + 2k_\mathrm{B}T\mu\left[t - m\mu\left(1 - e^{-\frac{t}{m\mu}}\right)\right]. \tag{1.15}$$

This MSD is not a proper equilibrium average, because it depends on the initial condition $v(0)$. Assuming that the particle is at equilibrium at $t = 0$, we can average over initial velocities, which results in MSD for a particle starting with arbitrary initial velocity in equilibrium. Performing this average, the first term vanishes (because $m\langle v^2(0)\rangle = k_\mathrm{B}T$) and the second one remains unchanged. We hence finally get

$$\left\langle [x(t) - x(0)]^2 \right\rangle = 2k_\mathrm{B}T\mu \left[t - m\mu \left(1 - e^{-\frac{t}{m\mu}} \right) \right]. \tag{1.16}$$

MSD (1.16) was first derived by L. S. Ornstein and R. Fürth [24–26], and it is valid for underdamped Brownian motion (i.e., for any m and μ). In the overdamped limit, $m\mu \ll t$, it reads

$$\lim_{m\mu \ll t} \left\langle [x(t) - x(0)]^2 \right\rangle = 2k_\mathrm{B}T\mu t. \tag{1.17}$$

A careful reader would notice that Eq. (1.17) is nothing else than Einstein formula for MSD (1.1) with

$$D = k_\mathrm{B}T\mu. \tag{1.18}$$

We have already mentioned that Einstein derived his formula using the diffusion equation [8], before Langevin proposed his equation (1.2). The comparison of the two derivations (that by Einstein and the one we reviewed above) leads to relation (1.18): equilibrium fluctuations described by the diffusion coefficient D are proportional to dissipation described by the friction coefficient $\gamma = \frac{1}{\mu}$. This is another, yet historically first, manifestation of the fluctuation-dissipation theorem. We note that Einstein himself found relation (1.18) using the balance between diffusion and external currents [3, 8]. Independent derivations were also given by W. Sutherland [27] and M. Smoluchowski [28]. Formula (1.18) is thus known as Sutherland-Einstein-Smoluchowski relation. In Subsec. 1.3.4, we provide an alternative derivation of formula (1.18) using linear response theory, demonstrating the connection between FDT and the linear response.

In the opposite limit, $m\mu \gg t$, when the particle has not started to feel friction yet (ballistic regime), one anticipates motion with a uniform velocity. Indeed, taking the limit of Eq. (1.16), one obtains

$$\lim_{m\mu \gg t} \left\langle [x(t) - x(0)]^2 \right\rangle = \frac{k_\mathrm{B}T}{m} t^2, \tag{1.19}$$

meaning that the particle moves the distance $\sqrt{\left\langle [x(t) - x(0)]^2 \right\rangle}$ with a constant equilibrium velocity $\sqrt{\langle v^2 \rangle} = \sqrt{\frac{k_\mathrm{B}T}{m}}$, a measurable quantity [14].

Formula (1.16) has been confirmed experimentally for a Brownian particle in a rarefied gas [13]. For a particle in a liquid, deviations from Eq. (1.16) are observed due to hydrodynamic memory effects [12, 15, 16], which are discussed in Subsec. 1.2.3.

1.2.2 Active Brownian particles – a nonequilibrium stochastic system

Passive versus active

A typical Brownian particle used in experimental studies of Brownian motion is a spherical particle of $\sim 1\ \mu m$ radius made of silica [12–17]. Such a particle has no driving mechanisms (i.e., it can not perform a directed motion), and it hence does not drive the system out of equilibrium. Its dynamics is fully determined by the fluctuation-dissipation of random and friction forces, as well as by external potentials. The particle thus fully "obeys its environment", i.e., it is passive, and its dynamics can be described by equilibrium Langevin equation (1.2).

On the other hand, consider some living microorganism such as a bacterium. A typical size of a bacterium is also $\sim 1\ \mu m$, and one can observe that a bacterium placed in some environment also performs erratic motion [29]. But is this motion similar to that of a silica particle? As any living organism, a bacterium has properties of life, and it is thus able to maintain a certain internal state as well as to perform motion according to its life needs, thereby being out of equilibrium with the environment. As regards the dynamics, one can observe clear differences between the motion of a bacterium

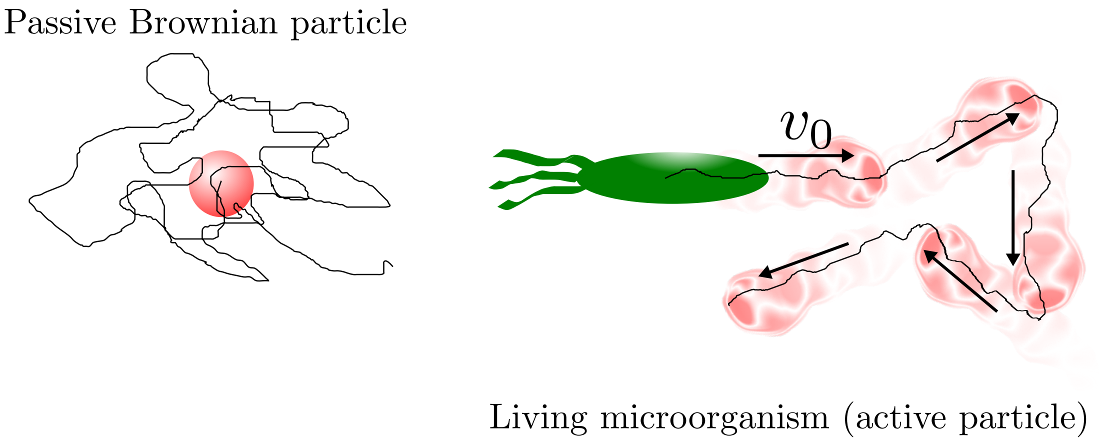

Figure 1.3. A comparison between passive and active particles. A passive Brownian particle performs random motion with no preferred direction, thereby being in equilibrium with its environment. In contrast, an active (or self-propelled) particle (e.g., a bacterium) has a driving mechanism, allowing the particle to perform a directed motion with self-propulsion velocity v_0[6]. This motion results in redistribution of energy from the particle to the environment (i.e., in local flows depicted as the red clouds), thereby violating detailed balance and driving the system out of equilibrium.

[6]Self-propelled motion is sometimes associated with swimming, and v_0 is also called swim velocity (speed).

and a passive particle. We shall not go into details, but for simplicity consider that a bacterium (or any other active particle) has a driving mechanism, i.e, an "engine" [30] capable to take up and convert energy from the environment into a directed motion [31–33]. This motion, which is usually called active or self-propelled, drives the system out of equilibrium (see Fig. 1.3 for an illustration), and the dynamics of active particles can thus not be described by standard Langevin equation (1.2).

Active matter

In recent years, the focus of statistical physics has been moving from equilibrium systems to nonequilibrium ones, in an attempt to solve "real life problems". Indeed, thermodynamic equilibrium is a rare exception in nature, in particular, concerning living systems [3]. This change of the focus towards nonequilibrium gave birth to many subdisciplines, on two of which, active matter and nonequilibrium response theory, Chapter 4 of this thesis is based. While response theory is reviewed in Sec. 1.3, let us now very briefly discuss active matter.

Active matter is a system composed of individual active agents (for example, a flock of birds or a cluster of bacteria), where each agent performs active motion, thereby individually driving the system out of equilibrium (see Fig. 1.3). This local form of driving and interactions between the agents lead to fascinating collective behaviors, such as flocking [34, 35], spontaneous bacterial flows [36, 37], dynamical clustering [38–40], or motility-induced phase separation [39–42]. Recently, a big progress has been made in fabrication of *artificial* active particles with various self-propulsion mechanisms, allowing to perform experimental studies of artificial active matter [31–33, 40].

Modeling active Brownian motion

There are many theoretical models for active matter, and most of them are based on statistical physics [31–33]. In this thesis, we focus on active Brownian particles (ABPs) model, which is an extension of passive Brownian motion described by Eq. (1.2). Let us first write down the corresponding Langevin equations for a general system of active Brownian particles (see Fig. 1.4) [43]:

$$m\dot{\mathbf{v}}_i = -\frac{1}{\mu}\mathbf{v}_i + \frac{1}{\mu}v_0\hat{\mathbf{u}}_i + \mathbf{F}_i^{\text{int}} + \mathbf{F}_i^{\text{ext}} + \mathbf{f}_i, \qquad \dot{\mathbf{r}}_i = \mathbf{v}_i, \tag{1.20}$$

$$\dot{\hat{\mathbf{u}}}_i = \mu_{\text{r}}\left(\mathbf{M}_i + \mathbf{g}_i\right) \times \hat{\mathbf{u}}_i. \tag{1.21}$$

Compared to Eq. (1.2), Eq. (1.20) has a new term, $\frac{1}{\mu}v_0\hat{\mathbf{u}}_i$, which models activity of particle i and can be formally interpreted as a self-propulsion force $\mathbf{F}_i^{\text{s-p}} = \frac{1}{\mu}v_0\hat{\mathbf{u}}_i$. $v_0\hat{\mathbf{u}}_i$ is the self-propulsion velocity, with v_0 and $\hat{\mathbf{u}}_i$ being the absolute value and the unit vector determining the direction, respectively (see Fig. 1.4). This unit vector $\hat{\mathbf{u}}_i$ obeys its own stochastic process described by Eq. (1.21), where μ_{r} is the rotational mobility. $\mathbf{M}_i$ is the torque acting on particle i, which can arise from interparticle and (or) external torque-potentials (e.g., imagine alignment between particles or alignment along a certain

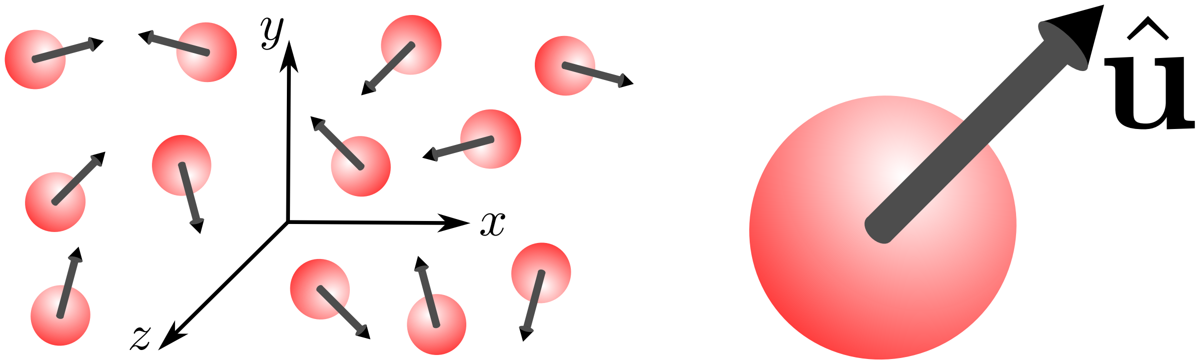

Figure 1.4. Interacting active Brownian particles, a nonequilibrium system studied in Chapter 4. Each particle performs self-propelled Brownian motion with self-propulsion velocity $v_0\hat{\mathbf{u}}$.

direction). $\mathbf{g}_i$ is the random torque modeled, as well as $\mathbf{f}_i$ in Eq. (1.3), by Gaussian white noise:

$$\langle \mathbf{g}_i(t)\rangle = 0, \qquad \langle \mathbf{g}_i(t) \otimes \mathbf{g}_j(t')\rangle = \frac{2D_\mathrm{r}}{\mu_\mathrm{r}^2}\mathbb{I}\delta_{ij}\delta(t-t'), \tag{1.22}$$

where D_r is the rotational diffusion coefficient determining how quickly $\hat{\mathbf{u}}_i$ is reoriented. We note that $\mathbf{f}_i$ and $\mathbf{g}_i$ are not correlated, and that, by not specifying D_r explicitly, we retain generality of the nature of angular noise (i.e., a particle can change the direction of its self-propulsion due to different mechanisms).

It has to be noted that active Brownian motion in three, two, and one dimensions are fundamentally different processes due to the structure of Eq. (1.21). In 3D, $\hat{\mathbf{u}}_i$ performs Brownian motion on a unit sphere, in 2D, it performs Brownian motion on a unit circle (see Sec. 4.1) [44], while in 1D, active Brownian motion is not defined (there is no continuous limit of Eq. (1.21) in one dimension) and is usually associated with one-dimensional run-and-tumble motion [45–48].

Dynamics of an active Brownian particle

Let us discuss the dynamics of a free ABP and show its differences compared to a passive particle. We consider an overdamped case and two space dimensions. Eqs. (1.20), (1.21), and (1.22) reduce to (setting $\mu_\mathrm{r} = 1$ for simplicity)

$$\dot{x} = v_0 \cos\varphi + \mu f_x, \tag{1.23a}$$
$$\dot{y} = v_0 \sin\varphi + \mu f_y, \tag{1.23b}$$
$$\dot{\varphi} = g, \tag{1.23c}$$

$$\langle g(t)\rangle = 0, \qquad \langle g(t)g(t')\rangle = 2D_\mathrm{r}\delta(t-t'). \tag{1.24}$$

Considering that the particle is at the origin at time $t = 0$ (i.e., $x(0) = y(0) = 0$) and that its orientation evolved from far away in the past, formal solutions of Eqs. (1.23a), (1.23b), and (1.23c) read

$$x(t) = v_0 \int_0^t ds \cos\varphi(s) + \mu \int_0^t ds f_x(s), \tag{1.25a}$$

$$y(t) = v_0 \int_0^t ds \sin\varphi(s) + \mu \int_0^t ds f_y(s), \tag{1.25b}$$

$$\varphi(t) = \varphi(-\infty) + \int_{-\infty}^t ds g(s). \tag{1.25c}$$

The $-\infty$-limit in Eq. (1.25c) makes relevant physical observables independent on the initial orientation, which is equivalent to the average over all initial orientations.

By computing the autocorrelation function of the orientation vector,

$$\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(t') \rangle = e^{-D_\mathrm{r}|t-t'|}, \tag{1.26}$$

we can see a clear physical interpretation of D_r: it quantifies the rate of particle reorientation. It is illustrative to define the persistence time

$$\tau_\mathrm{p} = \frac{1}{D_\mathrm{r}}, \tag{1.27}$$

showing how long a particle moves in approximately one direction on average, and the corresponding persistence length,

$$l_\mathrm{p} = v_0 \tau_\mathrm{p}, \tag{1.28}$$

the average distance covered due to this directed motion, indicated in Fig. 1.5. Compared to a passive particle, ABP thus has a finite time scale on which the particle persists its direction, although being slightly disturbed by the translational noise (see Fig. 1.5).

An experimentally accessible quantity allowing to compare passive and active Brownian motion is MSD. Whereas MSD for an overdamped passive particle is linear in time for all times [see Eq. (1.1)[7]], a finite time scale τ_p leads to an additional exponential term for the active case [32, 33],

$$\left\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \right\rangle = 4\left(D + \frac{v_0^2 \tau_\mathrm{p}}{2}\right) t - 2 v_0^2 \tau_\mathrm{p}^2 \left(1 - e^{-\frac{t}{\tau_\mathrm{p}}}\right), \tag{1.29}$$

similarly as the inertia time scale $\tau_m = m\mu$ leads to an exponential relaxation in the MSD for an underdamped passive particle [compare Eq. (1.16)]. For $t \ll \tau_\mathrm{p}$, MSD has both quadratic and linear terms,

$$\lim_{t \ll \tau_\mathrm{p}} \left\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \right\rangle = v_0^2 t^2 + 4Dt, \tag{1.30}$$

meaning that the particle performs a directed motion with the velocity v_0, but also tends to displace from the direction of this motion due to thermal fluctuations quantified by

[7]Note that in 2D the passive MSD is two times larger than in 1D.

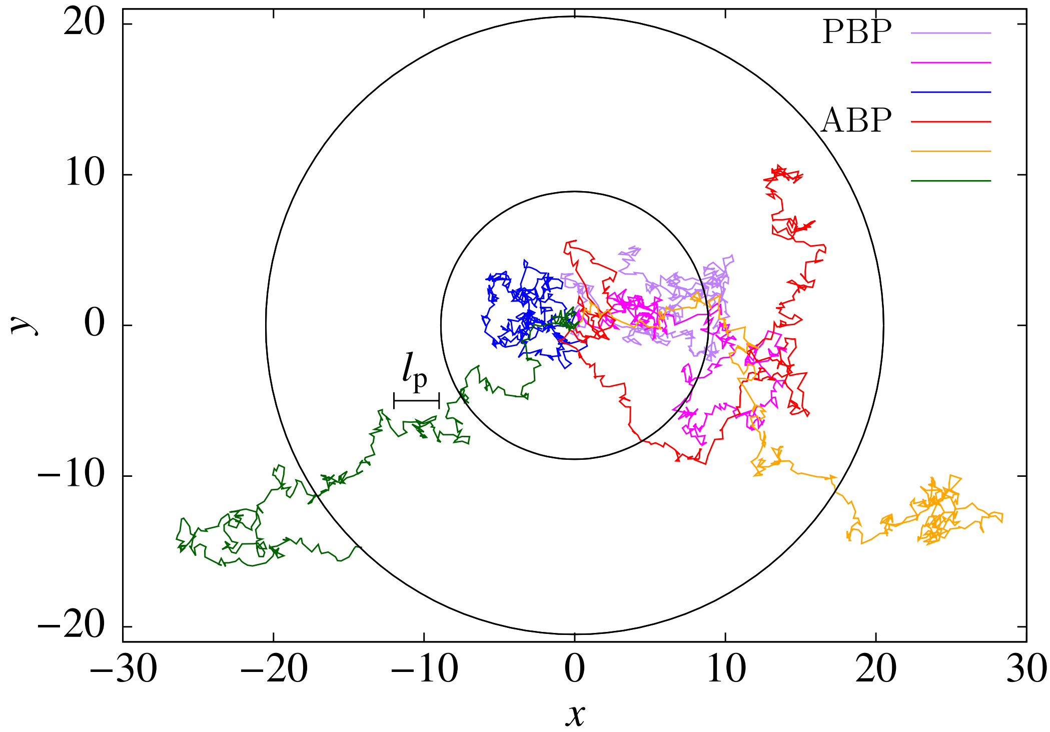

Figure 1.5. Comparison between two-dimensional simulation trajectories of a free passive Brownian particle (PBP) and a free active Brownian particle (ABP); the particles start at the origin; all the parameters are set to unity in the simulation, except $v_0 = 3$, simulation time $t = 20$, and the discretization time step $\Delta t = 5 \times 10^{-2}$. Circles, with radii equal to the square root of MSD of the particles (a smaller radius corresponds to the passive particle and a larger radius corresponds to the active particle) show the effective average area covered by the particles during the simulation time. l_p indicates the persistence length of the active particle.

D as discussed above (see the region spanned by l_p in Fig. 1.5). In the opposite limit, MSD is linear in time,

$$\lim_{t \gg \tau_\mathrm{p}} \left\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \right\rangle = 4 \left(D + \frac{v_0^2 \tau_\mathrm{p}}{2} \right) t, \tag{1.31}$$

indicating that the dynamics is the same as for the passive case (i.e., it is a diffusive motion)[8], but with a larger effective diffusion coefficient

$$D_\mathrm{a} = D + \frac{v_0^2 \tau_\mathrm{p}}{2}. \tag{1.32}$$

[8]Indeed, as can be seen from Fig. 1.5, a trajectory of ABP on a long time scale looks the same as a trajectory of a passive particle.

An active particle hence diffuses further than a passive one, i.e., it covers a larger effective area, as indicated by circles in Fig. 1.5.

Since for long times a free ABP behaves in the same way as a passive particle with a larger diffusion coefficient, one might think that steady-state active Brownian systems follow an equilibrium dynamics with the effective temperature (see, e.g., Refs. [30, 49–52] for theoretical and experimental studies of the effective temperature in various nonequilibrium systems)

$$T_{\mathrm{a}} = \frac{D_{\mathrm{a}}}{k_{\mathrm{B}}\mu} = T + \frac{v_0^2 \tau_{\mathrm{p}}}{2k_{\mathrm{B}}\mu}. \tag{1.33}$$

However, this naive intuition may work only for a free ABP or for a dilute many-particle active system with uniform external forces. As soon as interparticle interactions become important or external forces are spatially dependent, an effective equilibrium description fails, and one observes nonequilibrium phenomena like dynamical clustering [33].

1.2.3 How is the minimal model of Brownian motion connected to reality?

I was taught that a good theoretician should always ask whether the model he uses can describe real physical systems accessible in experiments. The model of Brownian motion, which we reviewed above, is the so-called *minimal* model. It describes essential features of real Brownian systems, and it is usually good enough to predict experimental results and physical phenomena *qualitatively*. However, this minimal model fails to *quantitatively* describe many relevant systems (see the discussions and references below). Let us figure out what the problem is.

As we mentioned in Subsec. 1.2.1, the essence of Brownian motion, interaction of a particle with the environment, is modeled by two forces, random force $\mathbf{f}$, and friction force $-\frac{1}{\mu}\mathbf{v}$, connected via Eq. (1.3). This modeling neglects two important effects of hydrodynamics: (i) hydrodynamic memory effect of a particle on itself; (ii) hydrodynamic interactions between particles.

Hydrodynamic memory effect

The first effect is present even in the case of a system containing a single Brownian particle. Expression $-\frac{1}{\mu}\mathbf{v}$ for friction force is valid if a particle moves with a constant velocity $\mathbf{v}$ [53]. However, due to inertia (i.e, acceleration) of a particle, the surrounding environment (gas or fluid formed by the molecules) is altered in such a way that it acts back on the particle at later times, as depicted in Fig. 1.6, – the particle experiences the so-called hydrodynamic memory effect [54, 55]. Therefore, friction force has to be modified accordingly: in addition to the term $\propto -\mathbf{v}$, it acquires other terms proportional to retarded particle's acceleration (i.e., friction force at time t depends on particle's acceleration at earlier times)[9].

[9]For a spherical particle of radius R and mass m, suspended in the environment with density ρ_{env} and viscosity η_{env}, the modified friction force can be obtained by solving Navier-Stokes equations and

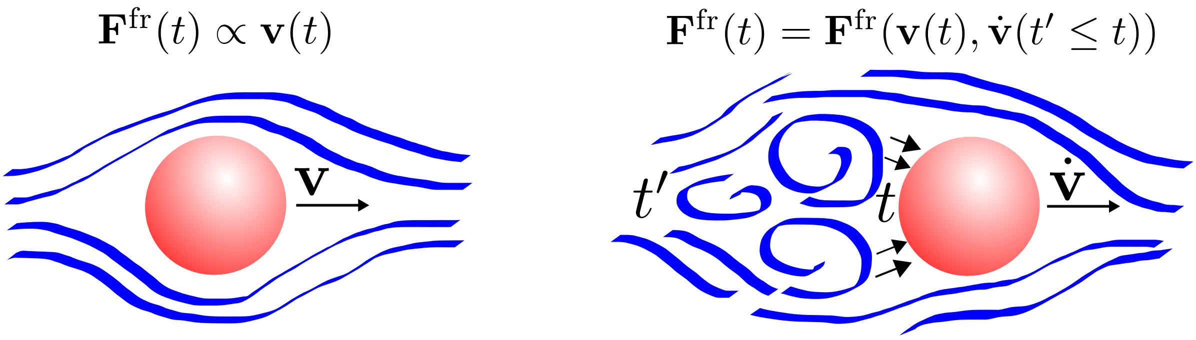

Figure 1.6. An illustration of hydrodynamic memory effect due to interaction of a Brownian particle with the environment (here, the environment is considered to be a fluid and depicted as fluid flow lines). The left panel shows motion of a particle with constant velocity $\mathbf{v}$; in this case, friction force is proportional instantaneously to the velocity, $\mathbf{F}^{\mathrm{fr}}(t) \propto \mathbf{v}(t)$ (this simple form of friction is used in this thesis). In reality (shown on the right panel), however, particle's inertia causes vorticity of the fluid at time t' (curled lines), which in turn affects the particle's motion at later time t, the effect known as hydrodynamic memory. Friction force has thus a more complicated form, accounting for the particle acceleration at earlier times [9].

Importance of including hydrodynamic memory in the model of Brownian motion can be clearly seen from experimental measurements of MSD of a passive Brownian particle in a liquid [12, 15–17, 60, 61]. MSD is modified due the corresponding modification of friction force [9]: a fast exponential relaxation from the ballistic to the diffusive regime, described by Eq. (1.16), is slowed down, having a more complicated form of an algebraic transition (and also bare mass m is replaced by effective mass m^*) [54, 55, 59]. However, for a particle in a gas, experimental results for MSD [13, 14] show a good quantitative agreement with Eq. (1.16) obtained from the minimal model. Indeed, hydrodynamic effects are more significant in dense and viscous media, such as fluid, while they become less relevant in the environment with low density and viscosity, such as gas (which can be also explicitly seen from the expression for the modified friction force [9]).

Hydrodynamic interactions

The second important effect which is not included in Langevin equations (1.2), (1.20), and (1.21) is hydrodynamic interactions [62, 63]. These are interactions between Brownian particles (and also between particles and the system potentials, e.g., confining walls) mediated by the environment (see Fig. 1.7): a particle moving in, for example, a fluid

reads $\mathbf{F}^{\mathrm{fr}}(t) = -6\pi\eta_{\mathrm{env}}R\mathbf{v}(t) - \frac{2}{3}\pi R^3\rho_{\mathrm{env}}\dot{\mathbf{v}}(t) - 6R^2\sqrt{\pi\rho_{\mathrm{env}}\eta_{\mathrm{env}}}\int_0^t \frac{dt'}{\sqrt{t-t'}}\dot{\mathbf{v}}(t')$ [56–59]. The first term corresponds to the simple friction force used in Eqs. (1.2) and (1.20), with the Stokes friction coefficient $\gamma = \frac{1}{\mu} = 6\pi\eta_{\mathrm{env}}R$; the second term accounts for pressure from the environment on the accelerated particle (bare mass m is replaced by effective mass $m^* = m + \frac{2}{3}\pi R^3\rho_{\mathrm{env}}$); the third term describes the mentioned hydrodynamic memory effect.

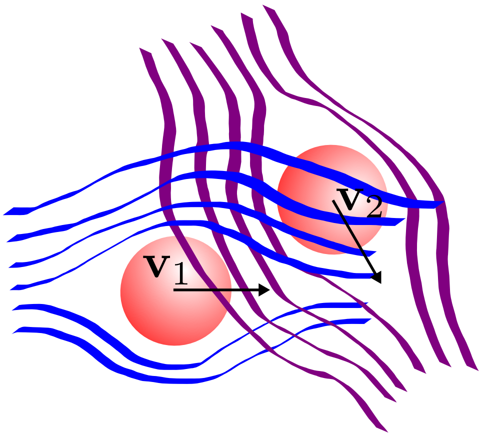

Figure 1.7. An illustration of hydrodynamic interactions between two Brownian particles. Particle 1 moving through a fluid creates a fluid flow (depicted as blue lines), thereby affecting the motion of particle 2. At the same time, particle 2 also creates a fluid flow (depicted as magenta lines), thereby affecting the motion of particle 1.

creates a fluid flow which in turn affects the motion of the other particles[10]. In the case of passive Brownian motion, hydrodynamic interactions can be modeled by generalizing the mobility μ in Eqs. (1.2) and (1.3) to a $DN \times DN$ matrix (where D and N are the number of dimensions and particles, respectively), with the entries depending on relative positions between particles (the functional form of this dependence is obtained by solving the corresponding Navier-Stokes equations describing the dynamics of the fluid as a continuous media) [62–66]. For active Brownian motion, a more complicated modification of Eqs. (1.20), (1.21), and (1.22) is required: in addition to generalization of μ and μ_r, one has to include the term describing the explicit effect of the particle activity on the environment, which depends on the swimming mechanism [31–33, 67].

Hydrodynamic interactions provide a significant contribution to the shear viscosity of Brownian suspensions, playing a major role for suspensions with short-ranged interparticle interactions and perturbed by large shear forces [68–70] (see Sec. 1.4 for a detailed discussion regarding the viscosity). They also play in important role in active particle dynamics [31–33, 71–77] as well as in collective behavior of active matter [31–33, 78–81].

Connection to reality

The above reviewed hydrodynamic effects are probably the most important missing ingredients in the minimal model of Brownian motion, but they are not the only ones. One can think of many other properties of real systems which are not captured by the model described in Subsecs. 1.2.1 and 1.2.2. However, no model describes reality exactly,

[10] Hydrodynamic interactions on a scale of Brownian motion are of the same nature as those which can be observed in everyday life. For example, swimmers in a swimming pool feel each other due to the disturbance of water they create while swimming, or a person walking down the street suddenly feels the air flow due to another person running by.

and it is the balance between the complexity and the validity which guides a theoretician towards the right choice.

To support the chosen minimal model of Brownian motion, we can say that it is the model which has only essential ingredients, and it is hence simple, clear, and relatively easy for making analytical and numerical computations. On the other hand, capturing most fundamental physics of Brownian motion by these essential ingredients, this model is able to predict important physical phenomena and quantities observed in experiments, both qualitatively and quantitatively. For example, as we mentioned above, MSD of a passive Brownian particle suspended in a gas agrees very well with the theoretical prediction given by Eq. (1.16) [13]; but even for a particle in a liquid, qualitative agreements can be found [12, 15]. The model is also able to predict collective phenomena intrinsic to active matter, where one might assume that hydrodynamic effects play a crucial role. For example, experimental observation of dynamical clustering and motility induced phase separation of a colloidal suspension of self-propelled particles is predicted by the minimal ABPs model [40]. Therefore, we conclude that the connection of the model to reality is strong enough.

Finally, it is important to note that we use a system of Brownian particles mainly to demonstrate our general results in linear response theory, most of which are supposed to be valid for a general stochastic system, rather than to predict concrete quantities and phenomena. Therefore, the chosen minimal model of Brownian motion should be treated here as an example but not a cornerstone for the main results of this dissertation.

1.3 Linear response theory in statistical physics

After discussing important aspects of statistical physics as well as introducing equilibrium and nonequilibrium stochastic systems, we can now turn to the topic of the thesis, which is "Linear response theory for equilibrium and nonequilibrium systems perturbed by nonconservative forces: The role of symmetries". In this section, we briefly introduce the linear response theory to the reader, to lay the foundation for our research presented in Chapter 2. In Chapter 3, the response theory will be discussed in more detail.

1.3.1 What is the linear response about?

Consider a general system of N particles given in some state at time $t = 0$ (for example, it can be a system of Brownian particles depicted in Fig. 1.1). Next, imagine that for time $t > 0$ the system is perturbed by forces $\{\mathbf{F}_i^{\text{ptb}}\}$ (which are usually, but not necessarily, external), with $\mathbf{F}_i^{\text{ptb}}$ acting on particle i. These forces can be in general explicitly time dependent: for example, the system can be perturbed by oscillating forces [82]. In this thesis, however, we mostly consider time-independent perturbations, but generalization to a time-dependent case is straightforward (see Sec. 3.2). If the system has rotational degrees of freedom [e.g., described by Eq. (1.21)], one can also consider perturbation torques. Due to the perturbation, the initial state of the system changes to a new one: the dynamics and the distribution depend on $\{\mathbf{F}_i^{\text{ptb}}\}$. As a result, for time $t > 0$, the average of an observable $A(\Gamma(t)) \equiv A(t)$ measured in the perturbed system, $\langle A(t)\rangle^{\text{ptb}}$, differs from its unperturbed average, $\langle A(t)\rangle$. The goal of the linear response theory is to find the difference $\langle A(t)\rangle^{\text{ptb}} - \langle A(t)\rangle$, i.e., the response of A to $\{\mathbf{F}_i^{\text{ptb}}\}$, up to the linear order in $\{\mathbf{F}_i^{\text{ptb}}\}$ in terms of an average computed in the unperturbed system.

It depends on the system and on $\{\mathbf{F}_i^{\text{ptb}}\}$, which quantity is averaged (we discuss different forms of response relations in the next chapters), but at the moment, let us restrict to a system being in equilibrium at $t = 0$ and perturbed by time-independent external forces $\{\mathbf{F}_i^{\text{ptb}}(\mathbf{r}_i)\}$. In this case, the linear response reads as [83, 84]

$$\langle A(t)\rangle^{\text{ptb}} - \langle A\rangle = \frac{1}{k_{\text{B}}T}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{N}\mathbf{F}_i^{\text{ptb}}(t')\cdot\dot{\mathbf{r}}_i(t')\right\rangle, \tag{1.34}$$

where $t \geq 0$, and a shorthand notation $A(t) \equiv A(\Gamma(t))$, $\mathbf{F}_i^{\text{ptb}}(t) \equiv \mathbf{F}_i^{\text{ptb}}(\mathbf{r}_i(t))$ is used. Note that the equilibrium average, $\langle A\rangle$, is time independent. Formula (1.34) is the starting point for our research presented in Chapter 2, and it is a typical linear response relation in statistical physics. The left-hand side is a formal expression for the response, the average we want to compute. The right-hand side is the desired result, the average computed in the unperturbed system of a quantity which is linear in $\{\mathbf{F}_i^{\text{ptb}}\}$. The physics of Eq. (1.34) will be discussed in Sec. 2.1, but the main conclusion about a typical structure of a linear response relation can be already drawn: the response is given by the time integral of an unperturbed correlation function of the considered observable with another quantity linear in $\{\mathbf{F}_i^{\text{ptb}}\}$.

1.3.2 The value of linear response theory, and its applications

Formula (1.34) states that, in order to compute the linear response of a system to an external *perturbation*, one can compute a correlation function for the *unperturbed* system. Although, from a purely mathematical point of view, this is simply a consequence of a series expansion of the average around perturbation forces (see Subsec. 1.3.3), physically, this is a wonderful approach for computing averages. The wonder and the value of this linear response approach is that one does not have to deal with the perturbed system to predict its response, but instead, one can compute correlations of the unperturbed system (see Fig. 1.8 for an illustration).

This value is for all three ways of computation: experimental, numerical, and analytical. Experimentally, the linear response approach is particularly useful in the cases when the direct measurement in the perturbed system is difficult to perform (e.g., due to difficulties to create the needed perturbation or to measure the desired observable affected by this perturbation [85–87]). In addition, measurements of unperturbed correlations are typically of higher accuracy and, for certain perturbations, they also allow to predict the response to arbitrary perturbation protocols from a single experiment [88]. As for numerical simulations, the linear response method has similar advantages. It may be a nontrivial task to realize a perturbation in simulations: for example, perturbing a bulk system by shear flow requires realization of more complex boundary conditions [89] than those used for an equilibrium system [11]. Also in terms of statistical accuracy,

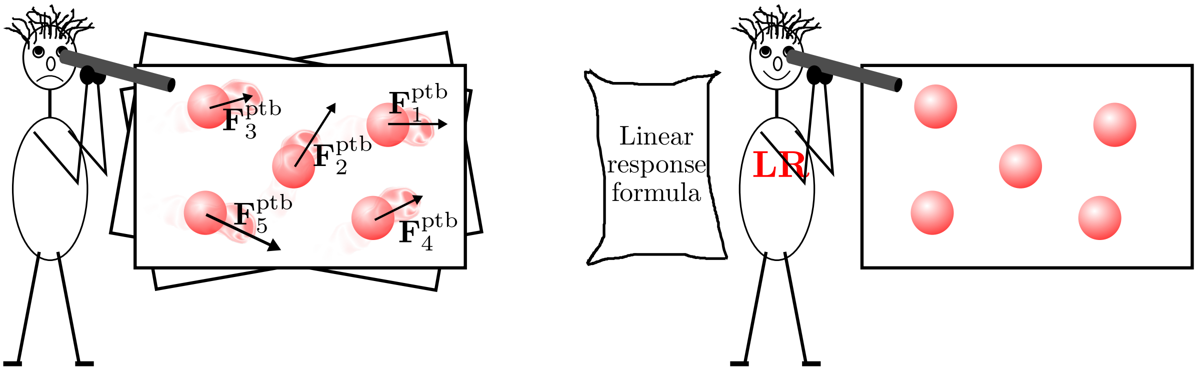

Figure 1.8. A physicist, who is interested in the response of a system to a small perturbation $\{\mathbf{F}_i^{\mathrm{ptb}}\}$, can compute the response in two ways. The direct computation (the left panel) requires perturbation of the system, while the linear response theory (the right panel) allows to compute the desired response by measuring fluctuations in the unperturbed system [compare the left-hand and right-hand sides of response formula (1.34)]. The linear response approach is usually advantageous, because it is typically more difficult to create the needed perturbation and to perform measurements in the perturbed system, rather than to evaluate unperturbed correlation functions [85–87].

and hence in terms of computational resources, numerical evaluation of equilibrium correlation functions is often advantageous over the direct computation of the considered observable in the system driven out of equilibrium, which we demonstrate in Sec 2.4. From the experience of the author, the value of the linear response is not so evident for analytical computations: it is sometimes easier to compute a perturbed average rather than the corresponding unperturbed correlation functions (see Sec. 2.7 and Subsec. 4.5.2). Nevertheless, response relations provide an alternative route for analytical computations of physical quantities.

Applications of linear response theory are mostly related to computation of transport coefficients, such as mobility (see Subsec. 1.3.4), viscosity (see Sec. 1.4), or electrical and thermal conductivity [3, 20, 21], as well as of other important macroscopic parameters, e.g., magnetic susceptibility [3, 90]. Apart from this, the change of a system dynamics [91] and structure (see Ref. [92] and Sec. 2.4) due to perturbations can be studied using the linear response. Linear response theory of statistical physics is found to be useful even in climate science [93, 94].

1.3.3 Some aspects of stochastic linear response

Everything revolves around statistics

The mathematical essence of response theory is a series expansion of the quantity of interest around perturbation forces. Clearly, this essence remains the same for any area of science: for example, perturbation theory in quantum mechanics [95] has similar principles as those used in stochastic linear response. Yet, the response theories are very different in many aspects, including mathematical formalisms for describing the systems, ways of derivation of the response relations, as well as methods for computing the responses. It is not our aim to make a detailed comparison between linear response theories for different subject areas, but we would like to stress some key features intrinsic to statistical physics.

As we mentioned above, statistical physics as about averaging. The desired average can be found from the distribution containing the information about the system's statistics. The change of the distribution due to a perturbation fully determines the change of any average, and the linear response is found by expanding the new distribution around perturbation forces. This is a fundamental difference to deterministic systems, where no distribution exists (alternatively, one can say that the distribution has a trivial form of delta-function), and where one has to perturb trajectories (i.e., the exact positions and velocities), as in classical mechanics, or energy levels and wave functions, as in quantum perturbation theory. Stochastic response theory has thus different mathematical formalism and physical interpretation compared to similar theories in other subject areas. It can be simply seen from the form of response relations (i.e., Eq. (1.34) contains average brackets and temperature). Also, derivation methods of stochastic response are based on statistical methods, including perturbation of Smoluchowski (Liouville) operator appearing in Smoluchowski (Liouville) equation for a probability distribution [20, 43, 96, 97], expansion of path weight describing the probability of a certain trajectory (see Sec. 3.2 and Refs. [98–102]), and Malliavin weight sampling (see Subsec. 3.2.5 and Ref. [103]). Although perturbation of trajectories can be, in principle, used also in statistical physics, it is disadvantageous and hardly applicable for stochastic systems (and is hence very uncommon) compared to conventional statistical methods (see Sec. 3.5 and Refs. [103, 104]).

Linearity

We hope that, after going through the above written text of this section, the reader has acquired some basic understanding of linear response theory in statistical physics (for details, we refer the reader to Refs. [1–3, 20, 21, 84]). However, two expected and important questions still remain unanswered: (i) "Does it make sense to consider only the linear order in the response?"; (ii) "Why do we consider only the linear order?"

These two questions are interconnected, and we have to first provide a positive answer to the first question before answering the second one. It depends on the strength of a perturbation, whether the *linear* response is valid or not. This strength has to be compared to the strength of fluctuations of the unperturbed system (i.e., to interparticle and external forces before perturbation is applied). The smaller the ratio of a perturbation to the fluctuations, the more is the validity of the linear response theory. Therefore, in situations where a perturbation is small compared to the fluctuations, it does make sense to consider only the linear order. But why do we stick to only the linear order? First, obviously because the linear order is the simplest one. Formula (1.34) contains *two*-point correlation function (i.e., correlation of quantities at *two* different times), while already the second order response requires evaluation of three-point correlations [87, 101]. In addition, the linear response has several remarkable properties absent in higher orders, as for example superposition principle (see Subsec. 2.2.3). And second, it turns out that in many situations linear response theory is enough to correctly predict physical phenomena and accurately estimate physical quantities [3], which we demonstrate throughout this thesis. However, for large perturbations, the linear response theory fails (see the inset plot of Fig. 2.3), and higher orders thus have to be considered.

1.3.4 The fluctuation-dissipation theorem and Green-Kubo relations

The energy given to a thermodynamic system due to an applied perturbation is distributed among the system components, and the system finally approaches a state with a new energy – the process called "dissipation". This distribution of energy depends on the system, i.e., on interparticle and particle-environment interactions, external forces, temperature and other system parameters. On the other hand, these properties determine fluctuations of the *unperturbed* system, i.e., systems with different interaction potentials have different correlation functions. For small perturbations (such that the linear order is a good approximation for the system response), dissipation and fluctuations determine each other, the statement known as the fluctuation-dissipation theorem (FDT).

Since linear response formula (1.34) connects the system response, which is the result of dissipation, and unperturbed fluctuations, linear response theory and FDT describe the same physical law and are usually considered as interchangeable concepts in the literature [1–3, 20, 21, 84, 105]. FDT is understood as a final result (statement, law, theorem, or formula), while linear response theory is the corresponding mathematical formalism to obtain this result. It should be noted, however, that there is a terminological ambiguity in the literature regarding the connection between FDT and general response relations: typical FDT is the linear response of an equilibrium system to a potential perturbation [20, 84, 105]; response formulas for nonconservative perturbations, giving expressions for transport coefficients, are usually associated with Green-Kubo relations [3, 20, 21, 96, 97, 106]; while the linear response of a nonequilibrium system is called "a generalized FDT" [98–100, 107, 108] or "a generalized Green-Kubo relation" [102]. In principle, any linear response relation can be considered as FDT from the physical point of view. At some stages of this thesis, we will specify what we mean by FDT to avoid possible confusions.

Sutherland-Einstein-Smoluchowski relation: the first manifistation of FDT

We have already mentioned that historically first (and also the most popular) manifestation of FDT is Sutherland-Einstein-Smoluchowski relation (1.18). A remarkable feature of this relation is that it connects dissipation and fluctuation via clear physical quantities, mobility and diffusion coefficient. Alternative to the derivation in Subsec. 1.2.1, here we derive Eq. (1.18) using linear response theory [9, 20, 21], shedding light on the connection between the linear response and FDT.

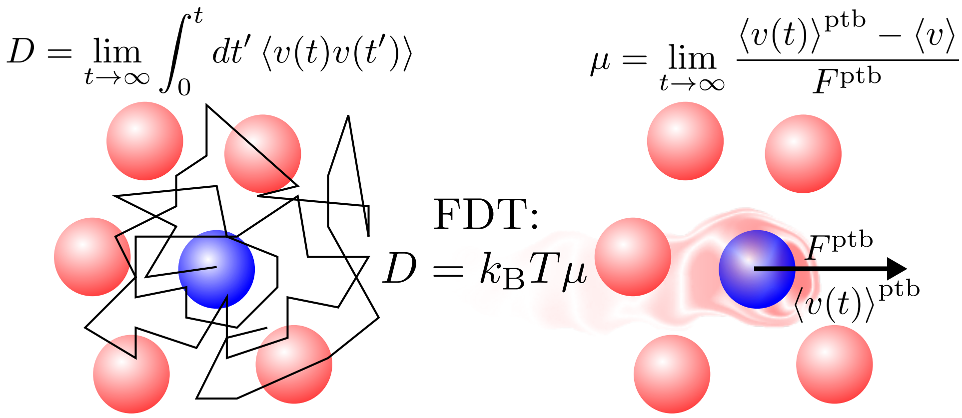

Figure 1.9. Illustration of Sutherland-Einstein-Smoluchowski relation, an example of FDT. The diffusion coefficient D, stemming from equilibrium velocity fluctuations of a tagged particle, is proportional to the particle mobility μ, characterizing the response (and the resulting dissipation depicted as the red cloud) of the system to the applied perturbation F^{ptb}.

Consider an arbitrary system of N (interacting) particles, being in equilibrium at time $t = 0$[11]. With no perturbation applied, the system remains in equilibrium for $t > 0$ (see the left panel of Fig. 1.9), and the one-dimensional diffusion coefficient of a tagged particle is defined as[12]

$$D = \lim_{t\to\infty} \frac{1}{2}\frac{d}{dt}\left\langle [x(t) - x(0)]^2 \right\rangle , \tag{1.35}$$

compatible with Einstein formula (1.1). Using simple mathematical manipulations, the diffusion coefficient in Eq. (1.35) can be related to the velocity autocorrelation function[13]:

$$D = \lim_{t\to\infty} \frac{1}{2}\frac{d}{dt}\left\langle [x(t) - x(0)]^2 \right\rangle = \lim_{t\to\infty} \langle v(t)[x(t) - x(0)]\rangle = \lim_{t\to\infty} \int_0^t dt' \langle v(t)v(t')\rangle . \tag{1.36}$$

Consider now that for time $t > 0$ the system is perturbed by a constant force F^{ptb} acting on a tagged particle in direction x (see the right panel of Fig. 1.9). We are interested in the change of the average particle velocity in the x direction due to this perturbation, namely $\langle v(t)\rangle^{\text{ptb}} - \langle v\rangle$. The ratio of this change to the applied force defines

[11]For a proper definition of diffusion coefficient and mobility, we assume that external potentials can be neglected, i.e., consider bulk system.

[12]Note that, due to interactions of a tagged particle with other particles, the diffusion coefficient D and mobility μ defined in Eqs. (1.35) and (1.37), respectively, differ from those of an isolated, i.e., noninteracting, Brownian particle appearing in Eq. (1.2) (the so-called bare diffusion coefficient and mobility). For interacting systems, D and μ are reduced compared to bare ones, because the particle motion is slowed down by the presence of other particles [109, 110].

[13]Remember (see the discussion in Sec. 1.2.1) that the instantaneous velocity is not well defined in the overdamped case. Therefore, in the overdamped limit, the diffusion coefficient in terms of MSD is preferable over that in terms of the velocity autocorrelation function.

the particle mobility μ,

$$\mu = \lim_{t\to\infty} \frac{\langle v(t)\rangle^{\text{ptb}} - \langle v\rangle}{F^{\text{ptb}}}. \tag{1.37}$$

On the other hand, according to linear response formula (1.34), we can compute the mobility using the time integral of the equilibrium correlation function:

$$\mu = \lim_{t\to\infty} \frac{\langle v(t)\rangle^{\text{ptb}} - \langle v\rangle}{F^{\text{ptb}}} = \frac{1}{k_{\text{B}}T} \lim_{t\to\infty} \int_0^t dt' \, \langle v(t)v(t')\rangle \,. \tag{1.38}$$

Substituting Eq. (1.36) into Eq. (1.38), we finally get[14]

$$\mu = \lim_{t\to\infty} \frac{\langle v(t)\rangle^{\text{ptb}} - \langle v\rangle}{F^{\text{ptb}}} = \frac{1}{k_{\text{B}}T} \lim_{t\to\infty} \int_0^t dt' \, \langle v(t)v(t')\rangle = \frac{D}{k_{\text{B}}T}, \tag{1.39}$$

which is nothing else than the famous Sutherland-Einstein-Smoluchowski relation (1.18). Formula (1.39) is physically insightful, as it represents the connection between linear response theory, FDT, and measurable physical quantities. Perturbation of the system results in dissipation which is characterized by the particle mobility defined as the linear response of the velocity to the applied force. According to linear response theory, the response is related to equilibrium velocity autocorrelation function given by the particle diffusion coefficient. This means that dissipation of the perturbation (described by the mobility) and equilibrium fluctuations (described by the diffusion coefficient) determine each other, the statement known as FDT. An illustration of Sutherland-Einstein-Smoluchowski relation is given in Fig. 1.9.

Development of FDT

Starting from Sutherland-Einstein-Smoluchowski relation (1.39) in 1905, FDT has undergone a multifaceted evolution, and it is of high unbroken interest nowadays. Among other prominent examples of the theorem are Johnson-Nyquist noise [111] and thermal radiation [112–117]. The first general formulation of FDT (which is also valid for quantum systems) has been given by H. B. Callen and T. A. Welton in 1951 [118], and progressed by J. Weber in 1956 [119]. Further development of FDT, and in particular the connection to linear response theory, has been discussed by R. Kubo in 1966 [105]. In recent years, the focus of FDT has been moving towards nonequilibrium systems, where fundamental differences to the equilibrium case appear (these differences are discussed throughout the thesis) [30, 98, 120, 121]. For a detailed review of FDT, we refer the reader to Ref. [84]

Green-Kubo relations

The linear response of a system to imposed flows or fields is given via transport coefficients. An electric field applied to a system of charged particles leads to an electric

[14] The consistency of formula (1.39) with Langevin equation (1.2) can be checked by plugging in the equilibrium velocity autocorrelation function of an isolated Brownian particle, $\langle v(t)v(t')\rangle = \frac{k_{\text{B}}T}{m} e^{-\frac{1}{m\mu}(t-t')}$.

current (response) characterized by the electrical conductivity, a temperature gradient imposed to a system results in a heat current described by the thermal conductivity, while a liquid perturbed by a shear flow experiences the shear stress along the flow gradient which is quantified by the fluid viscosity (see Sec. 1.4). The macroscopic transport coefficients characterizing the response, i.e., the electrical (thermal) conductivity and the viscosity, are related to equilibrium fluctuations of microscopic quantities via FDT (e.g., the electrical conductivity is given via electric current fluctuations of charged particles). In honor of M. S. Green and R. Kubo, being first who derived fluctuation-dissipation formulas for transport coefficients, these formulas are usually called Green-Kubo relations [3, 20, 21, 84, 90, 96, 97, 105, 106].

1.4 Response to shear flow: Rheology

1.4.1 Perturbing by shear

An important and, in the meantime, very illustrative perturbation is shear. Being a common perturbation in everyday life, it is intensively studied by physicists and engineers. The reader can realize shear by shifting the two sides of a book (or maybe even of this thesis!) in opposite directions. Another common example would be the flow of a fluid in a pipe, where the fluid velocity profile is not homogeneous, which is usually termed as shear flow. There are many types of shear, and they are modelled differently in different areas of physics.

In this thesis, we concentrate on linear shear flow (also called simple shear or Couette flow), whose velocity profile reads

$$\mathbf{V}(\mathbf{r}) = \dot{\gamma} \begin{pmatrix} y \\ 0 \\ 0 \end{pmatrix}, \tag{1.40}$$

where $\dot{\gamma} > 0$ is the shear rate (see Fig. 1.10). One typically realizes this flow by sliding two parallel plates, immersed in a fluid, in opposite directions. For a system of Brownian particles with mobility μ, the corresponding perturbation force can be written as

$$\mathbf{F}_i^{\text{ptb}} = \frac{\dot{\gamma}}{\mu} \begin{pmatrix} y_i \\ 0 \\ 0 \end{pmatrix}. \tag{1.41}$$

Linear response relations for perturbation by simple shear depend on the considered system, and we will explore these relations later. For now, let us start with the Green-Kubo relation for an equilibrium system of overdamped Brownian particles,

$$\langle A(t) \rangle^{(\dot{\gamma})} - \langle A \rangle = \frac{\dot{\gamma}}{k_{\text{B}}T} \int_0^t dt' \, \langle A(t') \sigma_{xy}(0) \rangle \,, \tag{1.42}$$

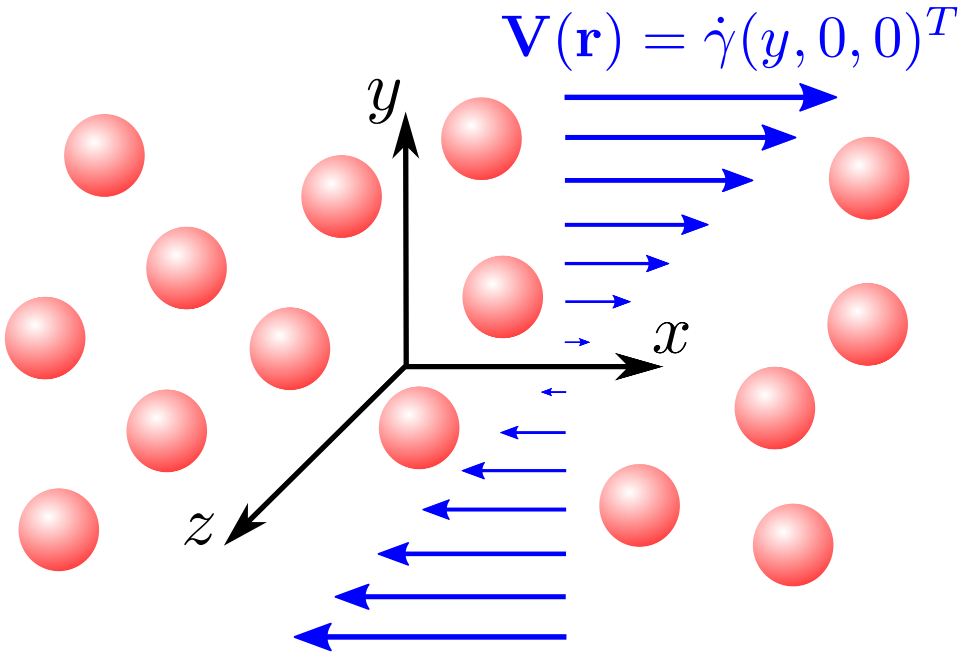

Figure 1.10. A system of particles perturbed by linear shear flow with the velocity profile $\mathbf{V}(\mathbf{r}) = \dot\gamma(y,0,0)^T$ depicted via blue arrows. $\dot\gamma > 0$ is the shear rate.

where $\langle A(t)\rangle^{(\dot\gamma)} \equiv \langle A(t)\rangle^{\text{ptb}}$ and σ_{xy} is the xy component of the stress tensor defined as

$$\sigma_{xy} = -\sum_{i=1}^{N}\left(F_{ix}^{\text{int}} + F_{ix}^{\text{ext}}\right) y_i. \tag{1.43}$$

Formula (1.42) can be derived using the Smoluchowski equation [96] or path integrals (see Sec. 3.6).

We use shear perturbation in Eq. (1.41) to demonstrate our general results in Chapter 2 and to study the response of active Brownian particles in Chapter 4.

1.4.2 Rheology

The response to shear tells us about one of the most important properties of the considered system – its viscosity. Roughly speaking, the larger the viscosity is, the more difficult it is to move one part of a system relative to another part, i.e., a system with a large viscosity is hardly deformable. For example, honey is much more viscous than water. Determination of viscosity and, more generally, investigation of deformation and flow of matter in different systems, are the goals of rheology [62, 122].

As for Brownian particles described by the minimal model, one distinguishes two viscosities: the bare viscosity of the solvent and the total viscosity of a Brownian suspension (i.e., the viscosity of the solvent and the particles as a whole). While the former is typically considered to be fixed and determined by the bare mobility μ, the latter depends on the system parameters, and it is what one aims to compute. How is this computation performed? In the case of passive overdamped Brownian suspensions, the resistance of a system to shear flow, and hence its viscosity, is characterized by the interaction part of the stress tensor (1.43),

$$\sigma_{xy}^{\text{int}} = -\sum_{i=1}^{N} F_{ix}^{\text{int}} y_i. \tag{1.44}$$

In general, the viscosity $\eta(t)$ is a function of time t after start of shear, and it depends on the shear rate $\dot{\gamma}$ [84, 123, 124],

$$\eta(t) = \frac{\left\langle \sigma_{xy}^{\text{int}}(t) \right\rangle^{(\dot{\gamma})}}{\dot{\gamma} V}, \tag{1.45}$$

where V is the volume of the considered bulk system[15]. Typically however, one is interested in the zero-shear limiting viscosity (also known as the Newtonian viscosity), where one assumes $\left\langle \sigma_{xy}^{\text{int}}(t) \right\rangle^{(\dot{\gamma})}$ to be linear in $\dot{\gamma}$, such that $\eta(t)$ does not depend on the shear rate. In this case, one can use linear response theory: setting $A = \sigma_{xy}^{\text{int}}$ in Eq. (1.42) and assuming $\left\langle \sigma_{xy}^{\text{int}} \right\rangle = 0$ (there are no flows in equilibrium), one gets the Green-Kubo relation for the shear viscosity [20, 21, 84, 97, 110, 123],

$$\eta(t) = \frac{1}{k_{\text{B}} T V} \int_0^t dt' \left\langle \sigma_{xy}^{\text{int}}(t') \sigma_{xy}^{\text{int}}(0) \right\rangle, \tag{1.46}$$

whose steady-state value is obtained in the limit $t \to \infty$.

The value of the shear viscosity as well as the form of Eqs. (1.44), (1.45), and (1.46) depend on the considered system and the chosen model. As discussed in Subsec. 1.2.3, hydrodynamic interactions play an important role here. Another interesting question is how the activity of the particles affects the viscosity. In that respect, active suspensions exhibit surprising properties: the active forces exerted by swimmers in a suspension can lead to an increase [125] or decrease [126] in the viscosity, even turning the suspension into a superfluid [127].

We do note study viscosity in this dissertation, but we think that this is the most optimal and important topic for an extension of the research presented here. Let us now finally take a look what this research is all about.

1.5 About this thesis

In this dissertation, based on theoretical statistical physics, we study the linear response of equilibrium and nonequilibrium systems, mostly concentrating on nonconservative

[15] For a proper measurement of viscosity, one has to avoid the boundary effects, i.e., external potentials. Therefore, the measurement has to be performed in a part of the system, where these effects can be neglected, the so-called bulk region with the volume V. In computer simulations, this measurement is performed using boundary conditions [11, 89].

perturbations, in particular, shear flow. Our research includes the method of restoring FDT for nonconservative forces, derivation of linear response relations for various systems, and investigation of specific cases using computer simulations and analytical computations. We hence hope that the thesis has a good balance between general results and concrete demonstrations.

In Chapter 2, focusing on equilibrium systems, we propose a method allowing to compute the response to a nonconservative perturbation via the response to a potential. Using this method, a response formula, alternative to and advantageous over the known Green-Kubo relation, is derived. To demonstrate the formula, we investigate the transient response of Brownian systems to shear flow, both analytically and in computer simulations, where several interesting features are observed.

In Chapter 3, we systemize the existing knowledge about linear response theory, paying a special attention to a path integral approach for deriving response relations. Discussing the response of equilibrium and nonequilibrium systems perturbed by conservative and nonconservative forces, we identify fundamental differences between the four cases. Furthermore, some aspects related to stochastic calculus, as well as the connection between deterministic and stochastic response theories are discussed.

Results of Chapters 2 and 3 are then combined in Chapter 4 to derive the response formulas for overdamped active Brownian particles perturbed by shear. Several active interacting systems are studied numerically, demonstrating the derived formulas and revealing interesting properties of active particles.

Finally, Chapter 5 summarizes the key results of the thesis in one compact and illustrative example, where all forms of the response studied in the previous chapters are revisited.

2 Nonconservative forces and the fluctuation-dissipation theorem (FDT)

In this chapter, we present a method of computing the linear response of an equilibrium system to nonconservative perturbation forces via the response to a potential, demonstrating that a conventional FDT for a potential perturbation can be also used for nonpotential perturbations. The work presented here is based on the research of the author, his supervisor (Matthias Krüger[1]) and collaborators, Christian M. Rohwer[2] and Alexandre P. Solon[3]. The first part of this chapter (Secs. 2.2, 2.3, and 2.4) is based on Ref. [128], and hence the content of this part is close to that reference. However, the results of the second part (Secs. 2.5, 2.6, and 2.7) are not included in Ref. [128].

2.1 Linear response for potential and nonpotential perturbations

Consider a classical system of N interacting particles, subject to external potentials and coupled to a heat bath at temperature T, in thermal equilibrium at time $t = 0$ (see Fig. 1.1). For time $t > 0$, the system is perturbed by, in general, nonconservative forces $\{\mathbf{F}_i^{\mathrm{ptb}}\}$, with $\mathbf{F}_i^{\mathrm{ptb}}$ acting on particle i at position $\mathbf{r}_i$. The linear response of an observable of interest A to the applied perturbation $\{\mathbf{F}_i^{\mathrm{ptb}}\}$ is given by formula (1.34), which we repeat here:

$$\langle A(t)\rangle^{\mathrm{ptb}} - \langle A\rangle = \frac{1}{k_{\mathrm{B}}T}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{N}\mathbf{F}_i^{\mathrm{ptb}}(t')\cdot\dot{\mathbf{r}}_i(t')\right\rangle, \tag{2.1}$$

where time dependence of $\mathbf{F}_i^{\mathrm{ptb}}$ and A is acquired through the phase space, i.e., we do not consider explicit time dependence. A careful reader may note that the equilibrium correlation function on the right-hand side of Eq. (2.1) is the correlation of A with the work $\int_0^t dt' \sum_{i=1}^N \mathbf{F}_i^{\mathrm{ptb}}(t')\cdot\dot{\mathbf{r}}_i(t')$ done by the applied perturbation forces on the system.

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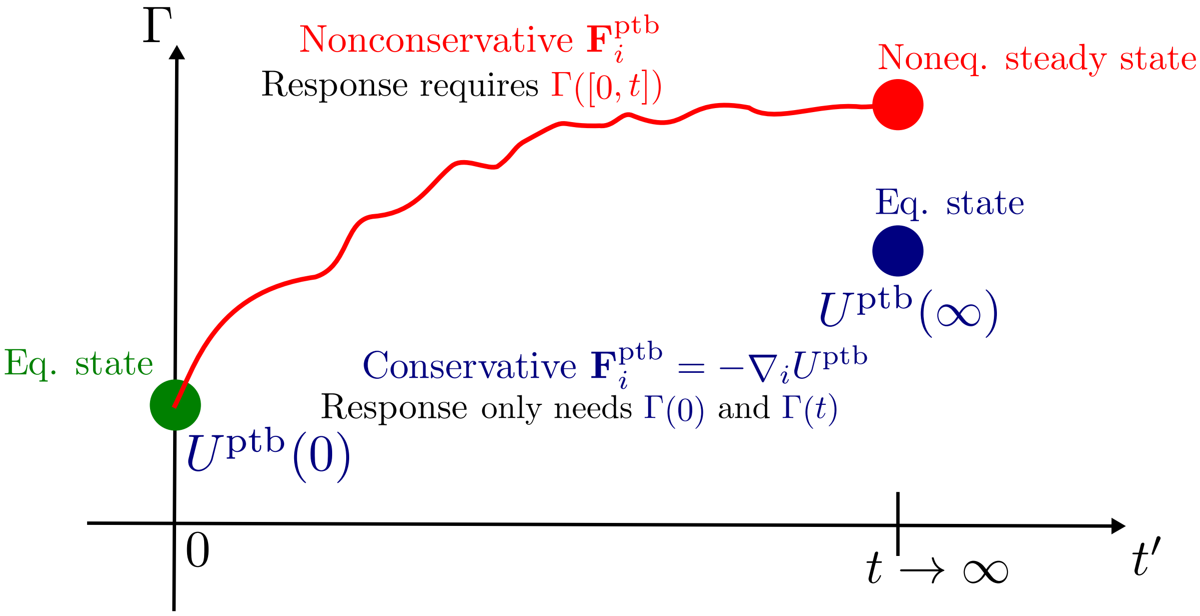

Figure 2.1. Illustration of nonconservative versus conservative perturbations on a phase space-time plot. When perturbing from the initial equilibrium state (green circle) by a nonconservative force, the linear response of the system depends on the path, and hence the time integral over this path has to be performed [see Eq. (2.1)]; the final state (red circle) is a nonequilibrium state. In contrast, in the case of a conservative perturbation, the response depends only on the initial and final states (green and blue circles, respectively) determined by the perturbation potential [see Eq. (2.3)]; the perturbed system approaches a new equilibrium.

On the other hand, the denominator contains thermal energy $k_{\text{B}}T$, characterizing the strength of equilibrium fluctuations. Response relation (2.1) has thus a clear physical meaning: the linear response of an equilibrium system to a perturbation force is determined by the ratio of the work done by this force (i.e., the energy given to the system) to equilibrium energy. The more work is performed, the larger the response is[4].

One can distinguish two cases for the linear response of equilibrium systems (see Fig. 2.1). The first case covers conservative (potential) perturbation forces, such that $\{\mathbf{F}_i^{\text{ptb}}\}$ arise from a potential U^{ptb}, $\mathbf{F}_i^{\text{ptb}} = -\nabla_i U^{\text{ptb}}$. In this situation, the work done on the system depends only on the initial and final configurations, namely

$$\int_0^t dt' \sum_{i=1}^{N} \mathbf{F}_i^{\text{ptb}}(t') \cdot \dot{\mathbf{r}}_i(t') = U^{\text{ptb}}(0) - U^{\text{ptb}}(t), \tag{2.2}$$

[4]The validity of considering only the linear order in the response, discussed in Subsec. 1.3.3, can be now formulated in a more quantitative form: the linear order term provides a good approximation for the total response if the work $\left\langle \int_0^t dt' \sum_{i=1}^N \mathbf{F}_i^{\text{ptb}}(t') \cdot \dot{\mathbf{r}}_i(t') \right\rangle$ done by a perturbation force is small compared to the characteristic energy of equilibrium fluctuations $k_{\text{B}}T$.

and formula (2.1) simplifies to[5]

$$\langle A(t)\rangle^{\mathrm{ptb}} - \langle A\rangle = -\frac{1}{k_{\mathrm{B}}T}\left[\langle AU^{\mathrm{ptb}}\rangle - \langle A(t)U^{\mathrm{ptb}}(0)\rangle\right]. \tag{2.3}$$

A remarkable feature of a potential perturbation is that the system relaxes to a new equilibrium. Indeed, the stationary limit of Eq. (2.3) can be derived from the equilibrium distribution the system relaxes to. In the second case, where perturbation forces are nonconservative (nonpotential), the work depends on the path [the integral in Eq. (2.2) remains], and the system is driven to a nonequilibrium steady state. While formula (2.3) is universal [20, 84], Eq. (2.1) can have different forms depending on the considered system and on the derivation method [see Refs. [43, 84, 96, 97, 103] and compare Eqs. (2.20), (2.26), and (3.37) for shear perturbation]. Therefore, in this section, we refer to response relation (2.3) as FDT, while treat formula (2.1) as a general linear response formula for perturbing equilibrium systems, although, formally, the latter represents FDT as well.

2.2 Restoring FDT

Our main message of this chapter is that, in certain cases (covering important scenarios), it is possible to use formula (2.3) even for nonconservative perturbations, as we demonstrate in this section.

2.2.1 Making a conservative force from nonconservative forces

Let us first assume that, for any particle i, the perturbation force $\mathbf{F}_i^{\mathrm{ptb}}$ has a partner force $\widetilde{\mathbf{F}}_i^{\mathrm{ptb}}$ such that adding the two forces results in a potential force with the corresponding potential $2U^{\mathrm{ptb}}$:

$$\mathbf{F}_i^{\mathrm{ptb}} + \widetilde{\mathbf{F}}_i^{\mathrm{ptb}} = -\nabla_i\left[2U^{\mathrm{ptb}}\right]. \tag{2.4}$$

2.2.2 The idea about symmetries

Next, consider that the system and the observable A are symmetric with respect to the application of $\{\mathbf{F}_i^{\mathrm{ptb}}\}$ and $\{\widetilde{\mathbf{F}}_i^{\mathrm{ptb}}\}$, such that the linear responses of the system to these perturbations are equivalent, i.e.,

$$\langle A(t)\rangle^{\mathrm{ptb}}\Big|_{\mathbf{F}_i^{\mathrm{ptb}}} = \langle A(t)\rangle^{\mathrm{ptb}}\Big|_{\widetilde{\mathbf{F}}_i^{\mathrm{ptb}}}. \tag{2.5}$$

[5]Note that time dependence of the first term in Eq. (2.3) is suppressed, because an equal-time equilibrium correlation function is time independent, i.e., $\langle A(t)U^{\mathrm{ptb}}(t)\rangle = \langle AU^{\mathrm{ptb}}\rangle$.

2.2.3 The wonder of linear response: superposition principle

Finally, we use the superposition principle of the linear response:

$$\langle A(t)\rangle^{\text{ptb}}\Big|_{\mathbf{F}_i^{\text{ptb}}+\widetilde{\mathbf{F}}_i^{\text{ptb}}} - \langle A\rangle = \left[\langle A(t)\rangle^{\text{ptb}}\Big|_{\mathbf{F}_i^{\text{ptb}}} - \langle A\rangle\right] + \left[\langle A(t)\rangle^{\text{ptb}}\Big|_{\widetilde{\mathbf{F}}_i^{\text{ptb}}} - \langle A\rangle\right]. \tag{2.6}$$

Assumptions (2.4) and (2.5), and property (2.6) allow us to make the central claim of this chapter: in certain cases [covered by Eqs. (2.4) and (2.5)], the linear response to a nonpotential perturbation $\{\mathbf{F}_i^{\text{ptb}}\}$ is equivalent to the linear response to a potential perturbation with the potential U^{ptb}, and it is given by FDT (2.3).

2.2.4 A method of restoring FDT

Based on the discussions of Subsecs. 2.2.1, 2.2.2 and 2.2.3, we can now provide a method for computing the linear response to a nonpotential perturbation via the response to a potential: (i) given a nonpotential perturbation force, find a partner force such that adding the two forces results in a potential; (ii) find conditions which allow for the responses to each of the two forces to be equivalent; (iii) under these conditions, the resulting response to the initial nonpotential perturbation is equivalent to the response to the half of the found potential, and it is given by FDT (2.3).

In Sec. 1.3, we learned that one can compute the linear response to some perturbation by looking at the correlation function for the unperturbed system, i.e., the perturbation does not have to be applied. The method presented in this section reveals another interesting feature of linear response theory: in order to compute the linear response to some perturbation, one can alternatively use another, fundamentally different, perturbation. Indeed, nonconservative and conservative perturbations, being fundamentally different in a way they drive the system out of equilibrium as well as in their mathematical representations via linear response relations, can still lead to the same response.

We further note that the presented method can be possibly used in quantum systems and, more generally, in any area of physics, as the ideas we employed are very general.

2.2.5 An alternative view: a freedom of adding forces

Aiming to formulate the method of restoring FDT in a more intuitive way, Matthias Krüger came up with the idea of a freedom of adding perturbation forces. Defining the force $\mathbf{G}_i^{\text{ptb}}$ as

$$\mathbf{G}_i^{\text{ptb}} = \frac{1}{2}\left(\widetilde{\mathbf{F}}_i^{\text{ptb}} - \mathbf{F}_i^{\text{ptb}}\right), \tag{2.7}$$

one can see from Eqs. (2.4), (2.5), and (2.6) that, while complementing the initial perturbation $\mathbf{F}_i^{\text{ptb}}$ to a potential U^{ptb}, the introduced $\mathbf{G}_i^{\text{ptb}}$ has no effect on the response, i.e., $\langle A(t)\rangle^{\text{ptb}}\Big|_{\mathbf{G}_i^{\text{ptb}}} = 0$. Therefore, adding $\mathbf{G}_i^{\text{ptb}}$ to $\mathbf{F}_i^{\text{ptb}}$, one makes the perturbation conservative without changing the response.

The method can be thus elegantly formulated via a freedom of adding perturbation forces. Namely, response formula (2.1) displays a freedom in $\mathbf{F}_i^{\text{ptb}}$: it allows adding perturbation forces $\mathbf{G}_i^{\rm ptb}$ whose work does not couple to the considered observable A, i.e.,

$$\int_0^t dt' \left\langle A(t) \sum_{i=1}^N \mathbf{G}_i^{\rm ptb}(t') \cdot \dot{\mathbf{r}}_i(t') \right\rangle = 0, \tag{2.8}$$

without changing the response of A. Therefore, if a force $\mathbf{G}_i^{\rm ptb}$ obeying Eq. (2.8) exists such that adding the two forces results in a potential $U^{\rm ptb}$,

$$\mathbf{F}_i^{\rm ptb} + \mathbf{G}_i^{\rm ptb} = -\nabla_i U^{\rm ptb}, \tag{2.9}$$

then, according to Eq. (2.1), the response of A to the nonconservative force $\mathbf{F}_i^{\rm ptb}$ is equivalent to the response to the potential $U^{\rm ptb}$ and given by FDT (2.3). It is this formulation which is presented in Ref. [128], and we use it throughout this chapter to study several examples.

We note that a similar freedom has been discussed in Ref. [121].

2.3 Perturbation by a linear force field. An important case: perturbing by shear flow

In this section, we demonstrate the presented method of restoring FDT for the case when the perturbation force is linear in particle coordinates $\mathbf{r}_i$, namely

$$\mathbf{F}_i^{\rm ptb} = \boldsymbol{\kappa} \cdot \mathbf{r}_i, \tag{2.10}$$

with the tensor $\boldsymbol{\kappa}$ independent of particle positions (here, $\cdot$ denotes the dot product). If $\boldsymbol{\kappa}$ is symmetric, $\mathbf{F}_i^{\rm ptb}$ derives from a generalized harmonic potential. The case of interest is that $\boldsymbol{\kappa}$ is not symmetric, such that $\mathbf{F}_i^{\rm ptb}$ in Eq. (2.10) is not conservative. One natural way of exploring the above-mentioned freedom is by using the transpose of $\boldsymbol{\kappa}$, i.e., it is promising to use

$$\mathbf{G}_i^{\rm ptb} = \frac{1}{2}\left(\boldsymbol{\kappa}^T - \boldsymbol{\kappa}\right) \cdot \mathbf{r}_i. \tag{2.11}$$

The sum of $\mathbf{F}_i^{\rm ptb}$ and $\mathbf{G}_i^{\rm ptb}$ is then immediately found,

$$\mathbf{F}_i^{\rm ptb} + \mathbf{G}_i^{\rm ptb} = \frac{1}{2}\left(\boldsymbol{\kappa} + \boldsymbol{\kappa}^T\right) \cdot \mathbf{r}_i = -\nabla_i U^{\rm ptb}(\{\mathbf{r}_i\}), \tag{2.12}$$

where the potential is identified as

$$U^{\rm ptb}(\{\mathbf{r}_i\}) = -\frac{1}{4}\sum_{i=1}^N \mathbf{r}_i \cdot \left(\boldsymbol{\kappa} + \boldsymbol{\kappa}^T\right) \cdot \mathbf{r}_i. \tag{2.13}$$

Our task now is to find the conditions under which Eq. (2.8) is satisfied.

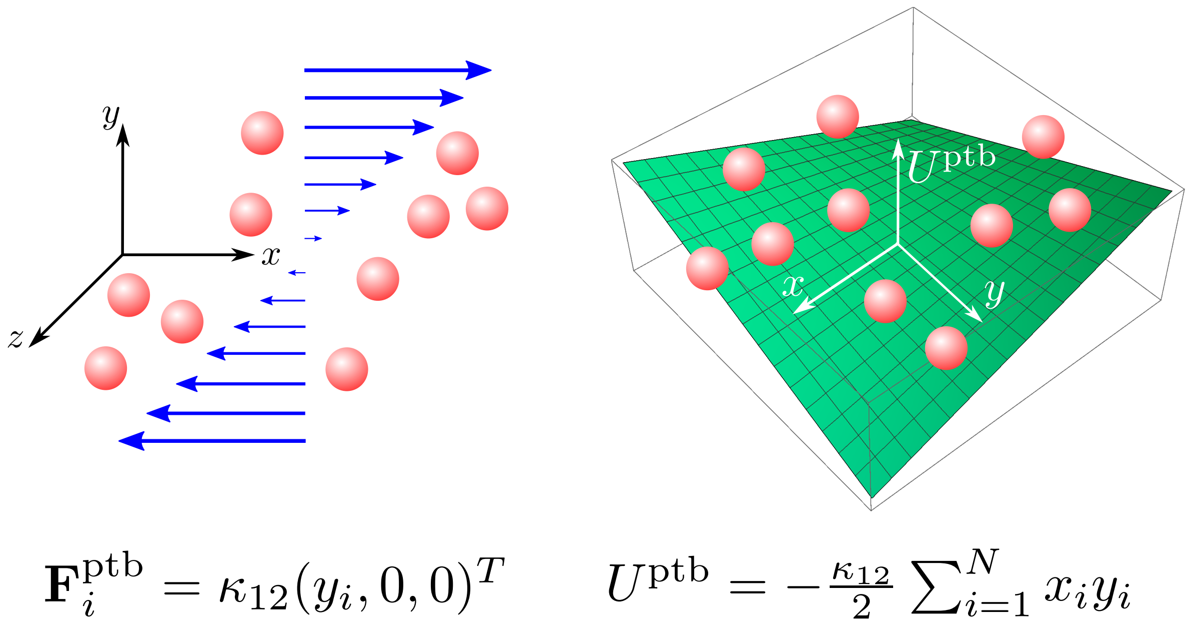

Figure 2.2. Illustration of the method of restoring FDT for the case of simple shear, $\mathbf{F}_i^{\text{ptb}} = \kappa_{12}(y_i, 0, 0)^T$. Superposition of $\mathbf{F}_i^{\text{ptb}}$ and $\mathbf{G}_i^{\text{ptb}}$ given by Eq. (2.11) results in the gradient of the potential $U^{\text{ptb}} = -\frac{\kappa_{12}}{2}\sum_{i=1}^N x_i y_i$. Note that this corresponds to superposition of the shear field with its image mirrored at the plane $x = y$. Given the symmetries detailed in the main text, the linear responses to $\mathbf{F}_i^{\text{ptb}}$ and U^{ptb} are identical.

For this, we regard $\boldsymbol{\kappa} = \kappa_{12}\hat{\mathbf{x}} \otimes \hat{\mathbf{y}}$ (with $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\otimes$ denoting unit vectors and the tensor product, respectively)[6], such that $\mathbf{F}_i^{\text{ptb}}$ in Eq. (2.10) corresponds to linear shear force in the x direction with gradient along y (see Fig. 2.2 for an illustration)[7], i.e.,

$$\mathbf{F}_i^{\text{ptb}} = \kappa_{12}(y_i, 0, 0)^T. \tag{2.14}$$

The partner force is identified as

$$\mathbf{G}_i^{\text{ptb}} = \frac{\kappa_{12}}{2}(-y_i, x_i, 0)^T. \tag{2.15}$$

From Eq. (2.13), the corresponding potential reads

$$U^{\text{ptb}} = -\frac{\kappa_{12}}{2}\sum_{i=1}^{N} x_i y_i, \tag{2.16}$$

[6]For concreteness, we assume that κ_{12}, as well as the shear rate $\dot{\gamma}$ introduced below, are nonnegative. However, in principle, these parameters can also be negative.

[7]We note that the considered case of shear force is a widely used example of a nonconservative perturbation. Because of this and the fact that a general linear force can be decomposed into a potential part and a sum of shear forces in different directions, the presented example of $\boldsymbol{\kappa} = \kappa_{12}\hat{\mathbf{x}} \otimes \hat{\mathbf{y}}$ can be regarded as an important and essential example of restoring FDT for a nonconservative linear force.

being a potential with one stable and one unstable direction in the xy plane (see Fig. 2.2). One direct way of fulfilling Eq. (2.8) is restricting to systems and observables which are symmetric under interchange of the x and y coordinates. These are systems for which interaction and external potentials remain the same under interchange $\{x_i\} \leftrightarrow \{y_i\}$, and observables which remain the same under interchange $\{x_i\} \leftrightarrow \{y_i\}$ and $\{v_{ix}\} \leftrightarrow \{v_{iy}\}$ (where v_{ix} denotes the x component of the velocity of particle i). Then condition (2.8) is fulfilled by symmetry[8]. For example, spherically symmetric potentials and observables like $A = \sum_{i=1}^{N} x_i y_i$, $A = \sum_{i=1}^{N} v_{ix} v_{iy}$, or the xy component of the stress tensor (see Eq. (2.27) and Ref. [20]) comprise these symmetries. Substituting Eq. (2.16) into Eq. (2.3), we find that, for these cases, the linear response to shear forcing is given by

$$\boxed{\langle A(t)\rangle^{\mathrm{ptb}} - \langle A\rangle = \frac{\kappa_{12}}{2k_{\mathrm{B}}T}\left[\left\langle A\sum_{i=1}^{N} x_i y_i\right\rangle - \left\langle A(t)\sum_{i=1}^{N} x_i(0) y_i(0)\right\rangle\right].} \tag{2.17}$$

Formula (2.17) thus provides the response of a general equilibrium stochastic system to a nonconservative force [shear force in Eq. (2.14)] via FDT.

As it was mentioned in Chapter 1, we use a system of Brownian particles to demonstrate our general results, and formula (2.17) in particular. For Brownian motion described by Eq. (1.2), *shear force* is usually understood as the force resulting from the external flow velocity field $\mathbf{V}(\mathbf{r}) = \dot{\gamma}(y,0,0)^T$, i.e., *shear flow* with shear rate $\dot{\gamma} > 0$. The corresponding shear force can be hence identified as $\mathbf{F}_i^{\mathrm{ptb}} = \frac{1}{\mu}\mathbf{V}(\mathbf{r}_i)$ [62] and reads

$$\mathbf{F}_i^{\mathrm{ptb}} = \frac{\dot{\gamma}}{\mu}(y_i, 0, 0)^T. \tag{2.18}$$

Comparing Eqs. (2.18) and (2.14), one can see that the specification to a system of Brownian particles is done by specifying $\kappa_{12} = \frac{\dot{\gamma}}{\mu}$. The linear response formula for an equilibrium system of Brownian particles perturbed by simple shear flow then follows immediately from Eq. (2.17), and, defining $\langle A(t)\rangle^{\mathrm{ptb}} = \langle A(t)\rangle^{(\dot{\gamma})}$, we obtain

$$\boxed{\langle A(t)\rangle^{(\dot{\gamma})} - \langle A\rangle = \frac{\dot{\gamma}}{2k_{\mathrm{B}}T\mu}\left[\left\langle A\sum_{i=1}^{N} x_i y_i\right\rangle - \left\langle A(t)\sum_{i=1}^{N} x_i(0) y_i(0)\right\rangle\right].} \tag{2.19}$$

Representing the method of restoring FDT for shear perturbation, response relations (2.17) and (2.19) are main results of this chapter. We note that Eq. (2.19) has been derived in Ref. [103] for a single overdamped Brownian particle by directly finding the nonequilibrium distribution function; for a system of interacting overdamped Brownian particles, Ref. [103] proposes an approximate expression which depends on the system parameters and is different from universal result (2.19). We further note that formula (2.19) is valid for both underdamped and overdamped Brownian systems,

[8]This can be understood from the fact that $\mathbf{G}_i^{\mathrm{ptb}} = \frac{\kappa_{12}}{2}(-y_i, x_i, 0)^T$ is a difference between shear forces in the y and x directions, whose works averaged with A are identical in the mentioned case of xy symmetry.

as no assumptions about the particle inertia have been made in the derivation (this can be also understood directly from Eq. (2.19): the formula does not contain the particle mass m explicitly). Eq. (2.19) is an alternative to the classical Green-Kubo relation for shear which, for the case of overdamped Brownian particles, reads as (see Refs. [3, 20, 21, 84, 90, 96, 97, 105, 106] for various Green-Kubo relations, and Sec. 1.4 and Ref. [96] for formula (2.20) in particular)

$$\langle A(t)\rangle^{(\dot\gamma)} - \langle A\rangle = \frac{\dot\gamma}{k_{\mathrm{B}}T}\int_0^t dt' \, \langle A(t')\sigma_{xy}(0)\rangle \,, \tag{2.20}$$

where σ_{xy} is the xy component of the stress tensor defined as

$$\sigma_{xy} = -\sum_{i=1}^{N}\left(F_{ix}^{\mathrm{int}} + F_{ix}^{\mathrm{ext}}\right) y_i. \tag{2.21}$$

FDT-formula (2.19) has several advantages over the Green-Kubo relation (2.20): first, there is no time integral in formula (2.19); second, forces do not have to be measured when using Eq. (2.19); and finally, for confined systems, formula (2.19) has a lower variance, which necessitates a smaller number of independent measurements to obtain the average response of the same statistical accuracy. The latter advantage is demonstrated in the next section.

We finally note that the symmetry conditions on the observable A defined above are not necessary if the system is spherically symmetric and A is a function of positions only (see Sec. 2.6).

2.4 Numerical example: comparing direct response, the Green-Kubo relation, and FDT

In this section, we numerically study the response of a confined system of Brownian particles to shear flow in terms of the change of the system spatial distribution. We confirm the validity of FDT (2.19) in the linear regime, as well as demonstrate its advantage in statistical accuracy over the Green-Kubo relation (2.20).

2.4.1 System and simulation details

We consider interacting overdamped Brownian particles in two space dimensions (for an illustration, see the snapshots in the inset plot of Fig. 2.3). For time $t \le 0$ the dynamics obeys Langevin equation (1.5), and at $t = 0$ the system is assumed to be in equilibrium. For $t > 0$, linear shear flow characterized by shear velocity $\mathbf{V}(\mathbf{r}_i) = \mu\boldsymbol{\kappa}\cdot\mathbf{r}_i$, with shear-rate tensor $\mu\boldsymbol{\kappa} = \dot\gamma\hat{\mathbf{x}}\otimes\hat{\mathbf{y}}$, is imposed (see the left panel of Fig. 2.2), such that the dynamics obeys the following Langevin equation:

$$\frac{\dot{\mathbf{r}}_i}{\mu} = \boldsymbol{\kappa}\cdot\mathbf{r}_i + \mathbf{F}_i^{\mathrm{int}} + \mathbf{F}_i^{\mathrm{ext}} + \mathbf{f}_i. \tag{2.22}$$

$$\mathbf{F}_i^{\text{int}} = -\nabla_i \frac{k^{\text{int}}}{2} \sum_{i=1}^{N} \sum_{j=1(j\neq i)}^{N} \frac{1}{r_{ij}} e^{-\frac{r_{ij}}{r_c}} \tag{2.23}$$

are interaction forces, chosen to arise from a screened Coulomb potential, with inter-particle distance $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$, interaction strength k^{int}, and interaction range r_c. The external force follows from a harmonic potential with spring constant k,

$$\mathbf{F}_i^{\text{ext}} = -\nabla_i \frac{k}{2} \sum_{i=1}^{N} |\mathbf{r}_i|^2, \tag{2.24}$$

providing a central confinement. $\mathbf{f}_i$ is a Gaussian white noise, with properties given by Eq. (1.3), which we repeat here:

$$\langle \mathbf{f}_i(t) \rangle = 0, \quad \langle \mathbf{f}_i(t) \otimes \mathbf{f}_j(t') \rangle = \frac{2k_{\text{B}}T}{\mu} \mathbb{I} \delta_{ij} \delta(t-t'), \tag{2.25}$$

where $\mathbb{I}$ is the identity matrix.

We set $k_{\text{B}}T = r_c = \mu = 1$, and $k^{\text{int}} = 25$. N, k, $\dot{\gamma}$, and the number of independent noise realizations C for performing averages are varied between measurements. The dynamics is simulated using the Euler method with the time step $\Delta t = 10^{-3}$. First, we simulate the dynamics of the unperturbed system starting with certain particle positions, and make sure that at time $t = 0$ the system reached equilibirum. Afterwards, we perform two types of simulations. In the first type, corresponding to the direct measurement of the response, we switch on shear and continue the simulation until the steady state is reached. In the second type, the system remains in equilibrium (i.e., no shear is applied), and the simulation is performed to get equilibirum correlation functions in order to compute the response using linear response theory.

We choose $A = \sum_{i=1}^{N} x_i y_i$, which is the lowest nontrivial moment of the particle distribution, characterizing the system morphology, i.e., the shape of the cluster of particles. Since the system and A are xy symmetric, condition (2.8) is fulfilled and formula (2.19) is hence valid.

2.4.2 Three routes to compute the response

We compute the response, $\langle A(t) \rangle^{(\dot{\gamma})} - \langle A \rangle$, via three different routes: by (i) applying finite shear, (ii) using equilibrium correlations according to the Green-Kubo formula (2.20), and (iii) using equilibrium correlations according to Eq. (2.19) (labeled "FDT" in the figures). Figure 2.3 compares these as a function of time t after start of shear. For small shear rate (main plot), all methods agree, thereby confirming formula (2.19). For large shear rate (inset plot), the deviation from the linear response is evident, also regarding the form of the response curve, which shows a characteristic "overshoot," i.e., a nonmonotonic behavior as a function of time, which has also been observed in sheared bulk systems [129]. Snapshots for equilibrium (black particles) and sheared (orange particles) systems illustrate the change of shape of the cluster of particles from circular to ellipsoidal: $\langle A \rangle = 0$, but $\langle A(t) \rangle^{(\dot{\gamma})} \geq 0$.

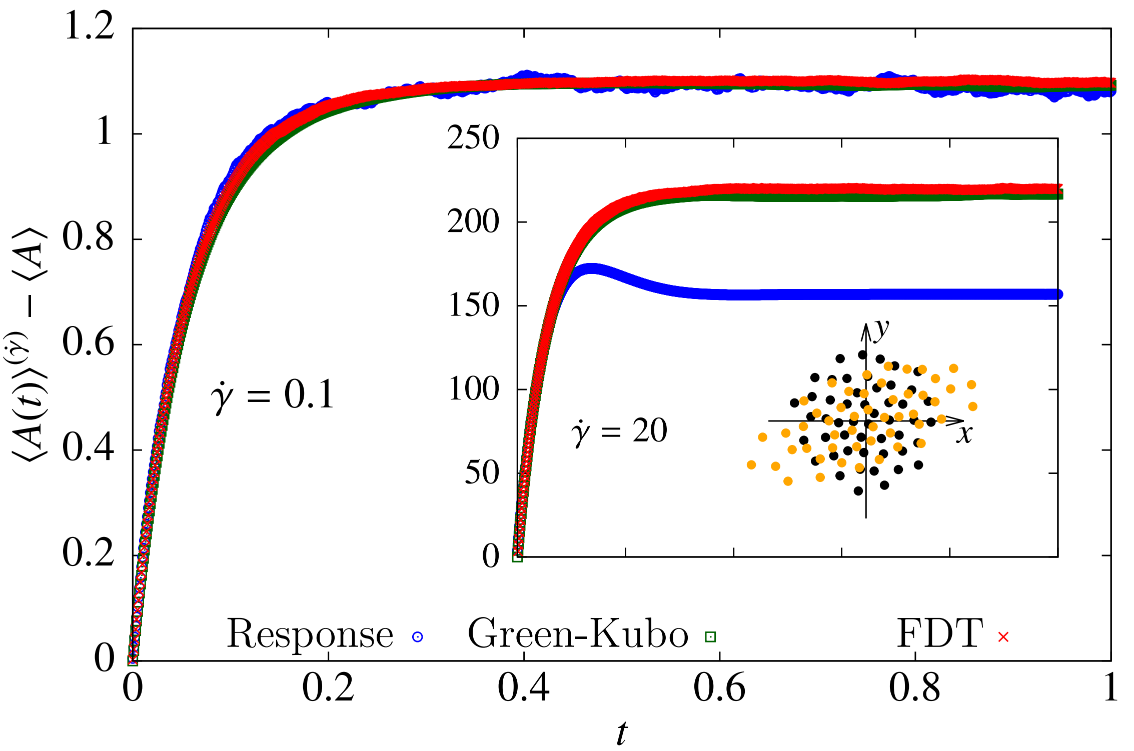

Figure 2.3. Response to shear flow for $A = \sum_{i=1}^{N} x_i y_i$ of a two-dimensional system of interacting Brownian particles confined in a harmonic trap. The main plot shows the linear (small $\dot{\gamma}$) response computed by shearing ("Response"), using the Green-Kubo formula (2.20), and using Eq. (2.19) ("FDT"). The inset plot shows a nonlinear (large $\dot{\gamma}$) response with the corresponding simulation snapshots demonstrating the effect of shear on the morphology of the system (black particles are in equilibrium, while orange particles are sheared). Parameters: $N = 50$, $k = 10$, and $C = 4 \times 10^5$.

2.4.3 Comparing the variances: Advantage of FDT

Panels (a) and (c) of Fig. 2.4 show the dependence on the confinement strength k and the number of particles N of the steady-state response, again confirming agreement between the three methods. From fits to the data, the response follows the scaling $\propto k^{-1.48}$ (compared to $\propto k^{-2}$, obtained analytically for $N = 1$) and $\propto N^{1.55}$ (for $N \gtrsim 4$).

Panels (b) and (d) of Fig. 2.4 show the corresponding variance, related to the statistical error of a single measurement using the different methods[9]. The variance shows a notable difference between the methods following scaling behaviors of $\propto k^{-0.64} N^{0.82}$,

[9]The variance is $s = \sqrt{\langle B^2 \rangle - \langle B \rangle^2}$, where $B = A(\dot{\gamma}) - A(\dot{\gamma} = 0)$ [here, noise realizations are chosen to be the same for $A(\dot{\gamma})$ and $A(\dot{\gamma} = 0)$], $B = \frac{\dot{\gamma}}{k_B T} \int_0^\tau dt' A(t') \sigma_{xy}(0)$, and $B = \frac{\dot{\gamma}}{2 k_B T \mu} A \sum_{i=1}^{N} x_i y_i$ for the three methods, respectively. τ is the time when the steady state of the corresponding mean, $\langle B \rangle$, is reached. We note that the variance for the Green-Kubo relation is not well defined, because it does not converge to a stationary value as a function of time.

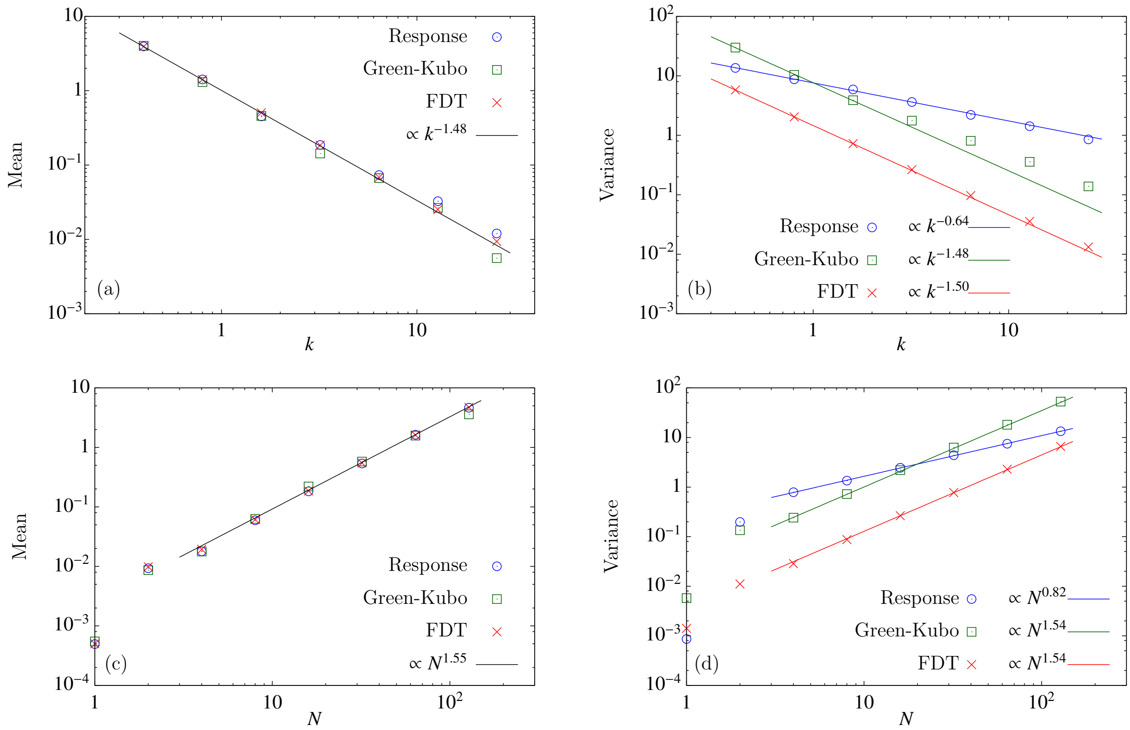

Figure 2.4. Dependence of the stationary linear response [(a), (c)] and its variance [(b), (d)] on the confinement strength k [(a), (b)] and the number of particles N [(c), (d)] obtained in the sheared system ("Response"), using the Green-Kubo formula (2.20), and using Eq. (2.19) ("FDT"). Straight lines correspond to power-law fits. Parameters: $N = 10$ and $\dot{\gamma} = 0.04$ for panels (a) and (b); $k = 10$ and $\dot{\gamma} = 0.1$ for panels (c) and (d); $C = 5 \times 10^3$ (in addition, averaging over time in the steady state is performed).

Table 2.1: Scaling behaviors of the relative variance for the three different computational methods (extracted from Fig. 2.4).

Method	Response	Green-Kubo	FDT
Power for k	0.84	0	−0.02
Power for N	−0.73	−0.01	−0.01

$\propto k^{-1.48}N^{1.54}$, and $\propto k^{-1.50}N^{1.54}$, respectively. The Green-Kubo relation and formula (2.19) scale similarly, but the latter has a notably lower variance.

Table 2.1 compares scaling behaviors of the relative variance (variance divided by the mean) for the three methods. The relative variance of the directly measured response grows with k and decreases with N. For the Green-Kubo relation (2.20) and for Eq. (2.19), the relative variance hardly depends on k and N, indicating that the statistical efficiency of Eqs. (2.20) and (2.19) is invariant with respect to changes of the effective system size and density, highlighting an interesting property of the linear response approach. For the set of parameters we used in our simulations, Eq. (2.19) has the lowest variance. Comparing it to the Green-Kubo relation (2.20), it thus needs a much smaller number of independent runs (roughly a factor of 100 here, estimated from the variance and the central limit theorem)[10], which is another important advantage of formula (2.19) over the Green-Kubo relation (2.20).

2.5 Universality of FDT, and the underdamped version of the Green-Kubo relation for shear perturbation of Brownian particles

In Secs. 2.3 and 2.4, we discussed several advantages of FDT for shear (2.19) over the Green-Kubo relation (2.20). The list of those advantages can be complemented by another important feature of FDT, which also applies to the general form (2.3), as mentioned in Sec. 2.1: FDT (2.3) is a universal response relation, whereas formula (2.1) takes different forms for different systems and perturbations.

To clarify what we mean, let us come back to the Green-Kubo relation (2.20), which is the form formula (2.1) takes in the case of overdamped Brownian particles perturbed by shear. Does this Green-Kubo relation remain the same if we consider a different system? To answer this question, let us simply consider *underdamped* Brownian particles. As shown in Sec. 3.6, the underdamped Green-Kubo relation differs from its overdamped analogue (2.20), and reads

$$\boxed{\begin{aligned}&\langle A(t)\rangle^{(\dot\gamma)} - \langle A\rangle \\ &= \frac{\dot\gamma}{k_{\mathrm{B}}T}\int_0^t dt'\,\langle A(t')\sigma_{xy}(0)\rangle + \frac{\dot\gamma m}{k_{\mathrm{B}}T}\left[\left\langle A\sum_{i=1}^N v_{ix}y_i\right\rangle - \left\langle A(t)\sum_{i=1}^N v_{ix}(0)y_i(0)\right\rangle\right],\end{aligned}} \tag{2.26}$$

where

$$\sigma_{xy} = -\sum_{i=1}^N \left[m v_{ix}v_{iy} + (F_{ix}^{\mathrm{int}} + F_{ix}^{\mathrm{ext}})y_i\right] \tag{2.27}$$

is the underdamped version of the stress tensor (2.21) [20, 21, 97, 130]. Note that in the limit $m \to 0$ Eq. (2.20) is recovered. The evident difference between Eqs. (2.20) and (2.26) answers the above-formulated question: the Green-Kubo relation for shear

[10] In other words, to obtain the average value of the same statistical error, FDT (2.20) requires much less computational resources (speed and memory of a computer).

perturbation depends on the considered system[11]. In contrast, FDT (2.19) is valid for both overdamped and underdamped Brownian particles.

The universality of FDT is apparent from the general expression (2.3), which is always used as it is, i.e., if a system is perturbed by a potential, there is no other response relation than formula (2.3). In contrast, in the case of a nonconservative perturbation, alternative formulas derived via various approaches are usually preferred to the general response relation (2.1) (e.g., to avoid the time derivative). These alternative formulas depend on the considered system (as we demonstrated above), the applied perturbation (compare Green-Kubo relations for perturbing by shear and by activity, Eq. (2.20) and Eq. (10) in Ref. [43], respectively), as well as on the derivation method (compare Eq. (2.20) and Eq. (3) in Ref. [103]).

2.6 Relaxing the symmetry conditions

The referee who reviewed the manuscript of Ref. [128] made a very important comment regarding the validity of formulas (2.17) and (2.19), emphasizing that the imposed symmetry conditions can be very specific. This comment motivated us to reconsider these conditions, and in this section we show, both physically and mathematically, that they can be relaxed.

2.6.1 Rotation force: How to make an important change without changing the distribution

Our first demonstration is based on a physical intuition behind the partner force $\mathbf{G}_i^{\mathrm{ptb}}$ in Eq. (2.15). Since this force is always orthogonal to the particle radius vector,

$$\mathbf{G}_i^{\mathrm{ptb}} \cdot \mathbf{r}_i = 0, \tag{2.28}$$

it is a rotation force, i.e., $\mathbf{G}_i^{\mathrm{ptb}}$ does not change the amplitude of $\mathbf{r}_i$. This means that the *spatial* distribution of a *spherically symmetric* system is unaffected by $\mathbf{G}_i^{\mathrm{ptb}}$. As an illustration, consider that the system of black particles in the inset of Fig. 2.3 is rotated: the clusters before and after the rotation cannot be distinguished.

Since the *spatial* distribution does not change, the mean of A, where A is a function of positions only, is unaffected by $\mathbf{G}_i^{\mathrm{ptb}}$. Therefore, adding $\mathbf{G}_i^{\mathrm{ptb}}$ to the shear force $\mathbf{F}_i^{\mathrm{ptb}}$ does not change the mean of $A = A(\{\mathbf{r}_i\})$ but gives the potential (2.16): formulas (2.17) and (2.19) are hence valid for any $A = A(\{\mathbf{r}_i\})$ if the unperturbed system is *spherically symmetric*.

We highlighted the words "spatial" and "spherically symmetric", because $\mathbf{G}_i^{\mathrm{ptb}}$ still affects the velocity distribution and changes the spatial nonspherical distribution (consider, e.g., an elliptical cluster). Since most realistic equilibrium systems have spherically

[11] It is interesting that, for Newtonian systems, the response to shear is given by either the first or the second term of Eq. (2.26) [20, 97, 130]. This means that the conventional Green-Kubo formula (2.20) is identical for overdamped Brownian systems and Newtonian systems (taking into account that the underdamped stress tensor (2.27) is used in the Newtonian case).

symmetric interaction and external potentials, formulas (2.17) and (2.19) have essentially no symmetry restrictions in the overdamped case, where $A = A(\{\mathbf{r}_i\})$. The situation is, however, different for underdamped systems where A can contain velocities: in this case, A has to be xy symmetric, as stated in Sec 2.3.

2.6.2 An important role of the symmetry of stress tensor

Our mathematical argument for the above statement regarding the validity of formulas (2.17) and (2.19) is based on the symmetry of the overdamped stress tensor (2.21). One can show that the stress tensor is symmetric for spherically symmetric potentials,

$$\sigma_{xy} = \sigma_{yx}. \tag{2.29}$$

The effect of $\mathbf{G}_i^{\text{ptb}}$ on the equilibrium distribution W^{eq} can be formulated in two ways (we consider overdamped Brownian dynamics). First, this effect can be written via the action of the corresponding Smoluchowski operator $\Omega_{\mathbf{G}_i^{\text{ptb}}}$ [96]:

$$\Omega_{\mathbf{G}_i^{\text{ptb}}} W^{\text{eq}} \propto (\sigma_{yx} - \sigma_{xy}) W^{\text{eq}}. \tag{2.30}$$

Second, it can be described via the Green-Kubo relation (2.20): since $\mathbf{G}_i^{\text{ptb}}$ is a difference between shear forces in the y and x directions, we can write

$$\langle A(t)\rangle^{\text{ptb}}\Big|_{\mathbf{G}_i^{\text{ptb}}} - \langle A\rangle \propto \int_0^t dt' \, \langle A(t') \, [\sigma_{yx}(0) - \sigma_{xy}(0)]\rangle \, . \tag{2.31}$$

If the system is spherically symmetric, we can substitute Eq. (2.29) into Eqs. (2.30) and (2.31) to get zero result. This means that $\mathbf{G}_i^{\text{ptb}}$ does not change a spherically symmetric W^{eq} up to linear order.

On the other hand, there will be an additional velocity term in Eqs. (2.30) and (2.31) in the underdamped case. For Eq. (2.31), this term stems from the second term in the underdamped Green-Kubo relation (2.26). Therefore, for underdamped systems, A must be xy symmetric in order to get zero result [see the example in Subsec 2.7.3 where formula (2.19) fails].

2.7 Analytical example: underdamped dynamics of a Brownian particle under shear

In this section, we demonstrate the usage of response formulas (2.19) and (2.26) for the case of a single underdamped Brownian particle confined in a harmonic potential and perturbed by linear shear flow (see Fig. 2.5), a scenario where the dynamics can be solved analytically [131–134]. Apart from demonstrating and confirming the response relations, this section complements the results of Refs. [131–134] with the transient response, i.e., we consider not only the steady-state sheared system, but evaluate the response for all

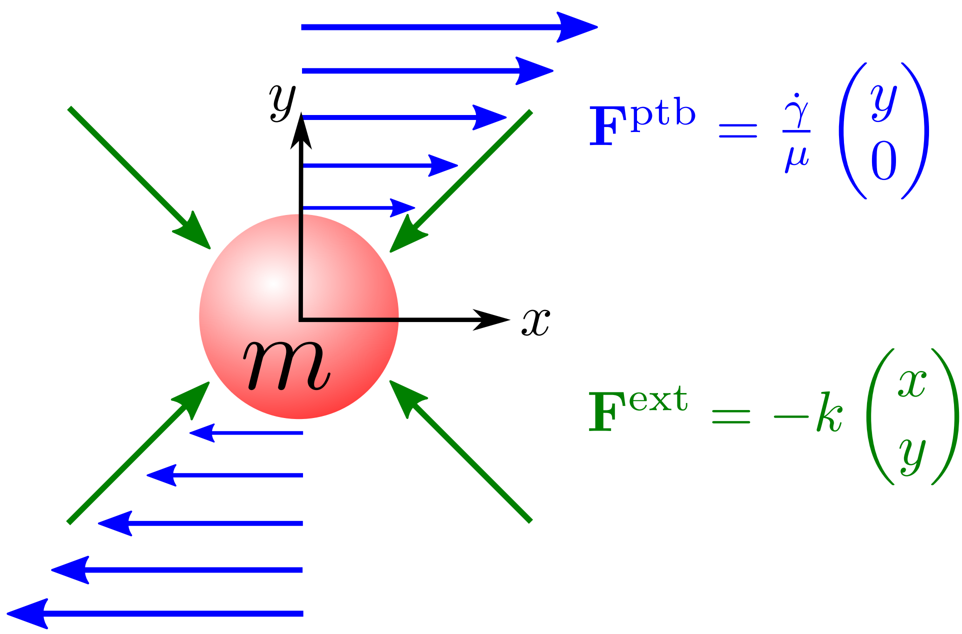

Figure 2.5. The system studied in Sec. 2.7: a single underdamped Brownian particle of mass m confined in a harmonic potential, leading to the external force $\mathbf{F}^{\mathrm{ext}} = -k(x, y)^T$, and perturbed by linear shear flow, with the corresponding perturbation force $\mathbf{F}^{\mathrm{ptb}} = \frac{\dot{\gamma}}{\mu}(y, 0)^T$.

times after start of shear, as in Fig. 2.3. As in Sec 2.4, we consider a two-dimensional system[12].

We begin by writing the equations of motion [following from Eq. (1.2), simplified to the case of a single particle, and additionally acquiring the shear force]:

$$m\ddot{x} = \frac{\dot{\gamma}}{\mu}y - \frac{1}{\mu}\dot{x} - kx + f_x, \qquad \dot{x} = v_x, \tag{2.32a}$$

$$m\ddot{y} = -\frac{1}{\mu}\dot{y} - ky + f_y, \qquad \dot{y} = v_y, \tag{2.32b}$$

where the shear force $\frac{\dot{\gamma}}{\mu}y$ is imposed for $t > 0$, k is the spring constant of the confining harmonic trap, and random force satisfies

$$\langle f_x(t)\rangle = \langle f_y(t)\rangle = 0, \qquad \langle f_\alpha(t) f_\beta(t')\rangle = \frac{2k_{\mathrm{B}}T}{\mu}\delta_{\alpha\beta}\delta(t - t'). \tag{2.33}$$

Assuming that the system is in equilibrium at $t = 0$, the solutions of Eqs. (2.32a) and (2.32b) are given by Eqs. (A.1), (A.2), (A.3), and (A.4) in Appendix A.1.

As in Sec. 2.4, our aim is to compare the response to shear computed via three different routes: by (i) using solutions (A.1), (A.2), (A.3), and (A.4) with finite shear

[12]In the case of a single particle, the results computed in 2D are also valid in 3D, because the z degree of freedom is decoupled from the x and y components.

rate, (ii) using equilibrium correlations according to the Green-Kubo formula (2.26), and (iii) using equilibrium correlations according to FDT (2.19). Since the system is xy symmetric, it is expected that the three methods agree in the linear regime if the observable A is also xy symmetric. In the subsections below, we demonstrate the computation for different observables.

2.7.1 Spatial distribution

We start with $A = xy$, which is xy symmetric and which characterizes the system spatial distribution. We note that $\langle xy \rangle = 0$ due to isotropicity of the equilibrium system, and hence do not consider this term in the response relations.

Response

First, we compute the response directly, using the dynamics of the sheared system, i.e., we evaluate the average under shear, $\langle x(t)y(t)\rangle^{(\dot\gamma)}$. Multiplying solutions (A.1) and (A.2), using Eq. (2.33), and performing time integrals, we obtain

$$\langle x(t)y(t)\rangle^{(\dot\gamma)} = \frac{2\dot\gamma k_{\mathrm{B}}T\mu}{1-4\mu^2 km}\Bigg\{ \left(\frac{\mu m}{1-\sqrt{1-4\mu^2 km}}\right)^2 \left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2 km}\right)t}\right) + \left(\frac{\mu m}{1+\sqrt{1-4\mu^2 km}}\right)^2 \left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2 km}\right)t}\right) - \frac{m}{2k}\left(1-e^{-\frac{t}{\mu m}}\right)\Bigg\}. \tag{2.34}$$

This result is valid for arbitrary $\dot\gamma$, meaning that the exact response of a single particle is linear in $\dot\gamma$, in contrast to a many-particle system (see Fig. 2.3). Although it is not directly evident from Eq. (2.34), one can show that it gives real and nonnegative result (see also Fig. 2.6).

It is insightful to take several limits of the response (2.34). In the overdamped limit, we have

$$\lim_{m\to 0}\langle x(t)y(t)\rangle^{(\dot\gamma)} = \frac{\dot\gamma k_{\mathrm{B}}T}{2\mu k^2}\left(1-e^{-2\mu kt}\right), \tag{2.35}$$

in agreement with Ref. [102]. At first glance an unclear behavior for $m = \frac{1}{4\mu^2 k}$ gives a finite result,

$$\lim_{m\to\frac{1}{4\mu^2 k}}\langle x(t)y(t)\rangle^{(\dot\gamma)} = \frac{\dot\gamma k_{\mathrm{B}}T}{2\mu k^2}\left[1-(1+2\mu kt)^2 e^{-4\mu kt}\right]. \tag{2.36}$$

The stationary limit

$$\lim_{t\to\infty}\langle x(t)y(t)\rangle^{(\dot\gamma)} = \frac{\dot\gamma k_{\mathrm{B}}T}{2\mu k^2} \tag{2.37}$$

agrees with Ref. [134], and it is m independent, as expected, because the dynamics for large times is diffusive, or overdamped [compare to the long-time limit of Eq. (1.16)]; limits (2.37) and (2.35) are hence commute.

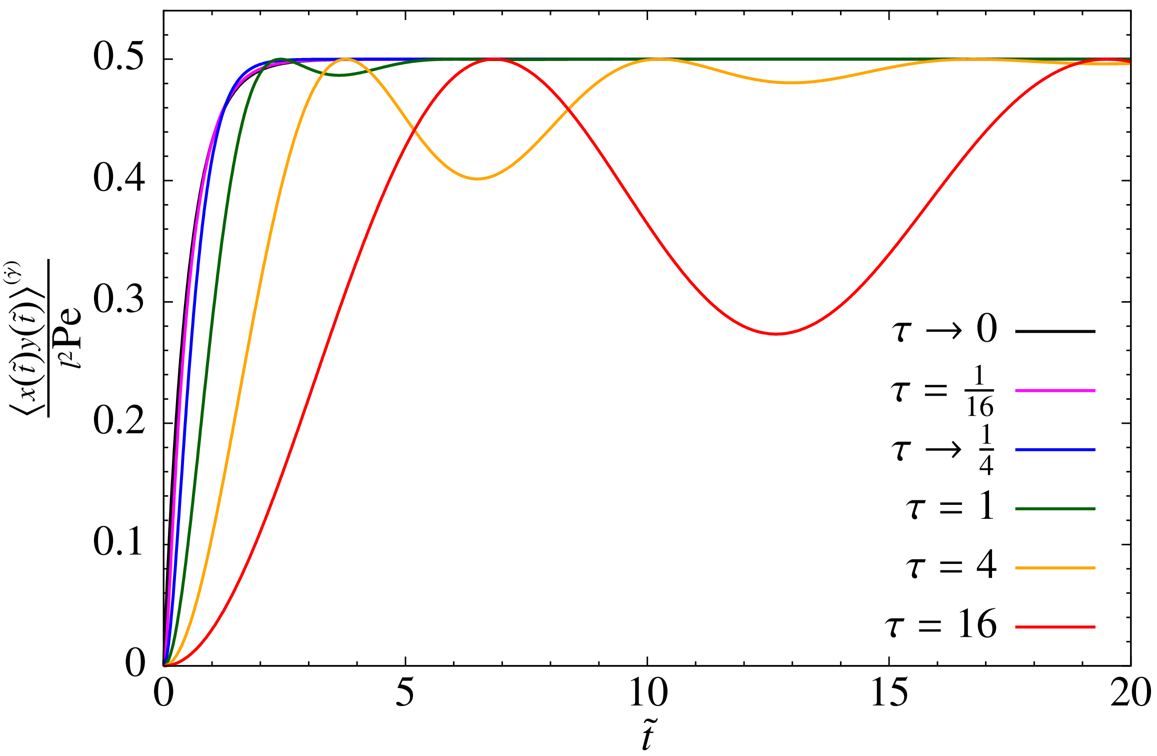

Figure 2.6. Rescaled response to shear flow for $A = xy$ of a single underdamped Brownian particle in a harmonic trap as a function of rescaled time $\tilde{t} \equiv \frac{t}{\tau_k} = \mu k t$ after the flow is applied, given by Eq. (2.38). The results are shown for different values of a characteristic ratio $\tau \equiv \frac{\tau_m}{\tau_k}$, which is the ratio between the inertia time $\tau_m = m\mu$ and the trap relaxation time $\tau_k = \frac{1}{\mu k}$.

In order to visualize expression (2.34), we rewrite it in terms of dimensionless parameters: $\tilde{t} \equiv \frac{t}{\tau_k}$ (describing time in units of the relaxation time of the trap $\tau_k = \frac{1}{\mu k}$), $\tau \equiv \frac{\tau_m}{\tau_k}$ (being the ratio between the inertia time $\tau_m = m\mu$ and the trap relaxation time τ_k), and $\mathrm{Pe} \equiv \dot\gamma\tau_k$ (giving the strength of the shear force relative to the confining force, known as the Péclet number). Rescaling $\langle x(t)y(t)\rangle^{(\dot\gamma)}$ by the unit of squared length, $l^2 \equiv k_\mathrm{B}T\mu\tau_k = \frac{k_\mathrm{B}T}{k}$, and dividing by Pe, we rewrite Eq. (2.34) as

$$\frac{\left\langle x\left(\tilde{t}\right) y\left(\tilde{t}\right)\right\rangle^{(\dot\gamma)}}{l^2\mathrm{Pe}} = \frac{2}{1-4\tau}\left\{\left(\frac{\tau}{1-\sqrt{1-4\tau}}\right)^2\left(1-e^{-\frac{\left(1-\sqrt{1-4\tau}\right)}{\tau}\tilde{t}}\right)\right.$$
$$\left. + \left(\frac{\tau}{1+\sqrt{1-4\tau}}\right)^2\left(1-e^{-\frac{\left(1+\sqrt{1-4\tau}\right)}{\tau}\tilde{t}}\right) - \frac{\tau}{2}\left(1-e^{-\frac{\tilde{t}}{\tau}}\right)\right\}. \qquad (2.38)$$

This function is plotted in Fig. 2.6 as a function of $\tilde{t}$ for different values of τ. As it is apparent from expression (2.38), one can distinguish two qualitatively different cases, $\tau \leq \frac{1}{4}$ and $\tau > \frac{1}{4}$. For $\tau \leq \frac{1}{4}$, the dynamics is overdamped [the particle position has no memory, i.e., it changes erratically (see Fig. 1.2)], and the response shows a purely exponential relaxation. Note, however, that for $\tau \to 0$ the derivative of the response at $\tilde{t} = 0$ is finite, whereas it is zero for any finite τ[13]. For $\tau > \frac{1}{4}$, the dynamics is underdamped [the particle position has memory, i.e., it changes smoothly (see Fig. 1.2)], and the response shows an oscillatory relaxation, typical for underdamped systems. The frequency of the oscillations decreases with τ, but their amplitude increases, meaning that the relaxation to the stationary state slows down with the increase of the particle inertia. However, in the limit $\tau \to \infty$ (a rigid particle), the response is zero, i.e., shear flow cannot move the particle.

Test Green-Kubo

Second, we demonstrate that the response, computed directly in Eq. (2.34), can be obtained using the underdamped Green-Kubo relation (2.26). For $A = xy$, the relation reads

$$\begin{aligned}\langle x(t)y(t)\rangle^{(\dot{\gamma})} = &-\frac{\dot{\gamma}m}{k_{\mathrm{B}}T}\int_0^t dt'\,\langle x(t')y(t')v_x(0)v_y(0)\rangle + \frac{\dot{\gamma}k}{k_{\mathrm{B}}T}\int_0^t dt'\,\langle x(t')y(t')x(0)y(0)\rangle \\ &+ \frac{\dot{\gamma}m}{k_{\mathrm{B}}T}\left[\langle xyv_xy\rangle - \langle x(t)y(t)v_x(0)y(0)\rangle\right]. \end{aligned} \tag{2.39}$$

Our aim is to show that the right-hand side of Eq. (2.39) equals that of Eq. (2.34). Using equilibrium correlation functions (A.5), (A.8), and (A.9), we get for the three terms

$$\begin{aligned}&-\frac{\dot{\gamma}m}{k_{\mathrm{B}}T}\int_0^t dt'\,\langle x(t')y(t')v_x(0)v_y(0)\rangle \\ &\quad= -\frac{\dot{\gamma}k_{\mathrm{B}}T\mu}{1-4\mu^2km}\left\{\frac{(\mu m)^2}{1-\sqrt{1-4\mu^2km}}\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)t}\right)\right. \\ &\qquad\left.+\frac{(\mu m)^2}{1+\sqrt{1-4\mu^2km}}\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)t}\right) - 2(\mu m)^2\left(1-e^{-\frac{t}{\mu m}}\right)\right\}, \end{aligned} \tag{2.40}$$

$$\begin{aligned}&\frac{\dot{\gamma}k}{k_{\mathrm{B}}T}\int_0^t dt'\,\langle x(t')y(t')x(0)y(0)\rangle \\ &\quad= \frac{4\dot{\gamma}k_{\mathrm{B}}T\mu}{1-4\mu^2km}\left\{\frac{(\mu m)^2\mu^2km}{\left(1-\sqrt{1-4\mu^2km}\right)^3}\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)t}\right)\right. \\ &\qquad\left.+\frac{(\mu m)^2\mu^2km}{\left(1+\sqrt{1-4\mu^2km}\right)^3}\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)t}\right) - \frac{(\mu m)^2}{2}\left(1-e^{-\frac{t}{\mu m}}\right)\right\}, \end{aligned} \tag{2.41}$$

[13] When we take a limit of τ, we assume μ and k to be fixed and finite, i.e., a limit of τ corresponds to a limit of m.

$$\frac{\dot{\gamma} m}{k_\mathrm{B}T}\left[\langle xyv_x y\rangle - \langle x(t)y(t)v_x(0)y(0)\rangle\right] = -\frac{2\dot{\gamma}k_\mathrm{B}T\mu}{1-4\mu^2 km}\left\{\frac{(\mu m)^2}{1-\sqrt{1-4\mu^2 km}}\right.$$
$$\left.\times\, e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2 km}\right)t} + \frac{(\mu m)^2}{1+\sqrt{1-4\mu^2 km}} e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2 km}\right)t} - \frac{m}{2k} e^{-\frac{t}{\mu m}}\right\}. \tag{2.42}$$

Adding Eqs. (2.40), (2.41), and (2.42) together, one gets Eq. (2.34), thereby confirming the underdamped Green-Kubo relation for $A = xy$.

Test FDT

Finally, we expect FDT (2.19) to hold, because the system and the observable are xy symmetric. Indeed, for $A = xy$, FDT reads

$$\langle x(t)y(t)\rangle^{(\dot{\gamma})} = \frac{\dot{\gamma}}{2k_\mathrm{B}T\mu}\left[\left\langle (xy)^2\right\rangle - \langle x(t)y(t)x(0)y(0)\rangle\right],$$

whose explicit expression computed using equilibrium correlator (A.5) agrees with the right-hand side of Eq. (2.34). Note how much easier it is to compute the response via FDT compared to the computation via the Green-Kubo relation: one has to know three correlation functions and perform time integrals when using the Green-Kubo formula, while it is enough to know one correlation function when using FDT.

2.7.2 Velocity distribution

In a similar to Subsec. (2.7.1) fashion, we investigate here the response for xy-symmetric observable $A = v_x v_y$, which describes the distribution of the velocity. Again, the term $\langle v_x v_y\rangle = 0$, and it is hence omitted in the response formulas.

Response

The direct computation using Eqs. (A.3) and (A.4) gives for the response

$$\langle v_x(t)v_y(t)\rangle^{(\dot{\gamma})} = \frac{\dot{\gamma}k_\mathrm{B}T\mu}{2\left(1-4\mu^2 km\right)}\left\{\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2 km}\right)t}\right)\right.$$
$$\left. + \left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2 km}\right)t}\right) - 2\left(1-e^{-\frac{t}{\mu m}}\right)\right\}, \tag{2.43}$$

valid for any $\dot{\gamma}$, and being real and nonpositive. In the overdamped limit, the absolute value of the response decays to zero exponentially after a jump at $t = 0$,

$$\lim_{m\to 0}\langle v_x(t)v_y(t)\rangle^{(\dot{\gamma})} = -\frac{\dot{\gamma}k_\mathrm{B}T\mu}{2}e^{-2\mu kt}, \tag{2.44}$$

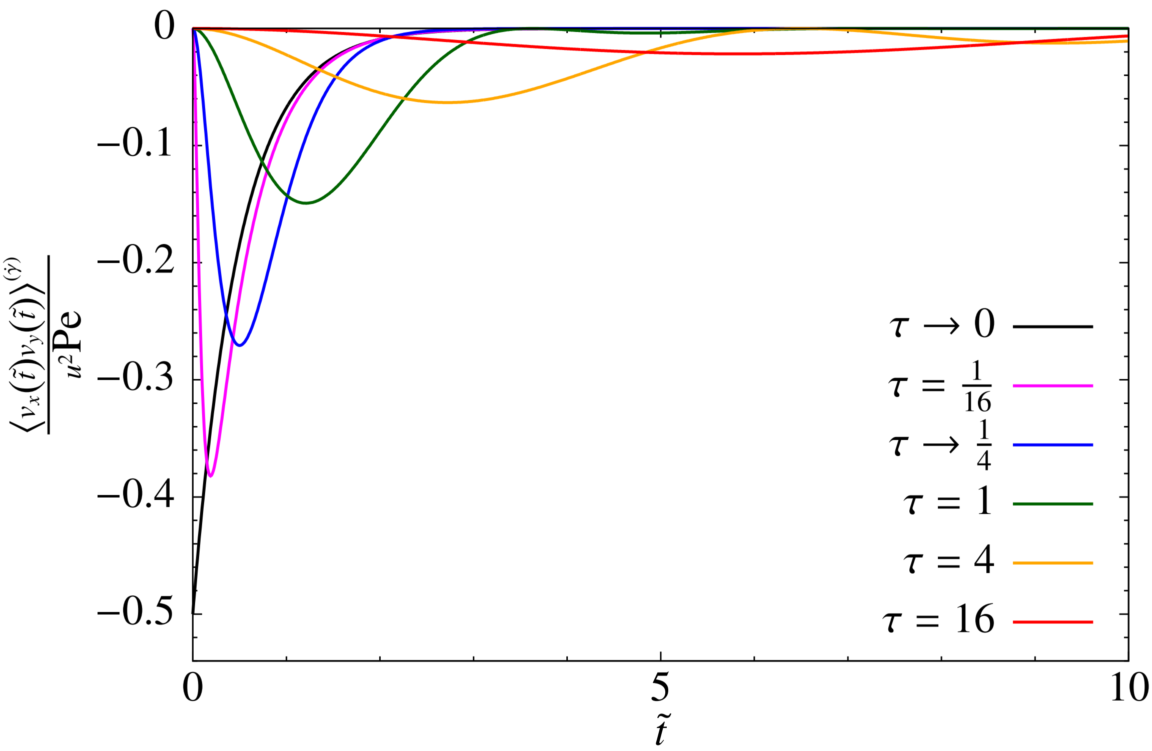

Figure 2.7. Rescaled response to shear flow for $A = v_x v_y$ of a single underdamped Brownian particle in a harmonic trap as a function of rescaled time $\tilde{t} \equiv \frac{t}{\tau_k} = \mu k t$ after the flow is applied, given by Eq. (2.47). The results are shown for different values of a characteristic ratio $\tau \equiv \frac{\tau_m}{\tau_k}$, which is the ratio between the inertia time $\tau_m = m\mu$ and the trap relaxation time $\tau_k = \frac{1}{\mu k}$.

meaning that the limits $m \to 0$ and $t \to 0$ do not commute, as for any finite m the absolute response increases *continuously* starting at $t = 0$ (see Fig. 2.7)[14]. The limit $m \to \frac{1}{4\mu^2 k}$ gives

$$\lim_{m \to \frac{1}{4\mu^2 k}} \langle v_x(t) v_y(t) \rangle^{(\dot{\gamma})} = -8\dot{\gamma} k_{\mathrm{B}} T \mu^3 k^2 t^2 e^{-4\mu k t}. \tag{2.45}$$

As mentioned above, the steady-state value is zero,

$$\lim_{t \to \infty} \langle v_x(t) v_y(t) \rangle^{(\dot{\gamma})} = 0, \tag{2.46}$$

and agrees with Ref. [134]. I.e., in contrast to the case $A = xy$ [see Eq. (2.37)], the cross moment of the steady-state *velocity* distribution is unaffected by shear. The re-

[14]Noncommutativity of the limits $m \to 0$ and $t \to 0$ for the observables involving velocities is a consequence of a qualitative difference between the velocity of underdamped and overdamped Brownian particles (see Fig. 1.2). In the former case, a particle has a well-defined velocity changing on a finite time scale $\tau_m = m\mu$, while in the latter case, the corresponding time scale is zero, leading to the velocity jumps.

sponse (2.43) is hence an illustrative example when the steady-state value is zero but the transient regime gives a finite result, indicating that it is also important to consider the relaxation towards a new steady state when computing the response.

As in Subsec. 2.7.1, to visualize the response (2.43), we rewrite it terms of dimensionless parameters τ and $\tilde{t}$, rescale by the unit of the squared velocity $u^2 \equiv \frac{l^2}{\tau_k^2} = k_{\rm B}T\mu^2 k$, and divide by the Péclet number Pe:

$$\frac{\left\langle v_x\left(\tilde{t}\right) v_y\left(\tilde{t}\right)\right\rangle^{(\dot\gamma)}}{u^2 \mathrm{Pe}} = \frac{1}{2(1-4\tau)}\left\{\left(1-e^{-\frac{(1-\sqrt{1-4\tau})}{\tau}\tilde{t}}\right)+\left(1-e^{-\frac{(1+\sqrt{1-4\tau})}{\tau}\tilde{t}}\right)-2\left(1-e^{-\frac{\tilde{t}}{\tau}}\right)\right\}, \quad (2.47)$$

plotted in Fig. 2.7 as a function of $\tilde{t}$ for different values of τ. As we already mentioned, the case $\tau \to 0$ is special: once shear is switched on at $\tilde{t} = 0$, the absolute response jumps to its maximum value and then monotonically relaxes to zero. For a finite τ, the relaxation is nonmonotonic, showing a single peak for $\tau \le \frac{1}{4}$ and an oscillatory behavior for $\tau > \frac{1}{4}$. The amplitude of peaks and oscillations decreases with increase of τ, but their width (period) increases (also maxima shift to the right), i.e., as for $\langle x(t)y(t)\rangle^{(\dot\gamma)}$, the relaxation to the stationary state of $\langle v_x(t)v_y(t)\rangle^{(\dot\gamma)}$ slows down with increase of m.

Test Green-Kubo

Let us show that $\langle v_x(t)v_y(t)\rangle^{(\dot\gamma)}$ in Eq. (2.43) agrees with the result given by the underdamped Green-Kubo relation (2.26). For $A = v_x v_y$, formula (2.26) reads

$$\langle v_x(t)v_y(t)\rangle^{(\dot\gamma)} = -\frac{\dot\gamma m}{k_{\rm B}T}\int_0^t dt'\,\langle v_x(t')v_y(t')v_x(0)v_y(0)\rangle + \frac{\dot\gamma k}{k_{\rm B}T}\int_0^t dt'\,\langle v_x(t')v_y(t')x(0)y(0)\rangle + \frac{\dot\gamma m}{k_{\rm B}T}\left[\langle v_x v_y v_x y\rangle - \langle v_x(t)v_y(t)v_x(0)y(0)\rangle\right]. \quad (2.48)$$

Using equilibrium correlation functions (A.6), (A.8), and (A.10), we get for the three terms

$$-\frac{\dot\gamma m}{k_{\rm B}T}\int_0^t dt'\,\langle v_x(t')v_y(t')v_x(0)v_y(0)\rangle = -\frac{\dot\gamma k_{\rm B}T\mu}{4\left(1-4\mu^2 km\right)}\left\{\left(1-\sqrt{1-4\mu^2 km}\right)\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2 km}\right)t}\right) + \left(1+\sqrt{1-4\mu^2 km}\right)\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2 km}\right)t}\right) - 8\mu^2 km\left(1-e^{-\frac{t}{\mu m}}\right)\right\}, \quad (2.49)$$

$$\frac{\dot{\gamma}k}{k_{\mathrm{B}}T}\int_0^t dt'\,\langle v_x(t')v_y(t')x(0)y(0)\rangle$$
$$= \frac{\dot{\gamma}k_{\mathrm{B}}T\mu}{1-4\mu^2km}\Bigg\{\frac{\mu^2km}{1-\sqrt{1-4\mu^2km}}\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)t}\right)$$
$$+\frac{\mu^2km}{1+\sqrt{1-4\mu^2km}}\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)t}\right)-2\mu^2km\left(1-e^{-\frac{t}{\mu m}}\right)\Bigg\}, \quad (2.50)$$

$$\frac{\dot{\gamma}m}{k_{\mathrm{B}}T}\left[\langle v_xv_yv_xy\rangle-\langle v_x(t)v_y(t)v_x(0)y(0)\rangle\right]=-\frac{\dot{\gamma}k_{\mathrm{B}}T\mu}{2\left(1-4\mu^2km\right)}\Bigg\{\left(1-\sqrt{1-4\mu^2km}\right)$$
$$\times\, e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)t}+\left(1+\sqrt{1-4\mu^2km}\right)e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)t}-2e^{-\frac{t}{\mu m}}\Bigg\}. \quad (2.51)$$

Adding Eqs. (2.49), (2.50), and (2.51) together, one gets Eq. (2.43), thereby confirming the underdamped Green-Kubo relation for $A = v_xv_y$.

Test FDT

The response evaluated via FDT (2.19), which for $A = v_xv_y$ takes the form

$$\langle v_x(t)v_y(t)\rangle^{(\dot{\gamma})}=\frac{\dot{\gamma}}{2k_{\mathrm{B}}T\mu}\left[\langle v_xv_yxy\rangle-\langle v_x(t)v_y(t)x(0)y(0)\rangle\right],$$

also agrees with the result in Eq. (2.43), as expected due to the xy symmetry of A.

2.7.3 The coupling between position and velocity

Finally, we investigate the response of $A = v_xy$ and $A = v_yx$, which are not xy symmetric. Both observables describe the coupling between position and velocity degrees of freedom under shear. As we show below, the coupling exists, giving a finite steady-state response which differs for the two observables by a minus sign.

Response

The direct computation in the sheared system, valid for any $\dot{\gamma}$, gives (again, the equilibirum terms vanish, $\langle v_xy\rangle = \langle v_yx\rangle = 0$)

$$\langle v_x(t)y(t)\rangle^{(\dot{\gamma})}=-\frac{\dot{\gamma}k_{\mathrm{B}}T\mu}{1-4\mu^2km}\Bigg\{\frac{\mu m}{1-\sqrt{1-4\mu^2km}}\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)t}\right)$$
$$+\frac{\mu m}{1+\sqrt{1-4\mu^2km}}\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)t}\right)-\frac{1-2\mu^2km}{\mu k}\left(1-e^{-\frac{t}{\mu m}}\right)\Bigg\}, \quad (2.52)$$

$$\langle v_y(t)x(t)\rangle^{(\dot\gamma)} = -\frac{\dot\gamma k_\mathrm{B}T\mu}{1-4\mu^2km}\Bigg\{\frac{\mu m}{1-\sqrt{1-4\mu^2km}}\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)t}\right)$$
$$+\frac{\mu m}{1+\sqrt{1-4\mu^2km}}\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)t}\right)-2\mu m\left(1-e^{-\frac{t}{\mu m}}\right)\Bigg\}. \tag{2.53}$$

First, we note that $\langle v_x(t)y(t)\rangle^{(\dot\gamma)} \neq \langle v_y(t)x(t)\rangle^{(\dot\gamma)}$, and also that $\langle v_x(t)y(t)\rangle^{(\dot\gamma)} \geq 0$, while $\langle v_y(t)x(t)\rangle^{(\dot\gamma)} \leq 0$.

In the overdamped limit, one has

$$\lim_{m\to 0}\langle v_x(t)y(t)\rangle^{(\dot\gamma)} = \frac{\dot\gamma k_\mathrm{B}T}{2k}\left(1+e^{-2\mu kt}\right), \tag{2.54}$$

$$\lim_{m\to 0}\langle v_y(t)x(t)\rangle^{(\dot\gamma)} = -\frac{\dot\gamma k_\mathrm{B}T}{2k}\left(1-e^{-2\mu kt}\right). \tag{2.55}$$

From Eq. (2.54), we conclude that the overdamped response for $A = v_x y$ has a jump at $t = 0$, and hence the limits $m \to 0$ and $t \to 0$ do not commute, similarly to $A = v_x v_y$ (see Subsec 2.7.2). In contrast, $\lim_{m\to 0}\langle v_y(t)x(t)\rangle^{(\dot\gamma)}$ is zero at $t = 0$, and the response changes continuously after start of shear[15]. The limit $m \to \frac{1}{4\mu^2 k}$ gives

$$\lim_{m\to\frac{1}{4\mu^2k}}\langle v_x(t)y(t)\rangle^{(\dot\gamma)} = \frac{\dot\gamma k_\mathrm{B}T}{2k}\left[1-\left(1-4\mu kt-8\mu^2k^2t^2\right)e^{-4\mu kt}\right], \tag{2.56}$$

$$\lim_{m\to\frac{1}{4\mu^2k}}\langle v_y(t)x(t)\rangle^{(\dot\gamma)} = -\frac{\dot\gamma k_\mathrm{B}T}{2k}\left[1-\left(1+4\mu kt+8\mu^2k^2t^2\right)e^{-4\mu kt}\right]. \tag{2.57}$$

The steady-state responses read

$$\lim_{t\to\infty}\langle v_x(t)y(t)\rangle^{(\dot\gamma)} = -\lim_{t\to\infty}\langle v_y(t)x(t)\rangle^{(\dot\gamma)} = \frac{\dot\gamma k_\mathrm{B}T}{2k}, \tag{2.58}$$

in agreement with Ref. [132]. Eq. (2.58) indicates the coupling between the particle position and velocity in the steady-state sheared system; this coupling is antisymmetric with respect to interchange of the degrees of freedom.

Aiming to visualize Eqs. (2.52) and (2.53), we rewrite them in terms of dimensionless parameters τ and $\tilde t$, and rescale by u, l and Pe (see Subsecs. 2.7.1 and 2.7.2 for definitions of these quantities). We get

$$\frac{\left\langle v_x\left(\tilde t\right)y\left(\tilde t\right)\right\rangle^{(\dot\gamma)}}{ul\mathrm{Pe}} = -\frac{1}{1-4\tau}\Bigg\{\frac{\tau}{1-\sqrt{1-4\tau}}\left(1-e^{-\frac{(1-\sqrt{1-4\tau})}{\tau}\tilde t}\right)$$
$$+\frac{\tau}{1+\sqrt{1-4\tau}}\left(1-e^{-\frac{(1+\sqrt{1-4\tau})}{\tau}\tilde t}\right)-(1-2\tau)\left(1-e^{-\frac{\tilde t}{\tau}}\right)\Bigg\}, \tag{2.59}$$

[15] The difference between Eqs. (2.54) and (2.55) for $t = 0$ is physically related to the fact that the two corresponding x degrees of freedom, directly affected by shear, behave different in the overdamped limit: v_x is a discontinuous function of time, while x is a continuous one.

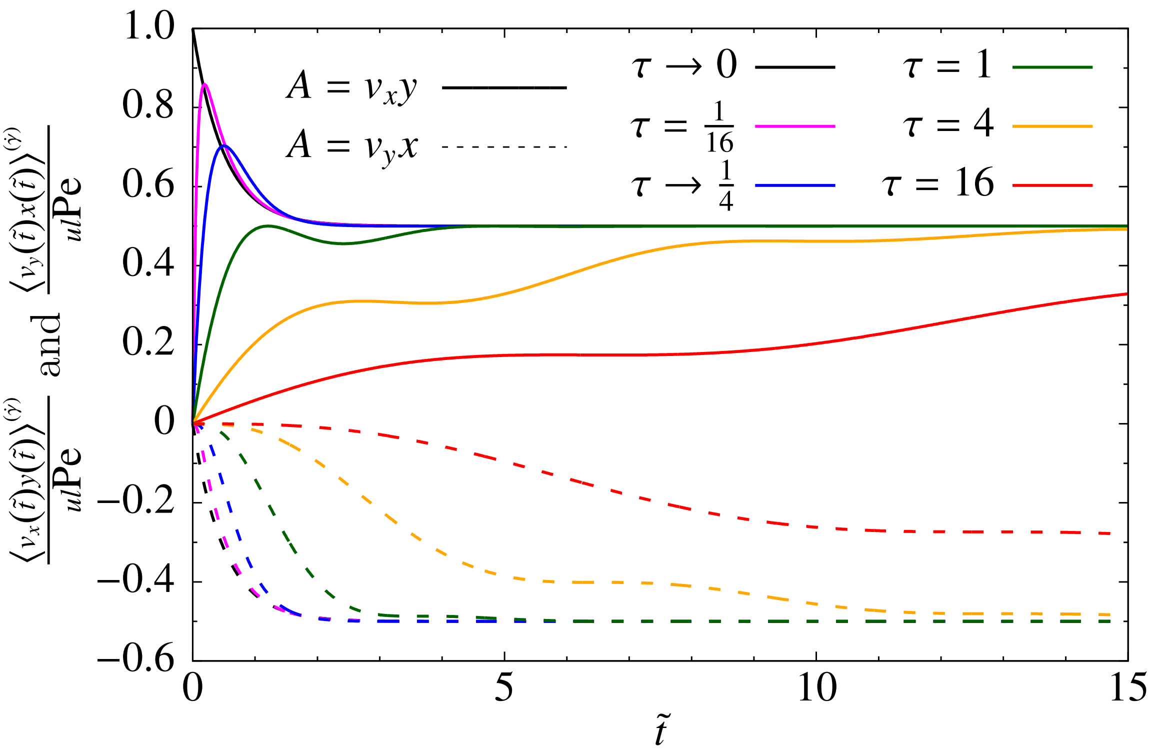

Figure 2.8. Rescaled response to shear flow for $A = v_x y$ (solid curves) and $A = v_y x$ (dashed curves) of a single underdamped Brownian particle in a harmonic trap as a function of rescaled time $\tilde{t} \equiv \frac{t}{\tau_k} = \mu k t$ after the flow is applied, given by Eqs. (2.59) and (2.60), respectively. The results are shown for different values of a characteristic ratio $\tau \equiv \frac{\tau_m}{\tau_k}$, which is the ratio between the inertia time $\tau_m = m\mu$ and the trap relaxation time $\tau_k = \frac{1}{\mu k}$.

$$\frac{\left\langle v_y\left(\tilde{t}\right) x\left(\tilde{t}\right)\right\rangle^{(\dot{\gamma})}}{ul\mathrm{Pe}} = -\frac{1}{1-4\tau}\left\{\frac{\tau}{1-\sqrt{1-4\tau}}\left(1-e^{-\frac{\left(1-\sqrt{1-4\tau}\right)}{\tau}\tilde{t}}\right)\right.$$
$$\left. + \frac{\tau}{1+\sqrt{1-4\tau}}\left(1-e^{-\frac{\left(1+\sqrt{1-4\tau}\right)}{\tau}\tilde{t}}\right) - 2\tau\left(1-e^{-\frac{\tilde{t}}{\tau}}\right)\right\}. \qquad (2.60)$$

Fig. 2.8 shows the responses in Eqs. (2.59) and (2.60) as functions of $\tilde{t}$ for different values of τ, thereby summarizing the above discussions. Note the pronounced peaks for $A = v_x y$ and $\tau < \frac{1}{4}$. Also note that the derivative at $\tilde{t} = 0$ is zero for $A = v_y x$, while it is finite for $A = v_x y$. Overall, although steady-state values are related via a minus sign for the two observables, their transient behaviors are qualitatively different.

Test Green-Kubo

Let us show that the Green-Kubo relation (2.26) correctly predicts the directly computed response in Eqs. (2.52) and (2.53). For $A = v_x y$, the relation reads

$$\langle v_x(t)y(t)\rangle^{(\dot\gamma)} = -\frac{\dot\gamma m}{k_\mathrm{B}T}\int_0^t dt'\,\langle v_x(t')y(t')v_x(0)v_y(0)\rangle$$
$$+\frac{\dot\gamma k}{k_\mathrm{B}T}\int_0^t dt'\,\langle v_x(t')y(t')x(0)y(0)\rangle + \frac{\dot\gamma m}{k_\mathrm{B}T}\left[\left\langle (v_x y)^2\right\rangle - \langle v_x(t)y(t)v_x(0)y(0)\rangle\right]. \quad (2.61)$$

Using correlators (A.7), (A.9), and (A.10), we get for the three terms

$$-\frac{\dot\gamma m}{k_\mathrm{B}T}\int_0^t dt'\,\langle v_x(t')y(t')v_x(0)v_y(0)\rangle = \frac{\dot\gamma k_\mathrm{B}T\mu}{2\left(1-4\mu^2 km\right)}\left\{\mu m\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2 km}\right)t}\right)\right.$$
$$\left.+\,\mu m\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2 km}\right)t}\right) - 2\mu m\left(1-e^{-\frac{t}{\mu m}}\right)\right\}, \quad (2.62)$$

$$\frac{\dot\gamma k}{k_\mathrm{B}T}\int_0^t dt'\,\langle v_x(t')y(t')x(0)y(0)\rangle$$
$$= -\frac{2\dot\gamma k_\mathrm{B}T\mu}{1-4\mu^2 km}\left\{\frac{(\mu^2 km)\mu m}{\left(1-\sqrt{1-4\mu^2 km}\right)^2}\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2 km}\right)t}\right)\right.$$
$$\left.+\,\frac{(\mu^2 km)\mu m}{\left(1+\sqrt{1-4\mu^2 km}\right)^2}\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2 km}\right)t}\right) - \frac{\mu m}{2}\left(1-e^{-\frac{t}{\mu m}}\right)\right\}, \quad (2.63)$$

$$\frac{\dot\gamma m}{k_\mathrm{B}T}\left[\left\langle (v_x y)^2\right\rangle - \langle v_x(t)y(t)v_x(0)y(0)\rangle\right] = \frac{\dot\gamma k_\mathrm{B}T\mu}{1-4\mu^2 km}\left\{-\mu m\left(1-e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2 km}\right)t}\right)\right.$$
$$\left.-\,\mu m\left(1-e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2 km}\right)t}\right) + \frac{1}{\mu k}\left(1-2\mu^2 km\right)\left(1-e^{-\frac{t}{\mu m}}\right)\right\}. \quad (2.64)$$

Adding Eqs. (2.62), (2.63), and (2.64) together, one gets Eq. (2.52), thereby confirming the underdamped Green-Kubo relation for $A = v_x y$. We note that Eq. (2.64) contributes to the steady state, i.e., the second term in formula (2.26) is crucial to get a correct steady-state response for the observables containing both positions and velocities, like $A = v_x y$.

Applying response relation (2.26) for $A = v_y x$, we get

$$\langle v_y(t)x(t)\rangle^{(\dot\gamma)} = -\frac{\dot\gamma m}{k_\mathrm{B}T}\int_0^t dt'\,\langle v_y(t')x(t')v_x(0)v_y(0)\rangle$$
$$+\frac{\dot\gamma k}{k_\mathrm{B}T}\int_0^t dt'\,\langle v_y(t')x(t')x(0)y(0)\rangle + \frac{\dot\gamma m}{k_\mathrm{B}T}\left[\langle v_y x v_x y\rangle - \langle v_y(t)x(t)v_x(0)y(0)\rangle\right]. \quad (2.65)$$

Since correlators (A.9) and (A.10) are symmetric with respect to interchange $v_x y \leftrightarrow v_y x$, the integral terms of the Green-Kubo relation are identical for $A = v_x y$ and $A = v_y x$:

$$-\frac{\dot{\gamma} m}{k_{\mathrm{B}} T} \int_0^t dt' \, \langle v_y(t') x(t') v_x(0) v_y(0) \rangle = -\frac{\dot{\gamma} m}{k_{\mathrm{B}} T} \int_0^t dt' \, \langle v_x(t') y(t') v_x(0) v_y(0) \rangle \,, \tag{2.66}$$

$$\frac{\dot{\gamma} k}{k_{\mathrm{B}} T} \int_0^t dt' \, \langle v_y(t') x(t') x(0) y(0) \rangle = \frac{\dot{\gamma} k}{k_{\mathrm{B}} T} \int_0^t dt' \, \langle v_x(t') y(t') x(0) y(0) \rangle \,. \tag{2.67}$$

It is thus the nonintegral term which makes the difference between the responses for $A = v_x y$ and $A = v_y x$: using correlator (A.8), we obtain

$$\begin{aligned} &\frac{\dot{\gamma} m}{k_{\mathrm{B}} T} \left[\langle v_y x v_x y \rangle - \langle v_y(t) x(t) v_x(0) y(0) \rangle \right] \\ &= \frac{\dot{\gamma} k_{\mathrm{B}} T \mu}{1 - 4\mu^2 k m} \mu m \left\{ e^{-\frac{1}{\mu m}\left(1 - \sqrt{1 - 4\mu^2 k m}\right) t} + e^{-\frac{1}{\mu m}\left(1 + \sqrt{1 - 4\mu^2 k m}\right) t} - 2 e^{-\frac{t}{\mu m}} \right\}. \end{aligned} \tag{2.68}$$

Adding Eqs. (2.66), (2.67), and (2.68) together, one gets Eq. (2.53), thereby confirming the underdamped Green-Kubo relation for $A = v_y x$.

Test FDT

In contrast to Subsecs. 2.7.1 and 2.7.2, we now expect FDT (2.19) to fail, because observables $A = v_x y$ and $A = v_y x$ are not xy symmetric. Let us demonstrate this failure. For $A = v_x y$ and $A = v_y x$, FDT (2.19) reads

$$\langle v_x(t) y(t) \rangle^{(\dot{\gamma})} = \frac{\dot{\gamma}}{2 k_{\mathrm{B}} T \mu} \left[\langle v_x y x y \rangle - \langle v_x(t) y(t) x(0) y(0) \rangle \right],$$

$$\langle v_y(t) x(t) \rangle^{(\dot{\gamma})} = \frac{\dot{\gamma}}{2 k_{\mathrm{B}} T \mu} \left[\langle v_y x x y \rangle - \langle v_y(t) x(t) x(0) y(0) \rangle \right].$$

Both equations give zero response in the limit $t \to \infty$, and they hence clearly disagree with Eqs. (2.52) and (2.53).

2.8 Summary and discussion

In this chapter, we discussed linear response theory for a general equilibrium system perturbed by conservative and nonconservative forces. We showed that the fluctuation-dissipation theorem (FDT), which is usually assumed to be applicable only for perturbations by a potential, can be also applied for nonpotential perturbations. This observation is a consequence of a remarkable property of the linear response: perturbation forces, whose work does not couple to the considered observable, can be added without changing the response. As a result, complementing the initial perturbation by these forces such that the total force derives from a potential, one finds that the linear response to the desired nonconservative perturbation is given by FDT.

Applying this finding to the case of Brownian particles perturbed by shear, we derived response formula (2.19) (FDT for shear), alternative to the well-known Green-Kubo relation (2.20); in the case of an arbitrary system, a more general form of Eq. (2.19), formula (2.17), has been also found. In contrast to the Green-Kubo relation, formulas (2.17) and (2.19) require specific symmetries of the considered system and observable. However, this requirement is usually met in many relevant physical situations. Furthermore, the Green-Kubo relation for underdamped Brownian systems, formula (2.26), has been given in this chapter (its derivation is postponed until Sec. 3.6).

We demonstrated the derived response relations both analytically and in numerical simulations. For a many-particle overdamped Brownian system, we numerically compared statistical efficiencies of the direct measurement in sheared system, the measurement performed using the Green-Kubo relation (2.20), and using FDT (2.19). For a single trapped underdamped particle, we analytically investigated the transient response to shear flow for several observables, and showed explicitly that this response can be computed via FDT (2.19) or the underdamped Green-Kubo relation (2.26).

Our demonstrations and discussions indicate that FDT (2.19) is advantageous over the Green-Kubo formulas in several aspects. First, it is directly evident from the response relations that FDT requires no time integration and involves simpler quantities to be measured [compare positions in Eq. (2.19) versus forces and velocities and Eqs. (2.19) and (2.26)]. Second, FDT shows more universality: it remains the same for both overdamped and underdamped Brownian dynamics, while the Green-Kubo formulas differ for the two cases. Finally, as demonstrated in numerical simulations, FDT has a lower variance, and it thus necessitates a smaller number of independent statistical measurements to compute the response.

We assume that all these advantages of FDT can be validated in experimental measurements, as experimental techniques to investigate the dynamics of a single trapped particle or several trapped interacting particles in shear flow already exist [135]. Note that the direct response to shear can be alternatively replaced by the direct response to the corresponding potential (2.16), which might be easier to realize in experiments[16]. We hence expect that the presented here general method of restoring FDT [and formulas (2.17) and (2.19) in particular] have a high potential to enrich and improve linear response theory from experimental side.

Future work may address the response of underdamped interacting Brownian particles (i.e., an extension of Sec. 2.7 to a many-body system), as well as application of formula (2.19) to the shear viscosity of Brownian suspensions[17]. Restoring FDT for various systems (including quantum ones) and perturbations is also a promising avenue to explore.

Finally, let us finish this chapter with a simple but an interesting fact: since one can use several response relations for the same perturbation (as we saw in this chapter), an

[16]The direct response to the potential (2.16) can be considered as the fourth route to compute the linear response to shear, in addition to the three routes defined in Subsec. 2.4.2 and investigated throughout this chapter.

[17]In addition to the Green-Kubo relations, the viscosity of particle suspensions can be computed via response relations of the form similar to MSD, the so-called Einstein relations for viscosity [136–141].

arbitrary normalized linear combination of these response relations can also be used [121]. For example, for overdamped Brownian particles perturbed by shear flow, one can write in the case of xy symmetry

$$\begin{aligned}&\langle A(t)\rangle^{(\dot{\gamma})}-\langle A\rangle\\&=c_1\frac{\dot{\gamma}}{2k_{\mathrm{B}}T\mu}\left[\left\langle A\sum_{i=1}^{N}x_iy_i\right\rangle-\left\langle A(t)\sum_{i=1}^{N}x_i(0)y_i(0)\right\rangle\right]+c_2\frac{\dot{\gamma}}{k_{\mathrm{B}}T}\int_0^t dt'\,\langle A(t')\sigma_{xy}(0)\rangle\,,\end{aligned} \tag{2.69}$$

where c_1 and c_2 are real numbers satisfying $c_1+c_2=1$. However, if the considered unperturbed system is out of equilibirum, $c_1=c_2=\frac{1}{2}$, as shown in Sec. 4.3 using path integrals (note that the stress tensor σ_{xy} is replaced by a generalized one, $\widetilde{\sigma}_{xy}$, for a nonequilibirum case). This is how we first found formula (2.19) [before we came up with the idea of restoring FDT]: after deriving Eq. (2.69) with $c_1=c_2=\frac{1}{2}$ for active Brownian particles perturbed by shear [see Eq. (4.11)], we realized that, in equilibrium, one can use only the first term with $c_1=1$. Applicable for both equilibrium and nonequilibrium systems, a path integral approach for deriving response relations gives the two terms, which are equal only in equilibrium. We thus invite the reader to Chapter 3, where the power of path integrals, features of nonequilibirum systems, and other advanced aspects of linear response theory are discussed.

3 Advanced linear response: nonequilibrium systems, path integrals, and more

In this chapter, we discuss general linear response theory in detail, aiming to put together and systemize the existing knowledge in order to get a complete and illustrative picture of the subject as well as to make a foundation for Chapters 4 and 5.

We start with a detailed derivation of a very general linear response formula based on stochastic Itô integral using a path integral method (Sec. 3.2). Next, in Sec. 3.3, we comprehensively explain the aspects of stochastic calculus related to the linear response and give the formula in terms of a more favorable stochastic Stratonovich integral. This general formula is then considered for different types of system and perturbation in Sec. 3.4, where certain simplifications can be applied, thereby allowing to use a simplified version of the formula for each scenario. Afterwards, in Sec. 3.5, we discuss the zero-temperature limit of the linear response, focusing on advantages of using the adjunct method in the deterministic case. Finally, we provide a derivation of the underdamped Green-Kubo relation in Sec. 3.6.

Most of the results of this chapter are known in the literature. The new contribution includes response formula (3.37) (a generalization of the formulas in Refs. [99–101] to a nonpotential perturbation and a detalization of the formula in Ref. [121] to the Stratonovich convention) and the underdamped Green-Kubo relation (2.26).

3.1 Equilibrium versus nonequilibrium

In Chapter 2, we studied the linear response of *equilibrium* systems. As discussed in Subsec. 1.2.1, nonequilibrium systems are fundamentally different from equilibrium ones, implying the difference between the responses. While the linear response of an equilibrium system is fully determined via the work done by the perturbation forces [see Eq. (2.1)], which is also called the *entropic* contribution (as it gives the excess entropy flux to the environment), this information is not enough for the nonequilibrium response. In the latter case, the response additionally contains the so-called *frenetic* term, quantifying the excess in activity due to the perturbation. The most prominent physical difference between the two terms is that they behave differently under the time reversal: the entropic term is time antisymmetric, whereas the frenetic one is time symmetric.

Let us postpone a more illustrative discussion regarding these differences to Sec. 3.4, where the response formulas are given. For a detailed study of nonequilibrium response theory, the reader may consult Refs. [98–101, 121].

It is interesting that the *second* order response of an *equilibrium* system also contains both, the entropic and frenetic, contributions: the linear (entropic) term is the linear equilibrium response, while the second-order (frenetic) term is constructed on the entropic and frenetic components of the nonequilibrium linear response [101]. Therefore, the linear response around nonequilibrium and the second-order response around equilibrium require measurements of similar quantities.

3.2 Linear response from the path integral representation

In this section, first, a path integral approach for computing averages is introduced. It is then used to derive linear response of Brownian particles (either in or out of equilibrium) to arbitrary perturbation. We note that the content of this section is close to that of Subsec. III B in Ref. [102].

3.2.1 The path integral formalism

The roots of the path integral formalism in statistical physics sprout from the famous Feynman path integral in quantum mechanics [3, 142]. The idea of the formalism is to write a statistical average via a functional (path) integral, where the statistics is encoded in the corresponding path weight (the distribution).

Consider a general stochastic system with some initial state $\Gamma(0)$ at time $t'=0$. For time $t'>0$, the system is perturbed by an external force quantified by a parameter λ (i.e., $\lambda=0$ is equivalent to the absence of the perturbation). Due to stochasticity of the dynamics, the system can evolve in different routes, i.e., there are many trajectories, or paths, the system can follow (see Fig. 3.1). Therefore, at time t, there are many possible values for $\Gamma(t)$ and hence for an observable $A(\Gamma(t))$. We are interested in the statistical average of A at time t given the initial condition $\Gamma(0)$[1], denoted as $\langle A(t)\rangle_0^{(\lambda)} \equiv \langle A(\Gamma(t))\rangle_0^{(\lambda)}$. According to the path integral formalism, this average can be written via the functional (path) integral [3, 102],

$$\langle A(\Gamma(t))\rangle_0^{(\lambda)} = \int_{\Gamma(0)} D\Gamma\, A(\Gamma(t)) W^{(\lambda)}(\{\Gamma\}), \tag{3.1}$$

where $D\Gamma$ is the functional integration measure and $W^{(\lambda)}(\{\Gamma\})$ is the path weight, with $\{\Gamma\}$ denoting the full history (the path) of the system on the time interval $[0,t]$.

The central object in Eq. (3.1) is the path weight $W^{(\lambda)}(\{\Gamma\})$, which describes the likelihood that the system follows a certain path $\{\Gamma\}$, playing the role of the distribution. Note that Γ is not the set of independent variables, but it is the set of functions of time,

[1] Apart from a typical initial condition where positions and velocities of particles are fixed to certain values, $\Gamma(0)$ can also correspond to a particular initial state, e.g., an equilibrium state or a nonequilibrium steady state.

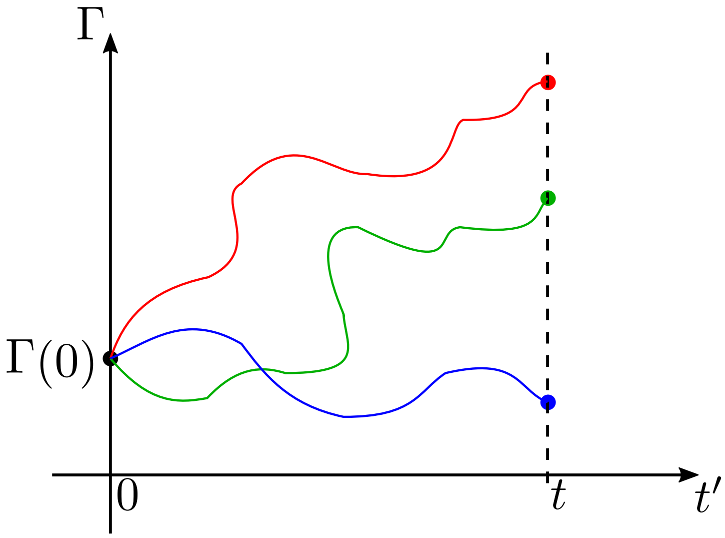

Figure 3.1. A sketch of paths (each path is represented by phase space Γ as a function of time t') for a general stochastic system. Starting with a particular configuration $\Gamma(0)$ at time $t' = 0$, the system can follow different trajectories, or paths (e.g., red, green, or blue), arriving at different configurations (red, green, or blue dots) at time t. The average of an observable $A(\Gamma(t))$ can be formulated as the average over the paths [see Eq. (3.1)].

implying that the integral is a functional one. To evaluate this functional integral, one typically performs time discretization, such that the integral turns into a usual multidimensional one [3, 143].

3.2.2 System: Brownian particles in or out of equilibrium

For now, Eq. (3.1) is just a formal mathematical expression. To proceed with the computation of the average, one has to specify the system under consideration. Depending on the system (or, equivalently, on the equations of motion), one has different forms of the path weight. Here, we consider a system of overdamped Brownian particles, being in nonequilibrium in general, as the system mostly used in this dissertation.

Let us write down the corresponding coupled equations of motion for $\widetilde{N}$ stochastic variables $\Gamma = \{x_1, \ldots, x_{\widetilde{N}}\}$:

$$\dot{x}_i(t) = F_i(\Gamma(t), t, \lambda) + f_i(t), \quad i = 1, \ldots, \widetilde{N}. \tag{3.2}$$

Here, $F_i(\Gamma(t), t, \lambda)$, which can depend explicitly on time as well as on the perturbation parameter λ, is the deterministic part, while f_i are independent Gaussian white noises with moments

$$\langle f_i(t) \rangle = 0, \quad \langle f_i(t) f_j(t') \rangle = 2\alpha_i \delta_{ij} \delta(t - t'), \tag{3.3}$$

where the noise variance α_i is assumed to be independent of Γ and t.

Eqs. (3.2) and (3.3) describe a process where each degree of freedom obeys an overdamped Brownian motion with Gaussian white noise. In principle, variables x_i can have any meaning. As for physical systems described in Sec. 1.2, Eqs. (3.2) and (3.3) cover overdamped passive Brownian particles, where x_i correspond to coordinates, and overdamped active Brownian particles in two space dimensions[2], where x_i correspond to coordinates and orientation angles (in both cases, $\widetilde{N} = 3N$).

3.2.3 The path weight

The path weight for Eqs. (3.2) and (3.3) follows from standard procedures, e.g., the Martin-Siggia-Rose-Janssen-de Dominicis approach [3, 143–146] or the Onsager-Machlup approach [143, 147, 148]. Defining

$$\mathcal{X}_i(t,\lambda) \equiv \dot{x}_i(t) - F_i(\Gamma(t),t,\lambda), \tag{3.4}$$

one obtains

$$\begin{aligned} &W(\{\Gamma\})^{(\lambda)} \propto e^{-\mathcal{A}(t,\lambda)}, \\ &\mathcal{A}(t,\lambda) = \int_0^t dt' \sum_{i=1}^{\widetilde{N}} \frac{1}{4\alpha_i} \mathcal{X}_i^2(t',\lambda), \end{aligned} \tag{3.5}$$

where $\mathcal{A}$ is the action of the system, and an underlying Itô time discretization (see Sec. 3.3) has been employed.

Let us point out several features of the structure of the path weight (3.5). First, the integration over time indicates the dependence on the full history of the dynamics. Second, the path weight has a Gaussian form[3], where $\mathcal{X}_i$ in Eq. (3.4) plays the role of the random variable, while the noise variance α_i corresponds to the variance of the distribution. This means that the most probable path is that without noise, i.e., $\mathcal{X}_i = 0$, and that the deviation from this path is quantified by the noise variance. In the limiting case $\alpha_i \to 0$ (deterministic scenario), the path weight acquires the form of a delta-distribution, indicating that the system can follow only one path, Eq. (3.2) with $f_i = 0$ (see Sec. 3.5 for discussions of this case).

3.2.4 Expanding the path weight: linear response

With Eqs. (3.1) and (3.5) at hand, we are now ready to derive a general linear response formula for a system described by Eqs. (3.2) and (3.3). Expanding the path weight (3.5)

[2] In 2D, the orientation vector, determining the direction of the self-propulsion, performs Brownian motion on a unit circle and can be hence parametrized by a single angle obeying Eqs. (3.2) and (3.3) (see Sec. 4.1). In 3D, however, where the orientation vector performs Brownian motion on a unit sphere, the angular dynamics cannot be described in terms of a simple Brownian process [44] – Eqs. (3.2) and (3.3) are not applicable.

[3] This is a direct consequence of the fact that the noise f_i is also Gaussian.

in powers of λ, we get

$$W^{(\lambda)}(\{\Gamma\}) = W(\{\Gamma\}) + \frac{\lambda}{2} W(\{\Gamma\}) \int_0^t dt' \sum_{i=1}^{\tilde{N}} \frac{1}{\alpha_i} \left[\dot{x}_i(t') - F_i(\Gamma(t'), t')\right] \frac{\partial F_i(\Gamma(t'), t', \lambda)}{\partial \lambda}\Big|_{\lambda=0} + \mathcal{O}(\lambda^2), \quad (3.6)$$

where $W(\{\Gamma\})$ is the path weight of the unperturbed system (given by Eq. (3.5) with $\lambda = 0$) and $F_i(\Gamma(t'), t') \equiv F_i(\Gamma(t'), t', \lambda = 0)$. Inserting Eq. (3.6) into Eq. (3.1), we get the linear response formula,

$$\langle A(t)\rangle_0^{(\lambda)} - \langle A(t)\rangle_0 = \frac{\lambda}{2}\, \text{Itô} \int_0^t dt' \left\langle A(t) \sum_{i=1}^{\tilde{N}} \frac{1}{\alpha_i} \left[\dot{x}_i(t') - F_i(\Gamma(t'), t')\right] \frac{\partial F_i(\Gamma(t'), t', \lambda)}{\partial \lambda}\Big|_{\lambda=0} \right\rangle_0, \quad (3.7)$$

where “Itô” indicates that the integral is a stochastic Itô integral, in accordance with the Itô time discretization employed to derive the path weight (3.5) (see Sec. 3.3). $\langle \cdots \rangle_0$ indicates average in the unperturbed system. Noticing that $\dot{x}_i(t') - F_i(\Gamma(t'), t')$ can be replaced by $f_i(t')$ according to Eq. (3.2), we can also write an alternative form of the response:

$$\langle A(t)\rangle_0^{(\lambda)} - \langle A(t)\rangle_0 = \frac{\lambda}{2}\, \text{Itô} \int_0^t dt' \left\langle A(t) \sum_{i=1}^{\tilde{N}} \frac{1}{\alpha_i} f_i(t') \frac{\partial F_i(\Gamma(t'), t', \lambda)}{\partial \lambda}\Big|_{\lambda=0} \right\rangle_0. \quad (3.8)$$

The transition from an abstract path integral (3.1) to practically useful response relations (3.7) and (3.8) reveals a big power of the path integral approach: once equations of motion and statistical properties of the considered system are specified, the response (not only linear but of any order) follows directly from the corresponding path weight, which, compared to a conventional nonequilibrium distribution function, is typically easy to find.

Equations (3.7) and (3.8) have been derived in the literature in similar ways (see, e.g., Refs. [98–100, 103, 120, 121]).

3.2.5 A similar approach: Malliavin weight sampling

Another powerful and interesting method to derive response relations is Malliavin weight sampling [103], which is similar to the path integral approach introduced above. According to this method, the response of A is given by its unperturbed weighted average, where the weight is given by an auxiliary variable, the so-called Malliavin weight[4]. To

[4] The resulting response relation has the form of Eq. (3.8), where the Malliavin weight q is identified as $q(t) = \frac{1}{2}\, \text{Itô} \int_0^t dt' \sum_{i=1}^{\tilde{N}} \frac{1}{\alpha_i} f_i(t') \frac{\partial F_i(\Gamma(t'), t', \lambda)}{\partial \lambda}\big|_{\lambda=0}$. The response can be hence written as the unperturbed weighted average: $\langle A(t)\rangle_0^{(\lambda)} - \langle A(t)\rangle_0 = \lambda \langle A(t) q(t)\rangle_0$.

compute the response, one thus has to track the evolution of A itself and of the Malliavin weight in the unperturbed system. For details of the method and its applications, we refer the reader to Ref. [103].

3.3 Some aspects related to stochastic calculus

3.3.1 An illustrative example

Consider an overdamped passive Brownian particle confined in a harmonic trap in one dimension and being in equilibrium at time $t = 0$. For time $t > 0$, the perturbation of the spring constant k of the trap is applied, i.e., $k \to k - \lambda$, where $k - \lambda \geq 0$, with $\lambda > 0$ ($\lambda < 0$) corresponding to a decrease (an increase) of the confinement strength (see Fig. 3.2). The Langevin equation reads

$$\dot{x} = -\mu k x + \mu \lambda x + \mu f, \tag{3.9}$$

where $\lambda \neq 0$ for $t > 0$ only, and random force f satisfies

$$\langle f(t) \rangle = 0, \qquad \langle f(t) f(t') \rangle = \frac{2 k_{\mathrm{B}} T}{\mu} \delta(t - t'). \tag{3.10}$$

Our goal is to find the linear response of x^2, i.e., how the mean squared position, quantifying the strength of particle fluctuations inside the trap, changes under the change of the trap stiffness. A more general problem, involving an active Ornstein-Uhlenbeck particle, has been studied in Ref. [149].

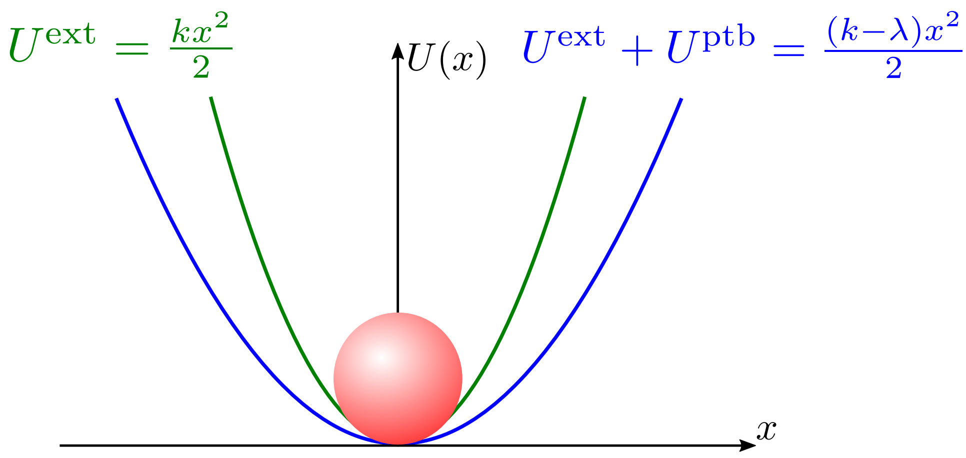

Figure 3.2. A particle confined in a harmonic potential $U^{\mathrm{ext}} = \frac{kx^2}{2}$ is subject to a potential perturbation $U^{\mathrm{ptb}} = -\frac{\lambda x^2}{2}$, i.e., the perturbation of the spring constant, $k \to k - \lambda$. Here, $\lambda > 0$ case is shown.

First, we compute the response directly, using the solution of Eq. (3.9) for $t \geq 0$ with finite λ,

$$x(t) = \mu e^{-\mu kt} \int_{-\infty}^{0} ds e^{\mu ks} f(s) + \mu e^{-\mu(k-\lambda)t} \int_{0}^{t} ds e^{\mu(k-\lambda)s} f(s). \tag{3.11}$$

Performing the average of the squared Eq. (3.11) and using $\langle x^2 \rangle = \frac{k_B T}{k}$, we find

$$\left\langle x^2(t) \right\rangle^{(\lambda)} - \left\langle x^2 \right\rangle = \frac{k_B T}{k} \frac{\lambda}{k-\lambda} \left[1 - e^{-2\mu(k-\lambda)t}\right], \tag{3.12}$$

whose linear order reads

$$\left\langle x^2(t) \right\rangle^{(\lambda)} - \left\langle x^2 \right\rangle = \lambda \frac{k_B T}{k^2} \left(1 - e^{-2\mu kt}\right), \tag{3.13}$$

in agreement with Ref. [149]. Since $\frac{\lambda}{k-\lambda} > (<)\ 0$ for $\lambda > (<)\ 0$, decreasing (increasing) the trap stiffness corresponds to increasing (decreasing) the mean squared position of the particle.

Next, we evaluate the linear response using the path-integral based response formula (3.7). Identifying $\widetilde{N} = 1$, $F(\Gamma(t'), t') = -\mu k x(t')$, $\left.\frac{\partial F_i(\Gamma(t'),t',\lambda)}{\partial \lambda}\right|_{\lambda=0} = \mu x(t')$, and $\alpha = k_B T \mu$, we rewrite the formula for our particular case:

$$\left\langle x^2(t) \right\rangle^{(\lambda)} - \left\langle x^2 \right\rangle = \frac{\lambda}{2k_B T} \text{ Itô} \int_0^t dt' \left\langle x^2(t) \left[\dot{x}(t') + \mu k x(t')\right] x(t') \right\rangle. \tag{3.14}$$

Since the integral in Eq. (3.14) is a stochastic Itô integral, care should be taken when computing it. The second term is not a problem: since this term does not involve time derivatives, its stochastic integral is a usual (Riemann) integral,

$$\frac{\lambda \mu k}{2k_B T} \text{ Itô} \int_0^t dt' \left\langle x^2(t) x^2(t') \right\rangle = \frac{\lambda \mu k}{2k_B T} \int_0^t dt' \left\langle x^2(t) x^2(t') \right\rangle. \tag{3.15}$$

Using unperturbed ($\lambda = 0$) solution of Eq. (3.9), we find

$$\left\langle x^2(t) x^2(t') \right\rangle = \left(\frac{k_B T}{k}\right)^2 \left[1 + 2e^{-2\mu k(t-t')}\right], \tag{3.16}$$

and hence

$$\frac{\lambda \mu k}{2k_B T} \int_0^t dt' \left\langle x^2(t) x^2(t') \right\rangle = \lambda \frac{k_B T}{2k^2} \left[\mu kt + \left(1 - e^{-2\mu kt}\right)\right]. \tag{3.17}$$

The issue related to stochastic calculus appears in the first term of Eq. (3.14), because it contains time derivative. Let us, however, for a moment ignore this issue and treat the integral as a usual one:

$$\frac{\lambda}{2k_B T} \text{ Itô} \int_0^t dt' \left\langle x^2(t) \dot{x}(t') x(t') \right\rangle \overset{\text{wrong}}{=} \frac{\lambda}{2k_B T} \int_0^t dt' \left\langle x^2(t) \dot{x}(t') x(t') \right\rangle. \tag{3.18}$$

The integral on the right-hand side of Eq. (3.18) can be easily evaluated:

$$\frac{\lambda}{2k_\mathrm{B}T}\int_0^t dt'\left\langle x^2(t)\dot{x}(t')x(t')\right\rangle = \frac{\lambda}{4k_\mathrm{B}T}\left\langle x^2(t)\int_0^t dt'\frac{dx^2(t')}{dt'}\right\rangle$$
$$= \frac{\lambda}{4k_\mathrm{B}T}\left\langle x^2(t)\left[x^2(t)-x^2(0)\right]\right\rangle = \frac{\lambda}{4k_\mathrm{B}T}\left[\left\langle x^4\right\rangle - \left\langle x^2(t)x^2(0)\right\rangle\right] = \lambda\frac{k_\mathrm{B}T}{2k^2}\left(1-e^{-2\mu k t}\right), \tag{3.19}$$

where in the last step we used correlator (3.16). Adding the two terms, Eqs. (3.19) and (3.17), together, we get for the linear response computed using linear response theory ignoring stochastic calculus:

$$\left\langle x^2(t)\right\rangle^{(\lambda)} - \left\langle x^2\right\rangle \overset{\text{wrong}}{=} \lambda\frac{k_\mathrm{B}T}{k^2}\left(1-e^{-2\mu k t}\right) + \lambda\frac{k_\mathrm{B}T\mu}{2k}t. \tag{3.20}$$

Comparing Eqs. (3.13) and (3.20), we conclude that the mistake we purposely made, Eq. (3.18), resulted in the wrong response, which differs from the correct value by the term $\lambda\frac{k_\mathrm{B}T\mu}{2k}t$, making the steady-state response divergent. Let us figure out why Eq. (3.18) is wrong.

3.3.2 Stochastic calculus in short

The physical origin of the fact that Brownian motion requires a special mathematical description can be seen in Fig. 1.2: the particle velocity is not a continuous function of time. This is in turn the consequence of Eq. (1.3), where the noise variance at equal times is infinite, implying an erratic nature of the collisions of a particle with the molecules of the environment. Up to now, based on Langevin equations for Brownian motion, we used conventional mathematics to successfully derive equations and compute concrete results. However, Subsec. 3.3.1 shows that usual calculus fails in Eq. (3.18). Indeed, the situation is tricky when one looks at the mathematics of Brownian motion in detail.

Revealing the trick by discretizing the Langevin equation

For making the analysis compact, let us restrict to a single degree of freedom, assume no explicit time dependence for F, and set $\lambda = 0$. Equations (3.2) and (3.3) thus simplify to

$$\dot{x}(t) = F(x(t)) + f(t), \tag{3.21}$$
$$\langle f(t)\rangle = 0, \quad \langle f(t)f(t')\rangle = 2\alpha\delta(t-t'), \tag{3.22}$$

Next, we consider the discretized version of Eqs. (3.21) and (3.22) [143]:

$$\frac{x_{n+1}-x_n}{\Delta t} = F(\widetilde{x}_n) + f_n, \tag{3.23}$$
$$\langle f_n\rangle = 0, \quad \langle f_n f_m\rangle = \frac{2\alpha\delta_{nm}}{\Delta t}, \tag{3.24}$$

where the subscripts index a time point, and Δt is the discretization time step. An important feature of this discretization procedure is that we consider F to be evaluated at an arbitrary point between x_n and x_{n+1}, such that we can parametrize $\widetilde{x}_n$ as follows [143]:

$$\widetilde{x}_n = cx_{n+1} + (1-c)x_n, \tag{3.25}$$

where $c \in [0, 1]$.

What is special about Eq. (3.23)? As we mentioned above, the peculiarity comes from the properties of the random force, i.e., Eq. (3.24): since $\langle f_n^2 \rangle = \frac{2\alpha}{\Delta t}$, f_n is of order $(\Delta t)^{-\frac{1}{2}}$, $f_n \sim (\Delta t)^{-\frac{1}{2}}$. This results to the fact that

$$\Delta x \equiv x_{n+1} - x_n = F(\widetilde{x}_n)\Delta t + f_n \Delta t \sim (\Delta t)^{\frac{1}{2}}\,, \tag{3.26}$$

in contrast to a conventional (nonstochastic) equation of motion, where $\Delta x \sim \Delta t$.

The tricky thing of stochastic calculus is that the property (3.26) makes certain mathematical operations dependent on the discretization parameter c in Eq. (3.25) even in the continuous limit ($\Delta t \to 0$) [143][5]. Let us show that the chain rule for computing derivatives of a composite function depends on c, and thereby identify the mistake we purposely introduced in Eq. (3.18).

The stochastic chain rule (Itô formula)

We consider a function $h(x(t))$, where $x(t)$ is a solution of Eq. (3.21), and aim to find its derivative with respect to time t, i.e., $\frac{dh(x(t))}{dt}$, by using the continuous limit of the discrete time derivative.

In the discrete version, the derivative yields [143]

$$\frac{\Delta h}{\Delta t} \equiv \frac{h(x_{n+1}) - h(x_n)}{\Delta t} = \frac{h\left[\widetilde{x}_n + (1-c)\Delta x\right] - h\left[\widetilde{x}_n - c\Delta x\right]}{\Delta t}. \tag{3.27}$$

Next, we make a Taylor expansion of Eq. (3.27) in powers of Δx, keeping in mind that $(\Delta x) \sim (\Delta t)^{\frac{1}{2}}$ according to Eq. (3.26) [143]:

$$\frac{h\left[\widetilde{x}_n + (1-c)\Delta x\right] - h\left[\widetilde{x}_n - c\Delta x\right]}{\Delta t} = \frac{\partial h(\widetilde{x}_n)}{\partial \widetilde{x}_n}\frac{\Delta x}{\Delta t} + \frac{1}{2}(1-2c)\frac{\partial^2 h(\widetilde{x}_n)}{\partial \widetilde{x}_n^2}\frac{(\Delta x)^2}{\Delta t} + \mathcal{O}\left[(\Delta t)^{\frac{1}{2}}\right]. \tag{3.28}$$

Substituting Δx given by Eq. (3.26) into the second term of Eq. (3.28), we get

$$\frac{\Delta h}{\Delta t} = \frac{\partial h(\widetilde{x}_n)}{\partial \widetilde{x}_n}\frac{\Delta x}{\Delta t} + \frac{1}{2}(1-2c)\frac{\partial^2 h(\widetilde{x}_n)}{\partial \widetilde{x}_n^2} f_n^2 \Delta t + \mathcal{O}\left[(\Delta t)^{\frac{1}{2}}\right]. \tag{3.29}$$

Assuming that $\frac{dh(x(t))}{dt}$ will be used only inside the average brackets, we can replace f_n^2 by its average $\langle f_n^2 \rangle = \frac{2\alpha}{\Delta t}$ [143]:

$$\frac{\Delta h}{\Delta t} = \frac{\partial h(\widetilde{x}_n)}{\partial \widetilde{x}_n}\frac{\Delta x}{\Delta t} + (1-2c)\alpha\frac{\partial^2 h(\widetilde{x}_n)}{\partial \widetilde{x}_n^2} + \mathcal{O}\left[(\Delta t)^{\frac{1}{2}}\right]. \tag{3.30}$$

[5] We note that the continuous limit of Eq. (3.23), Eq. (3.21), is unambiguous, as $F(\widetilde{x}_n)$ is independent of the choice of c once $\Delta t \to 0$. The situation changes, however, when one considers a multiplicative noise, i.e., $\alpha = \alpha(x)$ [143, 150].

Finally, taking the limit $\Delta t \to 0$, we obtain for the continuous time derivative [143]

$$\frac{dh(x(t))}{dt} = \frac{\partial h(x(t))}{\partial x(t)}\dot{x}(t) + (1-2c)\alpha\frac{\partial^2 h(x(t))}{\partial x^2(t)}. \tag{3.31}$$

Relation (3.31) is called the stochastic chain rule, or Itô formula [143, 151]. Compared to the usual chain rule, it has an additional term [the second one in Eq. (3.31)] depending on the discretization parameter c. This indicates that certain conventional mathematical operations has to be modified when using stochastic functions [143, 151, 152]. There are two standard discretization choices: the choice $c = 0$, which is also called Itô discretization (or Itô convention), and $c = \frac{1}{2}$ known as Stratonovich discretization (or Stratonovich convention). The Itô convention changes the usual chain rule,

$$\frac{dh(x(t))}{dt} \overset{\text{Itô}}{=} \frac{\partial h(x(t))}{\partial x(t)}\dot{x}(t) + \alpha\frac{\partial^2 h(x(t))}{\partial x^2(t)}, \tag{3.32}$$

while the Stratonovich convention remains it unchanged,

$$\frac{dh(x(t))}{dt} \overset{\text{Str.}}{=} \frac{\partial h(x(t))}{\partial x(t)}\dot{x}(t). \tag{3.33}$$

Stochastic integrals

Using rules (3.32) and (3.33), one can show the relation between the Itô and Stratonovich stochastic integrals [151–153]:

$$\text{Itô} \int_0^t dt'\dot{x}(t')h(x(t')) = \text{Str.} \int_0^t dt'\dot{x}(t')h(x(t')) - \alpha \int_0^t dt' \frac{\partial h(x(t'))}{\partial x(t')}, \tag{3.34}$$

where the last term is a normal (Riemann) integral, because it does not contain time derivatives (i.e., x, although being stochastic, is a well-behaved function compared to $\dot{x}$). Since the Stratonovich chain rule is the same as a usual one, the stochastic Stratonovich integral Str. $\int_0^t dt'\dot{x}h(x)$ obeys the same integration rules as a Riemann integral. For example, defining $h(x) = \frac{\partial H}{\partial x}$, one can write Str. $\int_0^t dt'\dot{x}\frac{\partial H}{\partial x} =$ Str. $\int_0^t dt'\frac{dH}{dt'} = H(x(t)) - H(x(0))$. From now on, we hence omit symbol "Str." for stochastic Stratonovich integrals. In contrast, an Itô integral does not in general obey normal integration rules [152].

It should be clear now why naive evaluation of Eq. (3.18) is wrong: the equation is not in agreement with the transition rule (3.34). Instead of Eq. (3.18), we had to write

$$\frac{\lambda}{2k_\mathrm{B}T}\ \text{Itô} \int_0^t dt' \left\langle x^2(t)\dot{x}(t')x(t')\right\rangle = \frac{\lambda}{2k_\mathrm{B}T}\int_0^t dt' \left\langle x^2(t)\dot{x}(t')x(t')\right\rangle - \frac{\lambda\mu}{2}\int_0^t dt' \left\langle x^2(t)\right\rangle, \tag{3.35}$$

where the second term $-\frac{\lambda\mu}{2}\int_0^t dt'\left\langle x^2(t)\right\rangle = -\lambda\frac{k_\mathrm{B}T\mu}{2k}t$ cancels the excess term $\lambda\frac{k_\mathrm{B}T\mu}{2k}t$ in the final expression (3.20), thereby resulting in the correct response (3.13).

3.3.3 An updated response formula

Since a Stratonovich integral obeys normal integration rules, it is useful to rewrite response relation (3.7) in terms of a Stratonovich integral. For this, we need a generalization of formula (3.34) applicable for Eqs. (3.2) and (3.3). According to Ref. [152], this generalization reads

$$\text{Itô} \int_0^t dt' \dot{x}_i(t') h(\Gamma(t'), t') = \int_0^t dt' \dot{x}_i(t') h(\Gamma(t'), t') - \alpha_i \int_0^t dt' \frac{\partial h(\Gamma(t'), t')}{\partial x_i(t')}. \tag{3.36}$$

Remember that we omit symbolizing a Stratonovich integral, Str. $\int_0^t dt' \dot{x}_i(t') h(\Gamma(t'), t') \equiv \int_0^t dt' \dot{x}_i(t') h(\Gamma(t'), t')$. Applying Eq. (3.36) to formula (3.7), we obtain[6]

$$\boxed{\begin{aligned} \langle A(t)\rangle_0^{(\lambda)} - \langle A(t)\rangle_0 &= \frac{\lambda}{2} \int_0^t dt' \left\langle A(t) \sum_{i=1}^{\tilde{N}} \frac{1}{\alpha_i} \dot{x}_i(t') \frac{\partial F_i(\Gamma(t'), t', \lambda)}{\partial \lambda}\Big|_{\lambda=0} \right\rangle_0 \\ - \frac{\lambda}{2} \int_0^t dt' &\left\langle A(t) \sum_{i=1}^{\tilde{N}} \left\{ \frac{1}{\alpha_i} F_i(\Gamma(t'), t') \frac{\partial F_i(\Gamma(t'), t', \lambda)}{\partial \lambda}\Big|_{\lambda=0} + \frac{\partial^2 F_i(\Gamma(t'), t', \lambda)}{\partial x_i(t') \partial \lambda}\Big|_{\lambda=0} \right\} \right\rangle_0 . \end{aligned}} \tag{3.37}$$

Apart from obeying the rules of standard calculus, formula (3.37) has another nice property absent in its Itô version (3.7): the first term in Eq. (3.37) is time antisymmetric, while the second one is time symmetric [152][7]. This property allows to simplify formula (3.37) for equilibrium systems, as we are going to show in the forthcoming section.

3.4 Discussion of the response formula regarding different systems and perturbations

Using response relation (3.37), we can identify fundamental differences between the linear responses for different systems and perturbations. We distinguish two types of systems, equilibrium and nonequilibrium, and two types of perturbations, conservative and nonconservative, – there are hence four cases in total.

[6] An alternative, direct way of deriving formula (3.37) implies using the Stratonovich convention when discretizing Eq. (3.2), where the path weight differs from the Itô path weight (3.5). Moreover, one can keep an arbitrary discretization [see Eq. (3.25)] to obtain a more general response relation depending on the discretization parameter (see Ref. [143] for the corresponding path weight).

[7] For discussions of the time reversal symmetry, we refer the reader to Refs. [98–101, 152].

Case I A: an equilibrium system perturbed by a potential

This is the least general but the simplest case, where the response relation (3.37) becomes FDT (2.3). First, we note that in equilibrium $F_i(\Gamma(t'),t') = F_i(\Gamma(t'))$, where $F_i(\Gamma(t'))$ derives from a potential, and $\alpha_i = \alpha$. Next, since an equilibrium state is time symmetric, the two terms in Eq. (3.37) yield identical contributions, such that the response is given by twice either term [98–101][8]. In addition, for a potential perturbation, $F_i(\Gamma(t'),t',\lambda) = F_i(\Gamma(t'),\lambda) = -\frac{\partial U(\Gamma(t'),\lambda)}{\partial x_i(t')}$. We thus have

$$\langle A(t)\rangle^{(\lambda)} - \langle A\rangle = -\frac{\lambda}{\alpha}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{\widetilde{N}} \dot{x}_i(t')\frac{\partial^2 U(\Gamma(t'),\lambda)}{\partial x_i(t')\partial\lambda}\Big|_{\lambda=0}\right\rangle. \tag{3.38}$$

Remember that that the absence of the subscript "0" for the average brackets means that the system is in equilibrium before a perturbation is applied. Since $\sum_{i=1}^{\widetilde{N}} \dot{x}_i \frac{\partial^2 U}{\partial x_i \partial\lambda}|_{\lambda=0}$ is the total time derivative, the integral in Eq. (3.38) can be performed, and we finally get

$$\langle A(t)\rangle^{(\lambda)} - \langle A\rangle = -\frac{\lambda}{\alpha}\left[\left\langle A(t)\frac{\partial U(t,\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right\rangle - \left\langle A(t)\frac{\partial U(0,\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right\rangle\right], \tag{3.39}$$

where we used a shorthand notation $U(\Gamma(t),\lambda) \equiv U(t,\lambda)$, as for A.

Formula (3.39) is an FDT, ant it represents the simplest form of general relation (3.37). Adapting it to a physical system of overdamped passive Brownian particles, we identify $\alpha = k_B T\mu$ and $\lambda\frac{\partial U(t,\lambda)}{\partial\lambda}|_{\lambda=0} = \mu U^{\mathrm{ptb}}(t)$, such that Eq. (2.3) is recovered.

Case I B: an equilibrium system perturbed by a nonconservative force

Here, Eq. (3.39) is not valid, but we can still use the fact that the two terms in Eq. (3.37) are identical. Therefore, there are two ways to calculate the response:

$$\langle A(t)\rangle^{(\lambda)} - \langle A\rangle = \frac{\lambda}{\alpha}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{\widetilde{N}} \dot{x}_i(t')\frac{\partial F_i(\Gamma(t'),t',\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right\rangle, \tag{3.40}$$

$$\langle A(t)\rangle^{(\lambda)} - \langle A\rangle = -\frac{\lambda}{\alpha}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{\widetilde{N}}\left\{F_i(\Gamma(t'))\frac{\partial F_i(\Gamma(t'),t',\lambda)}{\partial\lambda}\Big|_{\lambda=0} + \alpha\frac{\partial^2 F_i(\Gamma(t'),t',\lambda)}{\partial x_i(t')\partial\lambda}\Big|_{\lambda=0}\right\}\right\rangle. \tag{3.41}$$

Formula (3.40) contains a time-antisymmetric integral giving the entropic contribution to the response [98–101]. The response in Eq. (3.40) is hence quantified by the excess entropy flux to the environment, or the work done on the system by the perturbation

[8] Note that this statement cannot be applied to the Itô version of the response, Eq. (3.7), because an Itô integral does not possess a time reversal symmetry.

force. Identifying $\alpha = k_B T \mu$ and $\lambda \frac{\partial F_i(\Gamma(t'),t',\lambda)}{\partial \lambda}|_{\lambda=0} = \mu F_i^{\text{ptb}}(\Gamma(t')) \equiv \mu F_i^{\text{ptb}}(t')$, one recovers Eq. (2.1). In contrast, formula (3.41) contains a time-symmetric integral giving the frenetic contribution quantified by the excess in activity [98–101]. We repeat once again that the two contributions are identical because the unperturbed system is in equilibrium, such that the equilibrium response can be given by either the entropic or frenetic part [98–101].

Which response relation is better, the entropic formula (3.40) or the frenetic one (3.41)? There is no univocal answer to this question. Formula (3.40) contains instantaneous velocities $\dot{x}_i$, which are not well-behaved functions of time and which are typically not measurable in experiments. On the other hand, Eq. (3.41) involves more details of the unperturbed system, namely the forces $F_i(\Gamma(t'))$, such that one has to know how the particles interact and what the external potential is. The latter response formula is more frequently used in practice, and it represents a general Green-Kubo relation [3, 20, 21, 84, 90, 96, 97, 105, 106].

Case II A: a nonequilibrium system perturbed by a potential

In this case, since a nonequilibrium process is not invariant under time reversal, the two terms in Eq. (3.37) are not necessarily equal. However, the perturbation by a potential allows to simplify the first term for $\alpha_i = \alpha$, in the spirit of Case I A. We thus get

$$\langle A(t)\rangle_0^{(\lambda)} - \langle A(t)\rangle_0 \overset{\alpha_i=\alpha}{=} -\frac{\lambda}{2\alpha}\left[\left\langle A(t)\frac{\partial U(t,\lambda)}{\partial \lambda}\Big|_{\lambda=0}\right\rangle_0 - \left\langle A(t)\frac{\partial U(0,\lambda)}{\partial \lambda}\Big|_{\lambda=0}\right\rangle_0\right]$$
$$-\frac{\lambda}{2\alpha}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{\tilde{N}}\left\{F_i(\Gamma(t'),t')\frac{\partial F_i(\Gamma(t'),t',\lambda)}{\partial \lambda}\Big|_{\lambda=0} + \alpha\frac{\partial^2 F_i(\Gamma(t'),t',\lambda)}{\partial x_i(t')\partial \lambda}\Big|_{\lambda=0}\right\}\right\rangle_0 . \tag{3.42}$$

A large benefit of this simplification is that the formula does not contain time derivatives.

Case II B: a nonequilibrium system perturbed by a nonconservative force

This is the most general and the hardest case, where no simplifications can be applied. The response is hence given by Eq. (3.37) as it is.

Further discussions

We note that formula (3.7) has been given in Ref. [121]; response relation (3.37) is derived in Refs. [99–101] for a potential perturbation.

It is interesting that the path integral method always leads to a response relation with the two, entropic and frenetic, terms, even if one assumes from the start that the unperturbed system is in equilibrium. By this, the path integral approach differs from other derivation methods, where one obtains only one term[9], and it is, in this sense, more

[9] For example, derivation of the equilibrium response for a potential perturbation based on the Liouville equation gives only FDT (2.3) [20], while the derivation for shear perturbation via the Smoluchowski equation gives only the Green-Kubo formula (2.20) [96].

universal. As we mentioned in Sec. 2.8, this universality allowed us to draw attention to the entropic component of the response to shear (and, as a result, to restore FDT for shear later on), while typically only the Gree-Kubo relation based on the frenetic component is considered [20, 21, 84, 96, 97].

As for underdamped Brownian motion, the entropic term in Eq. (3.37) remains unchanged, while the frenetic one is modified due to the presence of time-symmetric inertia terms $\ddot{x}_i$ (see Sec. 3.6 and Ref. [100]). The above discussed simplifications regarding different systems and perturbations remain valid [100]. The underdamped version of the response relation in terms of the Malliavin weight is identical to the overdamped one [103].

3.5 Deterministic versus stochastic

3.5.1 Zero-temperature limit for the linear response

A crucial property of stochastic linear response is that the information about the change of the dynamics is fully determined by the distribution. As we mentioned in Subsec. 1.3.3 and saw in Sec. 3.1, the linear response is obtained by expanding the distribution around perturbation forces. As the parameters responsible for stochasticity and determining the variance of the distribution (e.g., the temperature) decrease, the distribution becomes sharper, indicating that one trajectory becomes more and more preferable over the others. An important question arises: what happens with the response in the limit of zero variance, or zero temperature?

An attempt to answer this question by taking the limit of a linear response relation directly fails for a simple reason: the linear response formula for a stochastic system is derived by a series expansion of a smooth function or functional [see, for example, Eq. (3.6)]; once the temperature becomes zero, this function (the distribution) acquires the form of a delta-distribution, and it hence cannot be expanded anymore; thus, the response relation is not valid for $T = 0$, and the direct limit does not make sense. Note, however, that the limit can be performed for a concrete scenario where the response is known as a function of temperature explicitly.

For taking the zero-temperature limit of a general linear response relation, one hence cannot expand the distribution, but one has to use an alternative approach applicable for both deterministic and stochastic systems. This approach, sometimes called as the adjunct method [103], is based on the expansion of the system trajectories, such that the mathematical interpretation of the response theory is changed: it is not the distribution which is perturbed, but the trajectories. The resulting response relations are hence different from the conventional ones studied before in this thesis. In the next subsection, we discuss the adjunct method in detail.

3.5.2 Linear response for deterministic systems: comparison to stochastic response

We consider an overdamped Brownian dynamics and, for simplicity, restrict to a single degree of freedom. The corresponding Langevin equation and the random force properties read

$$\dot{x}(t) = F(x(t), \lambda) + f(t), \tag{3.43}$$

$$\langle f(t) \rangle = 0, \quad \langle f(t) f(t') \rangle = 2\alpha\delta(t - t'), \tag{3.44}$$

where the parameter λ quantifying the perturbation is finite only for $t > 0$.

The adjunct method: perturbing trajectories to get the response

Let $x(t, \lambda)$ be a solution of Eq. (3.43), i.e., a trajectory satisfying the Langevin equation. The idea of the adjunct method is to use a series expansion of this solution:

$$x(t, \lambda) = x(t) + \lambda \frac{\partial x(t, \lambda)}{\partial \lambda}\Big|_{\lambda=0} + \mathcal{O}(\lambda^2). \tag{3.45}$$

Similarly, we can expand an observable of interest A,

$$A(x(t, \lambda)) = A(x(t)) + \lambda \frac{\partial A(x(t))}{\partial x(t)} \frac{\partial x(t, \lambda)}{\partial \lambda}\Big|_{\lambda=0} + \mathcal{O}(\lambda^2), \tag{3.46}$$

relating the response of A to the response of x. Next, since a solution $x(t, \lambda)$ satisfies Eq. (3.43), we can formally write

$$\dot{x}(t, \lambda) = F(x(t, \lambda), \lambda) + f(t). \tag{3.47}$$

To find the equation for $\frac{\partial x(t,\lambda)}{\partial \lambda}|_{\lambda=0}$, we substitute Eq. (3.45) into the left-hand side of Eq. (3.47), and expand the right-hand side of the latter:

$$\begin{aligned} \dot{x}(t) &+ \lambda \frac{d\left(\frac{\partial x(t,\lambda)}{\partial \lambda}\big|_{\lambda=0}\right)}{dt} + \mathcal{O}(\lambda^2) \\ &= F(x(t)) + \lambda \left[\frac{\partial F(x(t))}{\partial x(t)} \frac{\partial x(t, \lambda)}{\partial \lambda}\Big|_{\lambda=0} + \frac{\partial F(x(t), \lambda)}{\partial \lambda}\Big|_{\lambda=0} \right] + f(t) + \mathcal{O}(\lambda^2). \end{aligned} \tag{3.48}$$

In Eq. (3.48), $x(t)$ on the left-hand side cancels with $F(x(t)) + f(t)$ on the right-hand side, as they form the unperturbed equation of motion; the nonlinear in λ terms $\mathcal{O}(\lambda^2)$ are neglected; the rest gives the equation for $\frac{\partial x(t,\lambda)}{\partial \lambda}|_{\lambda=0}$. With this equation, and using relation (3.46), we can finally write the linear response formula:

$$\boxed{\begin{aligned} &\langle A(x(t, \lambda)) \rangle_0 - \langle A(x(t)) \rangle_0 = \lambda \left\langle \frac{\partial A(x(t))}{\partial x(t)} \frac{\partial x(t, \lambda)}{\partial \lambda}\Big|_{\lambda=0} \right\rangle_0, && (3.49) \\ &\frac{d\left(\frac{\partial x(t,\lambda)}{\partial \lambda}\big|_{\lambda=0}\right)}{dt} = \frac{\partial F(x(t))}{\partial x(t)} \frac{\partial x(t, \lambda)}{\partial \lambda}\Big|_{\lambda=0} + \frac{\partial F(x(t), \lambda)}{\partial \lambda}\Big|_{\lambda=0}, && (3.50) \end{aligned}}$$

where differential equation (3.50) is independent of λ (i.e., it is evaluated at $\lambda = 0$) and has the initial condition $\frac{\partial x(0,\lambda)}{\partial \lambda}|_{\lambda=0} = 0$.

Response relation (3.49) is valid for both stochastic and deterministic systems, as the expansion of trajectories can be performed for both systems and no assumptions about the random force $f(t)$ have been made (note that the relation does not contain α); formula (3.49) can hence be also considered as the $\alpha \to 0$ limit of formula (3.37). For a stochastic system, there are many possible trajectories, and one has to perform the average according to property (3.44); using our notation for averaging in stochastic response relations, one identifies $\langle A(x(t,\lambda))\rangle_0 \equiv \langle A(t)\rangle_0^{(\lambda)}$ and $\langle A(x(t)\rangle_0 \equiv \langle A(t)\rangle_0$. For a deterministic system, there is nothing to average over (i.e, there is only one trajectory), and the average brackets has thus to be dropped out. Note that using Eq. (3.49) one does not have to know the perturbed solution $x(t,\lambda)$, but instead one has to solve the adjunct equation (3.50) for an auxiliary variable $\frac{\partial x(t,\lambda)}{\partial \lambda}|_{\lambda=0}$, where no perturbed solution is required (hence the name "adjunct method"). Also note that formula (3.49) is very different from a conventional stochastic linear response relation [compare to Eq. (3.37)], although both have to give the same result. Generalization of Eqs. (3.49) and (3.50) to many degrees of freedom is straightforward (see Ref. [103]); the adjunct method can also be used for equations of motion different from Eq. (3.43) (for example, Ref. [104] studies the method for Newtonian dynamics).

Example I

Let us demonstrate response formula (3.49). In the first example, we consider the same unperturbed system as in Subsec. 3.3.1, i.e., an overdamped passive particle confined in a harmonic trap. Since equilibrium state cannot be defined for a deterministic system, we consider that the particle is located exactly at the trap minimum before the perturbation is applied, i.e., $x(0) = 0$. The perturbation we employ is $F^{\mathrm{ptb}} = \lambda$, with $\lambda > 0$ for concreteness, i.e., a constant force moving the particle to the right. Our goal is to check formula (3.49) and compare the linear responses of $A = x$ for the deterministic ($f = 0$, or equivalently $T = 0$) and stochastic (finite f or T) systems.

The Langevin equation is Eq. (3.9) with $\mu\lambda x$ replaced by $\mu\lambda$; the random force properties remain the same as in Eq. (3.10). The direct computation of the response reads

$$\langle x(t,\lambda)\rangle_0 - \langle x(t)\rangle_0 = \frac{\lambda}{k}\left(1 - e^{-\mu k t}\right), \tag{3.51}$$

valid for any λ, i.e., the linear order is the only finite one. Next, we compute the response using the stochastic response relation (3.42). For the considered system, the relation reads

$$\langle x(t,\lambda)\rangle_0 - \langle x(t)\rangle_0 = \frac{\lambda}{2k_{\mathrm{B}}T}\left[\left\langle x^2(t)\right\rangle_0 + \langle x(t)x(0)\rangle_0\right] + \frac{\lambda\mu k}{2k_{\mathrm{B}}T}\int_0^t dt'\langle x(t)x(t')\rangle_0. \tag{3.52}$$

Substituting the correlation function

$$\langle x(t)x(t')\rangle_0 = \frac{k_{\mathrm{B}}T}{k}e^{-\mu k t}\left(e^{\mu k t'} - e^{-\mu k t'}\right) \tag{3.53}$$

into Eq. (3.52), one obtains Eq. (3.51). Finally, we apply formula (3.49). Denoting the auxiliary variable $\frac{\partial x(t,\lambda)}{\partial \lambda}|_{\lambda=0} \equiv q(t)$, the adjunct equation (3.50) reads for our system

$$\dot{q} = -\mu k q + \mu, \tag{3.54}$$

whose solution is

$$q(t) = \frac{1}{k}\left(1 - e^{-\mu k t}\right). \tag{3.55}$$

Setting $A = x$ in Eq. (3.49) and substituting into there $\frac{\partial x(t,\lambda)}{\partial \lambda}|_{\lambda=0} \equiv q(t)$ given by Eq. (3.55), we obtain Eq. (3.51).

The response (3.51) is independent of T, and it is hence the same for the deterministic and stochastic systems. This is not the case in the next example, where we show that using formula (3.49) is advantageous over applying relation (3.37) when one restricts to the $T = 0$ case.

Example II

In this example, we consider a particle in a double-well potential

$$U^{\text{ext}}(x) = U_0\left[\left(\frac{x}{l_0}\right)^4 - 2\left(\frac{x}{l_0}\right)^2\right], \tag{3.56}$$

where U_0 is the barrier hight and l_0 gives the distance to the minima (see Fig. 3.3). This model is used to describe the stochastic resonance [154]. Initially, at time $t = 0$, the particle is located at the left minimum of the potential,

$$x(0) = -l_0. \tag{3.57}$$

For time $t > 0$ the constant perturbation force $F^{\text{ptb}} = \lambda$ is applied to the right (i.e., $\lambda > 0$), and we are interested in the linear response of the particle position, $\langle x(t,\lambda)\rangle_0 - \langle x(t)\rangle_0$. The Langevin equation for this scenario reads

$$\dot{x} = -4\mu\frac{U_0}{l_0^4}x^3 + 4\mu\frac{U_0}{l_0^2}x + \mu\lambda + \mu f, \tag{3.58}$$

with f determined by Eq. (3.10).

For a finite T, such that f is also finite, Eq. (3.58) is difficult to solve analytically. Indeed, the presence of the random force implies a nontrivial dynamics: depending on how strong the fluctuations are compared to the barrier height U_0, the motion of the particle is either restricted to the left well or extended to both wells. Evaluation of the linear response for a finite T is hence a difficult analytical problem, no matter which response relation, Eq. (3.37) or (3.49), is used.

The situation changes, however, when one restricts to the zero-temperature limit. In this case, the stochastic response relation (3.37) is still difficult to apply, as one has to keep f finite in that relation before taking the limit $T \to 0$. In contrast, the deterministic response formula (3.49) allows to set $f = 0$ from the beginning. Since for

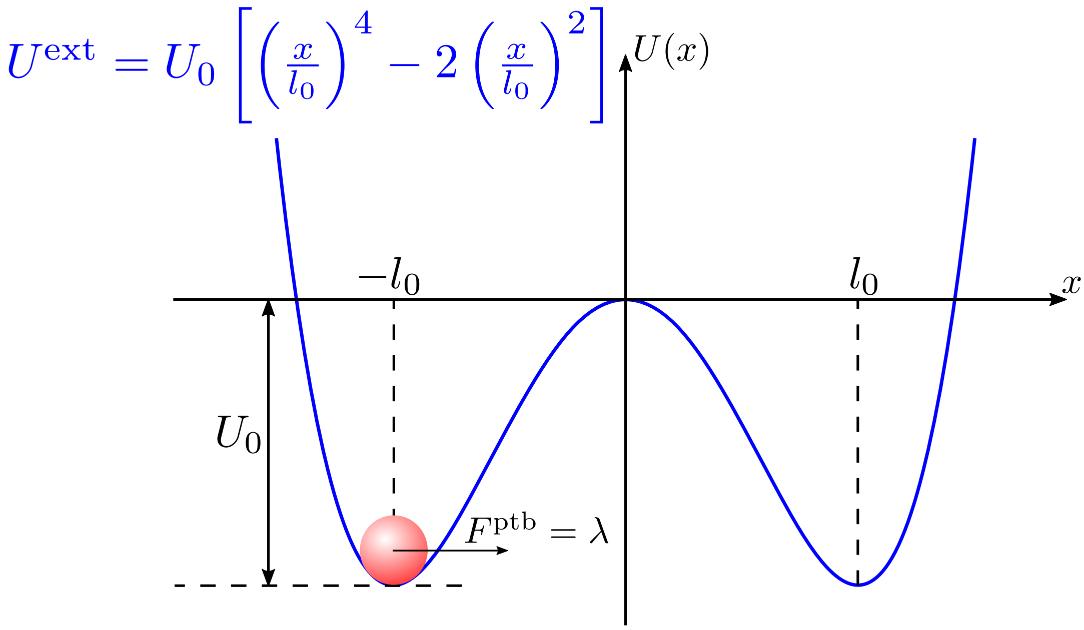

Figure 3.3. A particle confined in a double-well potential $U^{\text{ext}} = U_0\left[\left(\frac{x}{l_0}\right)^4 - 2\left(\frac{x}{l_0}\right)^2\right]$. Being located exactly at the left minimum at time $t = 0$, the particle is perturbed by a constant force $F^{\text{ptb}} = \lambda$ moving the particle to the right.

the unperturbed deterministic system the particle stays forever at the left minimum, the unperturbed deterministic solution is trivial, $x(t) = x(0) = -l_0$. The linear response can thus be easily evaluated. For our system, formula (3.49) reads [again denoting $\frac{\partial x(t,\lambda)}{\partial \lambda}|_{\lambda=0} \equiv q(t)$]

$$\langle x(t,\lambda)\rangle_0 - \langle x(t)\rangle_0 = x(t,\lambda) - x(t) = \lambda q(t), \tag{3.59}$$

$$\dot{q}(t) = 4\mu\frac{U_0}{l_0^2}\left[-\frac{3}{l_0^2}x^2(t) + 1\right]q(t) + \mu. \tag{3.60}$$

Since $x(t) = -l_0$, Eq. (3.60) simplifies to

$$\dot{q}(t) = -8\mu\frac{U_0}{l_0^2}q(t) + \mu, \tag{3.61}$$

whose solution reads

$$q(t) = \frac{l_0^2}{8U_0}\left(1 - e^{-8\mu\frac{U_0}{l_0^2}t}\right). \tag{3.62}$$

Substituting this solution into Eq. (3.59), we finally obtain for the linear response

$$x(t,\lambda) - x(t) = \frac{\lambda l_0^2}{8U_0}\left(1 - e^{-8\mu\frac{U_0}{l_0^2}t}\right), \tag{3.63}$$

where $x(t)$ can be replaced by $-l_0$.

Note that the direct computation of the deterministic linear response is much more difficult than using linear response theory demonstrated above: even if $f = 0$, a finite λ makes it still difficult to solve Eq. (3.58). Indeed, the dynamics for arbitrary λ is nontrivial, as the perturbed particle can move throughout the whole potential, whereas for small λ the perturbation force just slightly displaces the particle to the right, such that the perturbed particle does not move out of the left well. Therefore, in the linear regime, the problem reduces to a particle in a harmonic trap[10], and it is better to formally expand the trajectory first [formula (3.49)] rather than restrict to the linear order in the exact solution. The demonstrated example hence illustrates the advantage of linear response theory.

Remarks on the stability of the adjunct method[11]

The conventional statistical methods for the linear response, discussed before in this thesis, and the adjunct method, introduced in the current subsection, are fundamentally different. Unfortunately, since we studied here fairly simple examples, no effects of this difference was observed in a sense of efficiency and applicability of the two approaches (the only fact we learned is that the adjunct method is easier in the deterministic case). These effects do appear, however, when one looks at complex systems at finite temperature.

In some cases, especially when the dynamics is slow (i.e., a system relaxes to a steady state slowly), the adjunct method can be unstable in a sense that no reliable measurement using this method can be performed [104]. The reason for such an instability is the instability of an individual stochastic trajectory itself: a small perturbation can lead to a nonsmall change of a trajectory, especially for large times [21, 155]. In principle, this issue should disappear after the averaging, but the point is that it is very difficult to perform the averaging for unstable trajectories in practice. In contrast, perturbation of the distribution works well for such cases, and stochastic response relations are hence in general more widely applicable and more effective [103, 104].

3.5.3 A combination of stochastic and deterministic motions

We close this section by noticing that f_i in Eq. (3.2) can be zero for some set of i, but finite for the remaining set, meaning that some degrees of freedom are deterministic, while the others are stochastic. In this case, the response relation can be either Eq. (3.49) (generalized to many degrees of freedom), a superposition of Eqs. (3.49) and (3.37), or the other formula which is not discussed in this dissertation. This formula has a form which is intermediate between Eqs. (3.49) and (3.37). It is derived by transferring the expansion of a delta-distribution (corresponding to the deterministic degrees of freedom)

[10] Note that the adjunct equation (3.61) for an auxiliary variable q (which, according to Eq. (3.59), fully determines the linear response) is the same as the deterministic Langevin equation for x for a particle in a harmonic potential ($\dot{x} = -\mu k x + \mu\lambda$).

[11] My interest in the topic of these remarks originated from a fruitfull discussion with Grzegorz Szamel.

to the additional expansion of a smooth distribution (corresponding to the stochastic degrees of freedom). A nice example of such a combined linear response theory is the response of active Ornstein-Uhlenbeck particles studied in Ref. [149].

3.6 Application: a derivation of the underdamped Green-Kubo relation

In this section, we first generalize linear response relation (3.37) to underdamped systems, and then apply the underdamped formula to perform a derivation of the underdamped Green-Kubo relation for shear (2.26).

The generalization is straightforward. In the underdamped case, the function $\mathcal{X}_i(t,\lambda)$ changes to

$$\mathcal{X}_i(t,\lambda) \equiv \dot{x}_i(t) - F_i(\Gamma(t),t,\lambda) + \tau_{mi}\ddot{x}_i, \tag{3.64}$$

because Langevin equation (3.2) acquires the inertia term $\tau_{mi}\ddot{x}_i$, where τ_{mi} is the inertia time. This leads to the corresponding changes in Eqs. (3.5) and (3.6), such that the response relation is a simple modification of formula (3.7),

$$\begin{aligned}&\langle A(t)\rangle_0^{(\lambda)} - \langle A(t)\rangle_0 \\ &= \frac{\lambda}{2}\ \text{Itô}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{\tilde{N}}\frac{1}{\alpha_i}\left[\dot{x}_i(t') - F_i(\Gamma(t'),t') + \tau_{mi}\ddot{x}_i\right]\frac{\partial F_i(\Gamma(t'),t',\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right\rangle_0 .\end{aligned} \tag{3.65}$$

Regarding stochastic calculus, we note that $\dot{x}_i$ is a well-behaved variable if $\tau_{mi} \neq 0$, and hence the Itô integral containing $\dot{x}_i$ in Eq. (3.65) is equivalent to the Stratonovich one [100]. This equivalence also holds for the term containing $\ddot{x}_i$ if we assume that forces $F_i(\Gamma(t'),t',\lambda)$ do not depend on time derivatives, i.e., $F_i(\Gamma(t'),t',\lambda) = F_i(\mathbf{x}(t'),t',\lambda)$ [100]. Therefore, we can write [100]

$$\begin{aligned}&\langle A(t)\rangle_0^{(\lambda)} - \langle A(t)\rangle_0 \\ &\overset{\tau_{mi}\neq 0}{=} \frac{\lambda}{2}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{\tilde{N}}\frac{1}{\alpha_i}\left[\dot{x}_i(t') - F_i(\mathbf{x}(t'),t') + \tau_{mi}\ddot{x}_i\right]\frac{\partial F_i(\mathbf{x}(t'),t',\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right\rangle_0 .\end{aligned} \tag{3.66}$$

Finally, using the identity[12]

$$\sum_{i=1}^{\tilde{N}}\frac{\tau_{mi}}{\alpha_i}\ddot{x}_i\frac{\partial F_i}{\partial\lambda}\Big|_{\lambda=0} = \sum_{i=1}^{\tilde{N}}\frac{\tau_{mi}}{\alpha_i}\frac{d}{dt'}\left(\dot{x}_i\frac{\partial F_i}{\partial\lambda}\Big|_{\lambda=0}\right) - \sum_{i=1}^{\tilde{N}}\sum_{j=1}^{\tilde{N}}\frac{\tau_{mi}}{\alpha_i}\dot{x}_i\dot{x}_j\frac{\partial^2 F_i}{\partial x_j\partial\lambda}\Big|_{\lambda=0}, \tag{3.67}$$

we can get rid of accelerations $\ddot{x}_i$ (which are not well-behaved stochastic variables) in the response relation. The first term in Eq. (3.67) can be integrated out, and the response

[12] In Eq. (3.67), we assume that $F_i(\mathbf{x}(t'),t',\lambda) = F_i(\mathbf{x}(t'),\lambda)$ for simplicity. This assumption is, however, not necessary in order to get rid of $\ddot{x}_i$.

becomes [100]

$$\begin{aligned}\langle A(t)\rangle_0^{(\lambda)} - \langle A(t)\rangle_0 &\overset{\tau_{mi}\neq 0}{=} \frac{\lambda}{2}\int_0^t dt' \left\langle A(t)\sum_{i=1}^{\widetilde{N}} \frac{1}{\alpha_i}\dot{x}_i(t')\frac{\partial F_i(\mathbf{x}(t'),\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right\rangle_0 \\ &- \frac{\lambda}{2}\int_0^t dt' \left\langle A(t)\left[\sum_{i,j}^{\widetilde{N}} \frac{\tau_{mi}}{\alpha_i}\dot{x}_i(t')\dot{x}_j(t')\frac{\partial^2 F_i(\mathbf{x}(t'),\lambda)}{\partial x_j(t')\partial\lambda}\Big|_{\lambda=0} + \sum_{i=1}^{\widetilde{N}}\frac{F_i(\mathbf{x}(t'))}{\alpha_i}\frac{\partial F_i(\mathbf{x}(t'),\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right]\right\rangle_0 \\ &+ \frac{\lambda}{2}\left\{\left\langle A(t)\sum_{i=1}^{\widetilde{N}}\frac{\tau_{mi}}{\alpha_i}\dot{x}_i(t)\frac{\partial F_i(\mathbf{x}(t),\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right\rangle_0 - \left\langle A(t)\sum_{i=1}^{\widetilde{N}}\frac{\tau_{mi}}{\alpha_i}\dot{x}_i(0)\frac{\partial F_i(\mathbf{x}(0),\lambda)}{\partial\lambda}\Big|_{\lambda=0}\right\rangle_0\right\}.\end{aligned} \tag{3.68}$$

Using response formula (3.68), we are now ready to derive the Green-Kubo relation (2.26). The first term on the right-hand side of Eq. (3.68) is the entropic part, while the last two terms form the frenetic part. Therefore, in equilibrium, the response can be written as two times the last two terms (we need the frenetic part for the Green-Kubo relation). For a system of underdamped passive Brownian particles perturbed by shear (see Sec. 2.5), we identify $\widetilde{N} = 3N$, $\lambda = \dot{\gamma}$, $\tau_{mi} = m\mu$, $\alpha_i = k_{\mathrm{B}}T\mu$. A generalized variable x_i in Eq. (3.68) is either the x, y, or z component of the position of particle i, depending on N. Furthermore, $\frac{\partial F_i}{\partial\lambda}|_{\lambda=0} = \mu\frac{\partial F_{ix}^{\mathrm{ptb}}}{\partial\dot{\gamma}}|_{\dot{\gamma}=0} = y_i$ and $F_i = \mu\left(F_{ix}^{\mathrm{int}} + F_{ix}^{\mathrm{ext}}\right)$, where the index i on the right-hand sides indicates the number of particle. Therefore, $\sum_{i,j}^{\widetilde{N}}\frac{\tau_{mi}}{\alpha_i}\dot{x}_i\dot{x}_j\frac{\partial^2 F_i}{\partial x_j\partial\lambda}|_{\lambda=0} = \frac{m}{k_{\mathrm{B}}T}\sum_{i=1}^N v_{ix}v_{iy}$, $\sum_{i=1}^{\widetilde{N}}\frac{F_i}{\alpha_i}\frac{\partial F_i}{\partial\lambda}|_{\lambda=0} = \frac{1}{k_{\mathrm{B}}T}\sum_{i=1}^N\left(F_{ix}^{\mathrm{int}} + F_{ix}^{\mathrm{ext}}\right)y_i$, $\sum_{i=1}^{\widetilde{N}}\frac{\tau_{mi}}{\alpha_i}\dot{x}_i\frac{\partial F_i}{\partial\lambda}|_{\lambda=0} = \frac{m}{k_{\mathrm{B}}T}\sum_{i=1}^N v_{ix}y_i$, and we can write

$$\begin{aligned}&\langle A(t)\rangle^{(\dot{\gamma})} - \langle A\rangle \\ &\quad = \frac{\dot{\gamma}}{k_{\mathrm{B}}T}\int_0^t dt'\left\langle A(t)\left\{-\sum_{i=1}^N\left[m v_{ix}(t')v_{iy}(t') + \left(F_{ix}^{\mathrm{int}}(t') + F_{ix}^{\mathrm{ext}}(t')\right)y_i(t')\right]\right\}\right\rangle \\ &\quad + \frac{\dot{\gamma}m}{k_{\mathrm{B}}T}\left[\left\langle A\sum_{i=1}^N v_{ix}y_i\right\rangle - \left\langle A(t)\sum_{i=1}^N v_{ix}(0)y_i(0)\right\rangle\right].\end{aligned} \tag{3.69}$$

We note that the condition $m \neq 0$ in Eq. (3.69) [following from $\tau_{mi} \neq 0$ in Eq. (3.68)] is not necessary, because the Itô integral in Eq. (3.65) is equivalent to the Stratonovich one in the case of shear perturbation (the overdamped limit, $m \to 0$, can thus be safely taken). Finally, identifying the expression in the curly brackets of Eq. (3.69) as the stress tensor $\sigma_{xy}(t')$ in Eq. (2.27) and using the time-translation invariance of an equilibrium correlation function, we arrive at formula (2.26).

4 Response of active Brownian particles to shear flow

This chapter studies the linear response of active Brownian particles (ABPs) to simple shear flow. General linear response theory presented in the previous chapter is applied to this scenario, and the idea about symmetries introduced in Chapter 2 is used to remove time derivatives from the response formula; the results of Chapters 2 and 3 are hence combined here. The presented research is done by the author, his supervisor (Matthias Krüger) and collaborators, Christian M. Rohwer and Alexandre P. Solon, and it is originally published in Ref. [102]. Therefore, the content of this chapter is very close to that reference.

4.1 System: active Brownian particles in two space dimensions

We consider N overdamped ABPs, subject to interactions and external forces and torques, in two space dimensions. The choice of a *two*-dimensional system is due to simplicity reasons mentioned in Sec. 3.2.2: in 2D, all degrees of freedom perform a simple Brownian motion obeying Eqs. (3.2) and (3.3), such that we can directly apply the results of Chapter 3[1]. The generalization of the response formulas to ABPs in 3D and also to more general active particle models is given in Sec. 4.4.

We have already introduced the model for ABPs in Subsec. 1.2.2. In 2D, each particle has three degrees of freedom: two translational ones (in the x and y directions) and an angle φ parametrizing its heading $\hat{\mathbf{u}}(\varphi) = (\cos(\varphi), \sin(\varphi))^T$ in which the particle self-propels with velocity $v_0\hat{\mathbf{u}}(\varphi)$. For time $t > 0$, the particles are perturbed by simple shear flow which both advects and rotates them [62]. A schematic representation of the system is given in Fig. 4.1.

The dynamics of the ith particle is given by an overdamped two-dimensional version of Eqs. (1.20) and (1.21) [160, 161]:

$$\dot{x}_i = \dot{\gamma} y_i + v_0 \cos\varphi_i + \mu F_{ix}^{\text{int}} + \mu F_{ix}^{\text{ext}} + \mu f_{ix}, \tag{4.1a}$$

$$\dot{y}_i = v_0 \sin\varphi_i + \mu F_{iy}^{\text{int}} + \mu F_{iy}^{\text{ext}} + \mu f_{iy}, \tag{4.1b}$$

$$\dot{\varphi}_i = -\frac{\dot{\gamma}}{2} + \mu_{\text{r}}(M_i + g_i), \tag{4.1c}$$

[1] We note that a two-dimensional system of active particles is relevant to many experiments [156–159].

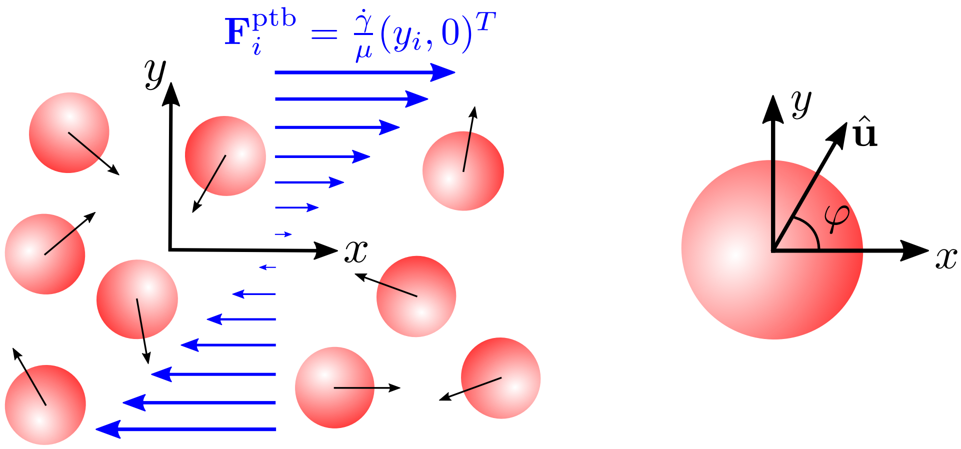

Figure 4.1. Active Brownian particles perturbed by simple shear flow in two space dimensions. Each particle performs a self-propelled motion with velocity $v_0\hat{\mathbf{u}}$ along its heading $\hat{\mathbf{u}}$ parametrized by an angle φ. Shear force $\mathbf{F}_i^{\mathrm{ptb}}$ both advects the particles and rotates them (their heading $\hat{\mathbf{u}}$).

where the terms containing $\dot{\gamma}$ are finite only for $t > 0$. We allow for very general forces, $\mathbf{F}_i^{\mathrm{int}}$ and $\mathbf{F}_i^{\mathrm{ext}}$, and torques, M_i, that do not have to arise from potentials and can depend on positions and orientations of the particles. The first term on the right-hand side of Eq. (4.1c) is the aforementioned rotation due to shear, where the prefactor of $\frac{1}{2}$ can be derived by considering an isolated particle in shear flow [62]. μ and μ_{r} denote bare translational and rotational mobilities, respectively. The stochastic terms $f_{i\alpha}$ and g_i are uncorrelated Gaussian white noises with moments

$$\langle f_{i\alpha}(t)\rangle = 0, \qquad \langle f_{i\alpha}(t) f_{j\beta}(t')\rangle = \frac{2D}{\mu^2}\delta_{ij}\delta_{\alpha\beta}\delta(t-t'), \tag{4.2a}$$

$$\langle g_i(t)\rangle = 0, \qquad \langle g_i(t) g_j(t')\rangle = \frac{2D_{\mathrm{r}}}{\mu_{\mathrm{r}}^2}\delta_{ij}\delta(t-t'), \tag{4.2b}$$

where $D = k_{\mathrm{B}}T\mu$ is the translational passive[2] diffusion coefficient [see Eq. (1.18)] and D_{r} is the rotational diffusion coefficient determining how quickly $\hat{\mathbf{u}}_i$ is reoriented. We note that even the unperturbed system ($\dot{\gamma} = 0$) is out of equilibrium because of activity.

[2]Due to activity, the effective diffusion coefficient is larger than D (see Subsec. 1.2.2 and Ref. [32]).

4.2 Linear response from the path integral representation: Formula I

The linear response of the considered ABPs system to shear flow reads directly from Eq. (3.37),

$$\begin{aligned}\langle A(t)\rangle_0^{(\dot\gamma)} - \langle A(t)\rangle_0 \\ &= \frac{\dot\gamma}{2D}\int_0^t dt' \left\langle A(t)\sum_{i=1}^N \left[\dot x_i(t') - v_0\cos\varphi_i(t') - \mu F_{ix}^{\mathrm{int}}(t') - \mu F_{ix}^{\mathrm{ext}}(t')\right] y_i(t')\right\rangle_0 \\ &- \frac{\dot\gamma}{4D_\mathrm{r}}\int_0^t dt' \left\langle A(t)\sum_{i=1}^N \left[\dot\varphi_i(t') - \mu_\mathrm{r} M_i(t')\right]\right\rangle_0 . \end{aligned} \tag{4.3}$$

The term $\propto \frac{\dot\gamma}{D}$ is the response due to the advection of the particles by the shear flow [described by $\dot\gamma y_i$ in Eq. (4.1a)], while the term $\propto \frac{\dot\gamma}{D_\mathrm{r}}$ is the response due to the rotation of the particles [described by $-\frac{\dot\gamma}{2}$ in Eq. (4.1c)]. Thus we see that, at linear order, shear translation and shear rotation do not couple, as expected from the superposition principle of the linear response [see Eq. (2.6)]. In the passive limit ($v_0 = \frac{1}{D_\mathrm{r}} = 0$), Eq. (4.3) reduces to the equilibrium Green-Kubo relation (2.20) if the unperturbed passive system is in equilibrium[3].

Formula (4.3) becomes more intuitive when introducing the generalized (total) force acting on particle i,

$$\widetilde{\mathbf{F}}_i = \mathbf{F}_i^{\text{s-p}} + \mathbf{F}_i^{\mathrm{int}} + \mathbf{F}_i^{\mathrm{ext}}. \tag{4.4}$$

Here, we have formally interpreted the self-propulsion velocity $v_0\hat{\mathbf{u}}_i$ as a self-propulsion (swim) force, $\mathbf{F}_i^{\text{s-p}} = \frac{1}{\mu}v_0\hat{\mathbf{u}}_i$. Similarly, we can introduce a generalized stress tensor, whose xy component reads

$$\widetilde{\sigma}_{xy} = -\sum_{i=1}^N \widetilde{F}_{ix} y_i = \sigma_{xy}^{\text{s-p}} + \sigma_{xy}^{\mathrm{int}} + \sigma_{xy}^{\mathrm{ext}}, \tag{4.5}$$

where $\sigma_{xy}^{(\cdots)} \equiv -\sum_{i=1}^N F_{ix}^{(\cdots)} y_i$. Compared to the stress tensor for passive systems, $\sigma_{xy} = \sigma_{xy}^{\mathrm{int}} + \sigma_{xy}^{\mathrm{ext}}$ in Eq. (2.21), $\widetilde{\sigma}_{xy}$ additionally contains the self-propulsion force, as in Ref. [162].

[3] If $v_0 = \frac{1}{D_\mathrm{r}} = 0$, we have from Eq. (4.3) $\langle A(t)\rangle_0^{(\dot\gamma)} - \langle A(t)\rangle_0 = \frac{\dot\gamma}{2D}\int_0^t dt' \left\langle A(t)\sum_{i=1}^N \dot x_i(t') y_i(t')\right\rangle_0 + \frac{\dot\gamma}{2k_\mathrm{B}T}\int_0^t dt' \langle A(t)\sigma_{xy}(t')\rangle_0$, where σ_{xy} is the stress tensor defined in Eq. (2.21). When the unperturbed system is in equilibrium, the two terms are equal (see Sec. 3.4), such that one can write $\langle A(t)\rangle^{(\dot\gamma)} - \langle A(t)\rangle = \frac{\dot\gamma}{k_\mathrm{B}T}\int_0^t dt' \, \langle A(t)\sigma_{xy}(t')\rangle$. Using the time-translation invariance of an equilibrium correlation function, one recovers formula (2.20).

Formula (4.3) then acquires the form

$$\langle A(t)\rangle_0^{(\dot\gamma)} - \langle A(t)\rangle_0 = \frac{\dot\gamma}{2D}\int_0^t dt' \left\langle A(t)\sum_{i=1}^N \dot x_i(t')y_i(t')\right\rangle_0 + \frac{\dot\gamma\mu}{2D}\int_0^t dt' \langle A(t)\widetilde\sigma_{xy}(t')\rangle_0 - \frac{\dot\gamma}{4D_\mathrm{r}}\int_0^t dt' \left\langle A(t)\sum_{i=1}^N [\dot\varphi_i(t') - \mu_\mathrm{r} M_i(t')]\right\rangle_0 . \tag{4.6}$$

Equation (4.6) have clear meanings when one compares it to its passive equilibrium analogue, Eq. (2.20): first, the term $\propto \frac{\dot\gamma}{D_\mathrm{r}}$ appears because shear rotates the particles; second, the entropic term with $\dot x_i$ appears because the system does not obey detailed balance; finally, the passive stress tensor σ_{xy} is replaced by the generalized one $\widetilde\sigma_{xy}$ because, being subject to interaction and external forces, the particle is additionally driven by the self-propulsion force.

4.3 Response formula without time derivatives using symmetries: Formula II

The linear response formula (4.6) contains instantaneous velocities, $\dot x_i$ and $\dot\varphi_i$, which are not present in the Green-Kubo formula (2.20) for overdamped equilibrium systems. While these derivatives emerge from a well-defined procedure (see Sec. 3.2) and can be measured in computer simulations, they are typically not measurable in experiments. We thus aim to give Eq. (4.6) only in terms of the positions and angles which we expect to be more easily accessible. According to the terminology of Sec. 3.4, formula (4.6) belongs to Case II B, and thus no simplifications of the formula can be applied in general. However, a simplification we need is possible for a specific class of systems and observables and is based on the two principles of the method of restoring FDT introduced in Sec. 2.2, the superposition principle (Subsec. 2.2.3) and the symmetries these systems and observables obey (Subsec. 2.2.2).

We consider a partner perturbation force to be the shear force in y direction with gradient in x, i.e., $\widetilde{\mathbf{F}}_i^{\mathrm{ptb}} = \frac{\dot\gamma}{\mu}(0, x_i)^T$. For this force, the linear response to shear translation is obtained by simply interchanging x and y in Eq. (4.6), while the response to shear rotation is minus that in Eq. (4.6), because the perturbation of interest $\mathbf{F}_i^{\mathrm{ptb}} = \frac{\dot\gamma}{\mu}(y_i, 0)^T$ and the partner force $\widetilde{\mathbf{F}}_i^{\mathrm{ptb}}$ exert opposite torques. Therefore, there is no net shear rotation when both are applied, and, according to the superposition principle (2.6), the linear response to the sum of the two forces reads (with $\langle A(t)\rangle_0^{(\widetilde{\dot\gamma})}$ denoting the response to $\widetilde{\mathbf{F}}_i^{\mathrm{ptb}}$)

$$\langle A(t)\rangle_0^{(\dot\gamma)} + \langle A(t)\rangle_0^{(\widetilde{\dot\gamma})} - 2\langle A(t)\rangle_0 = \frac{\dot\gamma}{2D}\int_0^t dt' \left\langle A(t)\sum_{i=1}^N [\dot x_i(t')y_i(t') + \dot y_i(t')x_i(t')]\right\rangle_0 + \frac{\dot\gamma\mu}{2D}\int_0^t dt' \langle A(t)\,[\widetilde\sigma_{xy}(t') + \widetilde\sigma_{yx}(t')]\rangle_0 . \tag{4.7}$$

Next, identifying the total time derivative,

$$\int_0^t dt' \left[\dot{x}_i(t')y_i(t') + \dot{y}_i(t')x_i(t')\right] = \int_0^t dt' \frac{d\left(x(t')y(t')\right)}{dt'} = x_i(t)y_i(t) - x_i(0)y_i(0), \quad (4.8)$$

we can write

$$\langle A(t)\rangle_0^{(\dot\gamma)} + \langle A(t)\rangle_0^{(\tilde{\dot\gamma})} - 2\langle A(t)\rangle_0 = \frac{\dot\gamma}{2D}\left\langle A(t)\sum_{i=1}^N \left[x_i(t)y_i(t) - x_i(0)y_i(0)\right]\right\rangle_0 + \frac{\dot\gamma\mu}{2D}\int_0^t dt' \langle A(t)\left[\widetilde{\sigma}_{xy}(t') + \widetilde{\sigma}_{yx}(t')\right]\rangle_0. \quad (4.9)$$

Thus, the response to $\mathbf{F}_i^{\mathrm{ptb}} + \widetilde{\mathbf{F}}_i^{\mathrm{ptb}}$ contains no time derivatives, which can be traced to the fact that the resulting perturbation is a potential one, $\mathbf{F}_i^{\mathrm{ptb}} + \widetilde{\mathbf{F}}_i^{\mathrm{ptb}} = -\nabla_i U^{\mathrm{ptb}}$, where $U^{\mathrm{ptb}} = -\frac{\dot\gamma}{\mu}\sum_{i=1}^N x_i y_i$.

Equation (4.9) is valid for any system and A, but it does not give the response to $\mathbf{F}_i^{\mathrm{ptb}}$ alone. To extract the desired response, we restrict to systems which are xy symmetric, i.e., the systems for which the external and interaction potentials, giving rise to $\mathbf{F}^{\mathrm{ext}}$ and $\mathbf{F}^{\mathrm{int}}$, respectively, as well as torques M_i are symmetric under interchange of x and y. These criteria allow, e.g., for alignment interactions between particles, as used in Eq. (4.27) below. If, additionally, the observable A is also symmetric under interchange of x and y, e.g., $A = \sum_{i=1}^N x_i y_i$, and the unperturbed system is in steady state[4], then, by symmetry, the responses to $\mathbf{F}_i^{\mathrm{ptb}}$ and $\widetilde{\mathbf{F}}_i^{\mathrm{ptb}}$ are equal, $\langle A(t)\rangle_0^{(\tilde{\dot\gamma})} = \langle A(t)\rangle_0^{(\dot\gamma)}$. Equation (4.9) then takes the desired response to shear,

$$\langle A(t)\rangle_{\mathrm{st}}^{(\dot\gamma)} - \langle A\rangle_{\mathrm{st}} = \frac{\dot\gamma}{4D}\left[\left\langle A\sum_{i=1}^N x_i y_i\right\rangle_{\mathrm{st}} - \left\langle A(t)\sum_{i=1}^N x_i(0)y_i(0)\right\rangle_{\mathrm{st}}\right] + \frac{\dot\gamma\mu}{4D}\int_0^t dt' \langle A(t)\left[\widetilde{\sigma}_{xy}(t') + \widetilde{\sigma}_{yx}(t')\right]\rangle_{\mathrm{st}}, \quad (4.10)$$

where in the first term we used the fact that a stationary correlation function is a function of time difference, such that an equal-time stationary correlator is time independent.

As a final simplification, we point out that, for spherically symmetric interaction and external potentials, the passive stress tensor σ is symmetric, $\sigma_{xy} = \sigma_{yx}$, and the terms $\sigma_{xy}^{\text{s-p}}$ and $\sigma_{yx}^{\text{s-p}}$ in Eq. (4.10) yield identical contributions, so that symmetrization of $\widetilde{\sigma}$ is

[4] The fact that the unperturbed system is in steady state allows to avoid the corresponding symmetry restrictions on the initial conditions which might be unrealistic. It is a natural and very common assumption.

not necessary. We thus have in this case

$$\boxed{\begin{aligned}&\langle A(t)\rangle_{\mathrm{st}}^{(\dot\gamma)} - \langle A\rangle_{\mathrm{st}} \\ &= \frac{\dot\gamma}{4D}\left[\left\langle A\sum_{i=1}^{N} x_i y_i\right\rangle_{\mathrm{st}} - \left\langle A(t)\sum_{i=1}^{N} x_i(0)y_i(0)\right\rangle_{\mathrm{st}}\right] + \frac{\dot\gamma\mu}{2D}\int_0^t dt' \langle A(t)\widetilde{\sigma}_{xy}(t')\rangle_{\mathrm{st}}.\end{aligned}} \tag{4.11}$$

Formula (4.11) is the most important result of this chapter. While Eq. (4.6) does not require the mentioned symmetries, Eq. (4.11) is much simpler, because it contains no time derivatives and no response to shear rotation.

At this point, it is insightful to discuss a chronological order of our research, which has been already shortly mentioned in Sec. 2.8. The research presented in this chapter was done before that presented in Chapter 2. Respectively, we derived formula (4.11) before we found formula (2.19) and proposed the method of restoring FDT. Once we had Eq. (4.11), we saw that in the equilibrium case it reduces to

$$\begin{aligned}\langle A(t)\rangle^{(\dot\gamma)} - \langle A\rangle = \frac{\dot\gamma}{4k_{\mathrm{B}}T\mu}&\left[\left\langle A\sum_{i=1}^{N} x_i y_i\right\rangle - \left\langle A(t)\sum_{i=1}^{N} x_i(0)y_i(0)\right\rangle\right] \\ &+ \frac{\dot\gamma}{2k_{\mathrm{B}}T}\int_0^t dt' \left\langle A(t')\sigma_{xy}(0)\right\rangle.\end{aligned} \tag{4.12}$$

Then we realized, without knowing any time-symmetry properties discussed in Chapter 3, that the two terms in Eq. (4.12) must be equal (this is because the equilibrium response is given by the Green-Kubo relation (2.20), and the second term in Eq. (4.12) is just the half of that relation). Therefore, the entire response can be given by two times the first term, i.e., by formula (2.19). The latter was hence originally derived as the limiting case of formula (4.11). Only afterwards we generalized the principles and observations described in this section to a general case of an equilibrium system perturbed by a nonconservative force, the research presented in Chapter 2. Therefore, formula (4.11) gave birth to all new results of Chapter 2.

Finally, we note that the details of the stochastic process underlying the angle φ given in Eq. (4.1c) do not appear explicitly in Eq. (4.11). We will explore this observation in the next subsection, thereby finding that the presented scheme is readily applied to a more general setup, yielding Eq. (4.16) below.

4.4 Three space dimensions and more general setups

While we have so far considered two spatial dimensions, we aim here to derive the analogue of Eq. (4.11) for more general setups of spherical particles. This is inspired by the mentioned observation that D_r and μ_r are absent in formula (4.11), suggesting its independence of the details of the dynamics of the swim-velocity vector.

We start with the multi-dimensional Langevin equation for position $\mathbf{r}_i = (x_i, y_i, \dots)^T$ of particle i,

$$\dot{\mathbf{r}}_i = \mu\boldsymbol{\kappa}\cdot\mathbf{r}_i + \mathbf{u}_i + \mu\mathbf{F}_i^{\mathrm{int}} + \mu\mathbf{F}_i^{\mathrm{ext}} + \mu\mathbf{f}_i, \tag{4.13}$$

where $\mu\boldsymbol{\kappa} = \dot{\gamma}\hat{\mathbf{x}}\otimes\hat{\mathbf{y}}$, given in terms of unit vectors, is the shear-rate tensor and $\mathbf{u}_i$ is the swim velocity. The Gaussian white noise $\mathbf{f}_i$ satisfies

$$\langle\mathbf{f}_i(t)\rangle = 0, \qquad \langle\mathbf{f}_i(t)\otimes\mathbf{f}_j(t')\rangle = \frac{2D}{\mu^2}\mathbb{I}\delta_{ij}\delta(t-t'), \tag{4.14}$$

with $\otimes$ denoting the tensor product and $\mathbb{I}$ being the identity matrix.

The swim velocity $\mathbf{u}_i$ obeys its own stochastic process. For the following arguments to be valid, we require the process for $\mathbf{u}_i$ to be random and unbiased in the absence of shear, and its stochastic properties (i.e., its noise) uncorrelated with the noise $\mathbf{f}_i$ in Eq. (4.14). Furthermore, with shear, $\mathbf{u}_i$ may be subject to a shear torque [as in Eq. (4.1c)]. When superposing two shear flows, $\mu\boldsymbol{\kappa} = \dot{\gamma}(\hat{\mathbf{x}}\otimes\hat{\mathbf{y}}+\hat{\mathbf{y}}\otimes\hat{\mathbf{x}})$, as done in Sec. 4.3, this shear torque drops out. For example, when perturbing ABPs by shear in three spatial dimensions, these conditions are naturally met, and Eq. (4.16) below is valid.

The total action $\mathcal{A}$ of the system can be written as the sum of the action $\mathcal{A}_\mathrm{t}$ following from Eq. (4.13), and $\mathcal{A}_\mathrm{r}$ deduced from the equation for the swim velocity $\mathbf{u}_i$,

$$\mathcal{A}(t,\dot{\gamma}) = \mathcal{A}_\mathrm{t}(t,\dot{\gamma}) + \mathcal{A}_\mathrm{r}(t,\dot{\gamma}). \tag{4.15}$$

These parts are additive if the noise for $\mathbf{r}_i$ in Eq. (4.14) is uncorrelated with the process of $\mathbf{u}_i$. When superposing the mentioned two shear flows, the dependence of $\mathcal{A}_\mathrm{r}$ on shear rate drops out. Performing the expansion of $\mathcal{A}_\mathrm{t}(t,\dot{\gamma})$, as done in Subsec. 3.2.4, and following the procedures described in Sec. 4.3, one obtains the form of Eq. (4.11) with $v_0\cos\varphi_i(t')$ replaced by a general $u_{ix}(t')$. Specifically,

$$\begin{aligned}&\langle A(t)\rangle_{\mathrm{st}}^{(\dot{\gamma})} - \langle A\rangle_{\mathrm{st}}\\ &= \frac{\dot{\gamma}}{4D}\left[\left\langle A\sum_{i=1}^{N} x_i y_i\right\rangle_{\mathrm{st}} - \left\langle A(t)\sum_{i=1}^{N} x_i(0)y_i(0)\right\rangle_{\mathrm{st}}\right] + \frac{\dot{\gamma}\mu}{2D}\int_0^t dt'\langle A(t)\widetilde{\sigma}_{xy}(t')\rangle_{\mathrm{st}},\end{aligned} \tag{4.16}$$

where the self-propulsion stress tensor in $\widetilde{\sigma}_{xy}$ is given by $\sigma_{xy}^{\text{s-p}} = -\sum_{i=1}^{N}\frac{1}{\mu}u_{ix}y_i$.

4.5 Analytical examples

The main purpose of this section is to demonstrate the use of response formulas (4.3) and (4.11) for solvable analytical cases, namely for a single active particle in free space or confined by a harmonic potential. Furthermore, we complement the previously known results, providing the transient regime of the response computed in Subsec. 4.5.2 as well as correlation functions in Appendix B.2. Throughout this section, we consider two-dimensional systems and set the torque $M = 0$ and the rotational mobility $\mu_\mathrm{r} = 1$ for simplicity.

4.5.1 Free active particle

We apply here Eq. (4.3) to compute the response to shear of the mean displacement, $\langle x(t)\rangle_0^{(\dot\gamma)} - \langle x(t)\rangle_0$, for a single free self-propelled particle, and show that the response formula reproduces the result of Ref. [160], directly computed in the sheared system.

Setting $A = x$ and $N = 1$ in Eq. (4.3), and using Eq. (4.1) to rewrite Eq. (4.3) in terms of random force and torque, one has

$$\langle x(t)\rangle_0^{(\dot\gamma)} - \langle x(t)\rangle_0 = \frac{\dot\gamma\mu}{2D}\int_0^t dt'\langle x(t)f_x(t')y(t')\rangle_0 - \frac{\dot\gamma}{4D_\mathrm{r}}\int_0^t dt'\langle x(t)g(t')\rangle_0. \tag{4.17}$$

Given the initial condition $\Gamma(0) = \{x(0), y(0), \varphi(0)\}$, the correlation functions appearing in Eq. (4.17) can be calculated explicitly:

$$\langle x(t)f_x(t')y(t')\rangle_0 = \frac{2D}{\mu}\left[y(0) + \frac{v_0\sin\varphi(0)}{D_\mathrm{r}}\left(1 - e^{-D_\mathrm{r}t'}\right)\right], \tag{4.18a}$$

$$\langle x(t)g(t')\rangle_0 = 2v_0\sin\varphi(0)\left[e^{-D_\mathrm{r}t} - e^{-D_\mathrm{r}t'}\right]. \tag{4.18b}$$

Finally, performing time integrals in Eq. (4.17), we obtain for the response

$$\langle x(t)\rangle_0^{(\dot\gamma)} - \langle x(t)\rangle_0 = \dot\gamma\left\{y(0)t + \frac{v_0\sin\varphi(0)}{D_\mathrm{r}}\left[t\left(1 - \frac{1}{2}e^{-D_\mathrm{r}t}\right) - \frac{1}{2D_\mathrm{r}}\left(1 - e^{-D_\mathrm{r}t}\right)\right]\right\}, \tag{4.19}$$

which reproduces Eq. (11) in Ref. [160] computed using the direct method.

4.5.2 Active particle in a harmonic trap

Using formula (4.11), we compute similarly the response to shear of a single active particle in a harmonic potential $U^\mathrm{ext} = \frac{k}{2}(x^2 + y^2)$ (see Fig. 4.2). The system is assumed to be in steady state before shear is applied. We consider $A = xy$, which characterizes the shape of the particle distribution. The the left- and right-hand sides of Eq. (4.11) are computed independently, such that the equation is verified explicitly. The stationary limit of the response was studied before in Ref. [161] and agrees with our findings.

For this system, Langevin equation (4.1) reduces to

$$\dot x = \dot\gamma y + v_0\cos\varphi - \mu k x + \mu f_x, \tag{4.20a}$$
$$\dot y = v_0\sin\varphi - \mu k y + \mu f_y, \tag{4.20b}$$
$$\dot\varphi = -\frac{\dot\gamma}{2} + g, \tag{4.20c}$$

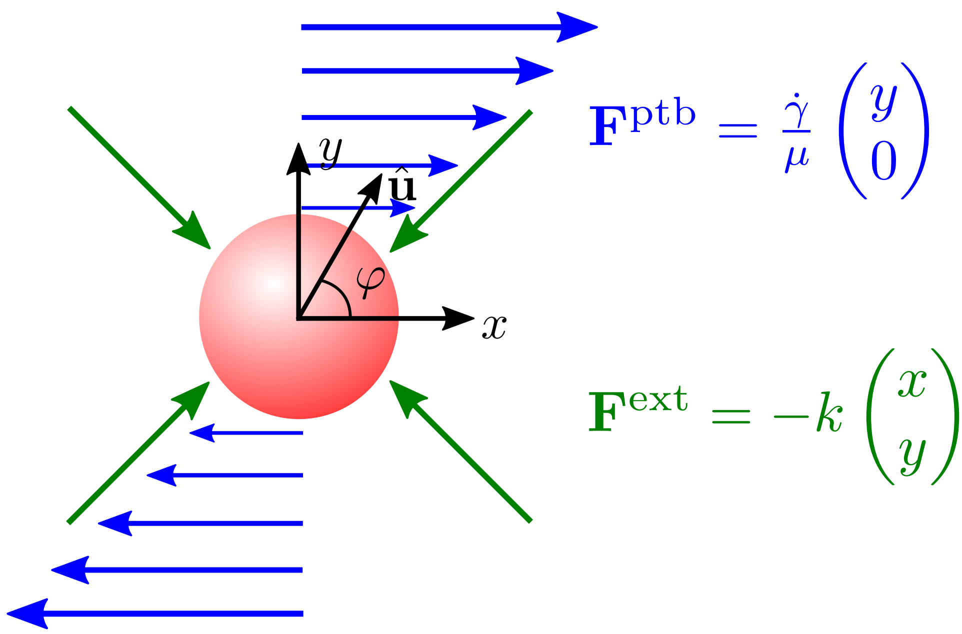

Figure 4.2. Active Brownian particle confined in a harmonic trap and perturbed by simple shear flow in two space dimensions. The self-propulsion velocity is $v_0\hat{\mathbf{u}} = v_0(\cos\varphi, \sin\varphi)^T$.

whose solutions for $t > 0$ read

$$x(t) = \dot{\gamma}e^{-\mu kt}\int_0^t dse^{\mu ks}y(s) + v_0e^{-\mu kt}\int_{-\infty}^t dse^{\mu ks}\cos\varphi(s) + \mu e^{-\mu kt}\int_{-\infty}^t dse^{\mu ks}f_x(s), \tag{4.21a}$$

$$y(t) = v_0e^{-\mu kt}\int_{-\infty}^t dse^{\mu ks}\sin\varphi(s) + \mu e^{-\mu kt}\int_{-\infty}^t dse^{\mu ks}f_y(s), \tag{4.21b}$$

$$\varphi(t) = \varphi(-\infty) - \frac{\dot{\gamma}}{2}t + \int_{-\infty}^t dsg(s). \tag{4.21c}$$

For $t \leq 0$, the first term on the right-hand side of Eq. (4.21a) and the second term on the right-hand side of Eq. (4.21c) are absent. Since $\varphi(t)$ never reaches a stationary value, this variable depends on the initial condition $\varphi(-\infty)$. However, any observable $A(x(t), y(t))$ depending only on the coordinates remains *independent* of $\varphi(-\infty)$ in both the unperturbed stationary state and the perturbed transient and stationary regimes, because this initial condition is forgotten for stationary values of $x(t)$ and $y(t)$. For the observable $A = xy$, Eq. (4.11) reads explicitly

$$\begin{aligned}\langle x(t)y(t)\rangle_{\text{st}}^{(\dot{\gamma})} - \langle xy\rangle_{\text{st}} &= \frac{\dot{\gamma}}{4D}\left[\left\langle x^2y^2\right\rangle_{\text{st}} - \langle x(t)y(t)x(0)y(0)\rangle_{\text{st}}\right] \\ &- \frac{\dot{\gamma}v_0}{2D}\int_0^t dt'\langle x(t)y(t)\cos\varphi(t')y(t')\rangle_{\text{st}} + \frac{\dot{\gamma}\mu k}{2D}\int_0^t dt'\langle x(t)y(t)x(t')y(t')\rangle_{\text{st}}.\end{aligned} \tag{4.22}$$

In the following, we verify Eq. (4.22) by independently computing its both sides.

We start by computing the left-hand side of Eq. (4.22) up to linear order in shear rate $\dot{\gamma}$. We provide here only the final result (computational details can be found in Appendix B.1),

$$\langle x(t)y(t)\rangle_{\mathrm{st}}^{(\dot{\gamma})} = \frac{\dot{\gamma}D}{2(\mu k)^2}\left(1-e^{-2\mu k t}\right) + \frac{\dot{\gamma}v_0^2}{4(\mu k)^2\left[D_{\mathrm{r}}^2-(\mu k)^2\right]}\left\{D_{\mathrm{r}}\left(1-e^{-2\mu k t}\right) - \frac{2(\mu k)^2}{D_{\mathrm{r}}+\mu k}\left(1-e^{-(D_{\mathrm{r}}+\mu k)t}\right)\right\}. \tag{4.23}$$

Here, the first term is a passive contribution, while the second term is due to activity (note the presence of v_0 and D_{r} and the absence of D). The term $\langle xy\rangle_{\mathrm{st}}$ in Eq. (4.22) vanishes by symmetry.

We then compute independently the right-hand side of Eq. (4.22) in Appendix B.2, and find it to be identical to Eq. (4.23). This verifies explicitly the validity of response relation (4.22).

Let us discuss the physics contained in Eq. (4.23). First, one can show that both terms ($\propto D$ and $\propto v_0^2$) in Eq. (4.23) are nonnegative, indicating that that the total response is not negative and that the activity increases the positive response of a passive particle. These facts mean that the shape of the particle spatial distribution changes from circular to ellipsoidal when shear is applied (similarly to the snapshot in Fig. 2.3), and that the activity increases this effect. Also note that passive and active contributions enter the response (4.23) independently, i.e., translational diffusion and activity are not coupled (there are no terms containing both D and v_0^2). We think that this could be a feature of the *linear* response, while in the nonlinear case one may observe a coupling between these two contributions.

In order to visualize Eq. (4.23), we rewrite it in terms of dimensionless parameters: $\tau \equiv \mu k t$ (describing time in units of the relaxation time $\frac{1}{\mu k}$ of the trap), $\mathrm{Pe} \equiv \frac{\dot{\gamma}}{\mu k}$ (Péclet number), $\widetilde{D}_{\mathrm{r}} \equiv \frac{D_{\mathrm{r}}}{\mu k}$ (normalizing rotational relaxation time $\frac{1}{D_{\mathrm{r}}}$ by the relaxation time $\frac{1}{\mu k}$ of the trap), $\tilde{v}_0^2 \equiv \frac{v_0^2}{D\mu k}$ (comparing the swim speed to translational diffusion and the strength of the trap). Rescaling $\langle x(t)y(t)\rangle_{\mathrm{st}}^{(\dot{\gamma})}$ by the unit of squared length, $l^2 \equiv \frac{D}{\mu k}$, and dividing by Pe, we rewrite Eq. (4.23) as

$$\frac{\langle x(\tau)y(\tau)\rangle_{\mathrm{st}}^{(\dot{\gamma})}}{l^2\mathrm{Pe}} = \frac{1}{2}\left(1-e^{-2\tau}\right) + \frac{\tilde{v}_0^2}{4\left(\widetilde{D}_{\mathrm{r}}^2-1\right)}\left\{\widetilde{D}_{\mathrm{r}}\left(1-e^{-2\tau}\right) - \frac{2}{\widetilde{D}_{\mathrm{r}}+1}\left(1-e^{-\left(\widetilde{D}_{\mathrm{r}}+1\right)\tau}\right)\right\}. \tag{4.24}$$

This function is plotted in Figure 4.3 as a function of τ for different values of $\tilde{v}_0^2$ and $\widetilde{D}_{\mathrm{r}}$, thereby summarizing the above discussions. One can see in Fig. 4.3 that the response increases as $\widetilde{D}_{\mathrm{r}}$ decreases, because the active motion becomes more persistent.

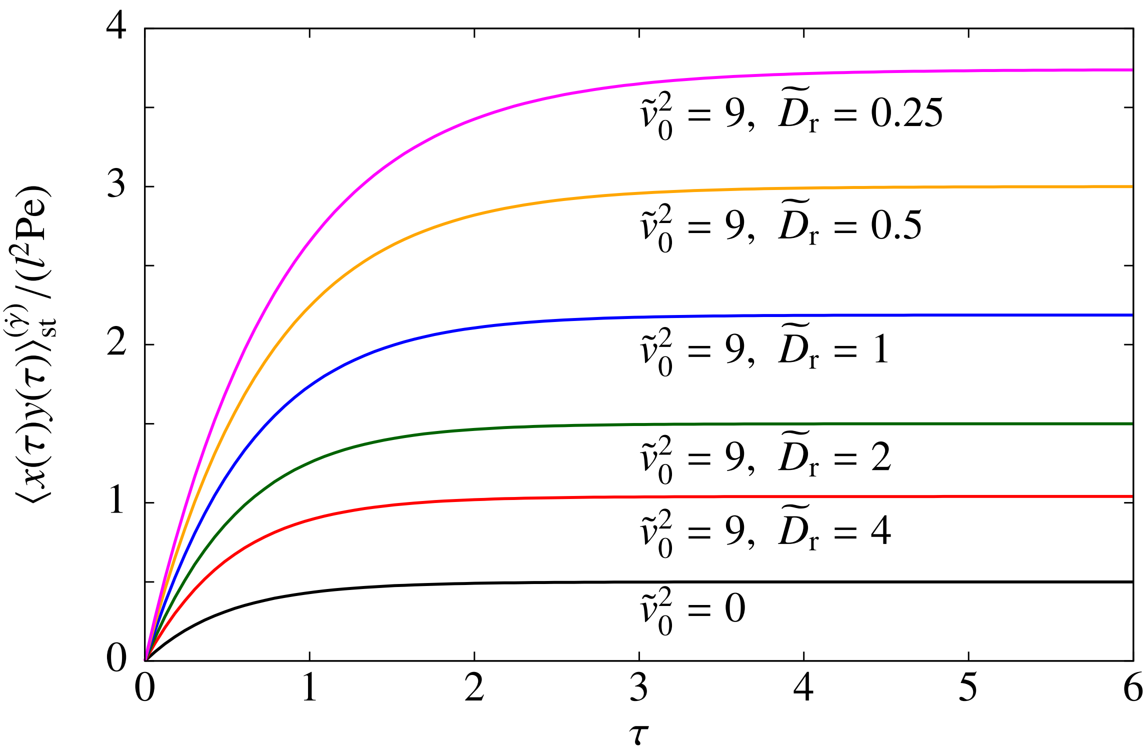

Figure 4.3. Rescaled response, given by Eq. (4.24), of a single active particle in a harmonic potential to shear flow as a function of rescaled time τ after the flow is applied. The results are given for different values of $\tilde{v}_0^2$ and $\widetilde{D}_{\rm r}$ (the case $\tilde{v}_0^2 = 0$ corresponds to a passive particle).

4.6 Numerical example: interacting particles in two space dimensions

The potential utility of response formula (4.11) lies in its application to experiments and computer simulations of interacting active particles, which we address in this section. We demonstrate this numerically for a two-dimensional system of particles trapped in a harmonic potential $U^{\rm ext} = \frac{k}{2}\sum_{i=1}^{N}(x_i^2+y_i^2)$, and interacting with a short-ranged harmonic repulsion, $U_{ij}^{\rm int}(r_{ij}) = \frac{k^{\rm int}}{2}(r_c - r_{ij})^2$ for $r_{ij} < r_c$ (where r_{ij} is the distance between particle i and particle $j \neq i$) and $U_{ij}^{\rm int} = 0$ otherwise. An illustration of the system can be seen in Fig. 4.4(a). The considered scenario is the extension of that studied in Sec. 2.4 to active particles. We take the radius of interaction $r_c = 1$ as our space unit, and choose $k = 1$ and the mobility $\mu = 1$, thus fixing the time and energy scales. The dynamics is simulated using the Euler method.

4.6.1 Morphology

First, we measure independently the two sides of Eq. (4.11) for $A(t) = \sum_{i=1}^{N} x_i(t)y_i(t)$ in steady state ($t \to \infty$) which characterizes the distortion of the density distribution (i.e., the system morphology) due to the shear flow. Note that, for the chosen parameters, $A = \sigma_{xy}^{\text{ext}}$. The correlator $\left\langle A(t) \sum_{i=1}^{N} x_i(0)y_i(0) \right\rangle_{\text{st}}$ in Eq. (4.11) must vanish for $t \to \infty$, and it is hence irrelevant. It is illustrative to split Eq. (4.11) into its different contributions,

$$\lim_{t\to\infty} \frac{\langle A(t) \rangle_{\text{st}}^{(\dot{\gamma})} - \langle A \rangle_{\text{st}}}{\dot{\gamma}} = \frac{C_1 + C_2 + C_3}{4D}, \tag{4.25}$$

where

$$C_1 = \left\langle A \sum_{i=1}^{N} x_i y_i \right\rangle_{\text{st}}, \tag{4.26a}$$

$$C_2 = -2v_0 \lim_{t\to\infty} \int_0^t dt' \left\langle A(t) \sum_{i=1}^{N} \cos\varphi_i(t') y_i(t') \right\rangle_{\text{st}}, \tag{4.26b}$$

$$C_3 = 2\mu \lim_{t\to\infty} \int_0^t dt' \langle A(t) \sigma_{xy}(t') \rangle_{\text{st}}. \tag{4.26c}$$

C_1 is the FDT term [see Eq. (2.19)], C_2 corresponds to a purely active contribution, while C_3 is the Green-Kubo term [see Eq. (2.20)]. Similarly to the case of a single particle, due to the isotropicity of the unsheared system, $\langle A \rangle_{\text{st}} = 0$.

The results obtained for $N = 10$ particles interacting with a spring constant $k^{\text{int}} = 0.5$ for various D are shown in Fig. 4.4 for both active (with $v_0 = D_{\text{r}} = \mu_{\text{r}} = 1$) and passive ($v_0 = 0$) particles. The linear response is first obtained by simulating the sheared system at different shear rates and extracting the small $\dot{\gamma}$ behavior as shown in Fig. 4.4(b). In Fig. 4.4(c) we then compare to the right-hand side of Eq. (4.25), obtained by measuring the appropriate correlation functions in the unperturbed system. We find that the two measurements agree. The response is positive and is increased by activity, as was observed for a single particle in Subsec. 4.5.2.

It is interesting to compare the limit $D \to 0$ in the passive and active cases, because they show qualitatively different behaviors. In the passive case, this corresponds to the zero-temperature limit so that the system becomes frozen in a minimal energy configuration (see Sec. 3.5). We find numerically that both C_1 and C_3 in Eqs. (4.26a) and (4.26c) are proportional to D in this limit (C_2 vanishes for passive particles). As a result, the two terms, $\frac{C_1}{4D}$ and $\frac{C_3}{4D}$, become constant at small D, as shown in Fig. 4.4(d). In contrast, active particles are still moving even at $D = 0$, so that the correlators C_i do not vanish. As a result, each of the terms on the right-hand side of Eq. (4.25) diverges when $D \to 0$ in such a way that the sum remains constant. This observation demonstrates the limitation of stochastic linear response theory, discussed in Sec. 3.5. Indeed, the derivation of formula (4.11) necessitates a finite D. However, D is often negligible in active systems, since the particles' motion in that case is primarily due to activity [156, 157, 163]. It may thus be desirable to obtain the formula valid for $D = 0$, the case discussed in Subsec. 3.5.3.

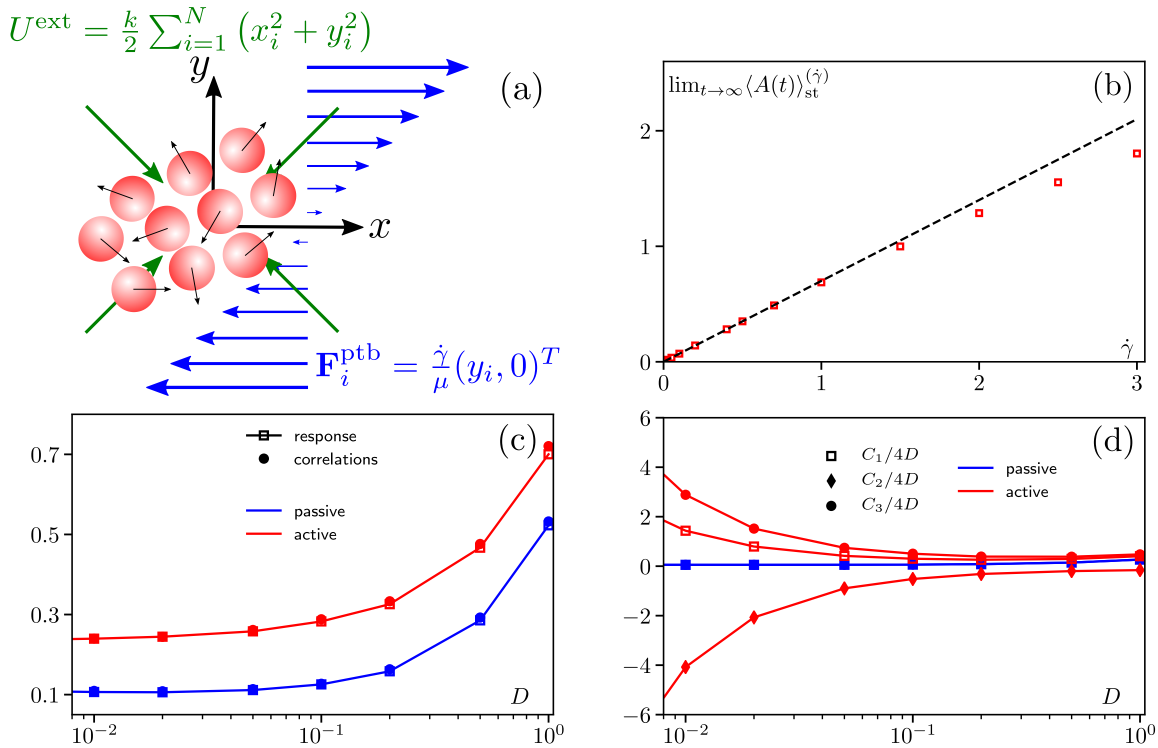

Figure 4.4. Numerical results for a suspension of interacting active particles ($M_i = 0$). **(a):** Illustration of the system: interacting active Brownian particles confined in a harmonic trap and perturbed by simple shear flow in two space dimensions. **(b):** Response measured in the sheared system for active particles with $D = 1$. The dashed line is a linear fit at small $\dot\gamma$. **(c):** Comparison of the response and correlations, i.e., the left-hand- and right-hand sides of Eq. (4.25), respectively. **(d):** Detail of each term on the right-hand side of Eq. (4.25). Parameters: $N = 10$ particles, $k = 1$, $k^{\rm int} = 0.5$, $\mu = 1$, and $v_0 = D_{\rm r} = \mu_{\rm r} = 1$ for active particles; time step $\Delta t = 0.02$.

4.6.2 Alignment and stresses

Next, we include alignment interactions modeled by torque

$$M_i = -J \sum_{j=1(j\neq i)}^{N} \sin(\varphi_i - \varphi_j), \tag{4.27}$$

where the sum runs over particles in contact, i.e., with the interparticle distance $r_{ij} < r_c$. This torque arises from a typical "spin"-interaction, formed by scalar products of particle orientation vectors $\hat{\mathbf{u}}_i$, and it is hence symmetric under interchange of x and y coordinates. Formula (4.11) can therefore be applied.

Additionally to $\sigma_{xy}^{\rm ext}$, we compute also $\sigma_{xy}^{\rm int}$ and $\sigma_{xy}^{\rm s\text{-}p}$ defined in Eq. (4.5). The results are given in Fig. 4.5. First, we note that the magnitudes of all stress tensor components increase with the alignment. We may expect that strong alignment renders the particle cloud into an elongated shape, which is more susceptible to shear. The saturation for

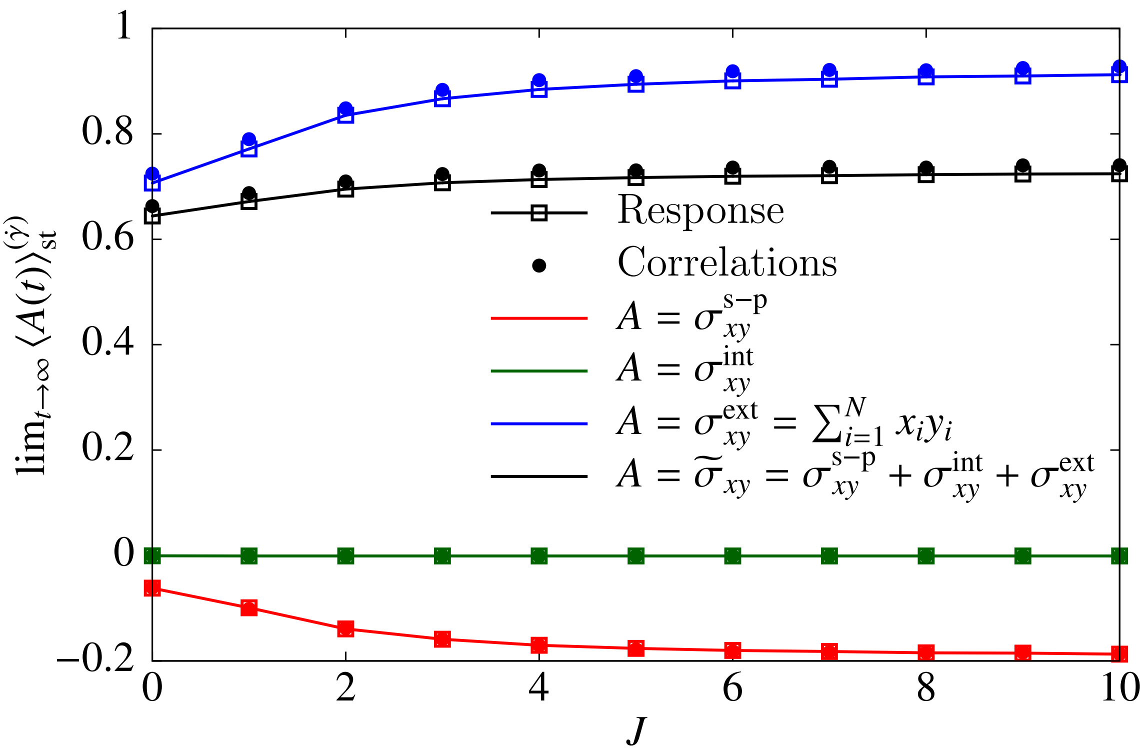

Figure 4.5. Numerical results for a suspension of interacting active particles [see Fig. 4.4(a)] subject to alignment interactions given in Eq. (4.27), as a function of strength of alignment J. Shown is the response of the terms appearing in the total stress tensor $\widetilde{\sigma}_{xy}$ defined in Eq. (4.5): the self-propulsion stress tensor $\sigma_{xy}^{\text{s-p}}$, the interaction stress tensor σ_{xy}^{int}, and the external stress tensor σ_{xy}^{ext}. The latter equals the observable studied in Fig. 4.4, i.e., $\sigma_{xy}^{\text{ext}} = \sum_{i=1}^{N} x_i y_i$. Parameters as in Fig. 4.4, and $D = 1$.

large values of J is also expected, as, once all velocities are perfectly aligned, increasing J has no effect. Notably, the interaction stress σ_{xy}^{int} shows a much smaller magnitude compared to the other two stress tensors.

4.7 Summary and discussion

In this chapter, we studied the linear response to simple shear flow of overdamped interacting active Brownian particles subject to external forces. The knowledge gained in Chapters 2 and 3 were combined to derive the linear response formulas for this scenario.

The path integral formalism introduced in Chapter 3 yields, in two space dimensions, linear response formula (4.6) relating any observable measured in the sheared system to correlation functions of the unsheared system. For systems and observables obeying xy symmetry, the symmetry ideas introduced in Chapter 2 allow to simplify formula (4.6) such that the final result, Eq. (4.16), contains no time derivatives, no response to shear rotation, and is valid in any space dimension and for a wider set of activity models. This form of the response formula is particularly advantageous, because it involves quantities that are typically easier to measure.

Next, we investigated the morphology and stresses of a two-dimensional cluster formed by N interacting active particles confined by a harmonic potential under shear. Performing analytical computations for $N = 1$ and numerical simulations for $N > 1$ particles, we found that the activity increases the effect of the change of the distribution shape from circular to ellipsoidal. We also found that increasing the persistence of activity (decreasing D_r) or adding alignment interactions between the particles increases the response to shear, so that the magnitudes of the found stresses increase.

Future work may consider the limit of zero translational diffusion, as well as the viscosity of a suspension of active Brownian particles. Finally, the extension to higher order responses is also a promising avenue to explore, since this could, for example, shed light on the coupling between shear translation and shear rotation.

5 The thesis in short: Brownian particles perturbed by shear revisited

Inspired by Section 6.3 in the Doctoral dissertation by Matthias Krüger [107], we decided to illustratively summarize the key results of this thesis in one example. The unperturbed system we consider is a two-dimensional system of overdamped Brownian particles, in general active, where interaction and external forces and torques arise from potentials. The nonconservative perturbation we choose is a simple shear flow studied intensively above. A schematic illustration of this scenario is given in Fig. 4.1, and the dynamics obeys Langevin equation (4.1).

5.1 Active particles, no symmetries

If the particles are active, the unperturbed system is out of equilibirum. For arbitrary interaction and external potentials and for an arbitrary observable A (i.e., no symmetries), the shear perturbation cannot be equivalently replaced by a potential one. The linear response is given by formula (4.6),

$$\langle A(t)\rangle_0^{(\dot\gamma)} - \langle A(t)\rangle_0 = \frac{\dot\gamma}{2k_\mathrm{B}T\mu}\int_0^t dt' \left\langle A(t)\sum_{i=1}^N \dot x_i(t')y_i(t')\right\rangle_0 + \frac{\dot\gamma}{2k_\mathrm{B}T}\int_0^t dt' \langle A(t)\widetilde\sigma_{xy}(t')\rangle_0 - \frac{\dot\gamma}{4D_\mathrm{r}}\int_0^t dt' \left\langle A(t)\sum_{i=1}^N [\dot\varphi_i(t') - \mu_\mathrm{r} M_i(t')]\right\rangle_0 . \tag{5.1}$$

Due to the absence of detailed balance, it contains both the entropic (with time derivatives) and frenetic contributions. Since the perturbation is nonconservative, time derivatives cannot be removed.

5.2 Active particles, perturbation-related symmetries

For spherically symmetric interaction and external potentials, and for an observable A which is symmetric under interchange of the x and y coordinates (the xy symmetric scenario), the linear response of a steady-state system to shear is equivalent to the response to a potential. Formula (5.1) simplifies to Eq. (4.11),

$$\begin{aligned}&\langle A(t)\rangle_{\mathrm{st}}^{(\dot{\gamma})} - \langle A\rangle_{\mathrm{st}} \\ &= \frac{\dot{\gamma}}{4k_{\mathrm{B}}T\mu}\left[\left\langle A\sum_{i=1}^{N} x_i y_i\right\rangle_{\mathrm{st}} - \left\langle A(t)\sum_{i=1}^{N} x_i(0)y_i(0)\right\rangle_{\mathrm{st}}\right] + \frac{\dot{\gamma}}{2k_{\mathrm{B}}T}\int_0^t dt' \langle A(t)\widetilde{\sigma}_{xy}(t')\rangle_{\mathrm{st}}.\end{aligned} \tag{5.2}$$

The response still contains both the entropic and frenetic contributions, but time derivatives are integrated out. In addition, the response to shear rotation is absent, because the corresponding perturbation potential does not exert a torque. Therefore, the linear response is such as if the system was originally perturbed by a potential.

5.3 Passive particles, no symmetries

If the particles do not perform a self-propelled motion, the unperturbed steady-state system is in equilibrium. Being a nonconservative perturbation, shear drives the system to a nonequilibrium state. The fluctuation-dissipation theorem thus cannot be applied, but the linear response can be given by either entropic or frenetic part. The latter is preferable, as it contains no time derivatives, and yields the famous Green-Kubo relation (2.20),

$$\langle A(t)\rangle^{(\dot{\gamma})} - \langle A\rangle = \frac{\dot{\gamma}}{k_{\mathrm{B}}T}\int_0^t dt' \,\langle A(t')\sigma_{xy}(0)\rangle\,. \tag{5.3}$$

5.4 Passive particles, perturbation-related symmetries

For xy symmetric systems and observables, the response to shear is equivalent to the response to a potential. Therefore, even though the original perturbation is nonconservative, the fluctuation-dissipation theorem can be applied, leading to response formula (2.19),

$$\langle A(t)\rangle^{(\dot{\gamma})} - \langle A\rangle = \frac{\dot{\gamma}}{2k_{\mathrm{B}}T\mu}\left[\left\langle A\sum_{i=1}^{N} x_i y_i\right\rangle - \left\langle A(t)\sum_{i=1}^{N} x_i(0)y_i(0)\right\rangle\right]. \tag{5.4}$$

Summary

In this thesis, we studied the linear response of stochastic systems to nonconservative perturbation forces.

For a system being initially in equilibrium, we proposed a method of restoring the fluctuation-dissipation theorem (FDT). The method is based on a freedom inherent to linear response theory: perturbation forces which perform work that does not couple statistically to the considered observable can be added to a nonconservative perturbation of interest without changing the response to the latter. By using this freedom, we found that, under certain conditions, the linear response to a nonconservative force can be equivalent to the response to a potential given by FDT. This means that the theorem can also be applied to perturbations by certain nonconservative forces, for which it is usually considered inapplicable. We discussed in detail the case of a nonconservative perturbation force linear in particle coordinates, where the mentioned freedom can be formulated in terms of perturbation-related symmetries.

In particular, for the case of a shear perturbation, the method leads to a new linear response formula, FDT for shear, which is an alternative to the known Green-Kubo relation. Using Brownian dynamics simulations, we demonstrated the formula for a confined system of interacting overdamped Brownian particles. Apart from several *explicit* advantages of the FDT over the Green-Kubo relation, this demonstration also showed that the former has a much lower variance, which makes it much more effective in terms of statistical accuracy. Analytical investigations of a single underdamped particle revealed several interesting features of the underdamped transient response and demonstrated that using the FDT is easier also in analytical computations.

Prior to proposing a similar method for a *nonequilibrium* system of active Brownian particles (ABPs), we reviewed and systemized the existing knowledge about general linear response theory. Specifically, we discussed a path integral approach for deriving response relations, the aspects of these relations related to stochastic calculus, and their zero-temperature limit. A classification of response relations with respect to the type of the system and perturbation was performed.

Using the path integral formalism, we derived a linear response formula for ABPs in two space dimensions perturbed by simple shear flow, Formula I. Following the principles of restoring FDT, we showed that, for xy symmetric systems and observables, the response of ABPs to shear can be equivalently replaced by the response to a potential. This observation leads to a new response relation, Formula II, which is advantageous over Formula I, as it contains no time derivatives and no response to shear rotation. Moreover, Formula II can be easily generalized to ABPs in 3D and to even more general active particle models.

Finally, the effect of a shear flow on the morphology and the stress of confined interacting ABPs was investigated numerically. The simulations showed that the activity increases the response compared to the passive case. Moreover, adding alignment interactions between the particles further increases the response. In these simulations, Formula II has been demonstrated.

Zusammenfassung

In der vorliegenden Dissertation untersuchen wir die lineare Antworttheorie von stochastischen Systemen, die durch nicht-konservative Kräfte gestört werden.

Für das ungestörte Gleichgewichtssystem verwenden wir eine Methode, die zu einer Form des bekannten Fluktuations-Dissipations-Theorems (FDT) führt. Diese Methode basiert auf einer speziellen Freiheit der linearen Antworttheorie: Störkräfte, die Arbeit am System verrichten, jedoch nicht an die zu untersuchende physikalische Observable statistisch koppeln, können in der Antwortrelation addiert werden, ohne die Antwort des Systems zu verändern. Unter Verwendung dieser Freiheit finden wir, dass die lineare Antwort auf eine nicht-konservative Kraft unter bestimmten Voraussetzungen äquivalent sein kann zu der Antwort auf eine Potentialkraft, die durch das FDT gegeben ist. Das bedeutet, dass man das Theorem auch für bestimmte Störungen durch nicht-konservative Kräfte verwenden kann, für die es normalerweise als nicht anwendbar angesehen wird. Wir diskutieren ausführlich den Fall, in dem eine nicht-konservative Störkraft linear in den Teilchenkoordinaten ist; in diesem Fall kann die genannte Freiheit durch störungsbedingte Symmetrien formuliert werden.

Insbesondere für eine Scherung führt die Methode zu einer neuartigen linearen Antwortformel, einem FDT für Scherung, das eine Alternative zur bekannten Green-Kubo-Relation ist. Um die Formel zu demonstrieren, führen wir Brownsche-Dynamik-Simulationen für überdämpfte interagierende Brownsche Teilchen in einem harmonischen Potential durch. Abgesehen von *einigen offenkundigen* Vorteilen der FDT gegenüber der Green-Kubo-Relation zeigt diese Analyse auch, dass die FDT-Relation eine viel bessere statistische Konvergenz aufweist und daher wesentlich effektiver ist. Analytische Untersuchungen eines einzelnen unterdämpften Teilchens zeigen mehrere interessante Merkmale der unterdämpften transienten Antwort und demonstrieren, dass die Verwendung des FDTs auch bei analytischen Berechnungen einfacher ist.

Bevor wir eine ähnliche Methode auch für ein *Nichtgleichgewichtssystem* [hier praktisch umgesetzt durch aktive Brownsche Teilchen (ABT)] vorschlagen, diskutieren wir zunächst bereits existierende Arbeiten zur allgemeinen linearen Antworttheorie. Insbesondere betrachten wir die Herleitung der Antwortrelationen im Rahmen des Pfadintegral-Formalismus und beleuchten dabei einige Aspekte der stochastischen Analyse und der Nulltemperaturgrenze. Außerdem klassifizieren wir die verschiedenen Antwortrelationen nach der Art des Systems und der Störung.

Unter Verwendung des Pfadintegral-Formalismus leiten wir die lineare Antwortrelation für ABT in zwei Raumdimensionen, die durch einen einfachen Scherfluss gestört werden, in Formel I her. Wir zeigen, dass die Antwort der ABT auf eine Störung durch Scherung äquivalent ist zur Antwort auf ein externes Potential, falls das System und die physikalische Observable xy-symmetrisch sind. Diese Beobachtung führt zu einer neuen Antwortrelation, Formel II, die gegenüber Formel I dahingehend vorteilhaft ist, da sie keine Zeitableitungen und keine Antwort auf Scherrotation enthält. Darüber hinaus kann Formel II auf ABT in 3D und sogar auf andere Modelle aktiver Teilchen leicht verallgemeinert werden.

Zu guter Letzt wird die Auswirkung eines Scherflusses auf die Morphologie und die Spannung interagierender ABT in einem harmonischen Potential numerisch untersucht. Die Simulationen zeigen, dass die Aktivität der Teilchen die Antwort im Vergleich zum passiven Fall erhöht. Außerdem erhöht das Hinzufügen von Ausrichtungswechselwirkungen zwischen den Teilchen die Antwort weiter. In diesen Simulationen wird Formel II demonstriert.

A Mathematical details of Section 2.7

A.1 Solutions of the Langevin equations

Given that the system is in equilibrium at time $t = 0$, we set the initial time to $-\infty$, such that the memory of the initial conditions is lost and the dynamics does not depend on these conditions. We further take into account that shear flow is applied for time $t > 0$. With these considerations, the solutions of Eqs. (2.32a) and (2.32b) read

$$\begin{aligned} x(t) = \frac{1}{m\sqrt{a^2-4b}} \Bigg\{ & e^{-\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)t} \int_{-\infty}^{t} ds e^{\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)s} f_x(s) \\ & - e^{-\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)t} \int_{-\infty}^{t} ds e^{\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)s} f_x(s) \Bigg\} \\ + \frac{\dot{\gamma} a}{m\left(a^2-4b\right)} \Bigg\{ & e^{-\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)t} \int_{0}^{t} ds_1 \int_{-\infty}^{s_1} ds_2 e^{\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)s_2} f_y(s_2) \\ & - e^{-\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)t} \int_{0}^{t} ds_1 \int_{-\infty}^{s_1} ds_2 e^{-\sqrt{a^2-4b}s_1} e^{\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)s_2} f_y(s_2) \\ & + e^{-\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)t} \int_{0}^{t} ds_1 \int_{-\infty}^{s_1} ds_2 e^{\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)s_2} f_y(s_2) \\ & - e^{-\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)t} \int_{0}^{t} ds_1 \int_{-\infty}^{s_1} ds_2 e^{\sqrt{a^2-4b}s_1} e^{\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)s_2} f_y(s_2) \Bigg\}, \end{aligned} \tag{A.1}$$

$$\begin{aligned} y(t) = \frac{1}{m\sqrt{a^2-4b}} \Bigg\{ & e^{-\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)t} \int_{-\infty}^{t} ds e^{\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)s} f_y(s) \\ & - e^{-\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)t} \int_{-\infty}^{t} ds e^{\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)s} f_y(s) \Bigg\}, \end{aligned} \tag{A.2}$$

$$
\begin{aligned}
v_x(t) = -\frac{1}{2m\sqrt{a^2-4b}}\Bigg\{ & \left(a-\sqrt{a^2-4b}\right) e^{-\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)t} \int_{-\infty}^{t} ds e^{\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)s} f_x(s) \\
& - \left(a+\sqrt{a^2-4b}\right) e^{-\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)t} \int_{-\infty}^{t} ds e^{\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)s} f_x(s) \Bigg\} \\
- \frac{\dot{\gamma}a}{2m\left(a^2-4b\right)}\Bigg\{ & \left(a-\sqrt{a^2-4b}\right) e^{-\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)t} \int_0^t ds_1 \int_{-\infty}^{s_1} ds_2 e^{\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)s_2} f_y(s_2) \\
& - \left(a-\sqrt{a^2-4b}\right) e^{-\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)t} \int_0^t ds_1 \int_{-\infty}^{s_1} ds_2 e^{-\sqrt{a^2-4b}s_1} e^{\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)s_2} f_y(s_2) \\
& + \left(a+\sqrt{a^2-4b}\right) e^{-\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)t} \int_0^t ds_1 \int_{-\infty}^{s_1} ds_2 e^{\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)s_2} f_y(s_2) \\
& - \left(a+\sqrt{a^2-4b}\right) e^{-\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)t} \int_0^t ds_1 \int_{-\infty}^{s_1} ds_2 e^{\sqrt{a^2-4b}s_1} e^{\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)s_2} f_y(s_2) \Bigg\},
\end{aligned}
\tag{A.3}
$$

$$
\begin{aligned}
v_y(t) = -\frac{1}{2m\sqrt{a^2-4b}}\Bigg\{ & \left(a-\sqrt{a^2-4b}\right) e^{-\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)t} \int_{-\infty}^{t} ds e^{\frac{1}{2}\left(a-\sqrt{a^2-4b}\right)s} f_y(s) \\
& - \left(a+\sqrt{a^2-4b}\right) e^{-\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)t} \int_{-\infty}^{t} ds e^{\frac{1}{2}\left(a+\sqrt{a^2-4b}\right)s} f_y(s) \Bigg\},
\end{aligned}
\tag{A.4}
$$

where $a \equiv \frac{1}{\mu m}$ and $b \equiv \frac{k}{m}$.

A.2 Equilibrium correlation functions required for the linear response formulas

All correlation functions given here are computed using solutions (A.1), (A.2), (A.3), and (A.4), with $\dot{\gamma} = 0$, Eq. (2.33), and the Isserlis' theorem, also known as the Wick's probability theorem[1]. They read

$$\langle x(t)y(t)x(t')y(t')\rangle = \frac{4(k_{\rm B}T)^2\mu^4m^2}{1-4\mu^2km}\Bigg\{\frac{1}{\left(1-\sqrt{1-4\mu^2km}\right)^2}e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)|t-t'|} + \frac{1}{\left(1+\sqrt{1-4\mu^2km}\right)^2}e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)|t-t'|} - \frac{1}{2\mu^2km}e^{-\frac{1}{\mu m}|t-t'|}\Bigg\}, \tag{A.5}$$

$$\langle v_x(t)v_y(t)v_x(t')v_y(t')\rangle = \frac{(k_{\rm B}T)^2}{4m^2\left(1-4\mu^2km\right)}\Bigg\{\left(1-\sqrt{1-4\mu^2km}\right)^2 e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)|t-t'|} + \left(1+\sqrt{1-4\mu^2km}\right)^2 e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)|t-t'|} - 8\mu^2kme^{-\frac{1}{\mu m}|t-t'|}\Bigg\}. \tag{A.6}$$

$$\langle v_x(t)y(t)v_x(t')y(t')\rangle = \langle v_y(t)x(t)v_y(t')x(t')\rangle = \frac{(k_{\rm B}T)^2}{km\left(1-4\mu^2km\right)}\Bigg\{-\mu^2km\left(e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)|t-t'|} + e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)|t-t'|}\right) + \left(1-2\mu^2km\right)e^{-\frac{1}{\mu m}|t-t'|}\Bigg\}. \tag{A.7}$$

$$\langle v_x(t)v_y(t)x(t')y(t')\rangle = -\langle v_x(t)y(t)v_y(t')x(t')\rangle = \frac{(k_{\rm B}T)^2\mu^2}{1-4\mu^2km}\Bigg\{e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)|t-t'|} + e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)|t-t'|} - 2e^{-\frac{1}{\mu m}|t-t'|}\Bigg\}, \tag{A.8}$$

$$\langle v_x(t)y(t)x(t')y(t')\rangle = \langle v_y(t)x(t)x(t')y(t')\rangle = -\frac{2(k_{\rm B}T)^2\mu^3m}{1-4\mu^2km}\Bigg\{\frac{1}{1-\sqrt{1-4\mu^2km}}e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)|t-t'|} + \frac{1}{1+\sqrt{1-4\mu^2km}}e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)|t-t'|} - \frac{1}{2\mu^2km}e^{-\frac{1}{\mu m}|t-t'|}\Bigg\}\mathrm{sgn}(t-t'), \tag{A.9}$$

[1]The Isserlis' theorem allows to compute higher-order moments of the normal distribution using the second moment [164]. For the random force in Eq. (2.33), one gets according to the theorem: $\langle f_a(t_1)f_b(t_2)f_c(t_3)f_d(t_4)\rangle = \langle f_a(t_1)f_b(t_2)\rangle\langle f_c(t_3)f_d(t_4)\rangle + \langle f_a(t_1)f_c(t_3)\rangle\langle f_b(t_2)f_d(t_4)\rangle + \langle f_a(t_1)f_d(t_4)\rangle\langle f_b(t_2)f_c(t_3)\rangle$, and odd moments are zero.

$$
\begin{aligned}
\langle v_x(t)v_y(t)v_x(t')y(t')\rangle &= \langle v_x(t)v_y(t)v_y(t')x(t')\rangle \\
&= \frac{(k_\mathrm{B}T)^2\mu}{2m(1-4\mu^2km)}\Bigg\{\left(1-\sqrt{1-4\mu^2km}\right)e^{-\frac{1}{\mu m}\left(1-\sqrt{1-4\mu^2km}\right)|t-t'|} \\
&+\left(1+\sqrt{1-4\mu^2km}\right)e^{-\frac{1}{\mu m}\left(1+\sqrt{1-4\mu^2km}\right)|t-t'|}-2e^{-\frac{1}{\mu m}|t-t'|}\Bigg\}\mathrm{sgn}(t-t'),
\end{aligned}
\tag{A.10}
$$

where $\mathrm{sgn}(t-t')$ is the sign function.

One can show that all these correlation functions are real. We note that correlators in Eqs. (A.5), (A.6), (A.7) and (A.8) are even functions of time difference, whereas correlators in Eqs. (A.9) and (A.10) are odd functions of $t-t'$. In the case $t=t'$, the correlators are in agreement with the equipartition theorem and the symmetry of the equilibrium distribution, i.e., from Eqs. (A.5), (A.6), and (A.7) one gets $\langle x^2y^2\rangle = \left(\frac{k_\mathrm{B}T}{k}\right)^2$, $\langle v_x^2v_y^2\rangle = \left(\frac{k_\mathrm{B}T}{m}\right)^2$, and $\langle v_x^2y^2\rangle = \langle v_y^2x^2\rangle = \frac{(k_\mathrm{B}T)^2}{km}$, respectively, while from Eqs. (A.8), (A.9), and (A.10) one gets $\langle v_xv_yxy\rangle = \langle v_xy^2x\rangle = \langle v_x^2v_yy\rangle = 0$. All the correlation functions decay to zero in the limit $|t-t'|\to\infty$. Finally, we note that the derivative with respect to $t-t'$ is not defined at $t=t'$ for $\langle v_x(t)v_y(t)v_x(t')v_y(t')\rangle$ and $\langle v_x(t)y(t)v_x(t')y(t')\rangle = \langle v_y(t)x(t)v_y(t')x(t')\rangle$: the limit of the derivative for $t-t'\to+0$ is negative, while for $t-t'\to-0$ it is positive.

B Detailed computation of the response in Subsection 4.5.2

B.1 Computation of the left-hand side of Equation (4.22)

First, one can show that

$$\langle \cos\varphi(s_1)\cos\varphi(s_2)\rangle_{\mathrm{st}}^{(\dot\gamma)} = \langle \sin\varphi(s_1)\sin\varphi(s_2)\rangle_{\mathrm{st}}^{(\dot\gamma)} = \frac{1}{2}\cos\left[\frac{\dot\gamma}{2}(s_1-s_2)\right]e^{-D_{\mathrm{r}}|s_1-s_2|} \quad \text{(B.1)}$$

and

$$\langle \cos\varphi(s_1)\sin\varphi(s_2)\rangle_{\mathrm{st}}^{(\dot\gamma)} = \frac{1}{2}\sin\left[\frac{\dot\gamma}{2}(s_1-s_2)\right]e^{-D_{\mathrm{r}}|s_1-s_2|}, \quad \text{(B.2)}$$

in agreement with Ref. [161]. For the unsheared correlators ($\dot\gamma = 0$), we hence have

$$\langle \cos\varphi(s_1)\cos\varphi(s_2)\rangle_{\mathrm{st}} = \langle \sin\varphi(s_1)\sin\varphi(s_2)\rangle_{\mathrm{st}} = \frac{1}{2}e^{-D_{\mathrm{r}}|s_1-s_2|} \quad \text{(B.3)}$$

and

$$\langle \cos\varphi(s_1)\sin\varphi(s_2)\rangle_{\mathrm{st}} = 0. \quad \text{(B.4)}$$

Results (B.1), (B.2), (B.3), and (B.4) do not depend on the initial angle $\varphi(-\infty)$, because we consider stationary correlation functions, i.e., we let the angle to evolve from far away in the past [$-\infty$ limit in Eq. (4.21c)] such that the initial angle is forgotten. We note that this limit does not commute with the limit $D_{\mathrm{r}} \to 0$ (for times smaller than $\frac{1}{D_{\mathrm{r}}}$ a particle remembers its initial orientation).

Due to Eq. (B.4),

$$\langle xy\rangle_{\mathrm{st}} = 0, \quad \text{(B.5)}$$

as in the case of a trapped passive particle. This result is intuitive, because the unsheared system is xy symmetric and the particle moves around the origin. For $\langle x(t)y(t)\rangle_{\mathrm{st}}^{(\dot\gamma)}$ linear in $\dot\gamma$, the relevant nonzero correlators are those given by Eqs. (B.1) and (B.2) linear in $\dot\gamma$, and $\langle f_y(s_1)f_y(s_2)\rangle = \frac{2D}{\mu^2}\delta(s_1-s_2)$. The contribution of correlator (B.2) is, however, zero due to the symmetry of time integrals containing it. Multiplying solutions (4.21a) and (4.21b), inserting the above mentioned correlators, and performing the integrals, one obtains result (4.23).

B.2 Computation of the right-hand side of Equation (4.22)

For the right-hand side of Eq. (4.22), we need the following correlation functions: $\langle x(t)y(t)x(t')y(t')\rangle_{\text{st}}$ and $\langle x(t)y(t)\cos\varphi(t')y(t')\rangle_{\text{st}}$, where $t \geq t'$.

For $\langle x(t)y(t)x(t')y(t')\rangle_{\text{st}}$, the relevant nonzero correlators are those given by Eq. (B.3), $\langle f_x(s_1)f_x(s_2)\rangle = \langle f_y(s_1)f_y(s_2)\rangle = \frac{2D}{\mu^2}\delta(s_1 - s_2)$, and

$$\begin{aligned}
&\langle \cos\varphi(s_1)\sin\varphi(s_2)\cos\varphi(s_3)\sin\varphi(s_4)\rangle_{\text{st}} \\
&= \frac{1}{8}\exp\Big\{-D_{\text{r}}\big[s_1 + s_2 + s_3 + s_4 + 2\min(s_1, s_2) - 2\min(s_1, s_3) - 2\min(s_1, s_4) \\
&\qquad - 2\min(s_2, s_3) - 2\min(s_2, s_4) + 2\min(s_3, s_4)\big]\Big\} \\
&+ \frac{1}{8}\exp\Big\{-D_{\text{r}}\big[s_1 + s_2 + s_3 + s_4 - 2\min(s_1, s_2) - 2\min(s_1, s_3) + 2\min(s_1, s_4) \\
&\qquad + 2\min(s_2, s_3) - 2\min(s_2, s_4) - 2\min(s_3, s_4)\big]\Big\} \\
&- \frac{1}{8}\exp\Big\{-D_{\text{r}}\big[s_1 + s_2 + s_3 + s_4 - 2\min(s_1, s_2) + 2\min(s_1, s_3) - 2\min(s_1, s_4) \\
&\qquad - 2\min(s_2, s_3) + 2\min(s_2, s_4) - 2\min(s_3, s_4)\big]\Big\},
\end{aligned} \tag{B.6}$$

where $\min(s_1, s_2) = s_1$ if $s_1 < s_2$ and $\min(s_1, s_2) = s_2$ if $s_2 < s_1$. Note that the second term in Eq. (B.6) equals minus the third one with either s_1 and s_2 or s_3 and s_4 interchanged. This leads to cancelation of these terms being integrated over either s_1 and s_2 or s_3 and s_4 in the same range. Therefore, these terms do not contribute to $\langle x(t)y(t)x(t')y(t')\rangle_{\text{st}}$ or to $\langle x(t)y(t)\cos\varphi(t')y(t')\rangle_{\text{st}}$ below . The final result for $\langle x(t)y(t)x(t')y(t')\rangle_{\text{st}}$ reads as

$$\begin{aligned}
\langle x(t)y(t)x(t')y(t')\rangle_{\text{st}} &= \frac{D^2}{(\mu k)^2}e^{-2\mu k(t-t')} + \frac{v_0^2 D}{(\mu k)^2\left[D_{\text{r}}^2 - (\mu k)^2\right]}\Big\{D_{\text{r}}e^{-2\mu k(t-t')} \\
&- \mu k e^{-(D_{\text{r}}+\mu k)(t-t')}\Big\} + \frac{v_0^4}{8(\mu k)^2\left[D_{\text{r}}^2 - (\mu k)^2\right]\left[4D_{\text{r}}^2 - (\mu k)^2\right][3D_{\text{r}} - \mu k][D_{\text{r}} + 3\mu k]} \\
&\times \Big\{2D_{\text{r}}^2[3D_{\text{r}} - \mu k][4D_{\text{r}} + 5\mu k]e^{-2\mu k(t-t')} - 12D_{\text{r}}\mu k\left[4D_{\text{r}}^2 - (\mu k)^2\right]e^{-(D_{\text{r}}+\mu k)(t-t')} \\
&+ (\mu k)^2[D_{\text{r}} - \mu k][D_{\text{r}} + 3\mu k]e^{-4D_{\text{r}}(t-t')}\Big\},
\end{aligned} \tag{B.7}$$

where the first term is the result for a passive particle, the second term stems from coupling between active motion and translational diffusion, and the third term is a purely active contribution.

For $\langle x(t)y(t)\cos\varphi(t')y(t')\rangle_{\text{st}}$, the relevant nonzero correlators are $\langle f_x(s_1)f_x(s_2)\rangle =$

$\langle f_y(s_1) f_y(s_2)\rangle = \frac{2D}{\mu^2}\delta(s_1 - s_2)$ and those given by Eqs. (B.3) and (B.6). We get

$$\langle x(t)y(t)\cos\varphi(t')y(t')\rangle_{\rm st} = \frac{v_0 D}{2\mu k\left[D_{\rm r}^2 - (\mu k)^2\right]}\Big\{2D_{\rm r}e^{-2\mu k(t-t')} - (D_{\rm r}+\mu k)\,e^{-(D_{\rm r}+\mu k)(t-t')}\Big\} + \frac{v_0^3}{8\mu k\left[D_{\rm r}^2 - (\mu k)^2\right]\left[4D_{\rm r}^2 - (\mu k)^2\right][3D_{\rm r}-\mu k]\,[D_{\rm r}+3\mu k]} \times \Big\{4D_{\rm r}^2\,[3D_{\rm r}-\mu k]\,[4D_{\rm r}+5\mu k]\,e^{-2\mu k(t-t')} - 6D_{\rm r}\left[4D_{\rm r}^2-(\mu k)^2\right][D_{\rm r}+3\mu k]\,e^{-(D_{\rm r}+\mu k)(t-t')} + \mu k\,[D_{\rm r}-\mu k]\,[2D_{\rm r}+\mu k]\,[D_{\rm r}+3\mu k]\,e^{-4D_{\rm r}(t-t')}\Big\}. \tag{B.8}$$

Using Eqs. (B.7) and (B.8), we find for the three terms on the right-hand side of Eq. (4.22)

$$\frac{\dot\gamma}{4D}\left[\langle x^2y^2\rangle_{\rm st} - \langle x(t)y(t)x(0)y(0)\rangle_{\rm st}\right] = \frac{\dot\gamma D}{4(\mu k)^2}\left(1-e^{-2\mu k t}\right) + \frac{\dot\gamma v_0^2}{4(\mu k)^2\left[D_{\rm r}^2-(\mu k)^2\right]} \times \Big\{D_{\rm r}\left(1-e^{-2\mu k t}\right) - \mu k\left(1-e^{-(D_{\rm r}+\mu k)t}\right)\Big\} + \frac{\dot\gamma v_0^4}{32D(\mu k)^2\left[D_{\rm r}^2-(\mu k)^2\right]\left[4D_{\rm r}^2-(\mu k)^2\right][3D_{\rm r}-\mu k]\,[D_{\rm r}+3\mu k]} \times \Big\{2D_{\rm r}^2\,[3D_{\rm r}-\mu k]\,[4D_{\rm r}+5\mu k]\left(1-e^{-2\mu k t}\right) - 12D_{\rm r}\mu k\left[4D_{\rm r}^2-(\mu k)^2\right] \times \left(1-e^{-(D_{\rm r}+\mu k)t}\right) + (\mu k)^2\,[D_{\rm r}-\mu k]\,[D_{\rm r}+3\mu k]\left(1-e^{-4D_{\rm r}t}\right)\Big\}, \tag{B.9}$$

$$-\frac{\dot\gamma v_0}{2D}\int_0^t dt'\langle x(t)y(t)\cos\varphi(t')y(t')\rangle_{\rm st} = -\frac{\dot\gamma v_0^2}{4(\mu k)^2\left[D_{\rm r}^2-(\mu k)^2\right]}\Big\{D_{\rm r}\left(1-e^{-2\mu k t}\right) - \mu k\left(1-e^{-(D_{\rm r}+\mu k)t}\right)\Big\} - \frac{\dot\gamma v_0^4}{16D(\mu k)^2\left[D_{\rm r}^2-(\mu k)^2\right]\left[4D_{\rm r}^2-(\mu k)^2\right][3D_{\rm r}-\mu k]\,[D_{\rm r}+3\mu k]} \times \Big\{2D_{\rm r}^2\,[3D_{\rm r}-\mu k]\,[4D_{\rm r}+5\mu k]\left(1-e^{-2\mu k t}\right) - \frac{6D_{\rm r}\mu k}{D_{\rm r}+\mu k}\left[4D_{\rm r}^2-(\mu k)^2\right][D_{\rm r}+3\mu k] \times \left(1-e^{-(D_{\rm r}+\mu k)t}\right) + \frac{(\mu k)^2}{4D_{\rm r}}\,[D_{\rm r}-\mu k]\,[2D_{\rm r}+\mu k]\,[D_{\rm r}+3\mu k]\left(1-e^{-4D_{\rm r}t}\right)\Big\}, \tag{B.10}$$

$$\begin{aligned}
\frac{\dot{\gamma}\mu k}{2D}\int_0^t dt'\langle x(t)y(t)x(t')y(t')\rangle_{\rm st} &= \frac{\dot{\gamma}D}{4(\mu k)^2}\left(1-e^{-2\mu k t}\right) + \frac{\dot{\gamma}v_0^2}{4(\mu k)^2\left[D_{\rm r}^2-(\mu k)^2\right]} \\
&\quad \times \left\{D_{\rm r}\left(1-e^{-2\mu k t}\right) - \frac{2(\mu k)^2}{D_{\rm r}+\mu k}\left(1-e^{-(D_{\rm r}+\mu k)t}\right)\right\} \\
&+ \frac{\dot{\gamma}v_0^4}{16D(\mu k)^2\left[D_{\rm r}^2-(\mu k)^2\right]\left[4D_{\rm r}^2-(\mu k)^2\right][3D_{\rm r}-\mu k][D_{\rm r}+3\mu k]} \\
&\quad \times \left\{D_{\rm r}^2[3D_{\rm r}-\mu k][4D_{\rm r}+5\mu k]\left(1-e^{-2\mu k t}\right) - \frac{12D_{\rm r}(\mu k)^2}{D_{\rm r}+\mu k}\left[4D_{\rm r}^2-(\mu k)^2\right]\right. \\
&\quad\quad \left.\times\left(1-e^{-(D_{\rm r}+\mu k)t}\right) + \frac{(\mu k)^3}{4D_{\rm r}}[D_{\rm r}-\mu k][D_{\rm r}+3\mu k]\left(1-e^{-4D_{\rm r}t}\right)\right\}. \qquad \text{(B.11)}
\end{aligned}$$

Adding the right-hand sides of Eqs. (B.9), (B.10), and (B.11) together, one finds that the terms proportional to $\frac{\dot{\gamma}v_0^4}{D(\mu k)^2}$ cancel and the rest gives Eq. (4.23). This completes our check of Eq. (4.22).

We also checked explicitly that $\langle x(t)y(t)\cos\varphi(t')y(t')\rangle_{\rm st} = \langle x(t)y(t)\sin\varphi(t')x(t')\rangle_{\rm st}$, thereby confirming, for this specific example, our statement in Subsec. 4.3 regarding the fact that the terms $\cos\varphi_i(t')y_i(t')$ and $\sin\varphi_i(t')x_i(t')$ in Eq. (4.10) give identical contributions.

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