Projection operators in statistical mechanics: a pedagogical approach

Michael te Vrugt$^1$ and Raphael Wittkowski$^{1, 2}$

$^1$Institut für Theoretische Physik, Center for Soft Nanoscience, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany

The Mori-Zwanzig projection operator formalism is one of the central tools of nonequilibrium statistical mechanics, allowing to derive macroscopic equations of motion from the microscopic dynamics through a systematic coarse-graining procedure. It is important as a method in physical research and gives many insights into the general structure of nonequilibrium transport equations and the general procedure of microscopic derivations. Therefore, it is a valuable ingredient of basic and advanced courses in statistical mechanics. However, accessible introductions to this method – in particular in its more advanced forms – are extremely rare. In this article, we give a simple and systematic introduction to the Mori-Zwanzig formalism, which allows students to understand the methodology in the form it is used in current research. This includes both basic and modern versions of the theory. Moreover, we relate the formalism to more general aspects of statistical mechanics and quantum mechanics. Thereby, we explain how this method can be incorporated into a lecture course on statistical mechanics as a way to give a general introduction to the study of nonequilibrium systems. Applications, in particular to spin relaxation and dynamical density functional theory, are also discussed.

I. INTRODUCTION

Although basic introductions to statistical mechanics tend to focus on thermodynamic equilibrium, a large part of modern research in this field is focused on nonequilibrium systems. These arise, e.g., in the study of driven and active soft matter. Transport equations for systems of this type are obtained either from phenomenological considerations or from derivations starting from the underlying microscopic equations of motion (e.g., Hamilton’s equations of motion). For working in this field, it is therefore important to have an understanding of both the structure of nonequilibrium transport equations and the way in which they can be derived.

It is a very remarkable and by no means obvious fact that the nonequilibrium dynamics of a very large class of systems can be described using only a small number of so-called “relevant” variables. For example, fluids are already well characterized by mass, momentum, and energy density, although the number of microscopic degrees of freedom is much larger. Moreover, nonequilibrium transport equations all share a general form. They consist of a reversible and an irreversible part, where the irreversible part is, for close-to-equilibrium systems, proportional to the functional derivative of a free energy. Another point is that most of these transport equations do not contain memory terms. It is interesting to understand both why they usually do not arise and under which circumstances they do. Finally, sometimes these equations contain noise terms, whose origin from the underlying deterministic dynamics is also a conceptually interesting question.

An excellent way to study these aspects is the Mori-Zwanzig formalism. It is a coarse-graining procedure, which allows to derive nonequilibrium transport equations in a systematic way from the underlying microscopic dynamics. The Mori-Zwanzig formalism has applications in a large number of fields, such as fluid mechanics, dynamical density functional theory, active matter physics, spin relaxation theory, and particle physics.

The formalism, originally developed by Sadao Nakajima, Robert Zwanzig, and Hajime Mori, exists in a large variety of forms and is known under different names, such as Zwanzig projection operator method, Nakajima-Mori-Zwanzig formalism, Mori-Zwanzig-Forster technique, or Kawasaki-Gunton method. Moreover, different forms differ in many technical details, although they all share the same general structure. Two main forms can be distinguished: methods where the projection operator is time-independent and methods where it is time-dependent.

This difference can form a major obstacle for students’ understanding, since these methods are typically presented and derived in different ways. For time-independent methods, one introduces the projection operator through the idea of a Hilbert space formed by all observables, in which, through an appropriate scalar product, one can project onto a certain subspace formed by the relevant variables. In the case of time-dependent projection operators, the idea of a Hilbert space or scalar product is used less frequently. Instead, the method is primarily discussed as a way to approximate the actual probability density of a system by means of a relevant probability density determined by macroscopically available information. Although both approaches are equivalent, and both approaches can be (and are) used in both cases, it requires a significant amount of calculation to see this (see Refs. for such cal-
II. MORI-ZWANZIG FORMALISM

A. General aspects of nonequilibrium transport equations

In the description of a many-particle system in statistical mechanics, one is typically not interested in the precise coordinates of every single particle. Instead, a system is typically described using only a few relevant variables that follow closed dynamical equations of motion. A good example is an incompressible fluid, where, rather than calculating position and momentum of all fluid molecules, one describes the system using the flow field \( \vec{u}(\vec{r}, t) \) (or, equivalently, the momentum density \( \rho \vec{u}(\vec{r}, t) \)) with position \( \vec{r} \) and time \( t \). The flow field follows the famous Navier-Stokes equation

\[
\frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \vec{\nabla}) \vec{u} = -\frac{\nabla p}{\rho} + \nu \Delta \vec{u},
\]

where \( \rho \) is the constant mass density, \( p(\vec{r}, t) \) the local pressure, and \( \nu \) the kinematic viscosity of the fluid.

Three things are notable here:

1. The complete system is described using only a single variable \( \vec{u}(\vec{r}, t) \). (This is based on the assumption of constant mass density and temperature, otherwise mass density and energy density would also come into play.) This variable is conserved, which implies that it varies on time scales that are much slower than those of microscopic fluctuations.

2. The equation consists of two parts. The first part, known as the Euler equation, is essentially Newton’s law for a fluid element (this is how it is often derived heuristically). It therefore describes reversible classical mechanics. The second part with the prefactor \( \nu \) describes irreversible dissipative dynamics, which increases the entropy.

3. The equation is memory-less, i.e., the rate of change of \( \vec{u}(\vec{r}, t) \) depends only on the current value \( \vec{u}(\vec{r}, t) \), but not on values \( \vec{u}(\vec{r}, s) \) at previous times \( s < t \).

Another example are the Bloch equations for a system of spins in a magnetic field \( \vec{B} \). Using the total spin \( \vec{S} \) as a relevant variable, it follows the Bloch equations

\[
\frac{dS_i}{dt} = \gamma (\vec{S} \times \vec{B})_i - \frac{S_i}{\tau_i}
\]

with the gyromagnetic ratio \( \gamma \) and the relaxation times \( \tau_i \) with \( i = x, y, z \). Again, we have a description that only requires one slow variable (although, this time, it is not conserved) and, again, we have a term for organized irreversible motion (precession of the spins in the magnetic field) as well as a term for dissipation, describing the irreversible relaxation to equilibrium. Moreover, again, we have an equation that contains no memory effects.

B. Mori theory

We now wish to extend these observations to a general formalism that allows us to derive such equations from the underlying microscopic dynamics in a systematic way. This formalism is known as the Mori-Zwanzig formalism. For introductory purposes, we present here only the simplest form (following Ref. [12]) and then discuss possible extensions. We present the method in quantum-mechanical form, since the classical case is essentially equivalent and not much simpler.

The main idea is that we can think of all the observables that we could use to describe the many-particle system as forming a Hilbert space. A Hilbert space, which should be familiar from quantum mechanics, is a vector space equipped with a scalar product. A simple example of a Hilbert space is \( \mathbb{R}^n \) with the scalar product \( \langle \vec{a}, \vec{b} \rangle = \vec{a} \cdot \vec{b} \). If we now have a vector \( \vec{x} \) in a Hilbert space and are, for some reason, only interested in the part which points in the direction of a vector \( \vec{c} \) (which does not have to be normalized), we can project \( \vec{x} \) onto \( \vec{c} \) by applying a projection operator \( P \):

\[
P\vec{x} = \frac{\vec{x} \cdot \vec{c}}{\vec{c} \cdot \vec{c}} \vec{c}.
\]

We now apply this idea to statistical mechanics. All our observables form a (very large-dimensional) Hilbert

---

3 Strictly speaking, this is a pre-Hilbert space. A Hilbert space additionally requires the convergence of every Cauchy sequence.
space. We are only interested in some particular observable $A$ (e.g., the momentum density in a fluid or the total magnetization in a spin system) that can be thought of as a “direction” in this large-dimensional Hilbert space. Defining an appropriate scalar product $(\cdot , \cdot )$, we then project an observable $X$ onto $A$ in the form

$$PX = (A, A)^{-1}(X, A)A.$$  \hfill (4)

For a set of relevant variables $\{A_i\}$, this generalizes to

$$PX = (A_j, A_k)^{-1}(X, A_t)A_j.$$  \hfill (5)

This form is constructed in complete analogy to Eq. (5). Note, however, that the form becomes more complicated for general projection operators, in particular if they are time-dependent.

We are left with two tasks:

1. What is a good definition of a “scalar product” in the Hilbert space of dynamical variables?

2. How does this help us to describe the dynamics of the system?

We start with the second task. For this, we need to think about what an observable is. In a classical system, it is a function $A(\vec{q}, \vec{p})$ on the phase space with conjugate position $\vec{q}$ and momentum $\vec{p}$, while in quantum mechanics, it is a Hermitian operator acting on wave functions. In the Heisenberg picture, the observables are time-dependent while the wave functions are not. This is the picture we use here, since we are interested in the time-evolution of the observables. We assume, for simplicity, that our quantum observable $A$ is not explicitly time-dependent. Then, the Heisenberg equation of motion reads

$$\frac{dA}{dt} = \frac{i}{\hbar}[H, A] = iLA,$$  \hfill (6)

where we have introduced the imaginary unit $i$, the reduced Planck constant $\hbar$, the commutator $[\cdot , \cdot ]$, the Hamiltonian $H$, and the corresponding Liouvillian $L$. In the classical case, we use the Poisson bracket $\{\cdot , \cdot \}$ instead of the commutator. The formal solution of Eq. (6) is the operator exponential

$$A(t) = e^{iLt}A.$$  \hfill (7)

To clarify the probably confusing notation, which is used also throughout the literature: By $A(t)$, we denote the time-dependent observable in the Heisenberg picture. This is related to the time-independent Schrödinger-picture observable by a time-dependent transformation (see Eq. (9) further below). One has to choose a certain time (here we use $t = 0$) at which the Heisenberg-picture observable coincides with the Schrödinger-picture observable [31]. By $A$ we denote the time-independent Schrödinger-picture observable. The same holds in the classical case, where a distinction between Heisenberg and Schrödinger picture also exists [32], although it is less well known there. In the classical case, the Schrödinger-picture observable is a phase-space function $A(\vec{q}, \vec{p})$, whereas the Heisenberg picture observable is a phase-space function $\hat{A}(\vec{q}(t), \vec{p}(t))$.

We now use the operator identity (“Dyson identity”)

$$e^{iLt} = e^{iQLt} + \int_0^t ds e^{iL(t-s)}P_iLe^{iQLs}$$  \hfill (8)

with the orthogonal projection operator $Q = 1-P$, which can be easily proven by differentiation (see Appendix A). Applying Eq. (5) to $QiLA_i$ gives the Mori-Zwanzig equation

$$\dot{A}_i(t) = \Omega_{ij}A_j(t) + \int_0^t ds K_{ij}(s)A_j(t-s) + F_i(t)$$  \hfill (9)

with the frequency matrix

$$\Omega_{ij} = (A_j, A_k)^{-1}(iLA_i, A_k),$$  \hfill (10)

the memory matrix

$$K_{ij}(s) = (A_j, A_k)^{-1}(iLF_i(s), A_k),$$  \hfill (11)

and the random force

$$F_i(t) = e^{iQLt}QiLA_i.$$  \hfill (12)

Equation (9) only contains the relevant variables $\{A_k\}$, but it is still formally exact. We have achieved this by a memory term: The present rate of change $\dot{A}_i(t)$ depends not only on the present value $A_i(t)$, as described by the term containing $\Omega_{ij}$, but also on the values $A_i(s)$ at previous times $s < t$, which is described by the term containing $K_{ij}$. $F_i(t)$ is a noise term. It describes the influence of those variables that we are not interested in.

Since the exact result (9) is a time-delayed integral-differential equation, it is, in general, extremely difficult to solve. We therefore make an approximation based on the assumption that the relevant variables are slow on macroscopic time scales. “Slow” means here that the rate of change is small. We can therefore make a Taylor expansion of Eq. (9) in $iLA_j$ up to second order. Since $K_{ij}$ is already of second order in $iLA_j$, we can write

$$A_j(t-s) = A_j(t) - \dot{A}_j(t) s + \cdots$$  \hfill (13)

and truncate the expansion after the first term. As this expression is integrated over in Eq. (9), we have to assume that the memory kernel $K_{ij}(s)$ vanishes very quickly on macroscopic time scales. In this case, the integrand in Eq. (9) vanishes for large times and there is

---

4 Throughout this article, we sum over each index appearing twice in a term.
no problem in extending the integral to \( s = \infty \). The resulting Markovian approximation gives the approximate transport equation

\[
\dot{A}_i(t) = \Omega_{ij} A_j(t) + D_{ij} A_j(t) + F_i(t)
\]

with the dissipative matrix \([12]\)

\[
D_{ij} = \int_0^\infty ds K_{ij}(s).
\]

As a further simplification, we can replace within \( K_{ij} \) the term \( e^{iQL_t} \) by \( e^{iLt} \), since \([12]\]

\[
iPLX \propto (iLX, A) = -(X, iLA),
\]

such that \( iPLX \) is of order \( iLA \) and can be dropped.

Equation (14), which is local in time, is much easier to solve than Eq. (9). Physically, the main difference is that we have replaced the memory integral by the simple term \( D_{ij} A_j(t) \). The fact that Eq. (14) only depends on the present state explains the name “Markovian approximation”: A Markov process is, in stochastics, a random process that has no memory.

The other task we had to address is the scalar product. For this, we first require the notion of a phase-space distribution function \( \rho(p, q, t) \). In the Gibbsian framework of statistical mechanics, where a many-particle system is described using an ensemble, which is a hypothetical set of infinitely many copies of the system with different initial conditions, this function specifies the probability that a system that is chosen at random from this ensemble is in a state specified by the phase-space coordinates \( q \) and \( p \) \([33]\). In the quantum-mechanical case, where the state of a system is specified by a wave function \( |\psi\rangle \), the many-particle system is instead described by the statistical operator \( \hat{\rho} = \sum_i p_i |\psi_i\rangle \langle \psi_i| \), where \( p_i \) is the probability that the system is in the quantum state \( |\psi_i\rangle \).

A standard choice is to use a generalized correlation function. For close-to-equilibrium quantum systems, this is given by the Mori product \([11]\)

\[
\langle X, Y \rangle = \int_0^1 d\alpha \text{Tr}(\hat{\rho} X e^{-\alpha \beta H} Y e^{\alpha \beta H})
\]

C. Mori-Zwanzig equation in a general context

If we take a look at the equation of motion (14), we see that we have arrived at the general form we were interested in:

1. The equations of motion depend only on the relevant variables \( \{A_i\} \).
2. They consist of a part \( \Omega_{ij} A_j \) that describes reversible organized motion and of a dissipative contribution \( D_{ij} A_j \).
3. They are memoryless, i.e., they only depend on the current state of the system.

Thus, Eq. (14) is a paradigmatic case for a transport equation in statistical mechanics. In fact, all relevant transport equations can be derived from this formalism. Moreover, we now have found a way to understand where the general structure described above comes from and under which conditions it holds.

Up to Eq. (9), our derivation was formally exact. If we describe a system not based on all microscopic degrees of freedom, but only with a reduced set of variables, the price we have to pay is that we need to know about the structure of the state at previous times to fully determine its temporal evolution. There are, however, certain circumstances under which this is not necessary, namely if the relevant variables are varying very slowly compared to other degrees of freedom. In this case, an approximate equation can be derived that gives a closed dynamics for the relevant variables without memory effects.

This requires that the set of relevant variables, which the formalism itself cannot determine, contains all slow macroscopic variables. For example, in the description of fluids, a reasonable choice is to use mass density, momentum density, and energy density \([11]\). If we restrict ourselves to one variable only – say, the mass density – we

---

5 Strictly speaking, the integral is extended to a time \( \tau_c \), which is much longer than the relaxation time scale \( \tau_R \), but smaller than the time scale of recurrence. “Recurrence” is the fact that a Hamiltonian system will, after a sufficiently long time, always return arbitrarily close to its initial state. Since recurrence occurs, for macroscopic systems, on time scales vastly longer than the age of the universe, this is no practical problem \([24]\) and we can simply set the upper integration boundary to infinity.

6 This matrix is also referred to as “diffusion matrix” \([13]\).

7 There is an alternative conceptual framework known as Boltzmannian statistical mechanics, which is not based on ensembles \([35]\). This framework is of historical and conceptual interest, but not frequently used in practical calculations.

8 From the general structure (14), it is not obvious that \( \Omega_{ij} A_j \) is reversible, while \( D_{ij} A_j \) is not. To see this, considerations on the symmetries of the coefficients \( \Omega_{ij} \) and \( D_{ij} \) under time reversal are required, which can be found in Ref. \([13]\).
make the strong assumption that all other variables relax on the time scale on which the chosen variable changes.  

The formalism does also allow to handle the case in which memory effects are relevant, since the memoryless case is just a particular approximation of the more general transport equation in which memory effects are present. Thus, memory kernel can be calculated systematically based on the formalism.

It is interesting that the Mori-Zwanzig formalism allows to derive irreversible macroscopic equations of motion from the reversible microscopic laws. As shown in Ref. [11], the dissipative terms lead to a monotonous increase of entropy and thus allow to prove a H-theorem, as long as the Markovian approximation holds (and only then). Thus, the assumption of Markovian behavior of the macroscopic variables is central to the emergence of macroscopic irreversibility. Moreover, as shown in Ref. [25], one also requires an assumption about initial conditions, namely that the irrelevant part of the probability density (see below) vanishes in the distant past. If we had made the same assumption for the future, we could have proven the unphysical statement that the entropy always decreases.

For this reason, projection operator methods have also attracted the attention of philosophers of physics who are interested in where, given the reversible microscopic physics, irreversibility comes from. Philosophers study projection operators due to the general insights they provide into the origin of irreversible transport equations. A matter of debate here is, roughly speaking, whether the fact that irreversible laws arise from coarse-graining methods, which are often justified by the disinterest in microscopic details, lead to some undesirable amount of subjectivity. After all, the fact that entropy always increases seems to be a physical matter of fact which is not related to our ignorance of microscopic details of a statistical-mechanical system. A recent philosophical discussion of this problem based on the Mori-Zwanzig projection operator method can be found in Ref. [40]. Moreover, it is discussed what precisely justifies the assumption of Markovian behavior. For a more detailed presentation of the debate in philosophy of physics, with an emphasis on how it relates to the one in statistical mechanics, see Ref. [41].

III. ADVANCED FORMS

Although the theory based on Eqs. (8, 9) is already a very powerful and, in principle, formally exact method, it has certain drawbacks. The most important one is that Eq. (12) is always a linear equation. As discussed in Ref. [12], the variables $A$ and $A^2$, although they are obviously related, are different variables in a Hilbert space of dynamical functions. Therefore, if we project onto $A$, the dependence on $A^2$ belongs to the orthogonal dynamics contained in memory and noise terms.

Nevertheless, most transport equations relevant for out-of-equilibrium systems, such as the Navier-Stokes equation, are nonlinear. These nonlinearities are very important for the dynamics of these systems, e.g., when studying pattern formation. Hence, it is a significant advantage if we are able to derive nonlinear equations. This is possible in two ways. One option is to project onto a larger set of relevant variables that also includes nonlinear functions of the $\{A_i\}$. This is the basic idea behind the derivation of Fokker-Planck equations within the Mori-Zwanzig formalism. The alternative, which we will present here, is to use time-dependent projection operators.

Another limitation of the standard method is that it is restricted to time-independent Hamiltonians. This is not the most general case, since time-dependent external fields can have an important influence on the microscopic structure and macroscopic dynamics of a system. Therefore, time-dependent Hamiltonians, discussed further below in Section 3.11, have become an active field of research in the context of Mori-Zwanzig theory, both for time-independent and time-dependent projection operators.

A. Relevant probability density

In the following, we focus on the time-dependent projection operator method presented in the classical textbook by Grabert [11]. It is a very general method applicable to nonlinear far-from-equilibrium dynamics, allows to describe also the dynamics of fluctuations, and has recently been extended to incorporate time-dependent Hamiltonians.

The time-dependent projection operator method is closely related to the usual methodology of statistical mechanics and extends it towards nonequilibrium systems. In statistical mechanics, the configuration of a many-particle system is described through a probability distribution $\rho$, which in classical mechanics is a function on phase space and in quantum mechanics a Hermitian operator ("density matrix"). For equilibrium systems, $\rho$ is constructed by optimizing a thermodynamic potential or the entropy. When choosing the microcanonical ensemble, the entropy, defined as $S = -k_B \text{Tr}(\rho \ln(\rho))$, is maximized with the constraint that the total energy of the system is fixed (or, more precisely, that the total energy is between $E$ and $E + \Delta E$ with $\Delta E/E \ll 1$).

In the information-theoretic approach to statistical mechanics, pioneered by E. T. Jaynes [42], this method of maximizing the entropy is given an epistemic justification: The probability distribution is introduced as a way incorporating what we know (and what we do not know) about the microscopic configuration of a system. It is, as he argues, rational to assign to all microscopic configurations that are, as far as we know, possible, the same probability. This is formalized by demanding that the probability distribution is chosen in such a way that
it maximizes the Shannon entropy
\[ \sigma = - \sum_i p_i \ln(p_i) \] (18)
with the probabilities \( p_i \) of the possible microscopic configurations. For example, if we consider a many-particle system about which we know nothing but the fact that it has total energy \( E \), particle number \( N \), and volume \( V \), then we can maximize the information entropy, i.e., a measure for how indifferent we are with respect to missing information, and arrive at the microcanoncal distribution. Likewise, if our macroscopic information is that we have an average energy \( E \), we recover, by the same procedure, the canonical distribution with the temperature \( T \) arising from the Lagrange multiplier fixing the average energy \( E \).

While this method thus gives the desired results for the equilibrium case, it can also be applied to nonequilibrium systems [28]. Assume that we have, like above, a set of available relevant variables \( \{ A_i \} \). Let their mean values be \( \{ a_i(t) \} \). These mean values are the macroscopic information we have about our system. Then, we choose our relevant probability density as [28]
\[ \bar{\rho}(t) = \frac{1}{Z(t)} e^{-\lambda_i(t)A_i} \] (19)
with the normalization \( Z(t) \) and the thermodynamic conjugates \( \{ \lambda_i(t) \} \). This density maximizes the information entropy with respect to the constraint that our macroscopic information is given by the mean values \( \{ a_i(t) \} \) of the relevant variables [16]. The normalization \( Z(t) \) ensures that
\[ \text{Tr}(\bar{\rho}(t)) = 1 \] (20)
and the thermodynamic conjugates \( \{ \lambda_j(t) \} \) are chosen in such a way that
\[ \text{Tr}(\bar{\rho}(t)A_i) = a_i(t), \] (21)
which is called the “macroequivalence condition”, stating that the relevant density gives the correct mean values for the relevant variables.

Although Eq. (19) is a standard choice, a relevant density can be any function of the mean values that satisfies Eqs. (20) and (21) [11]. It is helpful, in general, to choose the relevant density in such a way that it is a good approximation for the actual microscopic density, in particular if they coincide for \( t = 0 \).

### B. Time-dependent projection operators

For the time-dependent case, Grabert [11, 28] defines the projection operator by
\[ P(t)X = \text{Tr}(\bar{\rho}(t)X) + (A_j - a_j(t)) \text{Tr} \left( \frac{\partial \bar{\rho}(t)}{\partial a_j(t)} X \right). \] (22)
From this form of the projection operator, it is not immediately clear how it is related to the time-independent definition. It can be shown through a longer calculation (see Refs. [11, 28]) that the operator (22) contains the operator (3) as a limiting case and that it can be rewritten using a generalized scalar product. However, the general case can be more easily understood from the relevant-density point of view than from the scalar-product point of view.

We first make clear that \( P(t) \) defined by Eq. (22) is still a projection operator. It has the property
\[ P(t)P(t')X = P(t')X. \] (23)
This is a generalization of the usual projection operator property \( P^2X = PX \). (Note that the property (23) depends on the specific definition (22) of the projection operator and can be different for other definitions [13, 23].) Moreover, if we continue to think of the relevant variables \( \{ A_i \} \) as basis vectors in a Hilbert space of operators and add the identity to the set of relevant variables [11], then \( P(t)X \), thought of as an element of this Hilbert space, still points in a direction spanned by the relevant variables (including the identity, which gives the first term).

Now, we can use the more general projection operator (22) to derive the equations of motion for the relevant variables. For this purpose, we use instead of the Dyson identity (8) the more general identity [11]
\[ e^{Lt} = e^{iL}P(t) + \int_0^t ds e^{iL} \left( P(s)iQLQ(s) - \dot{P}(s) \right) G(s,t) + Q(0)G(0,t) \] (24)
with the orthogonal dynamics propagator
\[ G(s,t) = \exp_R \left( i \int_s^t dt' LQ(t') \right), \] (25)
where \( \exp_R(\cdot) \) denotes a right-time ordered exponential (see Section III). What might be confusing here is that the argument of the exponential is now \( LQ(t) \) rather than \( QL \) as in the time-independent case. The reason is that, for a time-independent projection operator, we have [12]
\[ QG(s,t) = Qe^{iLQ(t-s)} = Q \left( 1 + (t-s)QL + \frac{i^2}{2}(t-s)^2QQLQ + \cdots \right) = \left( Q + i(t-s)QL + \frac{i^2}{2}(t-s)^2QQLQ + \cdots \right) \] (26)
\[ = \left( 1 + i(t-s)QL + \frac{i^2}{2}(t-s)^2QQLQ + \cdots \right) Q = e^{iQL(t-s)}Q. \]
As we can see, if we compare this to Eq. (8), we have an additional operator \( Q \) at the end. For this reason, the identity (24) is applied to \( iLA \), while the identity (8) is applied to \( QQLA \).
Applying Eq. \((24)\) to \(i LA\) gives the equation of motion

\[
\dot{A}_i(t) = v_i(t) + \Omega_{ij}(t)\delta A_j(t) \nonumber + \int_0^t ds \left( K_{ij}(t, s) + \phi_{ij}(t, s)\delta A_j(s) \right) (27) 
+ F_i(t, 0),
\]

where we have introduced the organized drift

\[
v_i(t) = \text{Tr}(\bar{\rho}(t)i LA_i), (28) 
\]

the fluctuations \(\delta A_i(t) = A_i(t) - a_i(t)\), the collective frequencies

\[
\Omega_{ij}(t) = \text{Tr}\left( \frac{\partial \bar{\rho}(s)}{\partial a_j(t)} i LA_i \right), (29) 
\]

the after-effect functions

\[
K_{ij}(t, s) = \text{Tr}(\bar{\rho}(s)i LQ(s) G(s, t)i LA_i), (30) 
\]

the memory functions

\[
\phi_{ij}(t, s) = \text{Tr}\left( \frac{\partial \bar{\rho}(s)}{\partial a_j(s)} i LQ(s) G(s, t)i LA_i \right) - \dot{a}_k(s) \text{Tr}\left( \frac{\partial^2 \bar{\rho}(s)}{\partial a_j(s)\partial a_k(s)} G(s, t)i LA_i \right), (31) 
\]

and the random forces

\[
F_i(t, 0) = Q(0)G(0, t)i LA_i. (32) 
\]

In the more general formalism, we get separate equations of motion for the mean values and the fluctuations. From averaging Eq. \((27)\) we obtain \([11] \)

\[
\dot{a}_i(t) = v_i(t) + \int_0^t ds \, K_{ij}(s, t) + f_i(t) (33) 
\]

with the mean random force \(f_i(t) = \text{Tr}(\rho(0)F_i(t, 0))\). If we assume \(\rho(0) = \bar{\rho}(0)\), we have \(f_i(t) = 0\). Subtracting Eq. \((33)\) from Eq. \((27)\) gives for the fluctuations \([11]\)

\[
\delta \dot{A}_i(t) = \Omega_{ij}(t)\delta A_j(t) + \int_0^t ds \, \phi_{ij}(t, s)\delta A_j(s) \nonumber + \delta F_i(t, 0) (34) 
\]

with \(\delta F_i(t, 0) = F_i(t, 0) - f_i(t, 0)\).

Taking a look at Eqs. \((33)\) and \((34)\), we can notice that Eq. \((34)\), which describes the fluctuations, has a structure that is relatively similar to that of Eq. \((9)\), which we know from the time-independent case. The reason is that, for the fluctuations, we have written down a linear equation. In the close-to-equilibrium case, one can show that mean values and fluctuations follow similar equations of motion, such that Eq. \((9)\) can be recovered by adding them \([11, 13]\). Equation \((33)\), on the other hand, is a transport equation for the mean values of the observables/operators rather than for the operators themselves, as it was the case in Eq. \((9)\). For this reason, it is possible that the transport equations are nonlinear. Nonlinear equations do not always make sense for the microscopic observables, which are frequently defined microscopically as sums over delta functions. Moreover, the microscopic observables always follow a linear equation, namely the Liouville equation. No such restrictions hold, in general, for the mean values.

Of course, obtaining a transport equation for the mean values \(\{a_i(t)\}\) is also possible in the time-independent case by averaging over Eq. \((9)\). This transport equation will then be a linear equation, since the prefactors are time-independent and have no dependence on the macroscopic state determined by the \(\{a_i(t)\}\). Although it is always formally possible to apply the time-independent projection operator, it is therefore most useful if one is close to equilibrium, such that thermodynamic nonlinearities are not important \([13]\). The case of time-independent projection operators can be recovered from the time-dependent case, if one linearizes the relevant density in the thermodynamic conjugates, i.e., if one assumes deviations from equilibrium to be small \([11, 13]\).

C. Time-dependent Hamiltonians

An even more general case is one in which the Hamiltonian is time-dependent, which, in general, also leads to a time-dependent Liouvillian \([13]\). For time-independent projection operators, this case has been considered in Refs. \([22, 14, 17]\). Generalizations to time-dependent projection operators are derived in Refs. \([12, 34]\). We here present the method derived in Ref. \([13]\), which is applicable also to quantum systems.

This topic requires familiarity with time-ordered exponentials, which students will typically learn about in an advanced quantum mechanics or a quantum field theory course. However, when it comes to the Mori-Zwanzig formalism, certain subtleties become important that are typically ignored in the treatment of time-dependent Hamiltonians. The considerations relevant here thus can be a very valuable ingredient of a quantum mechanics course on time-dependent Hamiltonians, even if one is not interested in their use in statistical mechanics. Here, we explain how this can be done.

The starting point is, again, the Liouville equation

\[
\dot{A}(t) = i LH(t)A(t), (35) 
\]

where the Liouvillian is now time-dependent \([10]\). For \(t > 0\),

\[A(t) = \sum_b e^{\Omega_{ab}(t)} A_b(0) e^{-\Omega_{ab}(0)} \]

\[e^{\Omega_{ab}(t)} = \int_0^t ds \, e^{\Omega_{ab}(s)} \]

9 A more general equation is obtained by considering an initial time \(t = u\) rather than \(t = 0\). The physical significance of \(u\) is, in this case, that information about the history of the system from \(u\) onwards is taken into account \([23]\).

10 See below for a discussion of the subscript \(H\), which denotes the
we can integrate Eq. (35), giving
\[ A(t) = A_0 + i \int_0^t dt' L_H(t')A(t') \] (36)
with \( A_0 = A(0) \). This equation can be solved iteratively:
\[ A(t) = A_0 + \sum_{n=1}^{\infty} i^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} L_H(t_1) \cdots L_H(t_n)A_0 \]
\[ = \exp_L \left(i \int_0^t dt' L_H(t') \right) A_0, \] (37)
which defines the left-time-ordered exponential \( \exp_L(\cdot) \). In analogy, one can also define a right-time-ordered exponential \( \exp_R(\cdot) \), where later times are standing on the right.

When working with time-dependent Hamiltonians, it is important to distinguish between the Heisenberg picture and the Schrödinger picture of quantum mechanics. In the Schrödinger picture, the wave functions or statistical operators are time-dependent, while in the Heisenberg picture, the observables or operators are time-dependent. The operator \( A(t) \) in the Heisenberg picture is related to the corresponding Schrödinger-picture expression via
\[ A(t) = U(t)A(t)U(t) \] (39)
with the unitary time-evolution operator
\[ U(t) = \exp_L \left(-i \frac{\hbar}{\hbar} \int_0^t dt' H_S(t') \right), \] (40)
where \( H_S(t) \) denotes the Schrödinger-picture Hamiltonian. Since the Hamiltonian is time-dependent, the Hamiltonians at different points in time do not necessarily commute, such that there is a difference between the Schrödinger-picture Hamiltonian \( H_S(t) \) and the Heisenberg-picture Hamiltonian
\[ H_H(t) = U(t)H_S(t)U(t). \] (41)

As the Liouvillian is defined as the commutator with the Hamiltonian, one therefore needs to distinguish between a Heisenberg-picture Liouvillian \( L_H(t) \) and a Schrödinger-picture Liouvillian \( L_S(t) \), corresponding to the commutators with Schrödinger- and Heisenberg-picture Hamiltonians, respectively. Above, we have shown that in terms of Heisenberg-picture Liouvillians, the time evolution can be written as
\[ A(t) = \exp_L \left(i \int_0^t dt' L_H(t') \right) A_0. \] (42)
As is shown in Ref. [12], the time evolution can also be written as
\[ A(t) = \exp_R \left(i \int_0^t dt' L_S(t') \right) A_0. \] (43)

Remarkably, a right-time-ordered exponential of Schrödinger-picture Liouvillians is equivalent to a left-time-ordered exponential of Heisenberg-picture Liouvillians. A direct proof of this is sketched in Appendix [13]. For the right-time-ordered exponentials, one can prove the identity [13]
\[ \exp_R \left(i \int_0^t dt' L_S(t') \right) \]
\[ = \exp_R \left(i \int_0^t dt' L_S(t') \right) P(t) \]
\[ + \int_0^t ds \exp_R \left(i \int_0^s dt' L_S(t') \right) \]
\[ (P(s)iL_S(s)Q(s) - \dot{P}(s))G(s,t) \]
\[ + Q(0)G(0,t), \] (44)
which is a generalization of Eq. (24). Applying this to \( iL_S(t)A_0 \) again gives the general equation of motion (27).

**IV. APPLICATIONS**

In this section, we present two typical applications of the Mori-Zwanzig formalism to illustrate how it can be used. The Bloch equations are derived using a time-independent projection operator, while dynamical density functional theory is derived with a time-dependent projection operator.

**A. Spin relaxation and the Bloch equations**

The treatment of spin relaxation is a standard application of the Mori-Zwanzig formalism [13, 21, 22]. Here, we present a derivation that is a strongly simplified form of the one that can be found in Refs. [13, 21], which we will follow closely. Details on the spin algebra can be found in Ref. [13].

We consider \( N \) spins in a time-independent magnetic field \( \vec{B} = B_0\vec{e}_z \), where \( B_0 \) denotes the modulus of the Heisenberg picture.
field and \( \vec{e}_z = (0, 0, 1)^T \) its orientation. The system has a total spin \( \vec{S} \) given by the sum over the individual spin operators \( \{ \vec{S}_i \} \). We choose the relevant variables as

\[
\vec{A} = \begin{pmatrix}
S_+ \\
\Delta S_z \\
S_-
\end{pmatrix}
\]  

(45)

with \( \Delta S_z = S_z - \langle S \rangle_{\text{eq}} \) (the subscript eq denotes an equilibrium average) and the spin ladder operators \( S_\pm = S_x \pm i S_y \). Our Hamiltonian reads

\[
H = H_1 + H_{\text{sl}} - \gamma B_0 S_z.
\]  

(46)

\( H_1 \) describes lattice interactions commuting with the spin operator \( \vec{S} \), \( H_{\text{sl}} \) describes interactions of spin and lattice, and the last term accounts for the interaction with the magnetic field, where \( \gamma \) is the gyromagnetic ratio.

If we work in the high-temperature limit, the scalar product of two observables is the expectation value of the product of the two observables. In this case, we can easily calculate the normalization matrix

\[
\langle \vec{A} \vec{A}^\dagger \rangle_{\text{eq}} = \frac{1}{4} N \hbar^2 \begin{pmatrix}
2 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 2
\end{pmatrix}
\]  

(47)

and the frequency matrix

\[
\Omega = -i \gamma B_0 \begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & -1
\end{pmatrix}.
\]  

(48)

For the random force, we find

\[
\vec{F}(t) = e^{i Q L t} i Q L \vec{A} = e^{i Q L t} \frac{i}{\hbar} [H_{\text{sl}}, \vec{A}].
\]  

(49)

All that is left now is to calculate the memory matrix, the integral over which will – after a Markovian approximation – give the dissipative matrix. Due to the typical symmetries of the Hamiltonian, off-diagonal terms of the memory matrix vanish, leading to a decoupling of the equations for the three variables. We obtain, after some calculation, the memory-matrix diagonal elements

\[
K_{11}(t) = \frac{2}{N} \left\langle \frac{1}{\hbar^4} e^{i Q L t} [H_{\text{sl}}, S_+] \right\rangle_{\text{eq}} [S_-, H_{\text{sl}}],
\]  

(50)

\[
K_{22}(t) = \frac{4}{N} \left\langle \frac{1}{\hbar^4} e^{i Q L t} [H_{\text{sl}}, S_z] \right\rangle_{\text{eq}} [S_z, H_{\text{sl}}],
\]  

(51)

\[
K_{33}(t) = \frac{2}{N} \left\langle \frac{1}{\hbar^4} e^{i Q L t} [H_{\text{sl}}, S_-] \right\rangle_{\text{eq}} [S_+, H_{\text{sl}}].
\]  

(52)

Making the definitions

\[
\tau_1 = \int_0^{\infty} ds \ K_{22}(s),
\]  

(53)

\[
\tau_{2, +} = \int_0^{\infty} ds \ K_{11}(s),
\]  

(54)

we can, after a Markovian approximation and an averaging removing the random force, find the Bloch equations

\[
\dot{S}_z = -\frac{S_z - S_{z, \text{eq}}}{\tau_1},
\]  

(56)

\[
\dot{S}_\pm = \left( \mp \gamma B_0 - \tau_{2, \pm}^{-1} \right) S_\pm.
\]  

(57)

The terms \( \propto \gamma B_0 \) describe the precession in a magnetic field. Relaxation towards the equilibrium values is described by the terms \( \propto S_z/\tau_1 \) and \( \propto S_{\pm}/\tau_{2, \pm} \) with the relaxation times \( \tau_1 \) and \( \tau_{2, \pm} \).

B. Dynamical density functional theory

As an example for the application of the time-dependent projection operator technique, we use the derivation of classical dynamical density functional theory (DDFT) \[14, 15\]. DDFT is a theory for the time evolution of the one-body density \( n(\vec{r}) \) in a colloidal or atomic fluid which is based on a free-energy functional \( F(t) \). While the original derivations have started from Langevin \[48, 49\] or Smoluchowski \[50\] equations, projection operators have become an important tool in DDFT. In particular, since they can be applied to arbitrary variables, they can (and have been) used to derive extensions of DDFT towards additional variables, such as energy density \[17\], entropy density \[18\], and momentum density \[19\].

We suggest DDFT as an example for three reasons. First, it is relatively simple. Second, it is an extremely important theory in soft matter physics, such that students, in addition to learning about projection operators, also learn another method that is of more general importance. Third, DDFT is a good example of a rather general class of nonequilibrium theories known as “gradient dynamics theories” \[4, 5\], where the rate of change of a variable or set of variables is proportional to the gradient of the functional derivative of a free energy. Seeing the microscopic derivation of DDFT can thus further contribute to the general understanding of the microscopic origins of irreversible transport equations.

We follow closely the derivation by Español and Löwen presented in Ref. \[15\]. The considered system consists

\[11\] To make the presentation simpler, we have ignored one aspect that is discussed in Refs. \[14, 15\]. For a Markovian approximation to be allowed in the case of spin relaxation, one should first make a transformation to the rotating frame in order to remove fast precession effects, such that one can actually assume the variables to be slow.

\[12\] A difference in our presentation is that we use, for simplicity, the relevant density \[19\]. In Ref. \[15\], a more general density is used that, in addition, has a factor accounting for the equilibrium configuration.
of $N$ classical particles of mass $m$. As a relevant variable, we choose the number density:

$$
n(\vec{r},t) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i), \quad (58)
$$

where $\vec{r}_i$ is the position of the $i$-th particle. It deserves some comment, since it might not be clear to students, why we are able to derive a field theory for a variable $A(\vec{r},t)$ even though all our considerations were based on variables $\{A_i(t)\}$ that only depend on time. The basic idea is that a field $A(\vec{r},t)$ is an infinite number of variables indexed by the position $\vec{r}$. Thus, we can reuse all previous results for a set of variables $\{A_i\}$. Whenever we encounter a sum over the variables’ index, we have to perform an integral over $\vec{r}$, since this corresponds to a sum over all relevant variables. For the same reason, a time derivative $A_t$ becomes a partial time derivative $\partial A(\vec{r},t)/\partial t$, since $\vec{r}$ is essentially an index.

The mean value of $n(\vec{r})$ is

$$
n(\vec{r},t) = \text{Tr}(\hat{\rho}(t)n(\vec{r})), \quad (59)
$$

where the trace is now an integral over phase space. First, we need to calculate the microscopic current, which in the classical case is done using the Poisson bracket. We find

$$
iL n(\vec{r}) = \sum_{i=1}^{N} (\vec{\nabla}_{\vec{p}} H) \cdot (\vec{\nabla}_{\vec{r}_i} n(\vec{r})) = -\vec{\nabla} \cdot \vec{J}(\vec{r}) \quad (60)
$$

with the current

$$
\vec{J}(\vec{r}) = \sum_{i=1}^{N} \frac{\vec{p}_i}{m} \delta(\vec{r} - \vec{r}_i) \quad (61)
$$

and $\vec{p}_i$ being the momentum of the $i$-th particle.

Next, we calculate all terms in Eq. (58). We assume $\rho(0) = \hat{\rho}(0)$, which allows to drop the random force $f(t)$. The organized drift is

$$
\vec{v}(\vec{r},t) = -\vec{\nabla} \cdot \text{Tr}(\hat{\rho}(t)\vec{J}(\vec{r})) = 0. \quad (62)
$$

Here, the trace is a phase-space integral that, since the function $\vec{J}$ is odd in the momenta, vanishes. For the second term, we first use the fact that $-\hat{\rho}$ as is shown in Ref. [11] – the after-effect function [30] can be rewritten in the form

$$
K_i(t,s) = R_{ij}(t,s)\lambda_j(s), \quad (63)
$$

where the retardation matrix $R_{ij}(t,s)$ is, for classical systems, given by [12]

$$
R_{ij}(t,s) = \text{Tr}(\hat{\rho}(s)(G(s,t)Q(t)A_j(t)Q(s)iLA_j)). \quad (64)
$$

Inserting Eq. (63) into Eq. (58) and performing a Markovian approximation gives the equation of motion

$$
\dot{\lambda}_i(t) = v_i(t) + D_{ij}(t)\lambda_j(t) \quad (65)
$$

with the dissipative matrix [14]

$$
D_{ij}(t) = \int_0^\infty ds \text{Tr}(\hat{\rho}(t)(Q(t)iLA_j)e^{L_s}(Q(t)iLA_j)). \quad (66)
$$

The projected current is

$$
\bar{Q}(t)iL\dot{\lambda}(\vec{r}) = -\vec{\nabla} \cdot \vec{\bar{J}}(\vec{r}), \quad (67)
$$

which gives for the dissipative matrix the expression

$$
D(\vec{r},\vec{r}',t) = \vec{\nabla}_\vec{r} \cdot (\vec{\nabla}_{\vec{r}'} M(\vec{r},\vec{r}',t)) \quad (68)
$$

with the mobility

$$
M(\vec{r},\vec{r}',t) = \int_0^\infty ds \text{Tr}(\hat{\rho}(t))\vec{J}(\vec{r}') \otimes \vec{J}(\vec{r},s)), \quad (69)
$$

where $\otimes$ denotes a dyadic product. Assuming that the velocities $\{\vec{v}_i = \vec{p}_i/m\}$ of the individual particles are uncorrelated and that the positions vary slowly, this simplifies to [15]

$$
M(\vec{r},\vec{r}',t) = \int_0^\infty ds \text{Tr}(\hat{\rho}(s))\vec{J}(\vec{r}') \otimes \vec{J}(\vec{r},s)), \quad (69)
$$

Replacing in Eq. (69) the sum over $j$ by an integral over $\vec{r}'$, this gives

$$
\frac{\partial n(\vec{r},t)}{\partial t} = \int d^3r' \left( \vec{\nabla}_{\vec{r}'} \cdot (\vec{\nabla}_{\vec{r}'} M(\vec{r},\vec{r}',t)) \right) \lambda(\vec{r}',t)
$$

$$
= D_0 \vec{\nabla} \cdot \left( n(\vec{r},t) \int d^3r' \left( \vec{\nabla}_{\vec{r}'} \delta(\vec{r} - \vec{r}')) \lambda(\vec{r}',t) \right) \right)
$$

$$
= -D_0 \vec{\nabla} \cdot \left( n(\vec{r},t) \vec{\nabla} \lambda(\vec{r},t) \right). \quad (72)
$$

13 Although $\rho(\vec{r})$ is a more common notation for the number density than $n(\vec{r})$, we here use $n(\vec{r})$ in order to avoid confusion with the probability density.

14 The corresponding quantum-mechanical expression can be found in Refs. [11] [12]. It is slightly more complicated and not required here. The general structure remains the same.

15 In the Markovian approximation, one can replace $a_i(s)$ by $a_i(t)$, since variations of $a_i$ are of first order in $iLA_i$. The relevant value $\bar{\rho}(t)$ is a functional of the $\{a_i(t)\}$, such that we can also replace $\rho(t)$ by $\hat{\rho}(s)$ [11]. The same argument applies for the projection operators. Moreover, as in the case of time-independent projection operators, we replace $G(s,t)$ by $\exp(iL(t-s))$. Finally, we substitute $s \rightarrow t-s$ and switch integration boundaries.

16 Since we assume that the velocities vary quickly compared to the positions, we use $\bar{\rho}(t)$ for the expectation value of the positions and $\hat{\rho}(s)$ for the expectation value of the velocities.
where in the last step we have integrated by parts.

Finally, we can note that if we define a coarse-grained entropy as

\[ S = -k_B \text{Tr}(\tilde{\rho}(t) \ln(\tilde{\rho}(t))), \]

the thermodynamic conjugates \( \{ \lambda_i \} \) can be written as

\[ \lambda_i(t) = \frac{1}{k_B} \frac{\partial S}{\partial n_i(t)}. \]

For fields, the partial derivative becomes a functional derivative. Introducing a free energy \( F \) by the Legendre transformation

\[ F = U - TS \]

with the internal energy \( U \) and temperature \( T \), we can rewrite Eq. (72) as

\[ \frac{\partial n(\vec{r}, t)}{\partial t} = \beta D_0 \vec{V} \cdot \left( n(\vec{r}, t) \vec{V} \frac{\delta F}{\delta n(\vec{r}, t)} \right), \]

which is the traditional DDFT equation.

Since \( D_0 > 0 \), we can easily prove the H-theorem

\[ \frac{dF}{dt} = \int d^3 r \frac{\delta F}{\delta n(\vec{r}, t)} \frac{\partial n(\vec{r}, t)}{\partial t} = \int d^3 r \frac{\delta F}{\delta n(\vec{r}, t)} \beta D_0 \vec{V} \cdot \left( n(\vec{r}, t) \vec{V} \frac{\delta F}{\delta n(\vec{r}, t)} \right) \]

\[ = -\int d^3 r \beta D_0 n(\vec{r}, t) \left( \vec{V} \frac{\delta F}{\delta n(\vec{r}, t)} \right)^2 \leq 0. \]

We have thus – by virtue of restricting ourselves to one relevant variable and the approximation that this variable shows Markovian behavior – obtained an irreversible dissipative law, the DDFT equation, from the reversible Hamiltonian dynamics we started with. Moreover, the Mori-Zwanzig formalism provides a microscopic expression for the free energy.

The structure of Eq. (73), where the dynamics of the relevant variable is driven by the gradient of a thermodynamic conjugate, is a linear-response equation and a very general property of close-to-equilibrium systems. This can be shown with the Mori-Zwanzig formalism in a more general way [18]. General treatments also allow to show how generic features of nonequilibrium thermodynamics, such as irreversibility or the Onsager relations, arise from the microscopic physics in the Mori-Zwanzig formalism [11].

V. CONCLUSIONS

In this article, we have provided a compact introduction to the Mori-Zwanzig formalism, including both the standard, time-independent projection operator formalism and more advanced forms including time-dependent projection operators and time-dependent Hamiltonians. Particular attention has been paid on points that are, for someone who is new to the field, potentially difficult to understand, such as the relation between the scalar product and the relevant density approach. Relevant applications from the literature to spin relaxation and DDFT have also been presented.

We believe that the Mori-Zwanzig formalism, presented in this way, can form a valuable ingredient of basic and advanced courses in statistical mechanics and quantum mechanics. It is, in its simple forms, relatively easy to explain, and allows to introduce many important general ideas of theoretical physics, such as the origin and general structure of dissipative transport equations in statistical mechanics and the relation between Schrödinger picture and Heisenberg picture.

ACKNOWLEDGEMENTS

R.W. is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – WI 4170/3-1.

Appendix A: Proof of the Dyson identity

We here present the standard derivation of the Dyson identity [8], which can be found, e.g., in Ref. [22]. Consider the quantity

\[ W(t) = e^{-iLt} e^{iQLt} \]

and take the time derivative:

\[ \dot{W}(t) = -e^{-iLt} P_L e^{iQLt}. \]

Integrating this with respect to time from 0 to \( t \) gives

\[ W(t) = W(0) - \int_0^t ds e^{-iLs} P_L e^{iQLs}. \]

We use the initial condition \( W(0) = 1 \), insert Eq. (A1) into Eq. (A3), and multiply from the left by \( e^{iLt} \). This gives

\[ e^{iQLt} = e^{iLt} - \int_0^t ds e^{iLt(-s)} P_L e^{iQLs}, \]

which is the Dyson identity.

Appendix B: Relation between Heisenberg picture and Schrödinger picture

The identity [13]

\[ \exp_R \left( \int_0^t dt' iL_S(t') \right) = \exp_L \left( \int_0^t dt' iL_H(t') \right), \]

where
based on which a Mori-Zwanzig formalism for time-dependent Hamiltonians can be derived, can be proven in two ways. An indirect proof based on expectation values that is valid to all orders is given in Ref. [13]. Here, we sketch a different proof that is not written down there. It is more lengthy, but conceptually easier, since it is based on a direct calculation.

We show the derivation up to second order, which is the first nontrivial one. The Heisenberg-picture Hamiltonian reads

\[ H_B(t) = U^\dagger(t) H_S(t) U(t) \]

\[ = \exp \left( \frac{i}{\hbar} \int_0^t \text{d}t' H_S(t') \right) H_S(t) \]

\[ \exp_L \left( -\frac{i}{\hbar} \int_0^t \text{d}t' H_S(t') \right) \]  

(B2)

Up to second order, we can thus write

\[ H_B(t) = H_S(t) + \frac{i}{\hbar} \int_0^t \text{d}t' H_S(t') H_S(t) \]

\[ - \frac{i}{\hbar} \int_0^t \text{d}t' H_S(t) H_S(t') + \cdots \]  

(B3)

Using Eq. (B2), this gives for an arbitrary operator \( A \) the relation

\[ \exp_L \left( \int_0^t \text{d}t' i L_B(t') \right) A \]

\[ = \left( 1 + \int_0^t \text{d}t' i L_B(t') \right) \]

\[ + \int_0^t \text{d}t' \int_0^t \text{d}t'' i L_B(t') i L_B(t'') + \cdots \right) A \]

\[ = A + \frac{i}{\hbar} \int_0^t \text{d}t' \left[ H_B(t'), A \right] \]

\[ + \left( \frac{i}{\hbar} \right)^2 \int_0^t \text{d}t' \int_0^t \text{d}t'' \left[ H_B(t'), [H_B(t''), A] \right] + \cdots \]  

(B4)

The terms of second order in \( H_S \) can be rewritten as

\[ [H_S(t''), H_S(t'), A] - [H_S(t') H_S(t''), A] \]

\[ + [H_S(t'), [H_S(t''), A]] \]

\[ = H_S(t'') H_S(t') A + A H_S(t') H_S(t'') - H_S(t') A H_S(t'') \]

\[ - H_S(t'') H_S(t') A + H_S(t'') A H_S(t') \]

\[ = [H_S(t''), [H_S(t'), A]], \]

such that

\[ \exp_L \left( \int_0^t \text{d}t' i L_B(t') \right) A \]

\[ = A + \frac{i}{\hbar} \int_0^t \text{d}t' \left[ H_B(t'), A \right] \]

\[ + \left( \frac{i}{\hbar} \right)^2 \int_0^t \text{d}t' \int_0^t \text{d}t'' \left[ H_B(t'), [H_B(t''), A] \right] + \cdots \]  

(B6)

Since the operator \( A \) is arbitrary, we obtain from this Eq. (B4). We have thus shown, up to second order, that replacing the Heisenberg Liouvillian by the Schrödinger Liouvillian corresponds to switching from left time order to right time order.
[1] M. C. Marchetti, J. F. Joanny, S. Ramaswamy, T. B. Liverpool, J. Prost, M. Rao, and R. A. Simha, “Hydrodynamics of soft active matter,” Reviews of Modern Physics 85, 1143–1189 (2013).
[2] J. Uffink, “Issues in the foundations of classical statistical physics,” in Philosophy of Physics, Handbook of the Philosophy of Science, edited by J. Butterfield and J. Earman (Elsevier, Amsterdam, 2006) 1st ed.
[3] D. Forster, Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions, 1st ed., Frontiers in Physics, Vol. 47 (Addison Wesley, Redwood City, 1989).
[4] U. Thiele, A. J. Archer, and M. Flapp, “Thermodynamically consistent description of the hydrodynamics of free surfaces covered by insoluble surfactants of high concentration,” Physics of Fluids 24, 102107 (2012).
[5] U. Thiele, “Recent advances in and future challenges for mesoscopic hydrodynamic modelling of complex wetting,” Colloids and Surfaces A: Physicochemical and Engineering Aspects 553, 487–495 (2018).
[6] U. Thiele, T. Frohloff-Hülsmann, S. Engelkenkemper, E. Knobloch, and A. J. Archer, “First order phase transitions and the thermodynamic limit,” New Journal of Physics 21, 123021 (2019).
[7] R. Wittkowski, A. Tiribocchi, J. Stenhammar, R. J. Allen, D. Marenduzzo, and M. E. Cates, “Scalar φ⁴ field theory for active-particle phase separation,” Nature Communications 5, 4351 (2014).
[8] S. Nakajima, “On quantum theory of transport phenomena: steady diffusion,” Progress of Theoretical Physics 20, 948–959 (1958).
[9] R. Zwanzig, “Ensemble method in the theory of irreversibility,” Journal of Chemical Physics 33, 1338–1341 (1960).
[10] H. Mori, “Transport, collective motion, and Brownian motion,” Progress of Theoretical Physics 33, 423–455 (1965).
[11] H. Grabert, Projection Operator Techniques in Nonequilibrium Statistical Mechanics, 1st ed., Springer Tracts in Modern Physics, Vol. 95 (Springer, Berlin, 1982).
[12] R. Zwanzig, Nonequilibrium Statistical Mechanics, 3rd ed. (Oxford University Press, New York, 2001).
[13] M. te Vrugt and R. Wittkowski, “Mori-Zwanzig projection operator formalism for far-from-equilibrium systems with time-dependent Hamiltonians,” Physical Review E 99, 062118 (2019).
[14] A. Yoshimori, “Microscopic derivation of time-dependent density functional methods,” Physical Review E 71, 031203 (2005).
[15] P. Español and H. Löwen, “Derivation of dynamical density functional theory using the projection operator technique,” Journal of Chemical Physics 131, 244101 (2009).
[16] J. G. Anero, P. Español, and P. Tarazona, “Functional thermo-dynamics: a generalization of dynamic density functional theory to non-isothermal situations,” Journal of Chemical Physics 139, 034106 (2013).
[17] R. Wittkowski, H. Löwen, and H. R. Brand, “Extended dynamical density functional theory for colloidal mixtures with temperature gradients,” Journal of Chemical Physics 137, 224904 (2012).
[18] R. Wittkowski, H. Löwen, and H. R. Brand, “Microscopic approach to entropy production,” Journal of Physics A: Mathematical and Theoretical 46, 355003 (2013).
[19] D. Camargo, J. de la Torre, D. Duque-Zumajo, P. Español, R. Delgado-Buscalioni, and F. Chejne, “Nanoscale hydrodynamics near solids,” Journal of Chemical Physics 148, 064107 (2018).
[20] A. Liluashvili, J. Ónody, and T. Voigtmann, “Mode-coupling theory for active Brownian particles,” Physical Review E 96, 062608 (2017).
[21] D. Kivelson and K. Ogan, “Advances in magnetic resonance,” (Academic Press, New York, 1974) Chap. Spin relaxation theory in terms of Mori’s formalism, pp. 71–155, 1st ed.
[22] L. S. Bouchard, “Mori-Zwanzig equations with time-dependent Liouvillian,” preprint, arXiv:0709.1358v2 (2007).
[23] T. Koide, “Derivation of transport equations using the time-dependent projection operator method,” Progress of Theoretical Physics 107, 525–541 (2002).
[24] X. Huang, T. Kodama, T. Koide, and D. H. Rischke, “Bulk viscosity and relaxation time of causal dissipative relativistic fluid dynamics,” Physical Review C 83, 024906 (2011).
[25] H.-D. Zeh, The physical basis of the direction of time (Springer, Berlin, 1989).
[26] J. M. Dominy and D. Venturi, “Duality and conditional expectations in the Nakajima-Mori-Zwanzig formulation,” Journal of Mathematical Physics 58, 082701 (2017).
[27] K. Kawasaki and J. D. Gunton, “Theory of nonlinear transport processes: nonlinear shear viscosity and normal stress effects,” Physical Review A 8, 2048–2064 (1973).
[28] H. Grabert, “Nonlinear transport and dynamics of fluctuations,” Journal of Statistical Physics 19, 479–497 (1978).
[29] H. Meyer, T. Voigtmann, and T. Schilling, “On the non-stationary generalized Langevin equation,” Journal of Chemical Physics 147, 214110 (2017).
[30] H. Meyer, T. Voigtmann, and T. Schilling, “On the dynamics of reaction coordinates in classical, time-dependent, many-body processes,” Journal of Chemical Physics 150, 174118 (2019).
[31] R. Balian and M. Vénéroni, “Time-dependent variational principle for the expectation value of an observable: mean-field applications,” Annals of Physics 164, 334–410 (1985).
[32] B. Holian and D. J. Evans, “Classical response theory in the Heisenberg picture,” Journal of Chemical Physics 83, 3560–3566 (1985).
[33] R. Frigg, “A field guide to recent work on the foundations of statistical mechanics,” in The Ashgate Companion to Contemporary Philosophy of Physics, edited by D. Rickles (Ashgate, Aldershot, 2008) pp. 99–196.
[34] J.-P. Hansen and I. R. McDonald, Theory of Simple Liquids: with Applications to Soft Matter, 4th ed. (Elsevier Academic Press, Oxford, 2009).
[35] H. Grabert, P. Talkner, and P. Hänggi, “Microdynamics and time-evolution of macroscopic non-Markovian systems,” Zeitschrift für Physik B Condensed Matter 26, 389–395 (1977).
[36] H. Meyer, P. Pelagejev, and T. Schilling, “Non-
Markovian out-of-equilibrium dynamics: a general numerical procedure to construct time-dependent memory kernels for coarse-grained observables,” preprint, arXiv:1905.11753 (2019).

[37] A. J. Chorin, O. H. Hald, and R. Kupferman, “Optimal prediction with memory,” Physica D: Nonlinear Phenomena 166, 239–257 (2002).

[38] D. Wallace, “The arrow of time in physics,” in A Companion to the Philosophy of Time, edited by H. Dyke and A. Bardon (John Wiley & Sons, Chichester, 2013) Chap. 16, pp. 262–281.

[39] D. Wallace, “The quantitative content of statistical mechanics,” Studies in History and Philosophy of Modern Physics 52, 285–293 (2015).

[40] K. Robertson, “Asymmetry, abstraction, and autonomy: justifying coarse-graining in statistical mechanics,” British Journal for the Philosophy of Science 69, axy020 (2018).

[41] M. te Vrugt, “The five problems of irreversibility,” in preparation (2020).

[42] E. T. Jaynes, “Information theory and statistical mechanics,” Physical Review 106, 620–630 (1975).

[43] E. T. Jaynes, “Information theory and statistical mechanics. II,” Physical Review 108, 171–190 (1955).

[44] S. Nordholm and R. Zwanzig, “A systematic derivation of exact generalized Brownian motion theory,” Journal of Statistical Physics 13, 347–371 (1975).

[45] F. Shibata, Y. Takahashi, and N. Hashitsume, “A generalized stochastic Liouville equation. Non-Markovian versus memoryless master equations,” Journal of Statistical Physics 17, 171–187 (1977).

[46] T. Koide and M. Maruyama, “A new expansion of the Heisenberg equation of motion with projection operator,” Progress of Theoretical Physics 104, 575–594 (2000).

[47] C. Uchiyama and F. Shibata, “Unified projection operator formalism in nonequilibrium statistical mechanics,” Physical Review E 60, 2636–2650 (1999).

[48] U. Marini Bettolo Marconi and P. Tarazona, “Dynamic density functional theory of fluids,” Journal of Chemical Physics 110, 8032–8044 (1999).

[49] U. Marini Bettolo Marconi and P. Tarazona, “Dynamic density functional theory of fluids,” Journal of Physics: Condensed Matter 12, 413–418 (2000).

[50] A. J. Archer and R. Evans, “Dynamical density functional theory and its application to spinodal decomposition,” Journal of Chemical Physics 121, 4246–4254 (2004).