

Dynamic correlations in Brownian many-body systems

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For classical Brownian systems driven out of equilibrium, we derive inhomogeneous two-time correlation functions from functional differentiation of the one-body density and current with respect to external fields. In order to allow for appropriate freedom upon building the derivatives, we formally supplement the Smoluchowski dynamics by a source term, which vanishes at the physical solution. These techniques are applied to obtain a complete set of dynamic Ornstein-Zernike equations, which serve for the development of approximation schemes. The rules of functional calculus lead naturally to non-Markovian equations of motion for the two-time correlators. Memory functions are identified as functional derivatives of a unique space- and time-nonlocal dissipation power functional.

I. INTRODUCTION

In a standard procedure of equilibrium Statistical Mechanics, one generates static correlation functions of interacting many-body systems by functional differentiation. For example, differentiating the position-dependent average one-body density distribution, $\rho(\mathbf{r})$, with respect to an external potential field, $V_{\text{ext}}(\mathbf{r})$, yields the autocorrelation function of density fluctuations,¹

$$-\frac{\delta\rho(\mathbf{r}_1)}{\delta\beta V_{\text{ext}}(\mathbf{r}_2)} = \langle \hat{\rho}(\mathbf{r}_1)\hat{\rho}(\mathbf{r}_2) \rangle - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2), \quad (1)$$

where $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$ is the classical density operator, $\delta(\cdot)$ is the Dirac distribution, $\beta = 1/(k_B T)$, where k_B is the Boltzmann constant, T is absolute temperature, and the angular brackets denote an average over an appropriate statistical ensemble. Proving the equality (1) is straightforward, but requires as input the explicit form of the equilibrium (Boltzmann-Gibbs) probability distribution function in the grand canonical ensemble.

The situation for calculating *dynamic* two-body correlation functions is quite different; there is presently no standard method for identifying, in the spirit of (1), time-dependent microscopic correlation functions, such as the van Hove function,^{2,3} with functional derivatives of average quantities. In contrast to the static case, calculating dynamic correlations not only requires knowledge of the many-body probability distribution at a given time, but requires also the transition (conditional) probability between two states of the system at different times. The transition probability encodes the specific microscopic dynamics under consideration and is closely related to the propagator, which generates the time evolution of the distribution function. In a very recent publication,⁴ we have exploited this connection in order to obtain two-time correlations from functional derivatives of the one-body fields, focusing on the special case of many-body Brownian dynam-

ics and constructing a special external field for building the derivative.

A general rigorous identification of microscopic time-correlation functions with corresponding functional derivatives would have far-reaching consequences. In particular, such an identification would be essential when seeking to unify theories formulated on the one-body level, such as classical dynamical density functional theory (DDFT),¹ with the numerous approaches that aim to treat the dynamics of the two-time dynamical correlation functions, such as mode-coupling theory (MCT).⁵ In treating a dynamical problem, one often has access to an equation of motion for the time evolution of a given one-body average, such as the density or the current. While in very rare cases this may be exact, one is usually faced with an approximate expression. However, in both cases, differentiation of the one-body expression with respect to an external, time-dependent field constitutes a method to generate an equation of motion for the inhomogeneous two-time correlations. Here it is crucial that the functional derivatives involved have been identified with well-defined microscopic correlation functions. Clearly, if the one-body "parent" equation of motion is approximate in nature, then the derived "descendant" equation provides the dynamics of the two-time correlations on a similar level of description. If the parent equation is exact, then so too is the equation for the two-body correlations. The approach is general; higher-order members of a complete hierarchy are obtained by further differentiation.

The above strategy has been successfully applied to obtain a nonequilibrium Ornstein-Zernike (NOZ) equation for overdamped Brownian systems.⁴ The static Ornstein-Zernike (OZ) relation,³ utterly familiar from equilibrium liquid-state theory, is hence generalized to arbitrary dynamical situations, including bulk dynamics in equilibrium as a non-trivial special case. The NOZ equation is nonlocal in spacetime and incorporates memory functions, which play a role for the dynamics analogous to that of the equilibrium direct correlation function for the static structure. An unexpected and remarkable result is that the non-Markovian structure of the

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mode-coupling equation of motion for the bulk intermediate scattering function⁵ is recovered in a natural way, purely as a consequence of applying the rules of functional calculus. Furthermore, the present approach sheds light on the test-particle approach of Archer *et al.*⁶ It thus appears that the method of dynamical functional differentiation provides a powerful tool for generating new dynamical theories self-consistent on the one- and two-body level, as well as for extending existing theories of the one-body functions (such as DDFT) to the two-body level.

The restricted set of two-body correlation functions described in Ref. 4 were obtained by functional differentiation of the (Smoluchowski) propagator with respect to the special choice of one-body field,

$$\mathcal{V}(\mathbf{r}, t) \equiv \int_{t_0}^t dt' D_0 \nabla^2 V_{\text{ext}}(\mathbf{r}, t'), \quad (2)$$

where $V_{\text{ext}}(\mathbf{r}, t)$ is the (time-dependent) external potential, D_0 is the bare diffusion coefficient and t_0 is an initial time. Equation (2) amounts to the application of the diffusion operator to the external potential, which is necessary in order to “co-evolve” the external potential along the physical dynamics of the system. The choice to employ the field (2) was motivated by the desire to obtain the most direct mathematical route to the NOZ equation, but sacrificed the full generality of the approach.

In the present paper, we address the general case by differentiating with respect to the bare external fields, i.e., a non-conservative force field $\mathbf{X}(\mathbf{r}, t)$ and the temporal rate of change of an external potential, $\dot{V}_{\text{ext}}(\mathbf{r}, t)$ (which is in time-dependent situations a more natural quantity than the external potential itself). A key concept required for these calculations is that of a “sourced dynamics,” which can formally differ from the (Smoluchowski) dynamics of the physical system. The sourced dynamics is defined by a non-standard, many-body time evolution operator on configuration space which is not constrained by the many-body continuity equation. Physically meaningful two-point correlation functions are generated from functional differentiation of the sourced dynamics propagator, and imposing the continuity equation *a posteriori*. Following this procedure, we generate a complete set of dynamic correlation functions, the most important of which is the tensorial two-body current, auto-correlating the microscopic particle current at two different points in spacetime. Using the two-body current, we derive the most general NOZ equation for Brownian dynamics.

The paper is organized as follows. In Secs. II A–II C, we define the relevant correlation functions and specify the microscopic dynamics of interest. In Sec. II D, we give a detailed description of how two-time correlation functions are obtained as averages over configuration space. The sourced dynamics introduced in Sec. II E is used in Sec. II F to obtain two-time correlations, which are then (Sec. II G) interpreted physically as response functions. We next apply our strategy to develop NOZ equations for the two-time correlations, applying first an adiabatic approximation (Sec. II H), before proceeding to develop an exact superadiabatic expression involving “time-direct correlation functions,” which are memory functions that account for structural relaxation

(Sec. II I). In Sec. II J, we show that within the recently developed power functional theory,⁷ the time-direct correlation functions can be identified as functional derivatives of an excess (over ideal gas) power dissipation functional. A significant implication is that by approximating a single generating functional one can construct a consistent, non-adiabatic theory for both the one- and two-body nonequilibrium correlations. In Sec. III, we give concluding remarks and an outlook on future work.

II. THEORY

A. One-body correlations

For a classical many-body system subject to arbitrary microscopic dynamics, the one-body density and one-body current are described by the operators

$$\hat{\rho}(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (3)$$

$$\hat{\mathbf{J}}(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \hat{\mathbf{v}}_i(t), \quad (4)$$

respectively, where $\hat{\mathbf{v}}_i(t)$ is the time-dependent velocity of particle i and the sum runs over all particles, $i = 1, \dots, N$. The mathematical character of the velocity appearing in (4) depends upon whether one adopts a trajectory based (Newtonian or Langevin) picture of the dynamics, or a probabilistic phase space (Liouville or Smoluchowski) picture. In the case of the probabilistic interpretation of overdamped Langevin dynamics, which we will adopt henceforth, the particle velocity is a differential operator on configuration space.

The local conservation of particle number is expressed by the one-body continuity equation

$$\frac{\partial}{\partial t_1} \rho(1) = -\nabla_1 \cdot \mathbf{J}(1), \quad (5)$$

where the average density and current are given by $\rho(1) = \langle \hat{\rho}(1) \rangle$ and $\mathbf{J}(1) = \langle \hat{\mathbf{J}}(1) \rangle$, respectively. Here the angular brackets indicate a statistical average with respect to the appropriate distribution function, as specified below. We have introduced for brevity the shorthand notation $\hat{\rho}(1) \equiv \hat{\rho}(\mathbf{r}_1, t_1)$, and $\hat{\mathbf{J}}(1) \equiv \hat{\mathbf{J}}(\mathbf{r}_1, t_1)$ for spacetime points, and ∇_1 indicates the derivative with respect to \mathbf{r}_1 . The average one-body velocity is simply $\mathbf{v}(1) = \mathbf{J}(1)/\rho(1)$.

B. Two-body correlations

The most commonly studied dynamical two-body correlation function is the density-density correlation function introduced by van Hove.^{2,3} For spatially and temporally inhomogeneous situations, the van Hove function is defined as

$$G_{\text{vH}}(1, 2) = \rho(1)^{-1} \langle \hat{\rho}(1) \hat{\rho}(2) \rangle, \quad (6)$$

where the angular brackets indicate an appropriately defined (see below) two-time average over the nonequilibrium system, which evolves from the state at the earlier time t_2 to the later time t_1 .

While the van Hove function is very useful for characterizing relaxation to equilibrium, in general, as a scalar function

it does not provide a complete picture of the particle dynamics. Additional information is provided by the nonequilibrium two-body functions

$$\mathbf{J}_{\text{vH}}^{\text{f}}(1, 2) = \langle \hat{\mathbf{J}}(1) \hat{\rho}(2) \rangle, \quad (7)$$

$$\mathbf{J}_{\text{vH}}^{\text{b}}(1, 2) = \langle \hat{\rho}(1) \hat{\mathbf{J}}(2) \rangle, \quad (8)$$

which we will henceforth refer to as the front⁴ and back van Hove current, respectively, and we adopt the causality convention $t_1 \geq t_2$. The two correlation functions are not equivalent in general, because the particle current is a differential operator. Note further that the van Hove currents are particularly important for describing the dynamics in driven systems, such as, e.g., in the presence of a time-dependent external potential or non-conservative shear forces.

The analogue of (5) on the two-body level is constituted by two distinct continuity equations

$$\frac{\partial}{\partial t_1} \rho(1) G_{\text{vH}}(1, 2) = -\nabla_1 \cdot \mathbf{J}_{\text{vH}}^{\text{f}}(1, 2), \quad (9)$$

$$\frac{\partial}{\partial t_2} \rho(1) G_{\text{vH}}(1, 2) = -\nabla_2 \cdot \mathbf{J}_{\text{vH}}^{\text{b}}(1, 2), \quad (10)$$

which relate each vectorial van Hove current to the scalar van Hove function.

The most fundamental dynamic pair function, however, is the two-body current

$$\mathbf{J}_2(1, 2) = \langle \hat{\mathbf{J}}(1) \hat{\mathbf{J}}(2) \rangle. \quad (11)$$

This current-current correlation function is a second-rank tensor obtained by averaging the dyadic product of two one-body current operators. As we shall demonstrate below in Sec. II F, this tensorial correlation function can be related to a functional derivative of the current with respect to the nonconservative external force. Moreover, we will show that both the front and back van Hove currents, as well as the van Hove function, can be identified with functional derivatives.

From the two-body current the front and back van Hove currents can be determined, according to the continuity equations

$$\frac{\partial}{\partial t_1} \mathbf{J}_{\text{vH}}^{\text{b}}(1, 2) = -\nabla_1 \cdot \mathbf{J}_2(1, 2), \quad (12)$$

$$\frac{\partial}{\partial t_2} \mathbf{J}_{\text{vH}}^{\text{f}}(1, 2) = -\nabla_2 \cdot \mathbf{J}_2(1, 2). \quad (13)$$

The two-body current is thus fundamental for studying the dynamics of liquids, as all pair correlations of lower tensorial rank, namely (6)–(8), can be obtained by building the appropriate divergence in space and integrating in time. We demonstrate below (see Secs. II H and II I) that focusing on the two-body current enables the formulation of a general NOZ theory of the dynamic pair correlations.

C. Microscopic dynamics

We next specify the microscopic dynamics with which we will be concerned for the remainder of the paper. The state of the system is described by a time-dependent distribution function, $\Psi(\mathbf{r}^N, t)$, which gives the probability density to find

the N particles in the system at positions $\mathbf{r}^N \equiv \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ at time t . The total interparticle interaction potential is $U(\mathbf{r}^N)$ and the particles interact with their surrounding via an external potential $V_{\text{ext}}(\mathbf{r}, t)$ and via a non-conservative force field $\mathbf{X}(\mathbf{r}, t)$. We consider Brownian particles which undergo stochastic motion and are subject to a velocity-dependent friction force with force constant γ . The overdamped dynamics can be described via the continuity equation for the many-body distribution function,

$$\frac{\partial}{\partial t} \Psi(\mathbf{r}^N, t) = - \sum_i \nabla_i \cdot \hat{\mathbf{v}}_i(t) \Psi(\mathbf{r}^N, t), \quad (14)$$

where the velocity operator of particle i is defined as

$$\hat{\mathbf{v}}_i(t) = \gamma^{-1} [-(\nabla_i U(\mathbf{r}^N)) - k_{\text{B}} T \nabla_i - (\nabla_i V_{\text{ext}}(\mathbf{r}_i, t)) + \mathbf{X}(\mathbf{r}_i, t)]. \quad (15)$$

Here only the thermal term constitutes a differential operator; the two bracketed gradients each yield a vector-valued function, which then acts via multiplication only. Physically, the action of $\hat{\mathbf{v}}_i(t)$ on the distribution, $\Psi(\mathbf{r}^N, t)$, generates the noise averaged velocity of particle i .

Introducing the Smoluchowski operator,⁸ which is defined as

$$\hat{\Omega}(\mathbf{r}^N, t) = - \sum_i \nabla_i \cdot \hat{\mathbf{v}}_i(\mathbf{r}^N, t) \quad (16)$$

allows to write the Smoluchowski equation (14) in the alternative form

$$\frac{\partial}{\partial t} \Psi(\mathbf{r}^N, t) = \hat{\Omega}(\mathbf{r}^N, t) \Psi(\mathbf{r}^N, t). \quad (17)$$

The significant benefit of the rewriting is that a formal solution can be expressed as

$$\Psi(\mathbf{r}^N, t) = e_+^{\int_{t_0}^t ds \hat{\Omega}(\mathbf{r}^N, s)} \Psi(\mathbf{r}^N, t_0), \quad (18)$$

where e_+ indicates the time-ordered exponential operator,^{9,10} which acts on all functions to the right, and t_0 is an initial time, at which the many-body distribution is assumed to be known. The one-time average of an operator $\hat{f}(\mathbf{r}^N, t)$ on configuration space is thus given by

$$f(t) = \int d\mathbf{r}^N \hat{f}(\mathbf{r}^N, t) \Psi(\mathbf{r}^N, t), \quad (19)$$

$$= \int d\mathbf{r}^N \hat{f}(\mathbf{r}^N, t) e_+^{\int_{t_0}^t ds \hat{\Omega}(\mathbf{r}^N, s)} \Psi(\mathbf{r}^N, t_0), \quad (20)$$

where (20) follows from substitution of (18). Here and in the following, we have suppressed in the notation the possible dependence of a (dummy) operator $\hat{f}(\mathbf{r}^N, t)$ on further arguments, such as on position \mathbf{r} .

D. Two-time averages

We first recall that the correlation between two physical quantities, as represented by their corresponding operators \hat{f}

and \hat{g} on configuration space, is defined according to

$$C_{fg}(t, t') = \int d\mathbf{r}^N \int d\mathbf{r}'^N \hat{f}(\mathbf{r}^N, t) \hat{g}(\mathbf{r}'^N, t') \Psi_2(\mathbf{r}^N, t; \mathbf{r}'^N, t'), \quad (21)$$

where $\Psi_2(\mathbf{r}^N, t; \mathbf{r}'^N, t')$ is the joint probability to find configuration \mathbf{r}^N at time t and configuration \mathbf{r}'^N at time t' . Introducing the conditional (transition) probability $w(\mathbf{r}^N, t | \mathbf{r}'^N, t')$ to find the system in the unprimed state, given that it was in the primed state at the earlier time t' , the joint probability can be alternatively expressed as the product

$$\Psi_2(\mathbf{r}^N, t; \mathbf{r}'^N, t') = w(\mathbf{r}^N, t | \mathbf{r}'^N, t') \Psi(\mathbf{r}'^N, t'), \quad (22)$$

where $\Psi(\mathbf{r}'^N, t')$ is, as before, the instantaneous many-body distribution function. Note that for the case that the system was in equilibrium at the earlier time t' , such that $\Psi(\mathbf{r}'^N, t') = \Psi_{\text{eq}}(\mathbf{r}'^N)$, it is only via the transition probability that the specific details of microscopic dynamics (whether, e.g., Newtonian or Brownian) enter the expression (21) for the two-point correlator.

For many-body Brownian dynamics the transition probability evolves in time according to the (forward) time evolution equation¹¹

$$\frac{\partial}{\partial t} w(\mathbf{r}^N, t | \mathbf{r}'^N, t') = \hat{\Omega}(\mathbf{r}^N, t) w(\mathbf{r}^N, t | \mathbf{r}'^N, t'), \quad (23)$$

which is formally analogous to the equation of motion (17) for the distribution function. The formal solution of (23), subject to the initial condition $w(\mathbf{r}^N, t' | \mathbf{r}'^N, t') = \delta(\mathbf{r}^N - \mathbf{r}'^N)$, is given by

$$w(\mathbf{r}^N, t | \mathbf{r}'^N, t') = e_{+}^{\int_{t'}^t ds \hat{\Omega}(\mathbf{r}^N, s)} \delta(\mathbf{r}^N - \mathbf{r}'^N). \quad (24)$$

Inserting this expression into (22) allows to rewrite (21), upon carrying out the integral over the primed coordinates, as

$$C_{fg}(t, t') = \int d\mathbf{r}^N \hat{f}(\mathbf{r}^N, t) e_{+}^{\int_{t'}^t ds \hat{\Omega}(\mathbf{r}^N, s)} \hat{g}(\mathbf{r}^N, t') \Psi(\mathbf{r}^N, t'). \quad (25)$$

The benefits of the propagator form (25) over the bare definition (21) are that only a single integral over configuration space appears and that only the one-state distribution Ψ is required, rather than Ψ_2 . The complexity of the correlator is hence condensed into the propagator. This offers the advantage that all forces appear explicitly, cf. the definition (16). The structure of Eq. (25) can hence be exploited⁴ to calculate dynamical functional derivatives. In the following, we seek to develop a general method by which the inhomogeneous two-time functions (6)–(8) and (11) can be connected, by means of time-dependent functional differentiation (as laid out in Sec. II F), to the one-body level of description provided by the density, $\rho(1)$, and current, $\mathbf{J}(1)$.

Our approach to connecting one- and two-time correlators is based on the fact that taking a functional derivative of (20) with respect to an external field appearing in the propagator (i.e., the time-ordered exponential) can generate expressions with the same form as the right-hand side of (25). For particular choices of \hat{f} and \hat{g} and of external field, we can thus generate mathematical relations between physically meaningful one- and two-body correlators. Remarkably, within this approach the many-body Smoluchowski propagator, which was solely introduced to evolve the distribution function in

time, cf. (17), acts as a dynamical analogue of the Boltzmann factor for static properties in equilibrium.

Previous work focused on derivatives with respect to the special choice of external field (2) and did not reveal the full generality of dynamical functional differentiation. In the following, we present the complete picture and develop a general method for obtaining inhomogeneous two-time correlations from the one-body functions. This however requires modifying the underlying many-body dynamics.

E. Generalized many-body sourced dynamics

Here we construct a formal and more general time evolution operator, which retains the physical Smoluchowski dynamics (18) as a special case. As a motivation, we first rewrite (16) as

$$\hat{\Omega}(t) = \frac{\beta\gamma}{2} \sum_i (\hat{v}_i(t)^2 - \hat{v}_i^\dagger(t) \cdot \hat{v}_i(t)), \quad (26)$$

where for arbitrary functions, a and b , on configuration space the adjoint velocity operator $\hat{v}_i^\dagger(t)$ obeys

$$\int d\mathbf{r}^N a(\mathbf{r}^N) \hat{v}_i(t) b(\mathbf{r}^N) = \int d\mathbf{r}^N b(\mathbf{r}^N) \hat{v}_i^\dagger(t) a(\mathbf{r}^N). \quad (27)$$

As an aside, integration by parts yields the identity

$$\hat{v}_i^\dagger(t) = \hat{v}_i(t) + 2D_0 \nabla_i, \quad (28)$$

where $D_0 = k_B T / \gamma$ is the bare diffusion coefficient. Recognizing the self-adjoint nature of the second contribution in (26), we combine this together with external contributions into a source operator, defined as

$$\hat{S}(t) = \beta \sum_i \left(\frac{\gamma}{2} \hat{v}_i^\dagger(t) \cdot \hat{v}_i(t) - \dot{V}_{\text{ext}}(\mathbf{r}_i, t) + \alpha(\mathbf{r}_i, t) \right) + \lambda(\mathbf{r}^N, t), \quad (29)$$

where $\dot{V}_{\text{ext}}(\mathbf{r}, t)$ indicates the (partial) time derivative of the external potential, $\alpha(\mathbf{r}, t)$ is a scalar field of space and time, which represents a local one-body thermostat that either adds or removes power from the system, and $\lambda(\mathbf{r}^N, t)$ is an external many-body probability source field that is used below to restore the local particle conservation. Adding the source to the Smoluchowski operator, we arrive at a time evolution operator defined by

$$\begin{aligned} \hat{\Omega}_{\text{src}}(t) &= \hat{\Omega}(t) + \hat{S}(t) \\ &= \beta \sum_i \left(\frac{\gamma}{2} \hat{v}_i(t)^2 - \dot{V}_{\text{ext}}(\mathbf{r}_i, t) + \alpha(\mathbf{r}_i, t) \right) + \lambda(\mathbf{r}^N, t), \end{aligned} \quad (30)$$

which is free from the constraint of local particle number conservation. This constraint can easily be reinstated by requiring the source contribution to vanish, and hence the probability source field $\lambda(\mathbf{r}^N, t)$ to satisfy

$$\hat{S}(t) \psi(\mathbf{r}^N, t) = 0, \quad (31)$$

in which case the Smoluchowski and the sourced evolution operators become identical, $\hat{\Omega} = \hat{\Omega}_{\text{src}}$.

On the basis of (30), an alternative to (18) is a propagator that acts according to

$$\Psi(\mathbf{r}^N, t) = e_+^{\int_{t_0}^t ds \hat{\Omega}_{\text{src}}(s)} \Psi(\mathbf{r}^N, t_0). \quad (32)$$

Since the Smoluchowski equation (14) is simply the many-body continuity equation, integration of its formal solution, i.e., of the right-hand side of (18), over all particle coordinates yields unity for all times. This expresses the fact that the many-body distribution function is normalized at all times. However, the configurational integral over the right-hand side of (32) is in general, i.e., when $\lambda(\mathbf{r}^N, t)$ is prescribed such that (31) is not satisfied, not constant unity, but rather a function of time. We define the negative of this quantity as

$$\mathcal{R}(t) = - \int d\mathbf{r}^N e_+^{\int_{t_0}^t ds \hat{\Omega}_{\text{src}}(s)} \Psi(\mathbf{r}^N, t_0), \quad (33)$$

which carries an implicit functional dependence on the external fields $\alpha(\mathbf{r}, t)$ and $\hat{V}_{\text{ext}}(\mathbf{r}, t)$, as well as, via (15), on $V_{\text{ext}}(\mathbf{r}, t)$ and $\mathbf{X}(\mathbf{r}, t)$. As we show in the following, the functional (33) plays the role of a generator, in the sense that taking functional derivatives with respect to the external fields, followed by restoration of the physical Smoluchowski dynamics via (31), creates one-body averages of interest.

In order to illustrate the sourced dynamics further, we write (32) in differential form,

$$\frac{\partial}{\partial t} \Psi(\mathbf{r}^N, t) = (\hat{\Omega}(t) + \hat{S}(t)) \Psi(\mathbf{r}^N, t), \quad (34)$$

where the $\hat{S}(t)$ is given by (29). Equation (34) makes explicit that, in general, the continuity equation is violated by the introduction of the additional source term into the Smoluchowski equation of motion (14). Only for the case when the source term vanishes, we recover the physical dynamics. When expressed in the form (34) the modified dynamics becomes analogous to the Lindblad form of the quantum mechanical master equation, which describes the non-unitary time evolution of a reduced density matrix. In a quantum mechanical context, the appearance of source contributions in the time evolution equation represents interaction with the unresolved degrees of freedom which constitute the environment in which the system is embedded. In the present context, the use of the source term allows to enforce the many-body continuity equation, while allowing the necessary freedom from this constraint upon the ‘‘virtual’’ changes that are represented by the functional derivatives.

F. Dynamic functional derivatives

In order to perform dynamical functional differentiation, we use the chain rule for time-ordered exponentials, which in the form of a general operator identity reads

$$\frac{\delta}{\delta u(\mathbf{r}, t)} e_+^{\int_{t_1}^{t_2} ds \hat{O}(s)} = \int_{t_1}^{t_2} ds e_+^{\int_s^{t_2} ds' \hat{O}(s')} \frac{\delta \hat{O}(s)}{\delta u(\mathbf{r}, t)} e_+^{\int_{t_1}^s ds' \hat{O}(s')}, \quad (35)$$

where $\hat{O}(s)$ is a time-dependent operator with a functional dependence upon a field $u(\mathbf{r}, t)$. Using that for time-dependent fields $\delta u(\mathbf{r}, t) / \delta u(\mathbf{r}', t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t')$, and that further-

more one can obtain straightforwardly,

$$\frac{\delta \hat{\Omega}_{\text{src}}(s)}{\delta \beta \mathbf{X}(\mathbf{r}, t)} = \hat{\mathbf{J}}(\mathbf{r}, t) \delta(t - s), \quad (36)$$

$$\frac{\delta \hat{\Omega}_{\text{src}}(s)}{\delta \beta \alpha(\mathbf{r}, t)} = \hat{\rho}(\mathbf{r}, t) \delta(t - s), \quad (37)$$

we thus derive

$$- \frac{\delta \mathcal{R}(t)}{\delta \beta \mathbf{X}(\mathbf{r}, t)} = \mathbf{J}(\mathbf{r}, t), \quad (38)$$

$$- \frac{\delta \mathcal{R}(t)}{\delta \beta \alpha(\mathbf{r}, t)} = \rho(\mathbf{r}, t), \quad (39)$$

where we have used the fact that $\mathbf{X}(\mathbf{r}, t)$ is nonconservative, i.e., divergence-free.

Equations (38) and (39) suggest that well-defined two-time correlations can be obtained by further functional differentiation of (33) with respect to the conjugate fields. The time-ordered exponential (propagator) in (32) and the generating functional (33) then play a role similar to that of the Boltzmann factor and partition function, respectively, in equilibrium Statistical Mechanics.

Using (35), it is straightforward to show that the following functional derivative relations hold:

$$\frac{\delta \mathbf{J}(1)}{\delta \beta \mathbf{X}(2)} = D_0 \rho(1) \delta(1, 2) \mathbf{1} + \mathbf{J}_2(1, 2), \quad (40)$$

$$\frac{\delta \rho(1)}{\delta \beta \mathbf{X}(2)} = \mathbf{J}_{\text{vH}}^{\text{b}}(1, 2), \quad (41)$$

where causality requires $t_2 \leq t_1$, our notation is such that $\delta(1, 2) = \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(t_1 - t_2)$, and (40) is of second and (41) of first tensor rank. Furthermore, analogous reasoning and an additional integration by parts yields the derivatives with respect to $\alpha(\mathbf{r}, t)$, or equivalently with respect to the time derivative of the external potential,

$$\frac{\delta \mathbf{J}(1)}{\delta \beta \dot{V}_{\text{ext}}(2)} = D_0 \rho(1) \nabla_2 \delta(1, 2) + \mathbf{J}_{\text{vH}}^{\text{f}}(1, 2), \quad (42)$$

$$\frac{\delta \rho(1)}{\delta \beta \dot{V}_{\text{ext}}(2)} = \rho(1) G_{\text{vH}}(1, 2). \quad (43)$$

We have thus succeeded in identifying the inhomogeneous two-time correlation functions (6)–(8) and (11) as time-dependent functional derivatives of the one-body fields.

G. Response functions

The results for the dynamical functional derivatives, Eqs. (40)–(43), gain further physical significance when regarded as dynamic and in general nonlinear response functions. Consider first a perturbation of the current, $\delta \mathbf{J}(1)$, which is generated in response to a change in the externally applied nonconservative force, $\delta \mathbf{X}(2)$. Mathematically, this may be expressed via the integral relation

$$\delta \mathbf{J}(1) = \int d2 \frac{\delta \mathbf{J}(1)}{\delta \mathbf{X}(2)} \cdot \delta \mathbf{X}(2), \quad (44)$$

where the integral over spacetime point 2 is to be calculated up to the present (i.e., the one on the left-hand side of (44))

time, according to $\int d2 = \int d\mathbf{r}_2 \int_{-\infty}^{t_1} dt_2$. Substitution of (40) into (44) yields

$$\delta\mathbf{J}(1) = \frac{\rho(1)}{\gamma} \delta\mathbf{X}(1) + \beta \int d2 \mathbf{J}_2(1, 2) \cdot \delta\mathbf{X}(2), \quad (45)$$

which shows that the current perturbation consists of an instantaneous response to the local force acting at \mathbf{r}_1 (first term) and a retarded contribution (second term), arising from forces acting at more distant locations. The two-body current thus plays the role of a response function, which is related to the ‘‘creep compliance’’ employed in macroscopic rheology studies to calculate the deformation of a material caused by an applied stress field.¹² Equation (45) is nonlinear and exact, because the two-body current is itself a functional of the external forces. Linear response would be recovered by replacing $\mathbf{J}_2(1, 2)$ with the translationally invariant equilibrium function, $\mathbf{J}_2^{\text{eq}}(1-2)$. In contrast to the instantaneous current response, which is aligned with the force perturbation, the retarded contribution (the integral term in (45)) is in general not parallel to $\delta\mathbf{X}(2)$, due to mediated interactions.

A similar approach may be applied to calculating the change in density $\delta\rho(1)$ arising from a perturbation in the time-dependent external field, $\delta\dot{V}_{\text{ext}}(2)$. In this case the appropriate integral relation is given by

$$\delta\rho(1) = \int d2 \frac{\delta\rho(1)}{\delta\dot{V}_{\text{ext}}(2)} \delta\dot{V}_{\text{ext}}(2). \quad (46)$$

Insertion of Eq. (43) yields

$$\delta\rho(1) = \beta\rho(1) \int d2 G_{\text{vH}}(1, 2) \delta\dot{V}_{\text{ext}}(2), \quad (47)$$

which establishes that the van Hove function converts changes in the external potential rate into changes in the one-body density distribution.

Furthermore, expressions involving the van Hove currents are obtained by considering

$$\delta\rho(1) = \int d2 \frac{\delta\rho(1)}{\delta\mathbf{X}(2)} \cdot \delta\mathbf{X}(2), \quad (48)$$

$$\delta\mathbf{J}(1) = \int d2 \frac{\delta\mathbf{J}(1)}{\delta\dot{V}_{\text{ext}}(2)} \delta\dot{V}_{\text{ext}}(2), \quad (49)$$

from which, upon considering (41) and (42), one obtains

$$\delta\rho(1) = \int d2 \mathbf{J}_{\text{vH}}^{\text{b}}(1, 2) \cdot \delta\mathbf{X}(2), \quad (50)$$

$$\delta\mathbf{J}(1) = -\frac{\rho(1)}{\gamma} \nabla_1 \dot{V}_{\text{ext}}(1) + \beta \int d2 \mathbf{J}_{\text{vH}}^{\text{f}}(1, 2) \delta\dot{V}_{\text{ext}}(2). \quad (51)$$

As in the case of (45), the relationship (51) consists of a direct and mediated contributions, whereas (50) has no direct term.

The relations (45), (47), (50), and (51), provide a physical interpretation of the two-time correlators as mediators of changes in both external fields into resulting changes in the one-body density and current distribution. A very familiar case is that of linear response around the equilibrium state, where $\mathbf{X} = 0$ and $\dot{V}_{\text{ext}} = 0$. In general, however, the perturbations can be around any trajectory of the system, which is driven out of equilibrium by external forces.

H. Adiabatic approximation

The simplest theory for the average one-body current of interacting particles is the adiabatic dynamical density functional theory (DDFT), as originally proposed by Evans,¹ and subsequently rederived by both Marconi and Tarazona¹³ and Archer and Evans.¹⁴ DDFT assumes that the current,

$$\mathbf{J}_{\text{DDFT}}(1) = \frac{\rho(1)}{\gamma} \left(-\nabla \frac{\delta F[\rho]}{\delta\rho(1)} - \nabla V_{\text{ext}}(1) + \mathbf{X}(1) \right), \quad (52)$$

arises from a balance between forces generated by viscous friction, $\gamma\mathbf{v}(1)$, external fields, thermal motion, and interparticle interactions. The latter two contributions are generated from the intrinsic Helmholtz free energy functional $F[\rho]$. Substitution of (52) into the one-body continuity equation (5) yields a closed drift-diffusion equation for $\rho(1)$, which is local in time (i.e., Markovian¹⁵).

The functional derivative formalism developed above allows to generate two-point correlation functions within the adiabatic approximation. Using (52) to calculate the functional derivative $\delta\mathbf{J}(1)/\delta\mathbf{X}(3)$, employing the functional chain rule, and the relations (40) and (41) generates an adiabatic approximation to the two-body current,

$$\begin{aligned} \mathbf{J}_2^{\text{ad}}(1, 3) = & \mathbf{v}(1)\mathbf{J}_{\text{vH}}^{\text{b}}(1, 3) \\ & - D_0\rho(1)\nabla_1 \left(\frac{\mathbf{J}_{\text{vH}}^{\text{b}}(1, 3)}{\rho(1)} \right. \\ & \left. - \int d\mathbf{r}_2 c(1, 2_1)\mathbf{J}_{\text{vH}}^{\text{b}}(2_1, 3) \right), \quad (53) \end{aligned}$$

where the equilibrium direct correlation function is the second functional derivative of the excess (over ideal gas) part of the intrinsic Helmholtz free energy, $c(\mathbf{r}_1, \mathbf{r}_2) = -\delta^2\beta F^{\text{exc}}[\rho]/\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)$.¹ The argument 2_1 in (53) indicates position \mathbf{r}_2 and time t_1 ; the direct correlation function is hence evaluated at distinct values of the spatial arguments, but at the same time, i.e., $c(1, 2_1) \equiv c(\mathbf{r}_1, \mathbf{r}_2, t_1)$, and $\mathbf{v}(1)$ is given here by $\mathbf{J}_{\text{DDFT}}(1)/\rho(1)$. The three contributions to (53) represent a transport term, ideal decay, and an adiabatic spatial convolution that arises from the interparticle interactions. Equation (53) is the natural extension of the approximate one-body current (52) to the two-body level. External forces enter (53) only implicitly via the one-body density and current obtained by solving (5) with (52). When combined with (12), Eq. (53) provides a closed equation of motion for the back van Hove current.

Taking the divergence with respect to \mathbf{r}_3 in (53), using the two-body continuity equations (5) and (13), and integrating the entire history up to t_3 yields an approximation to the front van Hove current

$$\begin{aligned} \mathbf{J}_{\text{vH}}^{\text{f,ad}}(1, 3) = & \mathbf{J}(1)G_{\text{vH}}(1, 3) - D_0\rho(1)\nabla_1 \left(G_{\text{vH}}(1, 3) \right. \\ & \left. - \int d\mathbf{r}_2 c(1, 2_1)\rho(2_1) (G_{\text{vH}}(2_1, 3) - \rho(3_{-\infty})) \right), \quad (54) \end{aligned}$$

where $\rho(3_{-\infty}) \equiv \rho(\mathbf{r}_3, -\infty)$, a contribution $\nabla_1\rho(3_{-\infty})$ vanishes, and we have made the assumption that two-body

correlations factorize for widely separated time arguments, i.e., $\langle \hat{\rho}(\mathbf{r}, t) \hat{\rho}(\mathbf{r}', -\infty) \rangle = \rho(\mathbf{r}, t) \rho(\mathbf{r}', -\infty)$, which holds in the absence of an ideal glass transition.¹⁶ Substitution of (54) into the two-body continuity equation (9) yields a closed equation for the van Hove function, which is local in time but nonlocal in space. Equation (54) is identical to the result for the front van Hove current,⁴ derived by differentiating (52) with respect to the one-body field (2). This consistency demonstrates the flexibility of the method of dynamical functional differentiation.

I. Superadiabatic contributions

An exact theory for the two-body current should include a dependence on the history of both the one- and two-body correlation functions. Splitting the full two-body current into an adiabatic contribution (53) and a superadiabatic part, $\mathbf{J}_2 = \mathbf{J}_2^{\text{ad}} + \mathbf{J}_2^{\text{sup}}$, the most general expression for the latter is given by

$$\begin{aligned} \mathbf{J}_2^{\text{sup}}(1, 3) = & \rho(1)\mathbf{M}(1, 3)\rho(3) \\ & + \rho(1) \int d2 (\mathbf{M}(1, 2) \cdot \mathbf{J}_2(2, 3) \\ & + \mathbf{m}(1, 2)\mathbf{J}_{\text{vH}}^{\text{b}}(2, 3)), \end{aligned} \quad (55)$$

where we have introduced vectorial and tensorial direct time correlation functions, denoted by $\mathbf{m}(1, 2)$ and $\mathbf{M}(1, 2)$, respectively. The two-body current thus consists of a direct contribution, proportional to $\mathbf{M}(1, 2)$, and a convolution contribution of the respective direct time correlation function and a probabilistic correlation function. The non-Markovian equation (55) is the most general form that involves only one- and two-body functions which generate a tensor field from space-time convolutions of the van Hove current and the two-body current. The 2-integral in (55) runs over a spacetime slab from the earlier time t_3 to later time t_1 , consistent with causality. Unlike the approximate expression (54), the exact NOZ equation (55) is not closed and serves to define the direct time correlation functions $\mathbf{m}(1, 2)$ and $\mathbf{M}(1, 2)$.

As an aside, we note the close structural similarity between (55) and the equilibrium OZ equation,³

$$h(\mathbf{r}_1, \mathbf{r}_3) = c(\mathbf{r}_1, \mathbf{r}_3) + \int d\mathbf{r}_2 h(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2) c(\mathbf{r}_2, \mathbf{r}_3), \quad (56)$$

which defines the static direct correlation function, $c(\mathbf{r}_1, \mathbf{r}_2)$, in terms of the one-body density and the two-point correlation function $h(\mathbf{r}_1, \mathbf{r}_2) = \langle \hat{\rho}(\mathbf{r}_1) \hat{\rho}(\mathbf{r}_2) \rangle / (\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)) - 1$.

Building the divergence of the superadiabatic two-body current with respect to \mathbf{r}_3 and integrating in time t_3 yields

$$\begin{aligned} \mathbf{J}_{\text{vH}}^{\text{f, sup}}(1, 3) = & \mathbf{J}_{\text{vH}}^{\text{f, sup}}(1, 3_{-\infty}) - \rho(1) \int_{-\infty}^{t_3} dt'_3 \nabla_3 \cdot \mathbf{M}(1, 3') \rho(3') \\ & + \rho(1) \int d2 [\mathbf{M}(1, 2) \cdot (\mathbf{J}_{\text{vH}}^{\text{f}}(2, 3) - \mathbf{J}(2) \rho(3_{-\infty})) \\ & + \mathbf{m}(1, 2) \rho(2) (G_{\text{vH}}(2, 3) - \rho(3_{-\infty}))], \end{aligned} \quad (57)$$

where $\mathbf{J}_{\text{vH}}^{\text{f}} = \mathbf{J}_{\text{vH}}^{\text{f, ad}} + \mathbf{J}_{\text{vH}}^{\text{f, sup}}$. Closure of the theory requires (57) to be supplemented by two independent equations that relate

$\mathbf{m}(1, 2)$ and $\mathbf{M}(1, 2)$ to the van Hove function and its front current. One possible approach is to postulate a dynamical closure relation, in analogy to the procedure employed in equilibrium to obtain, e.g., the Percus-Yevick or hyper-netted-chain approximations.³ In Ref. 4, it was demonstrated that MCT can be viewed as a closure of this type. Alternatively, the power functional formalism⁷ can be exploited to relate the time-direct correlation functions to a generating functional, as outlined in the following.

J. Connection to power functional theory

The power functional theory⁷ is a recent approach to describing the dynamics of interacting Brownian systems by extending classical density functional theory to nonequilibrium situations. The theory rests on a dynamic generating functional (the free power), which is minimized with respect to either the current or the density, yielding a pair of complementary Euler-Lagrange equations. While the formulation is exact, obtaining a closed expression for the current requires knowledge of the excess (over ideal gas) power dissipation, $P_t^{\text{exc}}[\rho, \mathbf{J}]$, which is a functional of the history of $\rho(1)$ and $\mathbf{J}(1)$ prior to time t and accounts for dissipation that arises from interparticle interactions.

1. Euler-Lagrange equation for the current

Minimization of the dynamic free power functional with respect to the current yields a general and exact equation of motion,⁷

$$\mathbf{J}(1) = \mathbf{J}_{\text{DDFT}}(1) - \frac{\rho(1)}{\gamma} \frac{\delta P_t^{\text{exc}}[\rho, \mathbf{J}]}{\delta \mathbf{J}(1)}, \quad (58)$$

where $\mathbf{J}_{\text{DDFT}}(1)$ is defined via (52) and arises from differentiation of the ideal gas contribution to the power dissipation, $P_t^{\text{id}}[\rho, \mathbf{J}] = \int d\mathbf{r} \gamma \mathbf{J}(\mathbf{r}, t)^2 / (2\rho(\mathbf{r}, t))$, where the total free power functional consists of the sum $P_t[\rho, \mathbf{J}] = P_t^{\text{id}}[\rho, \mathbf{J}] + P_t^{\text{exc}}[\rho, \mathbf{J}]$.

Differentiating (58) with respect to $\mathbf{X}(3)$, observing (40), and comparing the result to the general form (55) yields the identification of the direct time correlation functions with second functional derivatives of the excess power dissipation via

$$\mathbf{m}(1, 2) = -\gamma^{-1} \frac{\delta}{\delta \rho(2)} \frac{\delta P_t^{\text{exc}}[\rho, \mathbf{J}]}{\delta \mathbf{J}(1)}, \quad (59)$$

$$\mathbf{M}(1, 2)^{\text{T}} = -\gamma^{-1} \frac{\delta}{\delta \mathbf{J}(2)} \frac{\delta P_t^{\text{exc}}[\rho, \mathbf{J}]}{\delta \mathbf{J}(1)}, \quad (60)$$

where the superscript T indicates the transpose. The relations (59) and (60) are identical to those previously derived in Ref. 4 via the less general method of differentiating with respect to the field (2). Equations (57)–(60) show that only a single mathematical object, the excess power dissipation functional, need be approximated to generate a closed and consistent set of equations for the dynamics of both the one- and two-body correlation functions. The DDFT (52) and the corresponding adiabatic approximation (54) are obtained by setting $P_t^{\text{exc}}[\rho, \mathbf{J}] = 0$. See Ref. 4 for the discussion of a

variety of systematic approximations beyond this dynamical ideal gas approximation.

2. Euler-Lagrange equation for the density

The generality of the theory that we have developed enables us to formulate a complete set of NOZ equations by observing that the power functional framework contains, in addition to (58), a second Euler-Lagrange equation,⁷

$$-\frac{\gamma \mathbf{J}(1)^2}{\rho(1)^2} + \frac{\delta P_t^{\text{exc}}[\rho, \mathbf{J}]}{\delta \rho(1)} + \frac{\delta \dot{F}[\rho]}{\delta \rho(1)} = \alpha(1) - \dot{V}_{\text{ext}}(1), \quad (61)$$

which follows from minimization of the free power with respect to the density distribution. As already mentioned in Sec. II F, the one-body function $\alpha(1)$ acts as a thermostat controlling the rate at which thermal energy is either removed from or input to the system at a given spatial location. The adiabatic approximation to (61), analogous to the DDFT, is obtained by setting $P_t^{\text{exc}}[\rho, \mathbf{J}] = 0$.

The linearity of (61) in $\dot{V}_{\text{ext}}(\mathbf{r}, t)$ suggests that the most natural way to generate an expression for the van Hove current is to differentiate (61) with respect to $\dot{V}_{\text{ext}}(\mathbf{r}, t)$, which is the field conjugate to the one-body density. Differentiating the adiabatic approximation to (61) with respect to $\dot{V}_{\text{ext}}(3)$ thus yields an approximate expression for the van Hove current

$$\begin{aligned} \mathbf{v}(1) \cdot \mathbf{J}_{\text{vH}}^{\text{f.ad}}(1, 3) &= \mathbf{v}(1) \cdot \mathbf{J}(1) G_{\text{vH}}(1, 3) \\ &\quad - D_0 \rho(1) \frac{\partial}{\partial t_1} \left(G_{\text{vH}}(1, 3) \right. \\ &\quad \left. - \int d\mathbf{r}_2 c(1, 2_1) \rho(2_1) G_{\text{vH}}(2_1, 3) \right), \quad (62) \end{aligned}$$

which complements our previous result (54) arising from the Euler-Lagrange equation for the current. If we now split, as we did previously, the van Hove current into adiabatic and superadiabatic contributions, $\mathbf{J}_{\text{vH}}^{\text{f}} = \mathbf{J}_{\text{vH}}^{\text{f.ad}} + \mathbf{J}_{\text{vH}}^{\text{f.sup}}$, the superadiabatic contribution satisfies

$$\begin{aligned} \mathbf{v}(1) \cdot \mathbf{J}_{\text{vH}}^{\text{f.sup}}(1, 3) &= \mathbf{J}(1) \cdot \mathbf{m}(1, 3) \rho(3) \\ &\quad + \rho(1) \int d2 (\mathbf{m}_b(1, 2) \cdot \mathbf{J}_{\text{vH}}^{\text{f}}(2, 3) \\ &\quad + m_0(1, 2) \rho(2) G_{\text{vH}}(2, 3)). \quad (63) \end{aligned}$$

Here the additional direct time correlation functions are given as functional derivatives of the excess dissipation functional

$$m_0(1, 2) = -\gamma^{-1} \frac{\delta}{\delta \rho(2)} \frac{\delta P_t^{\text{exc}}[\rho, \mathbf{J}]}{\delta \rho(1)}, \quad (64)$$

$$\mathbf{m}_b(1, 2) = -\gamma^{-1} \frac{\delta}{\delta \mathbf{J}(2)} \frac{\delta P_t^{\text{exc}}[\rho, \mathbf{J}]}{\delta \rho(1)}. \quad (65)$$

Knowledge of the excess dissipation functional is thus sufficient to generate all direct time correlation functions.

The Euler-Lagrange equation (61) can also be used to generate a vectorial expression involving the two-body current. Differentiating (61) with respect to $\mathbf{X}(3)$ yields the adia-

batic contribution

$$\begin{aligned} \mathbf{v}(1) \cdot \mathbf{J}_2^{\text{ad}}(1, 3) &= \mathbf{v}(1) \cdot \mathbf{J}(1) \mathbf{J}_{\text{vH}}^{\text{b}}(1, 3) \\ &\quad - D_0 \rho(1) \frac{\partial}{\partial t_3} \left(\mathbf{J}_{\text{vH}}^{\text{b}}(1, 3) \right. \\ &\quad \left. - \int d\mathbf{r}_2 c(1, 2_1) \rho(2_1) \mathbf{J}_{\text{vH}}^{\text{b}}(2_1, 3) \right), \quad (66) \end{aligned}$$

and the superadiabatic part

$$\begin{aligned} \nabla_3 \mathbf{v}(1) : \mathbf{J}_2^{\text{sup}}(1, 3) &= -\mathbf{J}(1) \cdot \frac{\partial}{\partial t_3} \mathbf{m}(1, 3) \rho(3) \\ &\quad + \rho(1) \nabla_3 \cdot \int d2 (\mathbf{m}_b(1, 2) \cdot \mathbf{J}_2(2, 3) \\ &\quad + m_0(1, 2) \rho(2) \mathbf{J}_{\text{vH}}^{\text{b}}(2, 3)). \quad (67) \end{aligned}$$

We thus have a obtained complete set of NOZ equations for the two-time correlation functions, based on both Euler-Lagrange equations.

III. CONCLUDING REMARKS

To summarize, we have presented a method for calculating dynamical functional derivatives and have applied this to derive general expressions for the two-body correlation functions, most significantly the tensorial two-body current. Our approach to calculating two-body correlations is based on differentiation of the propagator for the time evolution of the many-body distribution. Importantly, the dynamical operator which has to be considered when performing these variational calculations is not the physical Smoluchowski operator (16), but rather a more general sourced time evolution operator (30), which is only *a posteriori* constrained by the many-body continuity equation (14). The fact that the physical dynamics are enforced after performing the variation is in keeping with the spirit of the power functional theory,⁷ whereby derivatives with respect to the current are performed at fixed density and vice versa.

When applied to the approximate DDFT one-body current (52), the scheme yields an explicit, adiabatic approximation to the two-body current (53). Time integration of the divergence of the two-body current then yields an expression for the front van Hove current and thus, via (9), a closed expression for the van Hove function. Going beyond the adiabatic approximation and incorporating the physics of structural relaxation necessitates the introduction of time-direct correlation functions. The general result for the two-body current consists of the sum of adiabatic (53) and superadiabatic (55) contributions. In order to formulate a closed theory, additional expressions for the two time-direct correlation functions, $\mathbf{m}(1, 2)$ and $\mathbf{M}(1, 2)$, are required.

A possible way to apply the equations derived in this work is to view the general NOZ theory as a basis for the construction of nonequilibrium integral equation theories. However, a possibly preferable approach is provided by the power functional formalism,⁷ which enables the time-direct correlation functions to be identified as functional derivatives of the excess power dissipation functional. The challenge is to then find a suitable approximation to this fundamental

generating functional, cf. Ref. 7. As the same excess power dissipation generates the dynamics of the one-body fields, the power functional approach can be viewed as providing a unified (variational) framework for the calculation of one- and two-body dynamical correlation functions, both in and out of equilibrium.

In making a connection to the power functional theory,⁷ we have used the pair of Euler-Lagrange equations, which are obtained by minimizing the free power either with respect to the one-body current or the one-body density. Although both Euler-Lagrange equations provide expressions for the current and have an equivalent formal status, they differ in interpretation. The equation for the current, which was addressed also in Ref. 4, provides the most straightforward extension of the DDFT result (52), by supplementing this with an additional term arising from interaction-induced dissipation. The Euler-Lagrange equation (61) for the density describes the local rate of energy changes in the system. The right-hand side of (61) involves non-mechanical work arising from changes in the external potential at a given spacetime point, as well as energy injection or removal by a thermostat, as represented by the function $\alpha(1)$. Given that we are able to distinguish between various forms of work, it may prove fruitful to explore connections between the power functional formalism and fluctuation theory.^{17–19}

In Sec. II G, we interpreted the functional derivatives (40)–(43) as dynamic nonlinear response functions. This led directly to Eqs. (45), (47), (50), and (51), which demonstrate how the two-time correlators mediate external field perturbations into resulting changes in the one-body fields. These Green-Kubo-type formulae for the current and density response follow in a natural way from application of the dynamical functional calculus. However, the results presented here form only part of a more general picture. We expect to provide a unified variational framework for the generation of formal Green-Kubo relations for transport coefficients. Moreover, when applied to calculate the stress response to mechanical deformation a formal constitutive relation can be derived in a straightforward and physically intuitive fashion.²⁰ A full investigation of the connections between the present approach and the established Green-Kubo formalism^{21–24} is currently underway.

We have focused here on the special case of Brownian many-body dynamics. However, the functional differentiation of the dynamical propagator to generate two-body correlation functions is by no means limited to this particular choice of microscopic dynamics, but rather presents a general and powerful formalism. The application to Newtonian dynamics, as described by the Liouville propagator,³ should prove very instructive and may open the door to new studies of dynamical processes in atomic liquids. Work along these lines is also in progress.

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