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Power functional theory for Newtonian many-body dynamics

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We construct a variational theory for the inertial dynamics of classical many-body systems out of equilibrium. The governing (power rate) functional depends on three time- and space-dependent one-body distributions, namely, the density, the particle current, and the time derivative of the particle current. The functional is minimized by the true time derivative of the current. Together with the continuity equation, the corresponding Euler-Lagrange equation uniquely determines the time evolution of the system. An adiabatic approximation introduces both the free energy functional and the Brownian free power functional, as is relevant for liquids governed by molecular dynamics at constant temperature. The forces beyond the Brownian power functional are generated from a superpower (above the overdamped Brownian) functional. *Published by AIP Publishing.* https://doi.org/10.1063/1.5008608

I. INTRODUCTION

In two remarkable papers, Archer[1,2] formulated a microscopic approach for the description of the dynamics of atomic liquids or more generally: classical many-body systems, which are governed by Newtonian inertial dynamics. Systems that are appropriately described by his theory include dense atomic and molecular liquids. The approach is based on an equation of motion for the microscopic position- and time-dependent one-body density profile $\rho(\mathbf{r}, t)$, resolved on the particle time and length scale. The theory is based on arguments that are similar to those used in order to derive dynamical density functional theory (DDFT) for overdamped Brownian dynamics.[3–5] DDFT is a highly successful approach, which uses concepts from the exact formulation of equilibrium statistical mechanics via (equilibrium) density functional theory (DFT).[3,6–8] In equally remarkable papers, Marconi, Tarazona, and Melchionna[9–13] have developed again a microscopic approach that goes beyond the overdamped region of DDFT.

DFT for classical fluids and solids is based on the exact variational principle $\delta\Omega[\rho]/\delta\rho(\mathbf{r}) = 0$, where $\rho(\mathbf{r})$ is the equilibrium one-body density and $\Omega[\rho]$ is the grand potential functional.[3,8] The variational principal states that $\Omega[\rho]$ is minimized by the true equilibrium density distribution. Here an arbitrary position-dependent external potential $V_{\text{ext}}(\mathbf{r})$ can act on the system and, in general, will generate an inhomogeneous density distribution, $\rho(\mathbf{r}) \neq$ const. DFT addresses situations where a system is in equilibrium at constant temperature T and chemical potential μ. However, proper canonical information, at fixed particle number, can be obtained from DFT[14–16] and used in a dynamical, particle-conserving adiabatic theory.[17]

The DDFT for overdamped Brownian systems[3–5] describes the dynamics on the level of $\rho(\mathbf{r}, t)$. The effect of the internal interactions is represented by a one-body force field, $-\nabla\delta F[\rho]/\delta\rho(\mathbf{r}, t)$, where $F[\rho]$ is the intrinsic Helmholtz free energy functional. If the system is out of equilibrium, e.g., via the action of a dynamically varying external potential $V_{\text{ext}}(\mathbf{r}, t)$, then a nonvanishing one-body particle current distribution $\mathbf{J}(\mathbf{r}, t)$ develops. However, DDFT constitutes an approximation that only includes internal forces that originate from the free energy functional $F[\rho]$. Here, an adiabatic reference state is defined via the condition that its (equilibrium) density distribution is the same as that of the nonequilibrium system at a specific time. The difference between the full forces that act in nonequilibrium and the adiabatic forces constitute superadiabatic (over adiabatic) forces. Through explicit Brownian dynamics simulations, it was shown that the superadiabatic forces can be highly nontrivial:[18,19] they can be of a similar magnitude as the adiabatic forces and of the same or of the opposite sign.

Power functional theory (PFT)[20] goes beyond DDFT in that it provides a formally exact variational approach that derives the exact overdamped Brownian dynamics from an extremal principle of a power (energy per time) functional. The superadiabatic forces are obtained from an excess (over ideal gas and superadiabatic) "free" power functional $P_t^{\text{exc}}[\rho, \mathbf{J}]$. Here the functional depends nonlocally in space and in time on the density and the current, i.e., memory effects are accounted for. The framework has been used in a number of ways, such as to derive time-dependent nonequilibrium Ornstein-Zernike relations,[21] to obtain the nonequilibrium dynamics via formal functional integration,[22] and to express the dynamic test particle limit for the dynamic two-body liquid structure (van Hove function)[23,24] in an exact way.[25] Recent applications include the treatment of active Brownian particles.[26]

PFT was generalized to (nonrelativistic) quantum many-body systems,[27] as described by the Schrödinger equation. Such systems are conventionally treated using time-dependent quantum DFT.[28,29] The quantum PFT is fundamentally different from this approach, as it is based on an extremal principle for the time derivative of the current distribution, $\dot{\mathbf{J}}(\mathbf{r}, t)$. Using $\dot{\mathbf{J}}$ as the fundamental variational variable, instead of $\mathbf{J}$

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as in the over-damped (classical) case, permits to implement the inertial effects that are present in the quantum dynamics. The Schrödinger equation and the Smoluchowski (i.e., Fokker-Planck) equation for overdamped Brownian classical motion share many structural features, such as being both first order in time. However, the fact that the quantum mechanical wave function is complex-valued, as opposed to the real-valued probability distribution of the classical case, changes the nature of the motion from driven-diffusive in the classical case to inertial in the quantum case, where, e.g., waves can propagate without driving. While the interference phenomena of quantum mechanical motion are absent in the classical Newtonian dynamics, the effect of inertia are equally important in both cases. Hence one would expect that the inertial classical case also requires formulating the extremal principle for $\dot{\mathbf{J}}$ rather than for $\mathbf{J}$. The differences of both types of dynamics should however appear in the structure of the resulting equations of motion.

In the present paper, we derive such a variational theory for classical Newtonian systems. Our starting point is the (many-body) extremal principle due to Gauss, Appell, and Gibbs.[30] The presentation follows closely that of the quantum case.[27] We show how overdamped Brownian dynamics can be used as a reference for the present inertial systems. This strategy could be useful in situations where a global temperature is meaningful.

This paper is organized as follows. Our starting point is many-body Hamiltonians of the form described in Sec. II A. We formulate the dynamics of the relevant one-body distribution functions in Sec. II B. The one-body variational theory, based on the power rate functional, is presented in Sec. II C. For effectively isothermal situations, we describe in Sec. II D, how a Brownian reference system can be systematically incorporated via the power functional framework for overdamped dynamics. The additional forces, due to inertial effects, are then derived from a superpower (above Brownian power) functional.

II. VARIATIONAL THEORY

A. Many-body dynamics

We consider N classical point particles, with position coordinates $\mathbf{r}^N \equiv \{\mathbf{r}_1 \ldots \mathbf{r}_N\}$, and a many-body Hamiltonian of the form

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + u(\mathbf{r}^N) + \sum_i v^{\text{ext}}(\mathbf{r}_i, t), \tag{1}$$

where the sums run over all N particles, $u(\mathbf{r}^N)$ is the (intrinsic) interparticle interaction potential and $v^{\text{ext}}(\mathbf{r}, t)$ is a position- and time-dependent external one-body potential. The kinematic momentum of particle $i = 1 \ldots N$ is given by

$$\mathbf{p}_i = \boldsymbol{\pi}_i - q\mathbf{A}(\mathbf{r}_i, t), \tag{2}$$

where $\boldsymbol{\pi}_i$ is the canonical momentum of particle i, q is the electrical particle charge, and $\mathbf{A}(\mathbf{r}, t)$ is the position- and time-dependent magnetic vector potential. Phase space is spanned by the set $\{\mathbf{r}^N, \boldsymbol{\pi}^N\}$, where $\boldsymbol{\pi}^N = \{\boldsymbol{\pi}_1, \ldots, \boldsymbol{\pi}_N\}$.

Newton's equations of motion are

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m}, \tag{3}$$

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{f}_i, \tag{4}$$

where $\mathbf{f}_i$ is the force acting on particle i, given as a phase space function,

$$\mathbf{f}_i = -\nabla_i u - \nabla_i v_i^{\text{ext}} - q\dot{\mathbf{A}}_i + \frac{q}{m}\mathbf{p}_i \times \mathbf{B}_i, \tag{5}$$

where $v_i^{\text{ext}} = v^{\text{ext}}(\mathbf{r}_i, t)$ and the magnetic field acting on particle i is $\mathbf{B}_i \equiv \mathbf{B}(\mathbf{r}_i, t)$, obtained from the vector potential via $\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t)$; furthermore $\dot{\mathbf{A}}_i \equiv \partial \mathbf{A}(\mathbf{r}_i, t)/\partial t$. Equation (5) represents the sum of all forces that act on particle i, with contributions due to the interparticle interaction potential, the external potentials, and the Lorentz force. Note that $-q\dot{\mathbf{A}}(\mathbf{r}, t)$ constitutes a non-conservative external force field.

The time evolution of the probability distribution in phase space, $\Phi(\mathbf{r}^N, \boldsymbol{\pi}^N, t)$, is then governed by the Liouville equation,

$$\frac{\partial \Phi(\mathbf{r}^N, \boldsymbol{\pi}^N, t)}{\partial t} = -\sum_i \Big(\frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{f}_i \cdot \frac{\partial}{\partial \boldsymbol{\pi}_i} \Big) \Phi(\mathbf{r}^N, \boldsymbol{\pi}^N, t). \tag{6}$$

We next construct a description on the level of space- and time-dependent one-body fields.

B. One-body distribution functions

Consider first the density "operator" $\hat{\rho}_i(\mathbf{r}, t) = \delta(\mathbf{r} - \mathbf{r}_i)$ of particle i, where $\delta(\cdot)$ indicates the three-dimensional Dirac distribution. Here the term operator (and the caret symbol) indicates particular $\mathbf{r}$-dependent phase space functions that serve the purpose of building averages. The equation of motion for $\hat{\rho}_i(\mathbf{r}, t)$ is of continuity form,

$$\frac{d\hat{\rho}_i(\mathbf{r}, t)}{dt} = -\nabla \cdot \hat{\mathbf{J}}_i(\mathbf{r}, t), \tag{7}$$

where ∇ indicates the derivative with respect to $\mathbf{r}$, and the current operator of particle i is given by

$$\hat{\mathbf{J}}_i(\mathbf{r}, t) = \delta(\mathbf{r} - \mathbf{r}_i)\frac{\mathbf{p}_i}{m}, \tag{8}$$

where both $\mathbf{r}_i$ and $\mathbf{p}_i$ are evaluated at time t. Differentiating (8) in time yields, upon using (4),

$$m\frac{d\hat{\mathbf{J}}_i(\mathbf{r}, t)}{dt} = \delta(\mathbf{r} - \mathbf{r}_i)\mathbf{f}_i + \nabla \cdot \hat{\boldsymbol{\tau}}_i(\mathbf{r}, t), \tag{9}$$

where $\mathbf{f}_i$ is given by (5) and the one-body momentum current (or microscopic kinematic stress tensor) of particle i is defined as

$$\hat{\boldsymbol{\tau}}_i(\mathbf{r}, t) = -\frac{\mathbf{p}_i\mathbf{p}_i}{m}\delta(\mathbf{r} - \mathbf{r}_i), \tag{10}$$

where the pair of momentum vectors on the right-hand side forms a dyadic product. The second term on the right-hand side of (9) describes the transport effects that are due to the one-body description; note that transport effects are absent in the motion on the level of individual particles, as described by (4) and (5).

We build expectation values via the standard procedure, e.g., for the particle-labeled density operator $\hat{\rho}_i(\mathbf{r},t)$, the corresponding average is

$$\rho(\mathbf{r},t) = \left\langle \sum_i \hat{\rho}_i(\mathbf{r},t) \right\rangle \equiv \int d\mathbf{r}^N d\boldsymbol{\pi}^N \Phi(\mathbf{r}^N,\boldsymbol{\pi}^N,t) \sum_i \hat{\rho}_i(\mathbf{r},t), \tag{11}$$

where $\Phi(\mathbf{r}^N,\boldsymbol{\pi}^N,t)$ satisfies (6) and is normalized at all times, $\int d\mathbf{r}^N d\boldsymbol{\pi}^N \Phi(\mathbf{r}^N,\boldsymbol{\pi}^N,t) = 1$. Corresponding average expressions for the one-body current $\mathbf{J}(\mathbf{r},t)$ and momentum current tensor distribution $\boldsymbol{\tau}(\mathbf{r},t)$ are obtained by using $\hat{\mathbf{J}}_i(\mathbf{r},t)$ and $\hat{\boldsymbol{\tau}}_i(\mathbf{r},t)$, respectively, instead of $\hat{\rho}_i(\mathbf{r},t)$ in (11).

Building the expectation value of (7) and integrating in time yields

$$\rho(\mathbf{r},t) = \rho(\mathbf{r},t_0) - \int_{t_0}^{t} dt' \nabla \cdot \mathbf{J}(\mathbf{r},t'), \tag{12}$$

$$\mathbf{J}(\mathbf{r},t) = \mathbf{J}(\mathbf{r},t_0) + \int_{t_0}^{t} dt' \dot{\mathbf{J}}(\mathbf{r},t'), \tag{13}$$

where t_0 is an initial time, at which the state of the system is assumed to be known. Eqs. (12) and (13) allow one to determine $\rho(\mathbf{r},t)$ and $\mathbf{J}(\mathbf{r},t)$, provided that the time derivative of the current, $\dot{\mathbf{J}}(\mathbf{r},t)$, is known. One way of obtaining $\dot{\mathbf{J}}(\mathbf{r},t)$ is to build the expectation value of (9) and summing over i, which yields

$$\begin{aligned} m\dot{\mathbf{J}}(\mathbf{r},t) = \mathbf{f}^{\text{int}}(\mathbf{r},t) - \left(q\dot{\mathbf{A}}(\mathbf{r},t) + \nabla v^{\text{ext}}(\mathbf{r},t)\right)\rho(\mathbf{r},t) \\ + q\mathbf{J}(\mathbf{r},t) \times \mathbf{B}(\mathbf{r},t) + \nabla \cdot \boldsymbol{\tau}(\mathbf{r},t), \end{aligned} \tag{14}$$

where the interparticle interactions generate the intrinsic one-body force density field

$$\mathbf{f}^{\text{int}}(\mathbf{r},t) = -\left\langle \sum_i \delta(\mathbf{r}-\mathbf{r}_i)\nabla_i u \right\rangle. \tag{15}$$

The four additive contributions on the right-hand side of Eq. (14) have a clear interpretation: The first term is due to interparticle interactions, the second and the third terms represent the external force acting on the density distribution, and the fourth term constitutes a transport contribution.

C. Power rate functional for Newtonian dynamics

In the following, we construct an alternative to (14) and (15), by expressing the physical dynamics via a variational approach. We start on the many-body level and introduce a set of (real-valued) many-body acceleration fields on phase space, $\mathbf{a}^N \equiv \{\mathbf{a}_1(\mathbf{r}^N,\boldsymbol{\pi}^N,t)\ldots\mathbf{a}_N(\mathbf{r}^N,\boldsymbol{\pi}^N,t)\}$, which acts as variational variables. In the spirit of Gauss' principle of least constraint, as formalized independently by Appell and Gibbs,[30] we define an instantaneous functional of the acceleration fields as

$$\mathcal{G}_t = \int d\mathbf{r}^N d\boldsymbol{\pi}^N \sum_i \frac{(\mathbf{f}_i - m\mathbf{a}_i)^2}{2m}\Phi - \int d\mathbf{r} \frac{m}{2\langle\hat{\rho}\rangle}\left\langle \frac{d\hat{\mathbf{J}}}{dt}\right\rangle^2, \tag{16}$$

where $\hat{\rho}(\mathbf{r},t) = \sum_i \hat{\rho}_i(\mathbf{r},t)$, the total time derivative of $\hat{\mathbf{J}}(\mathbf{r},t)$ is given via (9) summed over all i and the probability distribution $\Phi(\mathbf{r}^N,\boldsymbol{\pi}^N,t)$ is evaluated at time t.

Minimizing (16) with respect to $\mathbf{a}^N$ at fixed time t implies that at the minimum

$$\frac{\delta\mathcal{G}_t}{\delta\mathbf{a}_i(\mathbf{r}^N,\boldsymbol{\pi}^N,t)} = 0, \tag{17}$$

for all $i = 1\ldots N$, and that the trial fields satisfy

$$m\mathbf{a}_i(\mathbf{r}^N,\boldsymbol{\pi}^N,t) = \mathbf{f}_i(\mathbf{r}^N,\boldsymbol{\pi}^N,t) \tag{18}$$

at time t. The equality in (17) and (18) is attained for the specific $\mathbf{a}^N$ at the minimum. Correspondingly, $\mathbf{p}^N$ and $\mathbf{r}^N$, and hence $\hat{\boldsymbol{\tau}}^N \equiv \hat{\boldsymbol{\tau}}_1\ldots\hat{\boldsymbol{\tau}}_N$ via (10), are then determined by integrating (3) and (4).

As a further central property, $\mathcal{G}_t$ acts as a generator for the one-body field of interest, via functional differentiation,

$$\frac{\delta\mathcal{G}_t}{\delta q\dot{\mathbf{A}}(\mathbf{r},t)} = \dot{\mathbf{J}}(\mathbf{r},t). \tag{19}$$

In order to connect the many-body description with the one-body level, we introduce a constraint on the acceleration fields $\mathbf{a}^N$ via imposing that

$$\dot{\mathbf{J}}(\mathbf{r},t) = \left\langle \sum_i \left(\mathbf{a}_i\delta(\mathbf{r}-\mathbf{r}_i) + \frac{\nabla\cdot\hat{\boldsymbol{\tau}}_i(\mathbf{r},t)}{m}\right)\right\rangle, \tag{20}$$

where $\dot{\mathbf{J}}(\mathbf{r},t)$ is regarded as a prescribed "target" one-body function. Hence in general, there will be many choices of $\mathbf{a}^N$ that are compatible with a given $\dot{\mathbf{J}}(\mathbf{r},t)$; we indicate this relationship (20) by $\mathbf{a}^N \to \dot{\mathbf{J}}$.

Performing a constrained search[31,32] for the minimum,

$$G_t[\rho,\mathbf{J},\dot{\mathbf{J}}] = \min_{\mathbf{a}^N\to\rho,\mathbf{J},\dot{\mathbf{J}}} \mathcal{G}_t, \tag{21}$$

establishes G_t as a functional of the three one-body fields $\rho(\mathbf{r},t)$, $\mathbf{J}(\mathbf{r},t)$, and $\dot{\mathbf{J}}(\mathbf{r},t)$. If $\mathbf{J}(\mathbf{r},t)$ and $\rho(\mathbf{r},t)$ have those values that correspond to the physical dynamics, then $G_t[\rho,\mathbf{J},\dot{\mathbf{J}}]$ is minimized by the true $\dot{\mathbf{J}}(\mathbf{r},t)$ and hence possesses vanishing (functional) derivative,

$$\left.\frac{\delta G_t[\rho,\mathbf{J},\dot{\mathbf{J}}]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)}\right|_{\rho,\mathbf{J}} = 0. \tag{22}$$

We proceed by splitting the total power rate (21) into intrinsic and external contributions,

$$\begin{aligned} G_t[\rho,\mathbf{J},\dot{\mathbf{J}}] = G_t^{\text{int}}[\rho,\mathbf{J},\dot{\mathbf{J}}] - \int d\mathbf{r}\,\dot{\mathbf{J}}(\mathbf{r},t) \\ \cdot\left(\frac{q\mathbf{J}(\mathbf{r},t)\times\mathbf{B}(\mathbf{r},t)}{\rho(\mathbf{r},t)} - q\dot{\mathbf{A}}(\mathbf{r},t) - \nabla v^{\text{ext}}(\mathbf{r},t)\right), \end{aligned} \tag{23}$$

where the intrinsic power rate functional $G_t^{\text{int}}[\rho,\mathbf{J},\dot{\mathbf{J}}]$ is independent of the external fields. Due to (19), the splitting (23) constitutes a Legendre transform from G_t to G_t^{int}. Inserting (23) into the one-body variational Eq. (22) yields an equality of (negative) internal and external contributions

$$\frac{\delta G_t^{\text{int}}[\rho,\mathbf{J},\dot{\mathbf{J}}]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)} = \frac{q\mathbf{J}(\mathbf{r},t)\times\mathbf{B}(\mathbf{r},t)}{\rho(\mathbf{r},t)} - q\dot{\mathbf{A}}(\mathbf{r},t) - \nabla v^{\text{ext}}(\mathbf{r},t), \tag{24}$$

where the left-hand side contains the interparticle interactions, as well as acceleration and transport effects. The right-hand side represents the sum of all external forces acting on the system.

We further decompose the intrinsic power rate functional $G_t^{\rm int}[\rho,\mathbf{J},\dot{\mathbf{J}}]$ into ideal (i.e., noninteracting) and excess (above ideal) contributions according to

$$G_t^{\rm int}[\rho,\mathbf{J},\dot{\mathbf{J}}] = G_t^{\rm id}[\rho,\mathbf{J},\dot{\mathbf{J}}] + G_t^{\rm exc}[\rho,\mathbf{J},\dot{\mathbf{J}}], \tag{25}$$

where the intrinsic contribution for ideal motion is

$$G_t^{\rm id}[\rho,\mathbf{J},\dot{\mathbf{J}}] = \int d\mathbf{r}\, \frac{\dot{\mathbf{J}}(\mathbf{r},t)}{\rho(\mathbf{r},t)} \cdot \left(\frac{m\dot{\mathbf{J}}(\mathbf{r},t)}{2} - \nabla\cdot\boldsymbol{\tau}^{\rm id}(\mathbf{r},t) \right), \tag{26}$$

with the ideal momentum current being a one-body field that we assume to have the factorized dyadic form

$$\boldsymbol{\tau}^{\rm id}(\mathbf{r},t) = -m\frac{\mathbf{J}(\mathbf{r},t)\mathbf{J}(\mathbf{r},t)}{\rho(\mathbf{r},t)}. \tag{27}$$

The excess contribution $G_t^{\rm exc}[\rho,\mathbf{J},\dot{\mathbf{J}}]$ in (25) contains both the effects of the interparticle interactions $u(\mathbf{r}^N)$ and the effects beyond the factorized form (27) of the ideal motion. Inserting (25) and (26) into (24) yields an exact relation for the time derivative of the current,

$$\begin{aligned} m\dot{\mathbf{J}}(\mathbf{r},t) = &-\rho(\mathbf{r},t)\frac{\delta G_t^{\rm exc}[\rho,\mathbf{J},\dot{\mathbf{J}}]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)} + \nabla\cdot\boldsymbol{\tau}^{\rm id}(\mathbf{r},t) \\ &+ q\mathbf{J}(\mathbf{r},t)\times\mathbf{B}(\mathbf{r},t) - \rho(\mathbf{r},t)(q\dot{\mathbf{A}}(\mathbf{r},t) + \nabla v^{\rm ext}(\mathbf{r},t)), \end{aligned} \tag{28}$$

which together with the continuity equations (12) and (13) forms a closed set of equations of motion for the one-body fields. Note that the splittings (23) and (25) define $G_t^{\rm int}[\rho,\mathbf{J},\dot{\mathbf{J}}]$ and $G_t^{\rm exc}[\rho,\mathbf{J},\dot{\mathbf{J}}]$, respectively. Hence these relations do not constitute assumptions. The dynamical problem is now encapsulated in the complexity of the dependence of $G_t^{\rm exc}[\rho,\mathbf{J},\dot{\mathbf{J}}]$ on its arguments. Comparing Eqs. (14) and (28) yields the identification

$$\frac{\delta G_t^{\rm exc}[\rho,\mathbf{J},\dot{\mathbf{J}}]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)} = \frac{\mathbf{f}^{\rm int}(\mathbf{r},t) + \nabla\cdot\left(\boldsymbol{\tau}(\mathbf{r},t) - \boldsymbol{\tau}^{\rm id}(\mathbf{r},t)\right)}{\rho(\mathbf{r},t)}, \tag{29}$$

where the functional derivative is evaluated at the minimum of the functional, i.e., for the true value of $\dot{\mathbf{J}}(\mathbf{r},t)$.

The (approximate) description of the effects of interparticle interactions can now be formulated using appropriate model forms for the excess power rate functional $G_t^{\rm exc}[\rho,\mathbf{J},\dot{\mathbf{J}}]$.

D. Brownian reference system

We next use an overdamped Brownian reference system. This could be useful in cases where molecular chaos has established an effective temperature T. Using a reference system is a well-established strategy for systematically constructing approximations. Recall that in the case of overdamped Brownian motion, the "adiabatic state" is used as a reference and treated via the corresponding equilibrium free energy functional, $F[\rho]$. Within the PFT for Brownian overdamped motion, the total time derivative $\dot{F}[\rho]$ forms a (an additive) contribution to the power functional. In particular, the time derivative of the excess free energy functional, $\dot{F}_{\rm exc}[\rho]$, represents the adiabatic effects of the internal interactions on the motion of the Brownian system. The nonequilibrium forces that act in addition to the adiabatic forces ("superadiabatic forces") are obtained from the superadiabatic excess power functional $P_t^{\rm exc}[\rho,\mathbf{J}]$. Neglecting these superadiabatic forces leads to the DDFT equation of motion. Here we perform a similar strategy, but use not only the adiabatic state as a reference for the dynamic system, but rather use an overdamped Brownian system as a reference for the Newtonian system. In order to facilitate this concept on the technical level, it is straightforward to convert the excess power functional contributions to power *rates* via a total time derivative.

Hence we split the interaction contribution to the power rate functional according to

$$G_t^{\rm exc}[\rho,\mathbf{J},\dot{\mathbf{J}}] = \ddot{F}_{\rm exc}[\rho] + \dot{P}_t^{\rm exc}[\rho,\mathbf{J}] + G_t^{\rm spo}[\rho,\mathbf{J},\dot{\mathbf{J}}]. \tag{30}$$

Here $F_{\rm exc}[\rho]$ is the excess (over ideal gas) intrinsic free energy density functional of equilibrium DFT, $P_t^{\rm exc}[\rho,\mathbf{J}]$ is the superadiabatic (excess) power functional of Ref. 20 that determines the dynamics of overdamped Brownian systems, and $G_t^{\rm spo}$ is the remaining ("superpower" or "superoverdamped") contribution, which is hence defined by (30). The overdots indicate total time derivatives.

We recall that the time derivative of the excess free energy functional is[20]

$$\dot{F}_{\rm exc}[\rho] = \int d\mathbf{r}\mathbf{J}\cdot\frac{\delta F[\rho]}{\delta\rho}, \tag{31}$$

where we use the short-hand notation $\delta F[\rho]/\delta\rho = \delta F[\rho]/\delta\rho(\mathbf{r})|_{\rho(\mathbf{r})=\rho(\mathbf{r},t)}$. Equation (31) can be obtained in a straightforward way by using the functional chain rule, then replacing, via the continuity equation, the occurring time derivative $\dot{\rho}(\mathbf{r},t)$ by the negative divergence of the current, and subsequently performing a spatial integration by parts. Note that (31) is an instantaneous (Markovian) expression, as one would expect from using the adiabatic state, which contains no detailed (memory) dynamic information.

Again via the functional chain rule and spatial integration by parts, the time derivatives can be carried out and one obtains the results

$$\begin{aligned} \ddot{F}_{\rm exc}[\rho] = &\int d\mathbf{r}\dot{\mathbf{J}}\cdot\nabla\frac{\delta F_{\rm exc}[\rho]}{\delta\rho} \\ &+ \int d\mathbf{r}d\mathbf{r}'\mathbf{J}'\mathbf{J}:\nabla\nabla'\frac{\delta^2 F_{\rm exc}[\rho]}{\delta\rho'\delta\rho}, \end{aligned} \tag{32}$$

$$\dot{P}_t^{\rm exc}[\rho,\mathbf{J}] = \int d\mathbf{r}\mathbf{J}\cdot\nabla\frac{\delta P_t^{\rm exc}[\rho,\mathbf{J}]}{\delta\rho} + \int d\mathbf{r}\dot{\mathbf{J}}\cdot\frac{\delta P_t^{\rm exc}[\rho,\mathbf{J}]}{\delta\mathbf{J}}, \tag{33}$$

where the arguments $\mathbf{r}$, t have been left away for clarity, the prime indicates dependence on $\mathbf{r}'$, t, and the colon indicates a double tensor contraction. The forces can now be obtained from functional derivatives as

$$-\frac{\delta\ddot{F}_{\rm exc}[\rho]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)} = -\nabla\frac{\delta F_{\rm exc}[\rho]}{\delta\rho(\mathbf{r},t)} = -\frac{\delta\dot{F}_{\rm exc}[\rho]}{\delta\mathbf{J}(\mathbf{r},t)}, \tag{34}$$

$$-\frac{\delta\dot{P}_t^{\rm exc}[\rho,\mathbf{J}]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)} = -\frac{\delta P_t^{\rm exc}[\rho,\mathbf{J}]}{\delta\mathbf{J}(\mathbf{r},t)}, \tag{35}$$

where the last expression in (34) is that used in the Brownian power functional, and the equality between the very left- and right-hand side of (34) already holds on general grounds.

We hence obtain the splitting of the excess force into adiabatic, overdamped Brownian, and superpower contributions as

$$-\frac{\delta G_t^{\mathrm{exc}}[\rho,\mathbf{J},\dot{\mathbf{J}}]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)} = -\frac{\delta}{\delta\dot{\mathbf{J}}(\mathbf{r},t)}(\ddot{F}_{\mathrm{exc}} + \dot{P}_t^{\mathrm{exc}} + G_t^{\mathrm{spo}})$$
$$= -\nabla\frac{F_{\mathrm{exc}}[\rho]}{\delta\rho(\mathbf{r},t)} - \frac{\delta P_t^{\mathrm{exc}}[\rho,\mathbf{J}]}{\delta\mathbf{J}(\mathbf{r},t)} - \frac{\delta G_t^{\mathrm{spo}}[\rho,\mathbf{J},\dot{\mathbf{J}}]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)}, \tag{36}$$

which can be input into (28).

III. CONCLUSIONS

In conclusion, we have presented a variational theory for the many-body dynamics of classical systems with inertial Newtonian dynamics. The theory complements the previously formulated cases of overdamped Browian[20] and nonrelativistic quantum systems.[27] The central equation of motion is of Euler-Lagrange form and contains the time derivative of the microscopic time-dependent current distribution, $\dot{\mathbf{J}}(\mathbf{r},t)$, as the central unknown field. Integration in time then yields both the current and the density distributions.

The presented theory is structurally very close to that for the quantum case. In particular, in the limit $\hbar \to 0$, the classical case is recovered. While this might be expected on general grounds (and is an indication for the self-consistency of the entire approach), on a technical level, it is nothing but surprising, given the difference in actual calculations, i.e., the bracket structure of the quantum mechanical expectation values. Note that the factorization (27) constitutes an approximation in the classical (statistical) problem.

Generalizing the nonequilibrium Ornstein-Zernike equation for overdamped motion[21] to the Newtonian case constitutes an exciting and challenging prospect for future work, as does developing concrete approximations. In particular, addressing viscosity and the presence of memory effects constitutes an important research task[33] for the future. Furthermore, making connections to the very recently developed approximation for the Brownian superadiabatic functional[34] should be very worthwhile. It also remains to be seen whether neglecting all excess contributions except for the adiabatic forces (as is done in DDFT) could be a useful approximation under certain conditions and whether in this case, connections to established models, such as, e.g., model H,[35] can be made.

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