

## Velocity Gradient Power Functional for Brownian Dynamics

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We present an explicit and simple approximation for the superadiabatic excess (over ideal gas) free power functional, admitting the study of the nonequilibrium dynamics of overdamped Brownian many-body systems. The functional depends on the local velocity gradient and is systematically obtained from treating the microscopic stress distribution as a conjugate field. The resulting superadiabatic forces are beyond dynamical density functional theory and are of a viscous nature. Their high accuracy is demonstrated by comparison to simulation results.

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The response of complex systems to external stresses is important, both from an applied point of view of control of flow properties, but also from a fundamental interest in understanding the collective nonequilibrium behavior of many-body systems [1]. In particular, colloidal dispersions, when exposed to shear flow, display a wealth of striking nonequilibrium phenomena, ranging from the nonlinear rheological behavior of fluids [1] and glasses [2] to shear banding phase transitions [3–5]. Much theoretical work has been carried out on the basis of the Smoluchowski many-body equation for overdamped Brownian systems [1]. On its basis dynamical density functional theory (DDFT) [6–9] has been used in order to study rheological properties of model fluids. Brader, Krüger, and their co-workers [10–15] have supplemented DDFT by further physically motivated contributions, such as, e.g., kinetic (flow kernel) considerations, in order to address a range of specific rheological problems. Their approach relies on considering two-point distribution functions, which they incorporate into DDFT.

Power functional theory (PFT) [16] is a formally exact and general dynamical approach that rather operates on the level of the time-dependent one-body density  $\rho(\mathbf{r}, t)$  and the current distribution  $\mathbf{J}(\mathbf{r}, t)$ . A minimization principle determines the current at position  $\mathbf{r}$  and time  $t$ , and hence the time evolution of the system. The many-body problem is encapsulated in the excess (over ideal gas) superadiabatic (over free energy) contribution to the free power functional  $P_i^{\text{exc}}[\rho, \mathbf{J}]$ , which is in general a spatially and temporally nonlocal functional of both density and current. The resulting (superadiabatic) forces are obtained from functional differentiation of  $P_i^{\text{exc}}$  with respect to  $\mathbf{J}(\mathbf{r}, t)$ , upon holding  $\rho(\mathbf{r}, t)$  fixed. The superadiabatic forces act in addition to the adiabatic forces; the latter are generated from the (equilibrium) free energy functional. On the basis of PFT, nonequilibrium Ornstein-Zernike relations [17,18] were systematically derived. However, the central object of the theory,  $P_i^{\text{exc}}$ , remains to a large extent unknown at present, which hampers the application of PFT to concrete problems.

In this Letter, we construct an explicit approximation for  $P_i^{\text{exc}}$ , based on a reformulation of PFT using the local velocity gradient field and the microscopic stress tensor as its conjugate field. This enables us to (i) connect PFT to rheology, and (ii) systematically construct an approximate superadiabatic excess functional. As we demonstrate, in rheological problems the superadiabatic forces describe viscous effects. These can be large and can even be the sole effects present, i.e., in cases where the adiabatic effects vanish, such as in bulk steady shear flow. Hence, rather than merely correcting DDFT, our current approach offers the study of entirely distinct areas of physics. To test the validity of our approach, we study the time evolution of a system of hard particles and find excellent agreement between theory and Brownian dynamics simulation results. We envisage future applications to nonequilibrium phenomena, such as shear ordering [3–5,10–15], laning transitions [19], active fluids [20], the dynamics of hard disks [21], hard spheres [22], and hard rods [23], magnetic transport [24], and the dynamics of colloidal sedimentation [25], of capacitive systems [26,27], of polymers [28], of protein adsorption [29], and of quantum systems [30].

The first part of the Letter is a fully microscopic and self-contained formulation of PFT using the velocity gradient field  $\nabla\mathbf{v}(\mathbf{r}, t)$ . We show that one can express the superadiabatic functional (i.e., the nonequilibrium contribution due to the interparticle interactions) as  $P_i^{\text{exc}}[\rho, \nabla\mathbf{v}]$ . Based on this, we present in Eqs. (29) and (30) explicit expressions, which are amenable to direct physical interpretation. In particular Eq. (30) is based on the symmetry arguments that apply to a simple fluid. We apply and test the theory subsequently in our model hard core system.

The starting point of PFT is a generator on the many-body level [16], defined as

$$\mathcal{R}_t = \int d\mathbf{r}^N \Psi(\mathbf{r}^N, t) \sum_i \left( \frac{\gamma}{2} \tilde{\mathbf{v}}_i^2 - \tilde{\mathbf{v}}_i \cdot \mathbf{F}_i + \dot{V}_{\text{ext},i} \right), \quad (1)$$

where  $\gamma$  is the friction constant,  $\Psi(\mathbf{r}^N, t)$  is the time-dependent many-body probability distribution in configuration space of  $N$  particles, spanned by  $\mathbf{r}^N \equiv \{\mathbf{r}_1 \dots \mathbf{r}_N\}$ , where  $\mathbf{r}_i$  is the position coordinate of particle  $i = 1, \dots, N$ ,  $\tilde{\mathbf{v}}_i(\mathbf{r}^N, t)$  is the trial velocity function of particle  $i$ ,  $\mathbf{F}_i(\mathbf{r}^N, t)$  is the total force acting on particle  $i$ , and  $\dot{V}_{\text{ext},i} \equiv \partial V_{\text{ext}}(\mathbf{r}_i, t)/\partial t$  is the partial time derivative of the external one-body potential  $V_{\text{ext}}$ . Below we demonstrate the connection of Eq. (1) to standard observables, such as the density profile and the current distribution. Before doing so, we first connect Eq. (1) to the many-body dynamics. The “real” velocity  $\mathbf{v}_i(\mathbf{r}^N, t)$  of particle  $i$  arises, in the overdamped limit with no hydrodynamic interactions considered here, as

$$\gamma \mathbf{v}_i(\mathbf{r}^N, t) = \mathbf{F}_i(\mathbf{r}^N, t), \quad (2)$$

where

$$\begin{aligned} \mathbf{F}_i(\mathbf{r}^N, t) = & -k_B T \nabla_i \ln \Psi(\mathbf{r}^N, t) - \nabla_i u(\mathbf{r}^N) \\ & - \nabla_i V_{\text{ext}}(\mathbf{r}_i, t) + \mathbf{X}(\mathbf{r}_i, t) + \gamma \mathbf{v}_{\text{sol}}(\mathbf{r}_i, t), \end{aligned} \quad (3)$$

where  $k_B$  is the Boltzmann constant,  $T$  is absolute temperature,  $\nabla_i$  indicates the derivative with respect to  $\mathbf{r}_i$ ,  $u(\mathbf{r}^N)$  is the interparticle interaction potential,  $\mathbf{X}(\mathbf{r}, t)$  is a nonconservative external force field, and  $\mathbf{v}_{\text{sol}}(\mathbf{r}, t)$  is the imposed velocity field of the (implicit) solvent; here,  $\mathbf{r}$  is the space coordinate. The many-body (free power) functional (1) is constructed in such a way that minimization with respect to all  $\tilde{\mathbf{v}}_i(\mathbf{r}^N, t)$  [i.e., imposing that  $\partial \mathcal{R}_t / \partial \tilde{\mathbf{v}}_i(\mathbf{r}^N, t) = 0$ ] sets each trial velocity equal to the corresponding real velocity,  $\tilde{\mathbf{v}}_i(\mathbf{r}^N, t) = \mathbf{v}_i(\mathbf{r}^N, t)$ , due to the quadratic dependence [Eq. (1)] of  $\mathcal{R}_t$  on  $\tilde{\mathbf{v}}_i$  [16]. Hence, the physical dynamics reside at the minimum of a parabola in the space of trial velocities. This process is carried out at each point in time, and the resulting dynamics for  $\Psi(\mathbf{r}^N, t)$  is equal to that given by the Smoluchowski equation [16]. The many-body functional (1) is significant as it acts as a generator of averages of interest, with one (primary) example being  $\delta \mathcal{R}_t / \delta \mathbf{X}(\mathbf{r}, t) = -\mathbf{J}(\mathbf{r}, t)$ , evaluated at the minimum, where the one-body current distribution is the microscopic average

$$\mathbf{J}(\mathbf{r}, t) = \int d\mathbf{r}^N \Psi(\mathbf{r}^N, t) \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{v}_i(\mathbf{r}^N, t) \quad (4)$$

with  $\delta(\cdot)$  being the (three-dimensional) Dirac distribution.

Here, we start by considering the functional derivative of  $\mathcal{R}_t$  with respect to the velocity gradient of the solvent, and obtain

$$\frac{\delta \mathcal{R}_t}{\delta \nabla \mathbf{v}_{\text{sol}}(\mathbf{r}, t)} = \boldsymbol{\sigma}(\mathbf{r}, t), \quad (5)$$

where the local and time-resolved stress distribution  $\boldsymbol{\sigma}(\mathbf{r}, t)$  is a one-body second-rank tensor field. Any microscopic definition of  $\boldsymbol{\sigma}(\mathbf{r}, t)$  is necessarily nonunique [31], as can be gleaned from the fact that the (driving) force density is obtained via the divergence,

$$\nabla \cdot \boldsymbol{\sigma}(\mathbf{r}, t) = \gamma \mathbf{J}(\mathbf{r}, t), \quad (6)$$

where  $\mathbf{J}(\mathbf{r}, t)$  is the average (4). Clearly, Eq. (6) is invariant under adding a divergenceless tensor field to  $\boldsymbol{\sigma}(\mathbf{r}, t)$ . In practice, carrying out the derivative (5) of Eq. (1) requires us to specify an inversion operation to  $\nabla$ . For simplicity, we choose this to be the convolution with a radial, inverse square distance vector field,

$$\nabla^{-1} f(\mathbf{r}) = \int d\mathbf{r}' \frac{\mathbf{r} - \mathbf{r}'}{4\pi |\mathbf{r} - \mathbf{r}'|^3} f(\mathbf{r}'), \quad (7)$$

where  $f(\cdot)$  is a test function.  $\nabla \cdot \nabla^{-1} f(\mathbf{r}) = f(\mathbf{r})$  is indeed the identity, as can easily be checked upon exploiting the identity  $\delta(\mathbf{r}) = \nabla \cdot [\mathbf{r}/(4\pi |\mathbf{r}|^3)]$ .

The specific form of  $\boldsymbol{\sigma}(\mathbf{r}, t)$  then emerges as a microscopic average from Eq. (5) upon spatial integration by parts,

$$\boldsymbol{\sigma}(\mathbf{r}, t) = \int d\mathbf{r}^N \Psi(\mathbf{r}^N, t) \sum_i \frac{(\mathbf{r} - \mathbf{r}_i) \mathbf{F}_i(\mathbf{r}^N, t)}{4\pi |\mathbf{r} - \mathbf{r}_i|^3}, \quad (8)$$

where the vector product on the right-hand side is a dyadic. For the special case of pairwise interparticle forces, the form (8) was suggested by Wajnryb *et al.* [32], but apparently not used further. A common alternative is that given by Irving and Kirkwood [33]; however, its extension to higher than two-body forces becomes increasingly cumbersome. Equation (8) does not suffer from this deficiency.

As a consequence of the structure of Eq. (8), the force density relationship (6) follows upon observing the factor  $\gamma$  from Eq. (2). The stress tensor distribution (8) carries further significance, as it allows us to define an integrated stress  $\boldsymbol{\Sigma}(t)$  via spatial integration of the stress distribution  $\boldsymbol{\sigma}(\mathbf{r}, t)$  over  $\mathbb{R}^3$ ,

$$\boldsymbol{\Sigma}(t) = \int d\mathbf{r} \boldsymbol{\sigma}(\mathbf{r}, t) \quad (9)$$

$$= -\frac{1}{3} \int d\mathbf{r}^N \Psi(\mathbf{r}^N, t) \sum_i \mathbf{r}_i \mathbf{F}_i(\mathbf{r}^N, t), \quad (10)$$

where the form (10) follows from inserting Eq. (8) into Eq. (9) and carrying out the  $\mathbf{r}$  integration. The negative trace of the stress tensor,  $-\text{Tr} \boldsymbol{\Sigma}(t)$ , is the (averaged) Clausius virial [34]. Equations (6) and (10) attest to the fact that Eq. (8) is a meaningful definition of a general local and time-resolved stress distribution. In the following we use Eq. (8) in order to formulate power functional theory on

the tensorial level of the microscopic stress distribution and the velocity gradient.

PFT elevates the variational principle on the one-body level, via constructing, from Eq. (1), a one-body “free power” functional  $R_t$  that depends on the one-body density distribution  $\rho(\mathbf{r}, t)$ , and on  $\mathbf{J}(\mathbf{r}, t)$ , and which can be split according to

$$R_t = P_t^{\text{id}} + P_t^{\text{exc}} + \dot{F} - X_t, \quad (11)$$

where  $P_t^{\text{id}}$  is the ideal dissipation functional,

$$P_t^{\text{id}} = \int d\mathbf{r} \frac{\gamma \mathbf{J}(\mathbf{r}, t)^2}{2\rho(\mathbf{r}, t)}, \quad (12)$$

and  $P_t^{\text{exc}}$  is the excess (over ideal) contribution, which arises from the presence of internal interactions,  $\dot{F} = \int d\mathbf{r} \mathbf{J}(\mathbf{r}, t) \cdot \nabla \delta F / \delta \rho(\mathbf{r}, t)$  [16] is the total time derivative of the (equilibrium) intrinsic Helmholtz free energy density functional  $F[\rho]$ , and  $X_t$  is the external power, given by the simple space- and time-local expression

$$X_t = \int d\mathbf{r} (\mathbf{J}(\mathbf{r}, t) \cdot \mathbf{f}_{\text{ext}}(\mathbf{r}, t) - \rho(\mathbf{r}, t) \dot{V}_{\text{ext}}(\mathbf{r}, t)), \quad (13)$$

where the total external force field is  $\mathbf{f}_{\text{ext}}(\mathbf{r}, t) = -\nabla V_{\text{ext}}(\mathbf{r}, t) + \mathbf{X}(\mathbf{r}, t) + \gamma \mathbf{v}_{\text{sol}}(\mathbf{r}, t)$ . Here,  $\rho(\mathbf{r}, t) = \int d\mathbf{r}^N \Psi(\mathbf{r}^N, t) \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$  is the microscopic one-body density distribution.

The variational principle [16] states that  $R_t$  is minimized by the true current at time  $t$ , at fixed density  $\rho(\mathbf{r}, t)$ , which implies that

$$\left. \frac{\delta R_t}{\delta \mathbf{J}(\mathbf{r}, t)} \right|_{\rho} = 0. \quad (14)$$

The density distribution can then be updated according to the continuity equation  $\partial \rho(\mathbf{r}, t) / \partial t = -\nabla \cdot \mathbf{J}(\mathbf{r}, t)$ . Inserting the decomposition (11) into Eq. (14) yields the equation of motion [16]

$$\gamma \mathbf{v}(\mathbf{r}, t) = -k_B T \nabla \ln \rho - \nabla \left. \frac{\delta F_{\text{exc}}}{\delta \rho(\mathbf{r}, t)} - \frac{\delta P_t^{\text{exc}}}{\delta \mathbf{J}(\mathbf{r}, t)} \right|_{\rho} + \mathbf{f}_{\text{ext}}(\mathbf{r}, t), \quad (15)$$

where the (negative) friction force (left-hand side) is balanced by the sum of ideal diffusive, excess adiabatic, superadiabatic, and external forces (right-hand side); here, the velocity field is defined as the ratio

$$\mathbf{v}(\mathbf{r}, t) = \mathbf{J}(\mathbf{r}, t) / \rho(\mathbf{r}, t). \quad (16)$$

The excess adiabatic force is  $\mathbf{f}_{\text{adx}}(\mathbf{r}, t) = -\nabla \delta F_{\text{exc}}[\rho] / \delta \rho(\mathbf{r}, t)$ , where the excess (above ideal) free

energy functional  $F_{\text{exc}}$  is defined via  $F[\rho] = F_{\text{exc}}[\rho] + k_B T \int d\mathbf{r} \rho (\ln(\rho \Lambda^3) - 1)$ , where  $\Lambda$  is the (irrelevant) de Broglie wavelength.

Although this (original) formulation of PFT (15) [16] permits us to obtain the full time evolution of the density and current fields of the system, the stresses that act do not appear. To provide access, we perform a change of variables, from the current  $\mathbf{J}(\mathbf{r}, t)$  to the gradient of the velocity field,  $\nabla \mathbf{v}(\mathbf{r}, t)$ . Using Eq. (7) and spatial integration by parts we can rewrite the external power (13) as

$$X_t = - \int d\mathbf{r} (\boldsymbol{\sigma}_{\text{ext}}(\mathbf{r}, t) : \nabla \mathbf{v}(\mathbf{r}, t) + \dot{V}_{\text{ext}}(\mathbf{r}, t) \rho(\mathbf{r}, t)), \quad (17)$$

where the colon indicates a double tensor contraction, and the external stress is defined as

$$\boldsymbol{\sigma}_{\text{ext}}(\mathbf{r}, t) = \nabla^{-1} [\rho(\mathbf{r}, t) \mathbf{f}_{\text{ext}}(\mathbf{r}, t)]. \quad (18)$$

Because of the structure of Eqs. (11) and (17), we can generate the velocity gradient tensor field via functional differentiation,

$$\frac{\delta R_t}{\delta \boldsymbol{\sigma}_{\text{ext}}(\mathbf{r}, t)} = \nabla \mathbf{v}(\mathbf{r}, t). \quad (19)$$

Using the splitting (11) further, we also perform integration by parts to express the ideal and adiabatic contributions, respectively, as

$$P_t^{\text{id}} = -\frac{1}{2} \int d\mathbf{r} \boldsymbol{\sigma}(\mathbf{r}, t) : \nabla \mathbf{v}(\mathbf{r}, t), \quad (20)$$

$$\dot{F} = \int d\mathbf{r} \boldsymbol{\sigma}^{\text{ad}}(\mathbf{r}, t) : \nabla \mathbf{v}(\mathbf{r}, t), \quad (21)$$

where the total stress  $\boldsymbol{\sigma}(\mathbf{r}, t)$  is a functional of  $\nabla \mathbf{v}(\mathbf{r}, t)$  and  $\rho(\mathbf{r}, t)$  via Eqs. (6) and (16), and the adiabatic stress  $\boldsymbol{\sigma}^{\text{ad}}(\mathbf{r}, t)$  is given by

$$\boldsymbol{\sigma}^{\text{ad}}(\mathbf{r}, t) = -\nabla^{-1} \rho(\mathbf{r}, t) \nabla \left. \frac{\delta F}{\delta \rho(\mathbf{r}, t)} \right|_{\rho}. \quad (22)$$

We can now reformulate the variational principle (14) as

$$\nabla \cdot \left. \frac{\delta R_t}{\delta \nabla \mathbf{v}(\mathbf{r}, t)} \right|_{\rho} = 0, \quad (23)$$

where the density  $\rho(\mathbf{r}, t)$  is kept fixed under the variation. An equivalent form is

$$\left. \frac{\delta R_t}{\delta \nabla \mathbf{v}(\mathbf{r}, t)} \right|_{\rho} = \boldsymbol{\sigma}_{\text{stat}}(\mathbf{r}, t), \quad (24)$$

where  $\sigma_{\text{stat}}(\mathbf{r}, t)$  is a “static” stress that generates vanishing force density,  $\nabla \cdot \sigma_{\text{stat}}(\mathbf{r}, t) = 0$ .

We next exploit the decomposition (11), and first consider the velocity gradient form of the ideal dissipation functional (20). Carrying out the functional derivative [at constant density  $\rho(\mathbf{r}, t)$ ] yields

$$\left. \frac{\delta P_t^{\text{id}}}{\delta \nabla \mathbf{v}(\mathbf{r}, t)} \right|_{\rho} = -\sigma(\mathbf{r}, t), \quad (25)$$

where the factor of 1/2 from Eq. (20) cancels with the two possibilities to carry out the integration by parts [i.e.,  $\sigma(\mathbf{r}, t)$  is not kept constant during the variation].

As the functional derivative of Eq. (17) and of Eq. (21) is straightforward, we are now in a position to rewrite Eq. (24) as

$$\sigma(\mathbf{r}, t) = \sigma^{\text{ad}}(\mathbf{r}, t) + \sigma^{\text{sup}}(\mathbf{r}, t) + \sigma^{\text{ext}}(\mathbf{r}, t) + \sigma^{\text{stat}}(\mathbf{r}, t), \quad (26)$$

where the superadiabatic stress tensor  $\sigma^{\text{sup}}(\mathbf{r}, t)$  is obtained from the superadiabatic excess functional via

$$\sigma^{\text{sup}}(\mathbf{r}, t) \equiv \left. \frac{\delta P_t^{\text{exc}}}{\delta \nabla \mathbf{v}(\mathbf{r}, t)} \right|_{\rho} \quad (27)$$

$$= -\nabla^{-1} \left( \rho(\mathbf{r}, t) \left. \frac{\delta P_t^{\text{exc}}}{\delta \mathbf{J}(\mathbf{r}, t)} \right|_{\rho} \right). \quad (28)$$

As a result of the variable transformation between  $\mathbf{J}$ ,  $\mathbf{v}$ , and  $\nabla \mathbf{v}$ , at fixed density, the excess free power functional can be alternatively and equivalently expressed as  $P_t^{\text{exc}}[\rho, \mathbf{J}]$ ,  $P_t^{\text{exc}}[\rho, \mathbf{v}]$ , or  $P_t^{\text{exc}}[\rho, \nabla \mathbf{v}]$ .

The theory laid out so far is an exact reformulation of the many-body problem in nonequilibrium. Its complexity is entirely contained in the functional form of  $P_t^{\text{exc}}$ . It requires approximations to make further progress. To lowest order in  $\nabla \mathbf{v}$ , we assume a bilinear form, which is nonlocal in space and time:

$$P_t^{\text{exc}} = k_B T \int d\mathbf{r} \int d\mathbf{r}' \int_0^t dt' \rho(\mathbf{r}, t) \nabla \mathbf{v}(\mathbf{r}, t) : \mathbf{M}(\mathbf{r} - \mathbf{r}', t - t') : \nabla \mathbf{v}(\mathbf{r}', t') \rho(\mathbf{r}', t'), \quad (29)$$

where  $\mathbf{M}(\mathbf{r}, t)$  is a fourth-rank tensor that carries no physical units and depends in general functionally on the density distribution; the state of the system is assumed to be known at the initial time  $t = 0$ . The bilinear form (29) implies the existence of a power series, and constitutes plausibly its lowest order term. Note that terms linear in the current (or equivalently in  $\nabla \mathbf{v}$ ) describe the external power  $X_t$  (13) and the (adiabatic) free energy rate  $\dot{F}[\rho]$ , cf. its explicit expression below (12).

On long time scales and for small inhomogeneities we may further approximate, and use a Markovian and spatially local approximation. Because of rotational symmetry we obtain the simple form

$$P_t^{\text{exc}} = \frac{1}{2} \int d\mathbf{r} \rho [n_{\text{rot}} (\nabla \times \mathbf{v})^2 + n_{\text{div}} (\nabla \cdot \mathbf{v})^2], \quad (30)$$

where  $n_{\text{rot}}$  and  $n_{\text{div}}$  are parameters with units of energy  $\times$  time. Hence, the dynamical shear and volume viscosity are given, respectively, by

$$\eta = \rho n_{\text{rot}}, \quad \zeta = \rho n_{\text{div}} \quad (31)$$

with units of Pa s = N s/m<sup>2</sup> = J s/m<sup>3</sup>. When starting from Eq. (29) the viscosities can then be obtained as moments of the memory kernel  $\mathbf{M}$ . The full (fourth-rank) viscosity tensor  $\eta(\mathbf{r}, \mathbf{r}', t, t')$  is obtained as the functional derivative

$$\eta = \left. \frac{\delta \sigma^{\text{sup}}(\mathbf{r}, t)}{\delta \nabla \mathbf{v}(\mathbf{r}', t')} \right|_{\rho} = \left. \frac{\delta^2 P_t^{\text{exc}}}{\delta \nabla \mathbf{v}(\mathbf{r}', t') \delta \nabla \mathbf{v}(\mathbf{r}, t)} \right|_{\rho}, \quad (32)$$

which then gives a response expression  $\sigma^{\text{sup}} = \int d\mathbf{r}' dt' \eta : \nabla \mathbf{v}$ . Note that  $\eta$  constitutes an abstract object that typically can be reduced by symmetry considerations. However, the general form arises quite naturally, see, e.g., the Boltzmann-type DDFT by Anero and Español [35], the coarse-graining approach by Hütter and Brader [36], and Olmsted’s review on shear banding [37].

Assuming constant viscosities and density, the superadiabatic force density that follows from Eq. (30) has the familiar Stokes form of hydrodynamics [34]:

$$\rho \mathbf{f}_{\text{sup}}(\mathbf{r}, t) \equiv - \frac{\delta P_t^{\text{exc}}}{\delta \mathbf{v}(\mathbf{r}, t)} \quad (33)$$

$$= \eta (\nabla^2 \mathbf{v} - \nabla \nabla \cdot \mathbf{v}) + \zeta \nabla \nabla \cdot \mathbf{v}. \quad (34)$$

In the more general case, without the above restrictions, Eq. (33) yields

$$\rho \mathbf{f}_{\text{sup}}(\mathbf{r}, t) = \nabla \rho n_{\text{rot}} \cdot \nabla \mathbf{v} - \nabla \rho n_{\text{rot}} \nabla \cdot \mathbf{v} + \nabla \rho n_{\text{div}} \nabla \cdot \mathbf{v}, \quad (35)$$

where the leftmost derivatives act on each entire expression.

As a proof of concept we apply the power functional approach developed here to a 1D system of hard particles, and compare the results to Brownian dynamics (BD) simulations. A 1D system of hard particles is an ideal test case since the exact equilibrium density functional is known [38]. Hence, differences between the time evolution predicted by PFT and that obtained with BD simulations are primarily due to the use of an approximate PFT. As our system contains a reduced number of particles, the use of

different statistical ensembles (grand canonical for the derivative of the free energy in PFT and canonical in BD) might, in principle, be an additional source of discrepancy between theory and simulations. To minimize this effect, we have selected cases for which the equilibrium density profiles obtained with density functional theory and BD are very similar. In other cases it would be necessary to first obtain the canonical data from grand canonical density functional theory [39,40].

We study the time evolution of a system of  $N$  hard particles of size  $L$  in a box of length  $H$  with periodic boundary conditions. The system is initially in equilibrium in an external potential given by  $V_{\text{ext}}(x) = V_0 \sin(2\pi x N/H)$  with  $x$  the spatial coordinate. At  $t = 0$  we switch off the external potential and study the time evolution both with BD and PFT. Here, we model the superadiabatic excess functional (30) by

$$P_t^{\text{exc}} = k_B T \frac{K(\bar{\rho}, t)}{2} \int_0^H dx \rho(x, t) [\partial_x v(x, t)]^2, \quad (36)$$

where the velocity profile is defined via Eq. (16) and  $K$  is a global prefactor (related to the kernel  $\mathbf{M}$ ) that depends on the average density  $\bar{\rho}$  and the time  $t$  and takes into account the memory effects. The superadiabatic force density  $I_{\text{sup}}(x, t)$ , which is neglected in DDFT, is given by the functional derivative (33) of  $P_t^{\text{exc}}$ , multiplied by the one-body density, i.e.,  $I_{\text{sup}} = \rho f_{\text{sup}}$ .

We apply the numerical method of Ref. [41] to measure  $I_{\text{sup}}(x, t)$  using BD simulations, and compare to the theoretical results. As we will see below, memory plays an important role during the time evolution of the system. We include memory effects in the time-dependent prefactor  $K(\bar{\rho}, t)$  of  $P_t^{\text{exc}}$ , cf. Eq. (36). The explicit dependence of  $K$  on time will be the focus of a future study. Here, we are only interested in the functional form of  $P_t^{\text{exc}}$  with the velocity profile. Hence, to compare theory and simulations we (i) obtain  $I_{\text{sup}}$  and the density profile  $\rho(x, t)$  at a given time  $t$  using BD simulations, and (ii) use  $\rho(x, t)$  as input of our PFT and find the value of  $K$  that best reproduces the simulation results. In other words, we fit the amplitude of the superadiabatic force, but nothing else.

Figure 1 shows the density and the excess adiabatic and superadiabatic force density profiles of systems with  $N = 15$  (a) and  $N = 20$  (b) at time  $t = 0.1\tau$  with  $\tau = L^2\gamma/(k_B T)$ , and  $H/L = 30$ . The excess adiabatic and superadiabatic force densities are of the same order of magnitude. In (a) superadiabatic and adiabatic forces are out of phase, whereas the opposite is true in (b). These examples highlight the important contribution of  $P_t^{\text{exc}}$  to the force balance: the magnitude of the superadiabatic force is not negligible and its structure is nontrivial. The agreement between PFT and BD is excellent in all cases analyzed.

The insets of Fig. 1 show the prefactor  $K$  of  $P_t^{\text{exc}}$ , which measures the magnitude of  $I_{\text{sup}}$ , as a function of time for

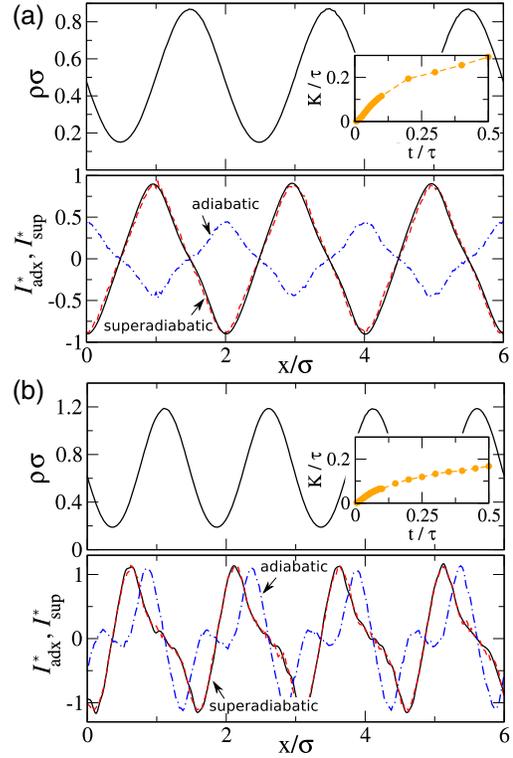


FIG. 1. (a) Density profile  $\rho(x, t)$  as a function of  $x$  (top panel) in a periodic system with  $N = 15$  and size  $H = 30$  obtained with Brownian dynamics simulations (only a small portion of the box is shown). The bottom panel of (a) shows the scaled excess (over ideal gas) adiabatic force density  $I_{\text{adx}}^* = \rho f_{\text{adx}} L^2 / (k_B T)$  (blue dash-dotted line) as a function of  $x$ . The scaled superadiabatic force density  $I_{\text{sup}}^* = I_{\text{sup}} L^2 / (k_B T)$  is also shown according to Brownian dynamics simulation (red dashed line) and the current power functional theory (black solid line). Data taken at time  $t = 0.1\tau$  after switching off the external potential. The inset in the top panel shows the time evolution of  $K$  (prefactor in  $P_{\text{exc}}$ ) as a function of the scale time  $t/\tau$ . In panels (b) we show the same data as in panels (a) for a system with  $N = 20$  and  $H = 30$ .

systems with  $N = 15$  and  $20$  ( $H/L = 30$  in both cases). As expected, the superadiabatic force vanishes for  $t = 0$  (since the system is at equilibrium at  $t = 0$ ) and reaches a plateau as time evolves due to the saturation of memory effects.

The reformulation of PFT in terms of the gradient of the velocity field, as presented here, is amenable to the study of stress-stress and strain rate–strain rate correlation functions via functional differentiation, and corresponding nonequilibrium Ornstein-Zernike relations [17,18].

In future work, the explicit study of memory effects is an important topic. Higher (than bilinear) order contributions to  $P_t^{\text{exc}}$  can be systematically constructed from combinations of the scalars  $\nabla \cdot \mathbf{v}$  and  $(\nabla \times \mathbf{v})^2$ . The resulting nonequilibrium forces go beyond the viscous forces that follow from Eq. (30). Work along these lines will be presented elsewhere [42]. Further possible interesting applications include gravitational collapse [43] of monolayers and active microrheology [44].

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