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ABSTRACT

The theory of nonlocal isothermal hydrodynamics near a solid object derived microscopically in the study by Camargo *et al.* [J. Chem. Phys. **148**, 064107 (2018)] is considered under the conditions that the flow fields are of macroscopic character. We show that in the limit of macroscopic flows, a simple pillbox argument implies that the reversible and irreversible forces that the solid exerts on the fluid can be represented in terms of boundary conditions. In this way, boundary conditions are derived from the underlying microscopic dynamics of the fluid-solid system. These boundary conditions are the impenetrability condition and the Navier slip boundary condition. The Green-Kubo transport coefficients associated with the irreversible forces that the solid exert on the fluid appear naturally in the slip length. The microscopic expression for the slip length thus obtained is shown to coincide with the one provided originally by Bocquet and Barrat [Phys. Rev. E **49**, 3079 (1994)].

I. INTRODUCTION

Field theories such as hydrodynamics are described with partial differential equations (PDEs) that, from a mathematical point of view, require for their solution the specification of boundary conditions. The boundary conditions select among the family of solutions of the PDE those that meet certain requirements that describe the physical conditions of the system. The boundary conditions are, in general, compact forms of describing the interaction of the system with that part of the world beyond the boundaries and which is not included in the description of the system.

It is obvious that hydrodynamics as a field theory is, in fact, a coarse-grained representation of fluid systems that at a microscopic level are composed of atoms and/or molecules. In Ref. 1, we have derived the equations of hydrodynamics from the microscopic Hamiltonian dynamics with the standard technique of projection operators.[2] A similar derivation for quiescent nonisothermal fluids has also been considered in Ref. 3. While this program has been done many times in the past for the case of "unconfined" fluids,[4,5] the novelty of Ref. 1 relies on the fact that the interactions with a solid object are considered explicitly. The resulting hydrodynamic equations contain additional terms that represent, in a coarse-grained way, the interaction of the solid with the fluid. These interactions are highly localized near the solid surface and have two components. The first component is purely reversible and responsible for the impenetrability of the solid by the fluid. It can be modeled with a coarse-grained potential of the hard core type in the free energy functional. The second component is irreversible and produces forces on the fluid proportional to both velocity gradients near the surface of the particle and velocity differences between the fluid velocity near the surface of the solid and the solid velocity. The irreversible forces contain transport "coefficients" that are given in terms of Green-Kubo expressions that can be explicitly computed, in principle, in molecular dynamic (MD) simulations. This, of course, requires a suitable discretization of the continuum equations that will be presented elsewhere.[6–9]

For situations in which the solid has macroscopic dimensions (as compared with molecular correlations) and the flow fields vary accordingly on these length scales, we expect that the coarse-grained solid-fluid interactions can be represented with boundary conditions

to be applied on the fluid region, slightly away from the surface of the solid. The purpose of this paper is to consider the application of the theory in Ref. 1 to macroscopic situations. Under simplifying symmetry assumptions about the interactions between the solid sphere and fluid, this leads to a derivation of boundary conditions for hydrodynamics from microscopic principles.

From a thermodynamic point of view, the issue of boundary conditions as emerging from "Physics" rather than "Numerical Analysis" has also been considered in the past[10–15] (see Ref. 16 for a review). In a pioneering work, Bedeaux, Albano, and Mazur[10] used linear irreversible thermodynamics to derive phenomenological equations for fluids with interfacial effects, an approach that naturally leads to boundary conditions that include in its formulation specific transport coefficients. Brenner[17] and Qian *et al.*[14] discuss the physics underlying boundary conditions and present singular perturbation methods and scaling arguments that enlighten the emergence of boundary conditions from a physical perspective. The above approaches are phenomenological, based on thermodynamic considerations.

From a statistical mechanics point of view, there has also been a large body of studies dealing with the problem of derivation of boundary conditions from either linear response theory[18–25] or from the comparison of measured correlations of hydrodynamic variables with analytical predictions of continuum hydrodynamics.[18,26] We refer to Ref. 1 for the discussion of this literature.

In this paper, we consider the theory presented in Ref. 1 in the limit of macroscopic geometries and flows. This allows us to obtain the boundary conditions to be satisfied by the flow field with explicit microscopic expressions for the different transport coefficients entering the slip boundary condition. This approach to obtain microscopic expressions for transport coefficients is very different and complementary to either linear response theory or the method of comparison of equilibrium correlation functions with analytical results.

This paper is organized as follows: In Sec. II, we advance the main results of this paper for the sake of clarity. In Sec. III, a summary of Ref. 1 is given as this is our starting point in the derivation of boundary conditions. In Sec. IV, we use a pillbox argument to obtain a mechanical balance condition. In Sec. V, we show that under the assumption of a linear velocity profile within the pillbox, the mechanical balance condition leads to the slip boundary condition with explicit expressions for the slip length in microscopic terms. In Sec. VI, we show that the resulting slip length is identical, with a suitable redefinition of the wall position, to the microscopic expression given by Bocquet and Barrat[18] (referred to as BB in the following).

II. SUMMARY

We advance the main results of the present paper, which are the boundary conditions for the velocity field of a fluid around a nonrotating solid sphere that has velocity $\mathbf{V}$. The sphere radius is much larger than molecular dimensions, and around a point $\mathbf{r}_{\rm wall}$ near the atomically fuzzy surface, we consider a very flat pillbox. In the scale of the pillbox, the surface of the sphere appears flat. It is assumed that the velocity field inside the pillbox takes a linear form

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_{\rm wall} + \dot{\boldsymbol{\gamma}} \cdot (\mathbf{r} - \mathbf{r}_{\rm wall}), \tag{1}$$

where $\dot{\boldsymbol{\gamma}}$ is the shear rate tensor and $\mathbf{v}_{\rm wall}$ is the value of the velocity field at the point $\mathbf{r}_{\rm wall}$. By using estimates of order of magnitude, a mechanical balance condition on the pillbox leads to the following boundary conditions to be satisfied by $\mathbf{v}_{\rm wall}$:

$$\begin{aligned} 0 &= \mathbf{n} \cdot (\mathbf{v}_{\rm wall} - \mathbf{V}), \\ \eta' \mathbf{t}_1 \cdot \left[\dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}}^T\right] \cdot \mathbf{n} &= \overline{\gamma}^{\parallel} \mathbf{t}_1 \cdot [\mathbf{v}_{\rm wall} - \mathbf{V}], \\ \eta' \mathbf{t}_2 \cdot \left[\dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}}^T\right] \cdot \mathbf{n} &= \overline{\gamma}^{\parallel} \mathbf{t}_2 \cdot [\mathbf{v}_{\rm wall} - \mathbf{V}], \end{aligned} \tag{2}$$

where $\mathbf{n}$ is a unit vector normal to the solid wall and $\mathbf{t}_1, \mathbf{t}_2$ are the unit tangent vectors to the sphere surface. The point $\mathbf{r}_{\rm wall}$ in Eq. (1) on which the boundary conditions apply has a microscopic expression in terms of a Green-Kubo-like formula

$$\mathbf{r}_{\rm wall} = \frac{1}{\overline{\gamma}^{\parallel} S} \int_0^{\Delta t} dt \left\langle \hat{\mathbf{F}}^{\parallel}(t) \sum_{ij'} \hat{\mathbf{F}}^{\parallel}_{ij'} \mathbf{r}_i \right\rangle. \tag{3}$$

In this expression, $\hat{\mathbf{F}}^{\parallel}_{ij'} = \mathbf{t} \cdot \hat{\mathbf{F}}_{ij'}$ is the tangent component (any of them) of the force that the solid atom j' exerts on the fluid atom i and $\hat{\mathbf{F}}^{\parallel} = \sum_{ij'} \hat{\mathbf{F}}^{\parallel}_{ij'}$, where the sums are over the atoms of the solid sphere that are within the pillbox. Unprimed indices refer to fluid particles, while primed indices like j' refer to any of the N' atoms in the solid. The position of the point $\mathbf{r}_{\rm wall}$ may be taken as a definition of the exact location of the "solid wall surface" out of an atomically fuzzy surface. The friction coefficient in (2) and (3) is defined in terms of a Green-Kubo formula

$$\overline{\gamma}^{\parallel} = \frac{1}{S} \int_0^{\Delta t} dt \left\langle \hat{\mathbf{F}}^{\parallel}(t) \hat{\mathbf{F}}^{\parallel} \right\rangle. \tag{4}$$

Finally, the modified shear viscosity $\eta' = \eta - \overline{G}^{(1)}$ is given in terms of the shear viscosity η defined in terms of the usual Green-Kubo expression

$$\eta = \frac{1}{V k_B T} \int_0^{\Delta t} dt \left\langle \hat{\boldsymbol{\sigma}}^{\parallel\perp}(t) \hat{\boldsymbol{\sigma}}^{\parallel\perp} \right\rangle, \tag{5}$$

where the bulk stress tensor of the fluid is given as

$$\hat{\boldsymbol{\sigma}} = \sum_i \mathbf{p}_i \mathbf{v}_i + \frac{1}{2} \sum_{ij} \hat{\mathbf{F}}_{ij} \mathbf{r}_{ij} \tag{6}$$

and $\hat{\boldsymbol{\sigma}}^{\parallel\perp} = \mathbf{t} \cdot \hat{\boldsymbol{\sigma}} \cdot \mathbf{n}$ is an off-diagonal component of this tensor. Finally, the last transport coefficient entering the boundary conditions is

$$\overline{G}^{(1)} = \frac{1}{S} \int_0^{\Delta t} dt \left\langle \hat{\mathbf{F}}^{\parallel}(t) \boldsymbol{\sigma}^{\parallel\perp} \right\rangle. \tag{7}$$

The upper limit Δt of the Green-Kubo integrals is not set to infinity in order to avoid the plateau problem. An in-depth discussion of the plateau problem and its solution is presented in a recent publication.[27]

Equations (2) are a set of three conditions that the velocity field has to satisfy at a point $\mathbf{r}_{\rm wall}$ that is "near the solid wall." The first equation in (2) is the impenetrability condition, while the second equation in (2) is the Navier slip boundary conditions in tensorial form, as was formulated many years ago by Liu and co-workers[12]

(see also recent reviews[28,29]). The tensorial representation allows one, for example, to compute curvature effects to the slip near a wall.[12]

The merit of this paper is not only the derivation of these boundary conditions from the hydrodynamic equations derived in Ref. 1 but also, more importantly, the formulation of the microscopic expressions (3)–(7) for the quantities entering the boundary conditions. Although the boundary conditions (2) have been obtained for a solid sphere, it is apparent from the arguments in Secs. IV–VI that they can be extended to any flow geometry, given that such a geometry is "macroscopic" (i.e., with length scales much larger than molecular dimensions). In order to compute from equilibrium MD simulations the microscopic expressions entering the slip boundary condition on a given atomic surface, the simplest and more convenient geometry is a planar channel. In this case, the pillbox can be taken as a thin slab covering all the solid-fluid interface and with area $S = L_x L_y$, where L_x, L_y, and L_z are the box dimensions. The volume V is the volume inside the channel for which the density field is constant (away from the molecular layering of the density near the wall).

Note that different definitions of the position $\mathbf{r}_{\rm wall}$ of the surface where the boundary condition is considered would give different forms of the boundary condition and, in particular, to the microscopic definitions of the objects entering it. We will show that the BB result[18] for the slip length based on linear response theory is obtained from our result (2) by a suitable redefinition of the wall position. Given the controversy raised in the literature about the proper definition of the friction coefficient of a fluid near a wall,[20–24] this alternative and very different way to obtain the BB result gives further confidence to the BB result, at least for macroscopic flows.

III. HYDRODYNAMIC THEORY FOR A SIMPLE LIQUID SURROUNDING A SOLID SPHERE

In this section, we give a brief summary of Ref. 1 which is the basis for the present work. By starting from the microscopic Hamiltonian dynamics of the system, and through the projection operator method,[2] we have derived in Ref. 1 the following hydrodynamic equations for a fluid surrounding a spherical solid particle:

$$\begin{aligned}
\partial_t \rho(\mathbf{r}) &= -\nabla\cdot\mathbf{g}(\mathbf{r}),\\
\partial_t \mathbf{g}(\mathbf{r}) &= -\nabla\cdot\mathbf{g}(\mathbf{r})\mathbf{v}(\mathbf{r}) - \rho(\mathbf{r})\nabla\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{r})}(\mathbf{r},\mathbf{R}), + \nabla\boldsymbol{\Sigma}(\mathbf{r}) + \mathcal{S}(\mathbf{r}),\\
\dot{\mathbf{R}} &= \mathbf{V},\\
\dot{\mathbf{P}} &= -\frac{\partial\mathcal{F}}{\partial\mathbf{R}} - \int d\mathbf{r}\mathcal{S}(\mathbf{r}),
\end{aligned} \tag{8}$$

where $\rho(\mathbf{r})$, $\mathbf{g}(\mathbf{r})$ are the mass and momentum density fields of the fluid, and $\mathbf{R}$, $\mathbf{P}$ are the position and momentum of the solid sphere and $\mathbf{V} = \mathbf{P}/M$ is the velocity of the sphere. It is assumed that the whole system of the fluid plus solid sphere is enclosed in periodic boundary conditions. The fields $\rho(\mathbf{r})$, $\mathbf{g}(\mathbf{r})$ are defined as the nonequilibrium average of the microscopic phase functions

$$\begin{aligned}
\hat{\rho}_{\mathbf{r}} &= \sum_i^N m_i\delta(\mathbf{r}-\mathbf{r}_i),\\
\hat{\mathbf{g}}_{\mathbf{r}} &= \sum_i^N \mathbf{p}_i\delta(\mathbf{r}-\mathbf{r}_i).
\end{aligned} \tag{9}$$

The average of the density field defined in terms of the Dirac delta function may vary over molecular length scales and can resolve, in principle, the well-known layering of a fluid near a wall.

Other quantities in (8) are the velocity field $\mathbf{v}(\mathbf{r}) = \mathbf{g}(\mathbf{r})/\rho(\mathbf{r})$, and the fluid stress tensor $\boldsymbol{\Sigma}(\mathbf{r})$ and the irreversible surface force $\mathcal{S}(\mathbf{r})$ given by

$$\begin{aligned}
\boldsymbol{\Sigma}^{\alpha\beta}(\mathbf{r}) &= \int d\mathbf{r}'\,\boldsymbol{\eta}^{\alpha\beta\alpha'\beta'}_{\mathbf{r}\mathbf{r}'}\nabla^{\beta'}_{\mathbf{r}'}\mathbf{v}^{\alpha'}(\mathbf{r}'),\\
\mathcal{S}^{\alpha}(\mathbf{r}) &= -\int d\mathbf{r}'\mathbf{G}^{\alpha\alpha'\beta'}_{\mathbf{r}\mathbf{r}'}\nabla^{\beta'}_{\mathbf{r}'}\mathbf{v}^{\alpha'}(\mathbf{r}')\\
&\quad + \int d\mathbf{r}'\left(\nabla^{\beta}_{\mathbf{r}}\mathbf{H}^{\alpha\beta\alpha'}_{\mathbf{r}\mathbf{r}'} - \boldsymbol{\gamma}^{\alpha\alpha'}_{\mathbf{r}\mathbf{r}'}\right)(\mathbf{v}^{\alpha'}(\mathbf{r}') - \mathbf{V}^{\alpha'}).
\end{aligned} \tag{10}$$

Here, α, β, etc., are Cartesian indices. The integrals extend over all space containing the fluid and the sphere. The nonlocal transport coefficients are given in terms of Green-Kubo formulae

$$\begin{aligned}
\boldsymbol{\eta}_{\mathbf{r}\mathbf{r}'} &\equiv \frac{1}{k_BT}\int_0^{\Delta t} dt\langle\mathcal{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle,\\
\mathbf{H}_{\mathbf{r}\mathbf{r}'} &\equiv \frac{1}{k_BT}\int_0^{\Delta t} dt\langle\mathcal{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t)\mathcal{Q}\hat{\mathbf{F}}_{\mathbf{r}'}\rangle,\\
\mathbf{G}_{\mathbf{r}\mathbf{r}'} &\equiv \frac{1}{k_BT}\int_0^{\Delta t} dt\langle\mathcal{Q}\hat{\mathbf{F}}_{\mathbf{r}}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle,\\
\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'} &\equiv \frac{1}{k_BT}\int_0^{\Delta t} dt\langle\mathcal{Q}\hat{\mathbf{F}}_{\mathbf{r}}(t)\mathcal{Q}\hat{\mathbf{F}}_{\mathbf{r}'}\rangle.
\end{aligned} \tag{11}$$

Here, $\langle\cdots\rangle$ denotes an equilibrium ensemble average and the action of the projector $\mathcal{Q}$ is defined explicitly in Ref. 1 and reproduced in the Appendix. The microscopic force density $\hat{\mathbf{F}}_{\mathbf{r}}$ that the solid exerts on the fluid and the microscopic stress tensor $\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$ in (11) are defined as

$$\begin{aligned}
\hat{\mathbf{F}}_{\mathbf{r}} &\equiv \sum_{ij'}^{NN'}\hat{\mathbf{F}}_{ij'}\delta(\mathbf{r}-\mathbf{r}_i),\\
\hat{\boldsymbol{\sigma}}_{\mathbf{r}} &\equiv \sum_i^N \mathbf{p}_i\mathbf{v}_i\delta(\mathbf{r}-\mathbf{r}_i) + \frac{1}{2}\sum_{ij}^N \mathbf{r}_{ij}\hat{\mathbf{F}}_{ij}\int_0^1 d\epsilon\,\delta(\mathbf{r}-\mathbf{r}_i+\epsilon\mathbf{r}_{ij}),
\end{aligned} \tag{12}$$

where $\mathbf{r}_i$, $\mathbf{p}_i$ are the position and momenta of the ith atom of the fluid in the system.

Note that the nonlocal transport coefficients $\mathbf{G}_{\mathbf{r}\mathbf{r}'}$, $\mathbf{H}_{\mathbf{r}\mathbf{r}'}$, $\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'}$ appearing in the surface force (10) and defined in (11) all involve correlations with the force density $\hat{\mathbf{F}}_{\mathbf{r}}$. This force density defined in (12) vanishes in a molecular scale away from the surface of the solid because the force $\hat{\mathbf{F}}_{ij'}$ between fluid and solid particles is short ranged. Therefore, the surface force $\mathcal{S}(\mathbf{r})$ is nonzero only in a layer of a molecular width near the solid surface.

The structure of the dissipative force $\nabla\boldsymbol{\Sigma} + \mathcal{S}$ in the momentum equation in Eq. (8) is due to the fact that, at a fundamental

level, the momentum of the fluid changes because of the action of forces exerted by the fluid and forces due to the solid. The former can be expressed in terms of the divergence of a microscopic stress tensor, but the latter cannot be expressed in terms of a stress tensor. As a consequence, the dissipative forces $\nabla\mathbf{\Sigma}$ that the fluid exerts on the fluid itself contain second derivatives of the velocity field (in a local approximation away from the walls, they produce the usual viscous terms in the Navier-Stokes equations), while the dissipative forces $\mathcal{S}$ that the solid exerts on the fluid in Eq. (10) contain terms that are proportional to the velocity differences between the fluid and solid (that is, friction forces associated with slip) and also terms that are proportional to gradients of the velocity field.

Finally, the free energy functional $\mathcal{F}[\rho, \mathbf{R}]$ appearing in (8) is defined microscopically in Ref. 1 and it is a natural generalization of the usual equilibrium free energy functional familiar in equilibrium Density Functional Theory (DFT),[30] where the effect of the solid particle is explicitly taken into account. In that sense, Eqs. (8) can be understood as a generalization of DFT to the dynamic realm for simple fluids in isothermal situations but not in mechanical equilibrium. Note that in the limit of infinite radius, the solid particle can be understood as a planar wall. Usually, the presence of a wall in DFT is modeled simply with an "external potential," which should be understood as a coarse-grained potential that accounts for all the eliminated degrees of freedom of the solid, assumed to be very fast as compared with the solvent degrees of freedom (i.e., there is no slow elastic response of the solid). A simple model for the free energy functional is

$$\mathcal{F}[\rho, \mathbf{R}] = \mathcal{F}[\rho] + \int d\mathbf{r} V(|\mathbf{r} - \mathbf{R}|)\rho(\mathbf{r}), \tag{13}$$

where $\mathcal{F}[\rho]$ is the standard free energy functional of the fluid in the absence of the solid sphere. One particularly simple model for the coarse-grained effect of the wall is through a hard core model given by $V(\mathbf{r}, \mathbf{R}) = \phi(|\mathbf{r} - \mathbf{R}| - a)$, where $\phi(r)$ is a short ranged potential of mean force describing the effective interaction between the solid and fluid and a is the effective radius of the solid sphere. For a planar wall, one may assume that this potential depends only on the distance of the point $\mathbf{r}$ to the wall, thus obviating any roughness effect from the wall.

Equations (8) govern the evolution of the nonlocal hydrodynamics of a simple isothermal fluid coupled with the motion of an immersed structureless solid sphere. The only approximation that has been taken in the derivation of Eqs. (8) in Ref. 1 is the Markovian approximation that neglects memory effects in the dissipative part of the dynamics. The reversible part of the dynamics is exact. We have observed in MD simulations, to be presented elsewhere,[8] that in the strict continuum limit the Markovian assumption breaks down near solid walls. Only when the hydrodynamic variables are defined with an intrinsic length scale which is larger than the radius of the atoms or molecules of the simple liquid, we recover a Markovian behavior. In the case of MD simulations that employ bins, the bin width needs to be larger than the molecular size. The counterpart in the present continuum theory involves a redefinition of the hydrodynamic fields (9) in terms of a coarse delta function $\bar{\delta}(\mathbf{r} - \mathbf{r}_i)$ of a bell shaped form with finite support of molecular dimension.[31] With the hydrodynamic fields defined in terms of the coarse delta function, one can go over the steps in Ref. 1 and obtain a set of equations identical to (8) for the new, coarser fields. The resulting Markovian equations should reproduce correctly the hydrodynamic behavior at scales larger than molecular dimensions.

When the density field $\hat{\rho}_\mathbf{r}$ in Eq. (9) is defined not with the Dirac delta function but with a coarse delta function, the free energy $\mathcal{F}[\rho]$ is no longer the exact free energy functional of DFT. The latter would allow one to predict the density layering which is blurred for the coarse density field. In DFT, there are many approximate expressions for the density functional $\mathcal{F}[\rho]$ of a simple structured liquid that range from the simplest local approximation, through the square gradient approximation, to weighted density approximations.[32] For the case of coarse density field in which correlations are blurred, we expect that a good model for the resulting free energy functional is given by the local density approximation

$$\mathcal{F}[\rho] = \int d\mathbf{r} f(\rho(\mathbf{r})), \tag{14}$$

where $f(\rho)$ is the bulk thermodynamic free energy density of the fluid. We will assume that the model (13) with (14) for the free energy functional is sufficiently good at macroscopic length scales, which are the ones we are concerned in this paper.

Once we assume the free energy model (13) and (14), we may compute the reversible coupling of the momentum density field with the motion of the sphere, which is given in Eq. (8) by the term

$$\begin{aligned} -\rho(\mathbf{r})\nabla\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{r})}[\rho, \mathbf{R}] &= -\rho(\mathbf{r})\nabla\left[f'(\rho(\mathbf{r})) + V(\mathbf{r})\right] \\ &= -\nabla P(\rho(\mathbf{r})) - n(\mathbf{r})\nabla V(\mathbf{r}), \end{aligned} \tag{15}$$

where we have introduced the number density $n(\mathbf{r}) = \rho(\mathbf{r})/m$ and the usual definition of the pressure of the fluid in terms of the free energy density

$$P(\rho) = \rho f'(\rho) - f(\rho), \tag{16}$$

where the prime denotes derivative. Therefore, the reversible term $-\rho\nabla\frac{\delta\mathcal{F}}{\delta\rho}$ is just the usual pressure gradient in the Navier-Stokes equations plus the body force exerted by the solid particle on the fluid through the CG potential V. When the size of the solid sphere is so small that it becomes comparable to the length scale of the structure of the fluid, then the local free energy model (14) is not appropriate and the concept of pressure is not as useful. A different approach is then required, as we have shown in Ref. 33.

IV. MECHANICAL BALANCE FROM A PILLBOX ARGUMENT FOR A MACROSCOPIC BODY

The approach that we take in order to formulate boundary conditions is a pillbox argument for mechanical balance. A more sophisticated and rigorous singular perturbation theory approach could be taken, as advocated by Brenner,[17] but the present heuristic arguments are sufficient at present. See also the discussion in Ref. 14 that bears resemblance on the arguments we present in what follows. As depicted in Fig. 1, the pillbox is a cylinder limited by the surface $\Sigma = \Sigma^1 + \Sigma^2 + \Delta\Sigma$. The area of the lids Σ^1 and Σ^2 is $\pi\epsilon^2$, while the area of the lateral surface $\Delta\Sigma$ is $4\pi\Delta\epsilon$, where ϵ is the radius of the cylinder and 2Δ its height. We assume that the pillbox is very flat, i.e., $2\Delta \ll \epsilon$. We also assume that $\epsilon \ll \lambda$, where λ is the length scale

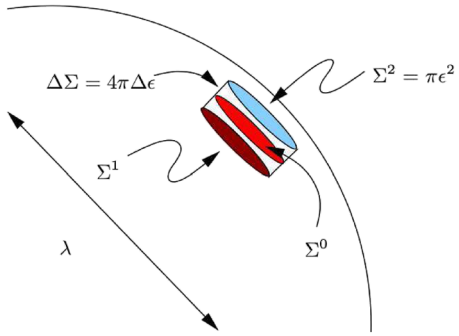

FIG. 1. A pillbox of height 2Δ, area $S = \pi\epsilon^2$, and lateral surface $\Delta\Sigma = 4\pi\epsilon\Delta$ intersects the surface of the solid sphere at Σ^0. The surface Σ^1 is inside the solid and Σ^2 is inside the fluid region. The separation between these two surfaces is 2Δ. The length scale λ of the flow field is assumed to be of the order of the radius of the macroscopic sphere. It is assumed that $\sigma_0 \ll 2\Delta \ll \epsilon \ll \lambda$. Finally, the center of the outer surface Σ^2 is located at $\mathbf{r}_0$.

of variation of the flow fields, typically of the order of the radius of the sphere, which is assumed to be macroscopic. In addition, the height of the cylinder is assumed to be much larger than a molecular diameter σ_0. We assume that the planar surface Σ^1 is inside the solid sphere, while the planar surface Σ^2 is outside the solid sphere, beyond the range of interaction between the solid atoms and fluid atoms, and where the density already has achieved its bulk value. The center of the circular surface Σ^2 is located at $\mathbf{r}_0$ within the bulk region of the fluid. Note that the irreversible surface force $\mathcal{S}(\mathbf{r})$, whose Green-Kubo transport coefficients (11) contain the force $\mathbf{F}_\mathbf{r}$ defined in (12), will vanish away from the solid object. Therefore, in the surface Σ^2, the surface force $\mathcal{S}(\mathbf{r})$ vanishes, while the stress tensor $\boldsymbol{\Sigma}(\mathbf{r})$ takes the bulk isotropic value. As it is clear, the overall shape of the macroscopic body (a sphere in this case) is irrelevant in the argument. For a macroscopic body, the pillbox "sees" the body as a planar wall.

We will make use of the well-known theorem for the time derivative of the integral of a function $A(\mathbf{r}, t)$ over a time-dependent volume $\Omega(t)$ that has $\Sigma(t)$ as its moving surface boundary

$$\frac{d}{dt}\int_{\Omega(t)} A(\mathbf{r},t)d\mathbf{r} = \int_{\Omega(t)} \frac{\partial}{\partial t}A(\mathbf{r},t)d\mathbf{r} + \int_{\Sigma(t)} dS\mathbf{n}\cdot\mathbf{v}^\Sigma(\mathbf{r})A(\mathbf{r},t). \tag{17}$$

The first term in the right-hand side exists even if the volume does not move and accounts for the time dependence of the function $A(\mathbf{r}, t)$. The second term is the variation on the amount of A that is inside the volume due to the sweeping of the surface $\Sigma(t)$ as it moves. In this expression, $\mathbf{n}$ is the normal of the surface pointing outwards and $\mathbf{v}^\Sigma(\mathbf{r})$ is the velocity of the surface at the point $\mathbf{r}$ on the surface. We will take as the volume $\Omega(t)$, the volume of the infinitesimal pillbox that intersects the boundary region between the solid and fluid, as shown in Fig. 1.

A. Impenetrability condition

When we take the density field $\rho(\mathbf{r})$ as the function $A(\mathbf{r})$ in the above theorem (17), we obtain

$$\frac{d}{dt}\int_\Omega \rho(\mathbf{r},t)d\mathbf{r} = \int_\Omega \frac{\partial}{\partial t}\rho(\mathbf{r},t)d\mathbf{r} + \int_\Sigma dS\mathbf{n}\cdot\mathbf{V}\rho(\mathbf{r},t), \tag{18}$$

where, for simplicity, we assume that the sphere does not rotate and, therefore, the velocity of any point of the sphere's surface coincides with the velocity $\mathbf{V}$ of the center of the sphere, i.e., $\mathbf{v}^\Sigma = \mathbf{V}$. By using the continuity equation and Gauss' theorem, we may write (18) as

$$\begin{aligned}\frac{d}{dt}\int_\Omega \rho(\mathbf{r},t)d\mathbf{r} = &\int_{\Sigma^1} dS\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t))\rho(\mathbf{r},t)\\ &+\int_{\Sigma^2} dS\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t))\rho(\mathbf{r},t)\\ &+\int_{\Delta\Sigma} dS\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t))\rho(\mathbf{r},t).\end{aligned} \tag{19}$$

The left-hand side is approximately given by $\frac{d}{dt}\rho(\mathbf{r}_0,t)\pi\epsilon^2\Delta$. This is of order Δ. The last integral over the lateral surface $\Delta\Sigma$ is proportional to $\epsilon\Delta$. The rest of the terms, on the right hand side of Eq. (19), are of order ϵ^2. We may neglect therefore the terms of order Δ [the lhs of (19) and the integral over $\Delta\Sigma$]. In addition, there can be no fluid inside the solid sphere because otherwise infinite forces would develop. Therefore, the density field evaluated on the surface Σ^1 vanishes. This implies

$$\int_{\Sigma^2} dS\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t))\rho(\mathbf{r},t) = 0, \tag{20}$$

which is approximately given by

$$\pi\epsilon^2\mathbf{n}\cdot(\mathbf{v}(\mathbf{r}_0,t)-\mathbf{V}(t))\rho(\mathbf{r}_0,t) = 0 \tag{21}$$

because all fields vary little, in the length scale $\lambda \gg \epsilon$. The density field $\rho(\mathbf{r}_0, t)$ is different from zero, and therefore,

$$\mathbf{n}\cdot(\mathbf{v}(\mathbf{r}_0,t)-\mathbf{V}(t)) = 0, \tag{22}$$

which is the usual impenetrability boundary condition. While this boundary condition is perfectly adequate for the macroscopic flows considered here, it has been questioned for flows of molecular scale.[34,35]

B. Mechanical balance condition

Let us move now to the boundary conditions that emerge when we consider theorem (17) for the momentum density field. We have

$$\frac{d}{dt}\int_\Omega \mathbf{g}(\mathbf{r},t)d\mathbf{r} = \int_\Omega \frac{\partial}{\partial t}\mathbf{g}(\mathbf{r},t)d\mathbf{r} + \int_\Sigma dS\mathbf{n}\cdot\mathbf{V}\mathbf{g}(\mathbf{r},t). \tag{23}$$

By using the momentum equation in Eq. (8) and Gauss' theorem for the convective part of the equation, one obtains

$$\begin{aligned}\frac{d}{dt}\int_\Omega \mathbf{g}(\mathbf{r},t)d\mathbf{r} = &\int_\Omega d\mathbf{r}[-\nabla P(\mathbf{r})+\nabla\cdot\boldsymbol{\Sigma}(\mathbf{r})]\\ &+\int_\Omega d\mathbf{r}[-n(\mathbf{r})\nabla V(\mathbf{r})+\mathcal{S}(\mathbf{r})]\\ &+\int_\Sigma dS\mathbf{n}\cdot(\mathbf{V}-\mathbf{v}(\mathbf{r}))\mathbf{g}(\mathbf{r},t),\end{aligned} \tag{24}$$

where we have used the local model for the free energy in Eq. (15). By using the impenetrability condition Eq. (22), we may express (24) in the form

$$\mathbf{F} = \mathbf{F}^{l\to l} + \mathbf{F}^{s\to l}, \tag{25}$$

where $\mathbf{F}$ is the total force on the portion of fluid that is within the pillbox and we have decomposed this force into the forces $\mathbf{F}^{l\to l}$ and $\mathbf{F}^{s\to l}$ that the fluid and solid exert on this portion, respectively. These forces are defined as

$$\begin{aligned}\mathbf{F}^{l\to l} &\equiv \int_\Omega d\mathbf{r}[-\nabla P(\mathbf{r}) + \nabla\boldsymbol{\Sigma}(\mathbf{r})],\\ \mathbf{F}^{s\to l} &\equiv \int_\Omega d\mathbf{r}[-n(\mathbf{r})\nabla V(\mathbf{r}) + \mathcal{S}(\mathbf{r})].\end{aligned} \tag{26}$$

Let us consider each term in (26) separately. The pressure term is

$$\begin{aligned}\int_\Omega d\mathbf{r}\nabla P(\rho(\mathbf{r})) = &\underbrace{\int_{\Sigma^1} dS\mathbf{n}P(\rho(\mathbf{r}))}_{=0} + \int_{\Sigma^2} dS\mathbf{n}P(\rho(\mathbf{r}))\\ &+ \underbrace{\int_{\Delta\Sigma} dS\mathbf{n}P(\rho(\mathbf{r}))}_{\simeq 0}.\end{aligned} \tag{27}$$

The first integral in the right-hand side vanishes because Σ^1 is inside the solid sphere, where no fluid exists and the density and pressure vanish. The third integral over the lateral surface $\Delta\Sigma$ is of order Δ and negligible in front of the rest of the terms.

The fluid stress contribution in the first equation of Eq. (26) is, after using Gauss' theorem,

$$\begin{aligned}\int_\Omega d\mathbf{r}\nabla\cdot\boldsymbol{\Sigma}(\mathbf{r}) = &\underbrace{\int_{\Sigma^1} dS\mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r})}_{=0} + \int_{\Sigma^2} dS\mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r})\\ &+ \underbrace{\int_{\Delta\Sigma} dS\mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r})}_{\simeq 0} \simeq \pi\epsilon^2\mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r}_0),\end{aligned} \tag{28}$$

where a reasoning similar to that used in Eq. (27) has been followed. Therefore, the force that the liquid exerts on the fluid in the pillbox is

$$\mathbf{F}^{l\to l} \simeq \pi\epsilon^2\mathbf{n}\cdot(P(\rho(\mathbf{r}_0))\boldsymbol{\delta} + \boldsymbol{\Sigma}(\mathbf{r}_0)), \tag{29}$$

where $\boldsymbol{\delta}$ is the identity matrix, $P(\rho(\mathbf{r}_0))$ is the bulk pressure near the solid sphere, and $\boldsymbol{\Sigma}(\mathbf{r}_0)$ is the bulk fluid stress tensor near the solid sphere.

Next, consider the reversible part of the force that the solid exerts on the fluid

$$\begin{aligned}\int_\Omega d\mathbf{r}n(\mathbf{r})\nabla V(\mathbf{r}) &= \int_\Omega d\mathbf{r}n(\mathbf{r})\mathbf{n}V'(\mathbf{r})\\ &= \pi\epsilon^2\mathbf{n}\int_{a-\Delta}^{a+\Delta} drn(r)V'(r).\end{aligned} \tag{30}$$

The integral (30) is not proportional to Δ because the forces $V'(r)$ are singular. Therefore, it cannot be neglected. In order to get some intuition for this term, consider the fluid as an ideal gas, for which the equilibrium value of the density field takes the barometric form

$$n(\mathbf{r}) = n_0 e^{-\beta V(\mathbf{r})}, \tag{31}$$

where n_0 is the fluid number density beyond the range of the singular potential. Therefore, the integral in (30) becomes

$$\begin{aligned}\int_{a-\Delta}^{a+\Delta} drn(r)V'(r) &= -n_0 k_B T\int_{a-\Delta}^{a+\Delta} dr\frac{d}{dr}e^{-\beta V(\mathbf{r})}\\ &= -n_0 k_B T\left[e^{-\beta V(\mathbf{r})}\right]_{a-\Delta}^{a+\Delta}\\ &= -n_0 k_B T,\end{aligned} \tag{32}$$

where we have used that inside the solid the potential is infinite and outside (in Σ_2) it vanishes. Therefore, this term gives a finite value independent of Δ. This argument with the equilibrium profile for the ideal gas makes it plausible that the singular potential contribution (30) gives a finite value for the resulting force, independent of Δ, even for a nonequilibrium nonideal fluid.

Note that the total force $\mathbf{F} \simeq \frac{d}{dt}\mathbf{g}(\mathbf{r}_0,t)\pi\epsilon^2\Delta$ scales as Δ, while the two forces $\mathbf{F}^{l\to l}$, $\mathbf{F}^{s\to l}$ scale independently of Δ. This means that we may neglect the force $\mathbf{F}$ and we have a balance between the two forces $\mathbf{F}^{s\to l} + \mathbf{F}^{l\to l} \simeq 0$. Such a balance is always satisfied in steady state situations. Therefore, the condition (25) with (29) and (30) gives the important mechanical balance relation

$$-\mathbf{n}(P_0 + \Delta P) + \mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r}_0) + \frac{1}{\pi\epsilon^2}\int_\Omega d\mathbf{r}\mathcal{S}(\mathbf{r}) = 0, \tag{33}$$

where we have introduced

$$\Delta P = \int_{a-\Delta}^{a+\Delta} drn(r)V'(r) \tag{34}$$

as the contribution to the pressure due to the wall potential. Equation (33) expresses the mechanical balance between the bulk forces due to the macroscopic stress tensor $-P\boldsymbol{\delta} + \boldsymbol{\Sigma}$ near the wall (but already in the bulk region) and the integrated singular surface forces.

We will need the normal and tangential components of this mechanical balance (33). The normal component is given after multiplication of Eq. (33) with respect to the normal vector $\mathbf{n}$

$$\begin{aligned}0 &= \mathbf{n}\cdot\mathbf{F}^{l\to l} + \mathbf{n}\cdot\mathbf{F}^{s\to l}\\ &= -P_0 - \Delta P + \mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r}_0)\cdot\mathbf{n} + \frac{1}{S}\int_\Omega d\mathbf{r}\mathbf{n}\cdot\mathcal{S}(\mathbf{r}),\end{aligned} \tag{35}$$

where $S = \pi\epsilon^2$ is the surface of the pillbox.

The tangential component is obtained by multiplying the mechanical balance equation (33) with respect to the two mutually perpendicular tangent unit vectors $\mathbf{t}_1$, $\mathbf{t}_2$. This leads to the equation,

$$\mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r}_0)\cdot\mathbf{t}_i + \frac{1}{S}\int_\Omega d\mathbf{r}\mathbf{t}_i\cdot\mathcal{S}(\mathbf{r}) = 0, \qquad i = 1,2. \tag{36}$$

C. The total force on the sphere

For completeness, we consider the calculation of the total force that the fluid exerts on the sphere in the present approximation. On one hand, the total force on the solid sphere is given by the last equation of Eq. (8), which has been obtained from microscopic considerations

$$\dot{\mathbf{P}} = -\frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \int d\mathbf{r}\mathcal{S}(\mathbf{r}). \tag{37}$$

With the local model (13) and (14) for the free energy density, this force becomes

$$\dot{\mathbf{P}} = -\int d\mathbf{r}\left[n(\mathbf{r})\frac{\partial}{\partial \mathbf{R}}\phi(|\mathbf{r}-\mathbf{R}|-a)+\mathcal{S}(\mathbf{r})\right], \tag{38}$$

where we recall that the integral over $\mathbf{r}$ extends over the whole periodic domain. Note, though, that the integrand contains functions that are highly localized in a layer between radii $a \pm \Delta$ around the surface of the solid sphere. For this reason, we may decompose the integral as follows:

$$\dot{\mathbf{P}} = -\int_{S_0} dS \int_{a-\Delta}^{a+\Delta} dr\left[n(\mathbf{r})\frac{\partial}{\partial \mathbf{R}}\phi(|\mathbf{r}-\mathbf{R}|-a)+\mathcal{S}(\mathbf{r})\right], \tag{39}$$

where S_0 is the spherical surface of radius a that contains the solid particle. By using the mechanical balance (33), we may write the force on the particle as

$$\dot{\mathbf{P}} = -\int_{S_0} dS[\mathbf{n}P_0 - \mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r}_0)]. \tag{40}$$

By virtue of Gauss' theorem, we have

$$\dot{\mathbf{P}} = \int' d\mathbf{r}\nabla\cdot\boldsymbol{\Pi}, \tag{41}$$

where $\boldsymbol{\Pi} = -P\boldsymbol{\delta} + \boldsymbol{\Sigma}$ is the total bulk stress of the fluid and the integral is now extended to the volume of the domain exterior to the solid particle (denoted with a prime). Equation (41) is a standard fluid dynamics expression for computing the force on a macroscopic sphere due to the interaction with the fluid. It is reassuring that it is consistent with the force (37) on the sphere predicted in the microscopically derived continuum hydrodynamic theory.

V. THE BOUNDARY CONDITIONS

The key assumption that will convert the mechanical balance (33) or equivalently expressions (35) and (36) into boundary conditions is that within the pillbox the velocity has an approximate linear form

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_0 + \dot{\boldsymbol{\gamma}}\cdot(\mathbf{r}-\mathbf{r}_0), \tag{42}$$

where $\mathbf{v}_0$ is the velocity at the point $\mathbf{r}_0$ on the upper lid of the pillbox and $\dot{\gamma}^{\alpha\beta} = \nabla^\alpha \mathbf{v}^\beta(\mathbf{r}_0)$ is the constant velocity gradient within the pillbox. This assumption is reasonable if the flows change slowly in the length scale of the pillbox in a way that a first order Taylor expansion around $\mathbf{r}_0$ is appropriate.

A. Symmetries in the stress tensor

The stress tensor in Eq. (36) is evaluated at the point $\mathbf{r}_0$ at the upper lid of the pillbox. By using the velocity profile (42), the stress tensor in Eq. (10) takes the form

$$\boldsymbol{\Sigma}^{\alpha\beta}(\mathbf{r}) = \boldsymbol{\eta}^{\alpha\beta\alpha'\beta'}(\mathbf{r}_0)\dot{\boldsymbol{\gamma}}^{\beta'\alpha'}, \tag{43}$$

where the local viscosity tensor is the integral of the viscosity kernel tensor

$$\boldsymbol{\eta}^{\alpha\beta\alpha'\beta'}(\mathbf{r}_0) \equiv \int d\mathbf{r}'\boldsymbol{\eta}^{\alpha\beta\alpha'\beta'}_{\mathbf{r}_0\mathbf{r}'}. \tag{44}$$

Because $\mathbf{r}_0$ is inside the bulk region, the fourth order viscosity tensor $\boldsymbol{\eta}^{\alpha\beta\gamma\delta}$ becomes independent of the position and takes a fully isotropic form. The isotropic fourth order tensor will be a linear combination of the tensor product of Kronecker deltas $\delta^{\alpha\beta}$ which is symmetric with respect to the first two indices and the last two indices and has the familiar form

$$\boldsymbol{\eta}^{\alpha\beta\gamma\delta} = \eta\left[\delta^{\alpha\gamma}\delta^{\beta\delta}+\delta^{\alpha\delta}\delta^{\beta\gamma}-\frac{2}{3}\delta^{\alpha\beta}\delta^{\gamma\delta}\right]+\zeta\delta^{\alpha\beta}\delta^{\gamma\delta}, \tag{45}$$

where η and ζ are the usual shear and bulk viscosities of the fluid, respectively. By using (45) into (43), the stress tensor in the bulk is given by the usual Newtonian viscous stress

$$\boldsymbol{\Sigma}^{\alpha\beta}(\mathbf{r}_0) = \eta\left(\dot{\boldsymbol{\gamma}}^{\alpha\beta}+\dot{\boldsymbol{\gamma}}^{\beta\alpha}\right)+\left(\zeta-\frac{2}{3}\eta\right)\delta^{\alpha\beta}\mathrm{Tr}[\dot{\boldsymbol{\gamma}}]. \tag{46}$$

The two components of the stress tensor entering the mechanical balance (35) and (36) become

$$\begin{aligned}\mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r}_0)\cdot\mathbf{n} &= 2\eta\mathbf{n}\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{n}+\left(\zeta-\frac{2}{3}\eta\right)\mathrm{Tr}[\dot{\boldsymbol{\gamma}}],\\ \mathbf{n}\cdot\boldsymbol{\Sigma}(\mathbf{r}_0)\cdot\mathbf{t}_i &= \eta\mathbf{n}\cdot(\dot{\boldsymbol{\gamma}}+\dot{\boldsymbol{\gamma}}^T)\cdot\mathbf{t}_i,\end{aligned} \tag{47}$$

where $\mathbf{t}_i$ with $i = 1, 2$ is any of the unit tangents to the solid surface.

B. Symmetries in the surface force

Let us now consider the integral over the pillbox volume of the irreversible surface force $\mathcal{S}(\mathbf{r})$ given in (10). We will use the fact that we are considering a macroscopic sphere and a small pillbox, in such a way that in the length scales of the pillbox, the surface of the sphere is planar. We may use, therefore, the particular form of $\mathcal{S}(\mathbf{r})$ for a planar isotropic wall. The tensorial structure of the tensors entering the irreversible surface force (10) for an isotropic planar wall is given in the Appendix

$$\begin{aligned}\mathbf{H}^{\alpha\beta\gamma}_{\mathbf{r}\mathbf{r}'} &= G^{(1)}_{\mathbf{r}\mathbf{r}'}\left[\mathbf{n}^\alpha\mathbf{T}^{\beta\gamma}+\mathbf{n}^\beta\mathbf{T}^{\alpha\gamma}\right]+G^{(2)}_{\mathbf{r}\mathbf{r}'}\mathbf{T}^{\alpha\beta}\mathbf{n}^\gamma+G^{(3)}_{\mathbf{r}\mathbf{r}'}\mathbf{n}^\alpha\mathbf{n}^\beta\mathbf{n}^\gamma,\\ \mathbf{G}^{\alpha\beta\gamma}_{\mathbf{r}\mathbf{r}'} &= G^{(1)}_{\mathbf{r}\mathbf{r}'}\left[\mathbf{T}^{\alpha\beta}\mathbf{n}^\gamma+\mathbf{T}^{\alpha\gamma}\mathbf{n}^\beta\right]+G^{(2)}_{\mathbf{r}\mathbf{r}'}\mathbf{n}^\alpha\mathbf{T}^{\beta\gamma}+G^{(3)}_{\mathbf{r}\mathbf{r}'}\mathbf{n}^\alpha\mathbf{n}^\beta\mathbf{n}^\gamma,\\ \boldsymbol{\gamma}^{\alpha\beta}_{\mathbf{r}\mathbf{r}'} &= \gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}\mathbf{T}^{\alpha\beta}+\gamma^{\perp}_{\mathbf{r}\mathbf{r}'}\mathbf{n}^\alpha\mathbf{n}^\beta,\end{aligned} \tag{48}$$

where $G^{(i)}_{\mathbf{r}\mathbf{r}'}, \gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}, \gamma^{\perp}_{\mathbf{r}\mathbf{r}'}$ are given in terms of Green-Kubo expressions detailed in Eqs. (A17) and (A20) in the Appendix. The tensor $\mathbf{T}$ is the projector on the plane of the wall, given by $\mathbf{T} = \boldsymbol{\delta} - \mathbf{nn} = \mathbf{t}_1\mathbf{t}_1 + \mathbf{t}_2\mathbf{t}_2$.

By inserting (48) into (10) and using the impenetrability condition (22), we obtain

$$\begin{aligned}
\mathbf{n}\cdot\mathcal{S}(\mathbf{r}) &= -\sum_i^2 \int d\mathbf{r}' G^{(2)}_{\mathbf{r}\mathbf{r}'}\mathbf{t}_i\cdot\nabla'\mathbf{v}(\mathbf{r}')\cdot\mathbf{t}_i - \int d\mathbf{r}' G^{(3)}_{\mathbf{r}\mathbf{r}'}\mathbf{n}\cdot\nabla'\mathbf{v}(\mathbf{r}')\cdot\mathbf{n} \\
&\quad + \sum_i^2 \mathbf{t}_i\cdot\nabla\int d\mathbf{r}' G^{(1)}_{\mathbf{r}\mathbf{r}'}\mathbf{t}_i\cdot(\mathbf{v}(\mathbf{r}')-\mathbf{V}), \\
\mathbf{t}_i\cdot\mathcal{S}(\mathbf{r}) &= -\int d\mathbf{r}' G^{(1)}_{\mathbf{r}\mathbf{r}'}\left[\mathbf{n}\cdot\nabla'\mathbf{v}(\mathbf{r}')\cdot\mathbf{t}_i + \mathbf{t}_i\cdot\nabla'\mathbf{v}(\mathbf{r}')\cdot\mathbf{n}\right] \\
&\quad + \int d\mathbf{r}'\left[\mathbf{n}\cdot\nabla G^{(1)}_{\mathbf{r}\mathbf{r}'} - \gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}\right]\mathbf{t}_i\cdot(\mathbf{v}(\mathbf{r}')-\mathbf{V}).
\end{aligned} \tag{49}$$

Observe that the surface force is a functional of the velocity field inside the pillbox. We now evaluate the functionals (49) at the assumed linear flow (42) with the result

$$\begin{aligned}
\mathbf{n}\cdot\mathcal{S}(\mathbf{r}) &= -G^{(2)}(\mathbf{r})[\mathbf{t}_1\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t}_1 + \mathbf{t}_2\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t}_2] - G^{(3)}(\mathbf{r})\mathbf{n}\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{n} \\
&\quad + \sum_i^2 \mathbf{t}_i\cdot\nabla\int d\mathbf{r}' G^{(1)}_{\mathbf{r}\mathbf{r}'}(\mathbf{r}'-\mathbf{r}_0)\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t}_i \\
&\quad + \sum_i^2 \mathbf{t}_i\cdot\nabla G^{(1)}(\mathbf{r})\mathbf{t}_i\cdot(\mathbf{v}_0-\mathbf{V}), \\
\mathbf{t}_i\cdot\mathcal{S}(\mathbf{r}) &= -G^{(1)}(\mathbf{r})[\mathbf{n}\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t}_i + \mathbf{t}_i\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{n}] \\
&\quad + \left[\mathbf{n}\cdot\nabla G^{(1)}(\mathbf{r}) - \gamma^{\parallel}(\mathbf{r})\right]\mathbf{t}_i\cdot(\mathbf{v}_0-\mathbf{V}) \\
&\quad + \mathbf{n}\cdot\nabla\int d\mathbf{r}' G^{(1)}_{\mathbf{r}\mathbf{r}'}(\mathbf{r}'-\mathbf{r}_0)\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t}_i \\
&\quad - \int d\mathbf{r}'\gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}(\mathbf{r}'-\mathbf{r}_0)\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t}_i,
\end{aligned} \tag{50}$$

where we have introduced the integrated local transport coefficients

$$\begin{aligned}
G^{(i)}(\mathbf{r}) &= \int d\mathbf{r}' G^{(i)}_{\mathbf{r}\mathbf{r}'}, \qquad i=1,2,3, \\
\gamma^{\parallel}(\mathbf{r}) &= \int d\mathbf{r}'\gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}.
\end{aligned} \tag{51}$$

The integral of the surface force (50) on the volume of the pillbox needed in the mechanical balance equation (36) is given by

$$\begin{aligned}
\frac{1}{S}\int_\Omega d\mathbf{r}\mathbf{n}\cdot\mathcal{S}(\mathbf{r}) &= -\overline{G}^{(2)}[\mathbf{t}_1\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t}_1 + \mathbf{t}_2\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t}_2] - \overline{G}^{(3)}\mathbf{n}\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{n} \\
&= -\overline{G}^{(2)}\mathrm{Tr}[\dot{\boldsymbol{\gamma}}] + \left(\overline{G}^{(2)} - \overline{G}^{(3)}\right)\mathbf{n}\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{n}, \\
\frac{1}{S}\int_\Omega d\mathbf{r}\mathbf{t}\cdot\mathcal{S}(\mathbf{r}) &= -\overline{G}^{(1)}\mathbf{n}\cdot\left[\dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}}^T\right]\cdot\mathbf{t} - \overline{\gamma}^{\parallel}\mathbf{t}\cdot(\mathbf{v}_0-\mathbf{V}) \\
&\quad - \frac{1}{S}\int_\Omega d\mathbf{r}\int d\mathbf{r}'\gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}(\mathbf{r}'-\mathbf{r}_0)\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t},
\end{aligned} \tag{52}$$

where $S=\pi\epsilon^2$ is the area of the lid of the pillbox, and the total integrated transport coefficients are defined as

$$\begin{aligned}
\overline{G}^{(i)} &= \frac{1}{S}\int_\Omega d\mathbf{r} G^{(i)}(\mathbf{r}), \qquad i=1,2,3, \\
\overline{\gamma}^{\parallel} &= \frac{1}{S}\int_\Omega d\mathbf{r}\gamma^{\parallel}(\mathbf{r}).
\end{aligned} \tag{53}$$

In Eq. (52), we take into account that

$$\begin{aligned}
\frac{1}{S}\int_\Omega d\mathbf{r}\mathbf{n}\cdot\nabla G^{(1)}(\mathbf{r}) &= 0, \\
\frac{1}{S}\int_\Omega d\mathbf{r}\mathbf{t}\cdot\nabla G^{(1)}(\mathbf{r}) &= 0.
\end{aligned} \tag{54}$$

This is easily seen because $G^{(1)}(\mathbf{r})$ is expected to vary only in the normal direction, i.e., $G^{(1)}(\mathbf{r}) = G^{(1)}(r)$, implying

$$\begin{aligned}
\frac{1}{S}\int_\Omega d\mathbf{r}\mathbf{n}\cdot\nabla G^{(1)}(\mathbf{r}) &= \frac{1}{S}\int_\Omega d\mathbf{r}\partial_r G^{(1)}(r) \\
&= \int_{a-\Delta}^{a+\Delta} dr\partial_r G^{(1)}(r) \\
&= G^{(1)}(a+\Delta) - G^{(1)}(a-\Delta) \\
&= 0.
\end{aligned} \tag{55}$$

This quantity vanishes because at $r=a+\Delta$ the force that the solid exerts on the fluid vanishes, while at $r=a-\Delta$, there is no fluid inside the solid. A similar argument shows that the third term in the right-hand side of (50) integrates also to zero.

The last term in (52) can be expressed as

$$\frac{1}{S}\int_\Omega d\mathbf{r}\int d\mathbf{r}'\gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}(\mathbf{r}'-\mathbf{r}_0) = \frac{1}{S}\int d\mathbf{r}'\gamma^{\parallel}(\mathbf{r}')(\mathbf{r}'-\mathbf{r}_0) \tag{56}$$

because $\gamma^{\parallel}_{\mathbf{r}\mathbf{r}'} = \gamma^{\parallel}_{\mathbf{r}'\mathbf{r}}$. Note that the local friction coefficient $\gamma^{\parallel}(\mathbf{r}')$, which is given in Eq. (A17) in terms of a Green-Kubo formula involving the correlations of the force $\hat{\mathbf{F}}_{\mathbf{r}}$, vanishes outside the range of interaction of this force. Therefore, $\gamma^{\parallel}(\mathbf{r}')$ is different from zero only in a shell around the solid sphere, of a molecular width. We introduce the vector

$$\mathbf{r}_{\mathrm{wall}} = \frac{\int_\Omega d\mathbf{r}'\gamma^{\parallel}(\mathbf{r}')\mathbf{r}'}{\int_\Omega d\mathbf{r}'\gamma^{\parallel}(\mathbf{r}')} \tag{57}$$

whose modulus r_{wall} is a good definition for "the radius of the surface of the solid sphere." This is an unambiguous way of defining the location of the surface of the solid sphere, even for an atomically fuzzy surface. At precisely this location, the velocity field (42) takes the value $\mathbf{v}_{\mathrm{wall}}$ given by

$$\mathbf{v}_{\mathrm{wall}} \equiv \mathbf{v}(\mathbf{r}_{\mathrm{wall}}) = \mathbf{v}_0 + \dot{\boldsymbol{\gamma}}\cdot(\mathbf{r}_{\mathrm{wall}} - \mathbf{r}_0). \tag{58}$$

Therefore, by using (56), with the two definitions (57) and (58), the last two terms in Eq. (52) become

$$\begin{aligned}
&-\overline{\gamma}^{\parallel}\mathbf{t}\cdot(\mathbf{v}_0-\mathbf{V}) - \frac{1}{S}\int d\mathbf{r}\int d\mathbf{r}'\gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}(\mathbf{r}'-\mathbf{r}_0)\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t} \\
&\quad = -\overline{\gamma}^{\parallel}\mathbf{t}\cdot(\mathbf{v}_0-\mathbf{V}) - \overline{\gamma}^{\parallel}(\mathbf{r}_{\mathrm{wall}}-\mathbf{r}_0)\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{t} \\
&\quad = -\overline{\gamma}^{\parallel}\mathbf{t}\cdot(\mathbf{v}_{\mathrm{wall}}-\mathbf{V}).
\end{aligned} \tag{59}$$

Finally, the tangential component of the force per unit area that the solid exerts on the fluid slab is given, from (52) and (59), by

$$\frac{1}{S}\mathbf{t}\cdot\mathbf{F} = \frac{1}{S}\int_\Omega d\mathbf{r}\mathbf{t}\cdot\mathcal{S}(\mathbf{r}) = -\overline{G}^{(1)}\mathbf{n}\cdot\left[\dot{\boldsymbol{\gamma}}+\dot{\boldsymbol{\gamma}}^T\right]\cdot\mathbf{t} - \overline{\gamma}^{\parallel}\mathbf{t}\cdot(\mathbf{v}_{\rm wall}-\mathbf{V}). \tag{60}$$

C. The final form of the boundary conditions

Note that in the impenetrability condition (22), we may approximate

$$0 = \mathbf{n}\cdot(\mathbf{v}_0-\mathbf{V}) \simeq \mathbf{n}\cdot(\mathbf{v}_{\rm wall}-\mathbf{V}) \tag{61}$$

because the difference between $\mathbf{v}_0$ and $\mathbf{v}_{\rm wall}$ is of order Δ and negligible. By collecting the impenetrability condition (61) and the mechanical balance equations (35) and (36) with (47), (52), and (60), we obtain

$$\begin{aligned} -P_0 - \Delta P + A\mathbf{n}\cdot\dot{\boldsymbol{\gamma}}\cdot\mathbf{n} + B{\rm Tr}[\dot{\boldsymbol{\gamma}}] &= 0,\\ \eta'\mathbf{n}\cdot\left[\dot{\boldsymbol{\gamma}}+\dot{\boldsymbol{\gamma}}^T\right]\cdot\mathbf{t}_1 - \overline{\gamma}^{\parallel}\mathbf{t}_1\cdot(\mathbf{v}_{\rm wall}-\mathbf{V}) &= 0,\\ \eta'\mathbf{n}\cdot\left[\dot{\boldsymbol{\gamma}}+\dot{\boldsymbol{\gamma}}^T\right]\cdot\mathbf{t}_2 - \overline{\gamma}^{\parallel}\mathbf{t}_2\cdot(\mathbf{v}_{\rm wall}-\mathbf{V}) &= 0,\\ \mathbf{n}\cdot(\mathbf{v}_{\rm wall}-\mathbf{V}) &= 0, \end{aligned} \tag{62}$$

where

$$\begin{aligned} A &= 2\eta + \overline{G}^{(2)} - \overline{G}^{(1)},\\ B &= \zeta - \frac{2}{3}\eta - \overline{G}^{(2)},\\ \eta' &= \eta - \overline{G}^{(1)}. \end{aligned} \tag{63}$$

The last three equations in (62) can be understood as conditions on the three components of the velocity at the surface and are, therefore, the boundary conditions to be imposed to the macroscopic hydrodynamic equations at the wall position defined by (57). The first equation does not gives an additional condition on the velocity because the term ΔP defined in (34) contains the integral of the density profile within the boundary zone which, from a macroscopic point of view, is unknown. In fact, this equation can be used to obtain ΔP but does not fix, nor over-determines, the value of the velocity.

In summary, under the assumption (42) that near the solid the velocity field is linear with a constant velocity gradient $\dot{\boldsymbol{\gamma}}$, the three components of the velocity field $\mathbf{v}_{\rm wall}$ at the location $\mathbf{r}_{\rm wall}$ satisfy the boundary conditions (2). Equations (2) are one of the main results of the present paper. They show how boundary conditions emerge from the theory presented in Ref. 1 which, in turn, derives from the microscopic dynamics of the system under appropriate conditions. Physically, the first equation of (2) represents impenetrability, while the second one balances the viscous stress at the wall with the friction force on the fluid exerted by the wall. The boundary conditions (2) are the Navier slip boundary conditions in tensorial form.[12]

VI. THE MICROSCOPIC EXPRESSION FOR THE SLIP LENGTH AND ITS EQUIVALENCE WITH BOCQUET AND BARRAT'S

The benefit of an approach based on microscopically derived hydrodynamic equations is that the coefficients appearing in the slip boundary conditions all have microscopic expressions in terms of Green-Kubo formulae.

The explicit microscopic expression for the viscosity η, for example, is obtained by averaging (44) over the volume $\mathcal{V}$ exterior to the sphere, which, on due account of (11), gives

$$\begin{aligned} \eta &= \frac{1}{\mathcal{V}k_BT}\int d\mathbf{r}_0\int d\mathbf{r}\int_0^{\Delta t} dt\left\langle \mathcal{Q}\hat{\boldsymbol{\sigma}}^{\parallel\perp}_{\mathbf{r}_0}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}^{\parallel\perp}_{\mathbf{r}}\right\rangle\\ &= \frac{1}{\mathcal{V}k_BT}\int_0^{\Delta t} dt\left\langle \hat{\boldsymbol{\sigma}}^{\parallel\perp}(t)\hat{\boldsymbol{\sigma}}^{\parallel\perp}\right\rangle, \end{aligned} \tag{64}$$

where the bulk stress tensor is given by (6). Equation (64) is the usual Green-Kubo expression for the shear viscosity. Note that, as explained in the Appendix, the projector $\mathcal{Q}$ has no effect on the off-diagonal components of the stress tensor due to symmetry reasons and drops out from the expression for the viscosity.

From Eqs. (51) and (53), we obtain that the coefficients $\overline{G}^{(1)}, \overline{\gamma}^{\parallel}$ entering the slip boundary condition (2) are

$$\begin{aligned} \overline{G}^{(1)} &= \frac{1}{S}\int_\Omega d\mathbf{r}\int d\mathbf{r}'\mathbf{G}^{(1)}_{\mathbf{r}\mathbf{r}'},\\ \overline{\gamma}^{\parallel} &= \frac{1}{S}\int_\Omega d\mathbf{r}\int d\mathbf{r}'\boldsymbol{\gamma}^{\parallel}_{\mathbf{r}\mathbf{r}'}. \end{aligned} \tag{65}$$

By inserting in these expressions the Green-Kubo formulae (11), performing the space integrals over the Dirac delta functions, and using Eqs. (A17) and (A20) in the Appendix, we finally obtain the explicit microscopic expressions (4) and (7) for the coefficients entering the slip boundary condition.

Note that the viscosity η' appearing in the slip boundary condition (2) is not the fluid viscosity η but rather a corrected viscosity η' defined in (63). As we will see in the rest of this section, whether to correct or not the viscosity depends on the actual definition of the wall position. In the process of showing this, we also demonstrate that the microscopic expression for the slip length obtained from the hydrodynamic theory of Ref. 1 coincides with the expression given by BB[18] from linear response theory.

As a first step, we need to extend our results for a sphere geometry to a planar shear flow with planar walls as considered by BB. Our pillbox derivation can be extended trivially from the sphere geometry to this parallel planar wall geometry. For a simple shear flow of the form $\mathbf{v}(\mathbf{r}) = (v^{\parallel}_{\rm wall} + \dot{\gamma}(z-z_{\rm wall}),0,0)$, the surface force (60) that the solid exerts on the fluid takes the form

$$\frac{1}{S}\mathbf{F}^{\parallel} = -\overline{G}^{(1)}\dot{\gamma} - \overline{\gamma}^{\parallel}v^{\parallel}_{\rm wall}, \tag{66}$$

where, for the sake of simplicity, we assume the wall at rest. For a planar wall, the position of the wall surface may be defined in a manner identical to the result (57) valid for a sphere. As the local friction coefficient $\gamma(\mathbf{r}')$ will be different from zero only in the region within the range of interaction of the forces that the solid particles exert on the fluid particles, a reasonable definition is

$$z_{\text{wall}} = \frac{\int d\mathbf{r}' \gamma^{\parallel}(\mathbf{r}') z'}{\int d\mathbf{r}' \gamma^{\parallel}(\mathbf{r}')} = \frac{1}{\bar{\gamma}^{\parallel} S k_B T} \int_0^t ds \left\langle \hat{\mathbf{F}}^{\parallel}(s) \sum_i^N z_i \hat{\mathbf{F}}_i^{\parallel} \right\rangle, \tag{67}$$

where (51) and (11) have been used.

According to the mechanical balance (36), the surface force (66) is balanced by the force that the fluid exerts on the fluid, which is given by the stress tensor component

$$\mathbf{n} \cdot \boldsymbol{\Sigma}(\mathbf{r}_0) \cdot \mathbf{t} = \eta \dot{\gamma}. \tag{68}$$

The tensorial slip boundary condition (2) for the simple shear flow is given by the balance of (66) and (68), leading to

$$\eta \dot{\gamma} = \bar{G}^{(1)} \dot{\gamma} + \bar{\gamma}^{\parallel} v_{\text{wall}}^{\parallel}, \tag{69}$$

which is the boundary condition (2) for this flow field, and that can be written as

$$\delta \dot{\gamma} = v_{\text{wall}}^{\parallel}, \tag{70}$$

where the slip length is

$$\delta = \frac{\eta - \bar{G}^{(1)}}{\bar{\gamma}^{\parallel}}. \tag{71}$$

In order to compare with the above results, we now revisit the linear response calculation of BB[18] and express it in a notation as close as ours as possible. BB consider a planar shear flow with planar walls and add to the unperturbed Hamiltonian $\hat{H}_0$ of the system (fluid plus solid walls) a perturbation of the form $\hat{H}_1 = -\dot{\gamma}\hat{M}$ with

$$\hat{M} = \sum_i^N (z_i - z_0) \mathbf{p}_i^{\parallel}, \tag{72}$$

where z_0 is a parameter, and z_i is the vertical coordinate of the fluid particle i and $\mathbf{p}_i^{\parallel}$ is a component of its momentum parallel to the wall. To first order in the perturbation, linear response theory gives the time dependent average $B(t)$ of any phase function $\hat{B}$ (with zero equilibrium average) as[36]

$$B(t) = \frac{\dot{\gamma}}{k_B T} \int_0^t ds \left\langle \left(iL_0 \hat{M}\right) \left(\exp\{iL_0 s\} \hat{B}\right) \right\rangle, \tag{73}$$

where iL_0 is the Liouville operator corresponding to the unperturbed Hamiltonian (fluid plus solid walls) and $\langle \cdots \rangle$ is the corresponding canonical equilibrium ensemble average. Note that we may integrate by parts the Liouville operator inside the equilibrium ensemble and recognize a time derivative that can be integrated out leading to the result

$$B(t) = \frac{\dot{\gamma}}{k_B T} \left[\left\langle \hat{M} \hat{B} \right\rangle - \left\langle \hat{M} \hat{B}(t) \right\rangle \right]. \tag{74}$$

By taking in (74) $\hat{B}$ equal to the tangential component of the microscopic momentum density field $\hat{\mathbf{g}}_{\mathbf{r}}^{\parallel} = \sum_i^N \mathbf{p}_i^{\parallel} \delta(\mathbf{r} - \mathbf{r}_i)$, one easily arrives at the conclusion that at long times the system develops an average flow field in the tangential direction given by

$$\mathbf{g}^{\parallel}(z) = \rho(z) \dot{\gamma}(z - z_0), \tag{75}$$

where $\rho(z)$ is the equilibrium average density field. The velocity field generated by the perturbation is, therefore,

$$\mathbf{v}^{\parallel}(z) = \dot{\gamma}(z - z_0), \tag{76}$$

where the parameter z_0 in the perturbation (72) is now recognized as the position of the plane where the velocity field vanishes. Petravic and Harrowell in Ref. 20 claimed that there was an error in BB when they assume that the perturbation (72) to the Hamiltonian of a fluid in contact with solid walls leads to the velocity field (76). The above argument shows that such an assumption is, in fact, correct. BB then apply the linear response result (73) to the total force that the solid exerts on the fluid, i.e., $\hat{B} = \hat{\mathbf{F}}^{\parallel}$, where

$$\hat{\mathbf{F}}^{\parallel} = \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'}^{\parallel}. \tag{77}$$

The result is

$$\mathbf{F}^{\parallel}(t) = \frac{\dot{\gamma}}{k_B T} \int_0^t dt' \left\langle \left(iL_0 \hat{A}\right) \hat{\mathbf{F}}^{\parallel}(t') \right\rangle. \tag{78}$$

The time derivative $iL_0\hat{A}$ is given by

$$iL_0 \hat{A} = \hat{\boldsymbol{\sigma}}^{\parallel \perp} + \sum_i^N (z_i - z_0) \hat{\mathbf{F}}_i^{\parallel}, \tag{79}$$

where the off-diagonal component of the total fluid stress tensor is given, from Eq. (12), by

$$\hat{\boldsymbol{\sigma}}^{\parallel \perp} = \sum_i^N \mathbf{p}_i^{\parallel} \mathbf{v}_i^{\perp} + \frac{1}{2} \sum_{ij}^N z_{ij} \hat{\mathbf{F}}_{ij}^{\parallel}. \tag{80}$$

This is the total stress tensor of the fluid and it depends only on the coordinates and momenta of fluid particles. Instead of using this natural definition of the stress tensor, which is the one that enters the Green-Kubo expression (64) for the viscosity of the fluid, BB use a different stress tensor, defined as

$$\hat{\boldsymbol{\sigma}}^{BB} = \hat{\boldsymbol{\sigma}}^{\parallel \perp} + \sum_i^N z_i \hat{\mathbf{F}}_i^{\parallel}, \tag{81}$$

which includes a "stress" contribution due to the force that the solid exerts on the liquid. In terms of this stress tensor, the time derivative (79) is given by

$$iL_0 \hat{A} = \hat{\boldsymbol{\sigma}}^{BB} - z_0 \hat{\mathbf{F}}^{\parallel}. \tag{82}$$

By inserting (82) into (78), one obtains the BB result for the average force

$$\mathbf{F}^{\parallel}(t) = -\frac{\dot{\gamma}}{k_B T}\int_0^t ds\left\langle \hat{\mathbf{F}}^{\parallel}(s)\hat{\boldsymbol{\sigma}}^{BB}\right\rangle + \frac{\dot{\gamma}z_0}{k_B T}\int_0^t ds\left\langle \hat{\mathbf{F}}^{\parallel}(s)\hat{\mathbf{F}}^{\parallel}\right\rangle$$
$$= -S\overline{\gamma}^{\parallel}\dot{\gamma}(z_{\text{wall}}^{BB} - z_0)$$
$$= -S\overline{\gamma}^{\parallel}v_{\text{wall}}^{BB}, \tag{83}$$

where the velocity v_{wall}^{BB} at the effective wall position z_{wall}^{BB} is defined as

$$v_{\text{wall}}^{BB} = \dot{\gamma}(z_{\text{wall}}^{BB} - z_0) \tag{84}$$

and the effective wall position z^{BB} is defined as

$$z_{\text{wall}}^{BB} = \frac{\int_0^t ds\left\langle \hat{\mathbf{F}}^{\parallel}(s)\hat{\boldsymbol{\sigma}}^{BB}\right\rangle}{\int_0^t ds\left\langle \hat{\mathbf{F}}^{\parallel}(s)\hat{\mathbf{F}}^{\parallel}\right\rangle}. \tag{85}$$

Equation (83) is the original expression given by BB for the friction force on the wall per unit area.

We now seek an alternative form for expression (83) given by BB that makes close contact with our result given by the force (66) obtained from the hydrodynamic theory. The effective wall position defined by BB is related to the wall position defined from the friction coefficient (67) as follows. Consider (85) with (81)

$$z_{\text{wall}}^{BB} = \frac{\int_0^t ds\left\langle \hat{\mathbf{F}}^{\parallel}(s)\left(\hat{\boldsymbol{\sigma}}^{\parallel\perp} + \sum_i^N z_i\hat{\mathbf{F}}_i^{\parallel}\right)\right\rangle}{\int_0^t ds\left\langle \hat{\mathbf{F}}^{\parallel}(s)\hat{\mathbf{F}}^{\parallel}\right\rangle}. \tag{86}$$

By using expression (67), we have

$$z_{\text{wall}}^{BB} = \frac{\overline{G}^{(1)}}{\overline{\gamma}^{\parallel}} + z_{\text{wall}}. \tag{87}$$

For a shear flow, the relationship between the velocity v_{wall}^{BB} at z_{wall}^{BB} and $v_{\text{wall}}^{\parallel}$ at z_{wall} is given by

$$v_{\text{wall}}^{BB} = v_{\text{wall}}^{\parallel} + \dot{\gamma}(z_{\text{wall}}^{BB} - z_{\text{wall}}), \tag{88}$$

which, by using (87) is

$$v_{\text{wall}}^{BB} = v_{\text{wall}}^{\parallel} + \dot{\gamma}\frac{\overline{G}^{(1)}}{\overline{\gamma}^{\parallel}}. \tag{89}$$

The combination of (83), (87), and (88) gives

$$\frac{1}{S}\mathbf{F}^{\parallel}(t) = -\overline{\gamma}^{\parallel}v_{\text{wall}}^{\parallel} - \overline{G}^{(1)}\dot{\gamma}. \tag{90}$$

The force on the wall given by BB in (83) has the form (90) that coincides with our result (66) obtained from the hydrodynamic theory of Ref. 1. As the balance of this force with the viscous force gives the boundary condition, we have shown that our microscopic expression for the slip length (71) coincides with that of BB, with a suitable redefinition of the wall position.

VII. CONCLUSIONS

In this paper, we have shown how the theory of hydrodynamics near solid objects presented in Ref. 1 leads to the usual slip boundary conditions when applied to situations of macroscopic flow. The effect of the solid walls is described in the theory through reversible and irreversible forces located near the "surface" of the solid. When the flows are macroscopic, the effect of these surface forces can be reinterpreted in terms of boundary conditions that express the impenetrability and mechanical balance near the solid surface. The mechanical balance leads to the usual slip boundary condition. Because of the microscopic underpinning of the hydrodynamics theory, the boundary conditions contain two parameters (slip length and wall position) that are given in molecular terms through Green-Kubo formulae. We have shown that the microscopic definition of the slip length obtained by us coincides with the one given by BB under a suitable redefinition of the wall position. The validity of the BB expression is confirmed here for flows that are of macroscopic character in the sense that the pillbox used encloses any possible density layering near the walls and the velocity profile is approximately linear within the pillbox.

In a forthcoming series of publications,[6–9] we will present a discrete version of the continuum theory in Ref. 1 that allows us to measure through MD simulations the different nonlocal transport kernels and compare with predictions for shear flow, thus validating the present theoretical results under the hypothesis used to derive them.

As a final remark, we note that the slip of a fluid near a wall can be looked upon from two different perspectives, as a condition at the boundary or as a boundary condition.[17] In the first perspective, one has a phenomenological observation of a linear relationship between the velocity and the velocity gradient of the fluid near the wall. The quantification of this observation requires, of course, to specify the wall position for an atomically fuzzy surface and to ensure that the gradient is constant "near the wall." Different wall positions and different ways of defining the gradient (particularly in unsteady situations) will give different slip lengths. This phenomenological perspective is the one used in most MD simulation studies where the slip length, understood as a particular property of the flow, is measured. The second perspective is to make use of this linear relationship between the value of the field and its derivatives at the boundary as a way to specify a Robin boundary condition in order to solve the partial differential equations of hydrodynamics. This second perspective, of course, assumes implicitly that those equations are valid. Only in this second perspective, it makes sense to speak about the slip boundary condition.

For highly confined fluids in between parallel walls, requiring the use of very thin bins to resolve the density layering near the wall, nonlocal effects become important. Space nonlocality has been studied in depth recently in Refs. 37–39. We will show in Ref. 9 that time nonlocality also becomes an issue at the scales that resolve the density layering. In fact, the hydrodynamic equations are non-Markovian at these scales. If the theory is non-Markovian, transport coefficients are meaningless and, instead, memory "kernels" should be used. As the hydrodynamic equations are non-Markovian at these scales, the Green-Kubo expression for transport coefficients is then not very useful. In that case, to find a microscopic expression for the slip length in terms of Green-Kubo formulae as in the BB result may not be very fruitful, as the very concept of a boundary condition to be applied to physically incorrect (at these scales) partial differential equations becomes futile.

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APPENDIX: ISOTROPIC TRANSPORT KERNELS

In this appendix, we review what tensors of second and third order are invariant under a rotation $\mathcal{R}$ around a given axis $\mathbf{n}$. We know that the Kronecker tensor $\boldsymbol{\delta}$ with components given by the Kronecker symbol $\boldsymbol{\delta}^{\alpha\beta}$ and the permutation tensor $\boldsymbol{\epsilon}^n$ of order n with components given by the Levi-Civita symbol $\epsilon^{\underbrace{\alpha\cdots\gamma}_{n}}$ are invariant under an arbitrary rotation. If $\mathcal{R}^{\alpha\alpha'}$ is the orthogonal matrix that represents the rotation around a fixed axis, we have

$$\begin{aligned}\mathcal{R}^{\alpha\alpha'}\mathbf{n}^{\alpha'} &= \mathbf{n}^{\alpha}\\ \mathcal{R}^{\alpha\alpha'}\mathcal{R}^{\beta\beta'}\boldsymbol{\delta}^{\alpha'\beta'} &= \boldsymbol{\delta}^{\alpha\beta}\\ \mathcal{R}^{\alpha\alpha'}\mathcal{R}^{\beta\beta'}\mathcal{R}^{\gamma\gamma'}\epsilon^{\alpha'\beta'\gamma'} &= \epsilon^{\alpha\beta\gamma}\\ &\vdots\end{aligned} \tag{A1}$$

Here, the first order tensor $\mathbf{n}$ (with components $\mathbf{n}^{\alpha}$) is the unit vector determining the axis of rotation of the rotation matrix $\mathcal{R}$, which is obviously left invariant under a rotation. Of course, any contraction of $\mathbf{n}$, $\boldsymbol{\delta}$, $\boldsymbol{\epsilon}^n$ will produce a tensor that is also invariant under the rotation $\mathcal{R}$. The only nontrivial contractions are the order m tensors $\mathbf{n}^{(m)}$ with components $n^{(m)\alpha\cdots\beta} = \epsilon^{(m+1)}_{\alpha\cdots\beta\gamma}\mathbf{n}^{\gamma}$.

In addition to rotations, we may consider the invariance with respect to a plane. For example, consider the inversion of the axis $x \to -x$ which is represented by the matrix

$$\mathcal{I} = \begin{pmatrix} -1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}. \tag{A2}$$

Clearly, the Kronecker tensor is invariant under plane inversion

$$\mathcal{I}^{\alpha\alpha'}\mathcal{I}^{\beta\beta'}\delta^{\alpha'\beta'} = \delta^{\alpha\beta}. \tag{A3}$$

However, the Levy-Civita symbol changes sign. Let us sketch the proof by considering the element 1, 2, 3 of the transformed symbol

$$\epsilon'_{123} \equiv \underbrace{\mathcal{I}^{1\alpha}\mathcal{I}^{2\beta}\mathcal{I}^{3\gamma}\epsilon_{\alpha\beta\gamma}}_{(\mathcal{I}_2\times\mathcal{I}_3)_{\alpha}} = -1 = -\epsilon^{123}, \tag{A4}$$

where $\mathcal{I}^2$ is the second column vector of the parity matrix.

Therefore, tensors that are invariant under rotations around a fixed axis and parity around any plane containing the axis will be combinations of the corresponding tensors formed out of $\boldsymbol{\delta}$ and $\mathbf{n}$, but will not contain any antisymmetric combination involving the permutation tensor $\boldsymbol{\epsilon}^n$ of order n.

For future reference, it is convenient to introduce the following two symmetric second order tensors, which we call tangential and normal projectors, respectively:

$$\begin{aligned}\mathbf{T}^{\alpha\beta} &\equiv \boldsymbol{\delta}^{\alpha\beta} - \mathbf{n}^{\alpha}\mathbf{n}^{\beta}\\ \mathbf{N}^{\alpha\beta} &\equiv \mathbf{n}^{\alpha}\mathbf{n}^{\beta}\end{aligned} \tag{A5}$$

Recall that the unit tensor may be written as

$$\boldsymbol{\delta} = \mathbf{t}_1\mathbf{t}_1^T + \mathbf{t}_2\mathbf{t}_2^T + \mathbf{n}\mathbf{n}^T, \tag{A6}$$

where $\mathbf{t}_1$, $\mathbf{t}_2$ are unit vectors tangent to the surface and mutually orthonormal. We take the convention that $\mathbf{t}_1 \times \mathbf{t}_2 = \mathbf{n}$, $\mathbf{t}_2 \times \mathbf{n} = \mathbf{t}_1$, and $\mathbf{n} \times \mathbf{t}_1 = \mathbf{t}_2$. Therefore, the tangential projector $\mathbf{T}$ becomes

$$\mathbf{T}^{\alpha\beta} = \mathbf{t}_1^{\alpha}\mathbf{t}_1^{\beta} + \mathbf{t}_2^{\alpha}\mathbf{t}_2^{\beta}. \tag{A7}$$

This projector satisfies

$$\begin{aligned}\mathbf{T}^{\alpha\beta}\mathbf{T}^{\beta\gamma} &= \mathbf{T}^{\alpha\gamma},\\ \mathbf{T}^{\alpha\beta}\mathbf{n}^{\alpha} &= 0,\\ \mathbf{T}^{\alpha\beta}\mathbf{n}^{\beta} &= 0,\\ \mathbf{T}^{\alpha\alpha} &= 2,\\ \mathbf{T}^{\alpha\beta}\mathbf{T}^{\alpha\beta} &= 2,\end{aligned} \tag{A8}$$

where repeated indices are summed over.

1. Second and third order tensors

In order to construct the most general second order tensor that is invariant around arbitrary rotations around a fixed axis $\mathbf{n}$ and parity, we have to construct all possible tensorial products of $\mathbf{n}^{\alpha}$, and $\boldsymbol{\delta}^{\alpha\beta}$. The possible combinations that form a second order tensor are

$$\boldsymbol{\delta}^{\alpha\beta}\mathbf{n}^{\alpha}\mathbf{n}^{\beta}. \tag{A9}$$

In this way, the most general second order tensor $\mathbf{A}$ which is invariant under rotation around the axis $\mathbf{n}$ is of the form

$$\mathbf{A} = a_1\boldsymbol{\delta} + a_2\mathbf{n}\mathbf{n}, \tag{A10}$$

where a_1, a_2 are arbitrary coefficients. Instead of the 9 independent components of a general second order tensor, the invariant tensor has only two independent components. If the tensor is required to be fully isotropic, it means that it cannot depend on the actual axis $\mathbf{n}$, and this implies $a_2 = 0$.

The assumption of isotropy around a normal axis implies that the second order friction tensor $\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'}$ is a linear combination of the unit tensor $\boldsymbol{\delta}$ and the dyadic $\mathbf{n}\mathbf{n}^T$, or, alternatively, of $\mathbf{T}$, $\mathbf{N}$, that is,

$$\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'} = \gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}\mathbf{T} + \gamma^{\perp}_{\mathbf{r}\mathbf{r}'}\mathbf{N} \tag{A11}$$

Next, let us consider the most general third order tensor that is invariant around parity and arbitrary rotations around a fixed axis $\mathbf{n}$, we have to construct all possible tensorial products of $\mathbf{n}^{\alpha}$, and $\boldsymbol{\delta}^{\alpha\beta}$ giving third order tensors. These are

$$\boldsymbol{\delta}^{\alpha\beta}\mathbf{n}^{\gamma}, \quad \boldsymbol{\delta}^{\alpha\gamma}\mathbf{n}^{\beta}, \quad \boldsymbol{\delta}^{\beta\gamma}\mathbf{n}^{\alpha}, \quad \mathbf{n}^{\alpha}\mathbf{n}^{\beta}\mathbf{n}^{\gamma}. \tag{A12}$$

Any linear combination of the above tensors will produce a third order tensor that is invariant under rotation around a fixed axis. In this way, such a tensor, instead of having 27 independent components, has only 4. Instead of the above tensors, it is more convenient to use the tangential tensor

$$\mathbf{T}^{\alpha\beta}\mathbf{n}^{\gamma}, \quad \mathbf{T}^{\alpha\gamma}\mathbf{n}^{\beta}, \quad \mathbf{T}^{\beta\gamma}\mathbf{n}^{\alpha}, \quad \mathbf{n}^{\alpha}\mathbf{n}^{\beta}\mathbf{n}^{\gamma}. \tag{A13}$$

Now consider a third order tensor $\mathbf{G}$ that is symmetric with respect to its last two indices, i.e., $\mathbf{G}^{\alpha\beta\gamma} = \mathbf{G}^{\alpha\gamma\beta}$. The most general third order tensor invariant with respect to rotations around $\mathbf{n}$ and with the above index symmetry has the following structure (we do not display the dependence on $\mathbf{r}$, $\mathbf{r}'$):

$$\mathbf{G}^{\alpha\beta\gamma} = G^{(1)}\left[\mathbf{T}^{\alpha\beta}\mathbf{n}^{\gamma} + \mathbf{T}^{\alpha\gamma}\mathbf{n}^{\beta}\right] + G^{(2)}\mathbf{n}^{\alpha}\mathbf{T}^{\beta\gamma} + G^{(3)}\mathbf{n}^{\alpha}\mathbf{n}^{\beta}\mathbf{n}^{\gamma}. \tag{A14}$$

Similarly, a third order tensor $\mathbf{H}$ that is symmetric with respect to its first two indices, i.e., $\mathbf{H}^{\alpha\beta\gamma} = \mathbf{H}^{\beta\alpha\gamma}$, and which is invariant with respect to rotations around $\mathbf{n}$ should have the following form:

$$\mathbf{H}^{\alpha\beta\gamma} = H^{(1)}\left[\mathbf{n}^{\alpha}\mathbf{T}^{\beta\gamma} + \mathbf{n}^{\beta}\mathbf{T}^{\alpha\gamma}\right] + H^{(2)}\mathbf{T}^{\alpha\beta}\mathbf{n}^{\gamma} + H^{(3)}\mathbf{n}^{\alpha}\mathbf{n}^{\beta}\mathbf{n}^{\gamma}. \tag{A15}$$

2. The Green-Kubo expressions

In this isotropic approximation, from the nine components of the friction tensor only two of them are independent and different from zero. The Green-Kubo expressions for these independent and nonzero components $\gamma^{\perp}_{\mathbf{r}\mathbf{r}'}, \gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}$ of the friction tensor are obtained by multiplying the tensor $\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'}$ with $\mathbf{T}$ and $\mathbf{N}$ and by taking its trace. We obtain

$$\begin{aligned}\gamma^{\perp}_{\mathbf{r}\mathbf{r}'} &= \mathbf{n}\cdot\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'}\cdot\mathbf{n},\\ \gamma^{\parallel}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{2}\left[\mathbf{t}_1\cdot\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'}\cdot\mathbf{t}_1 + \mathbf{t}_2\cdot\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'}\cdot\mathbf{t}_2\right].\end{aligned} \tag{A16}$$

As we know the Green-Kubo expression for $\boldsymbol{\gamma}_{\mathbf{r}\mathbf{r}'}$ given in (11), the above expressions provide the corresponding molecular expressions for $\gamma^{\perp}_{\mathbf{r}\mathbf{r}'}, \gamma^{\parallel}_{\mathbf{r}\mathbf{r}'}$

$$\begin{aligned}\gamma^{\perp}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{k_BT}\int_0^{\Delta t} dt\left\langle \mathcal{Q}\hat{\mathbf{F}}^{\perp}_{\mathbf{r}}(t)\mathcal{Q}\hat{\mathbf{F}}^{\perp}_{\mathbf{r}'}\right\rangle,\\ \gamma^{\parallel}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{k_BT}\int_0^{\Delta t} dt\left\langle \mathcal{Q}\hat{\mathbf{F}}^{\parallel}_{\mathbf{r}}(t)\mathcal{Q}\hat{\mathbf{F}}^{\parallel}_{\mathbf{r}'}\right\rangle,\end{aligned} \tag{A17}$$

where we have defined

$$\begin{aligned}\hat{\mathbf{F}}^{\parallel} &\equiv \mathbf{t}\cdot\hat{\mathbf{F}},\\ \hat{\mathbf{F}}^{\perp} &\equiv \mathbf{n}\cdot\hat{\mathbf{F}},\end{aligned} \tag{A18}$$

and $\mathbf{t}$ is any of the two $\mathbf{t}_1, \mathbf{t}_2$.

The kernels $G^{(1)}$, $G^{(2)}$, and $G^{(3)}$ in (A14) can be obtained from full contractions of the third order tensor $\mathbf{G}$ with $\mathbf{n}$, $\mathbf{T}$

$$\begin{aligned}\mathbf{T}^{\alpha\beta}\mathbf{G}^{\alpha\beta\gamma}\mathbf{n}^{\gamma} &= 2G^{(1)},\\ \mathbf{n}^{\alpha}\mathbf{G}^{\alpha\beta\gamma}\mathbf{T}^{\beta\gamma} &= 2G^{(2)},\\ \mathbf{n}^{\alpha}\mathbf{G}^{\alpha\beta\gamma}\mathbf{n}^{\beta}\mathbf{n}^{\gamma} &= G^{(3)}.\end{aligned} \tag{A19}$$

We may now use Eq. (11) in order to find Green-Kubo expressions for these kernels

$$\begin{aligned}G^{(1)}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{k_BT}\int_0^{\Delta t} dt\left\langle \mathcal{Q}\hat{\mathbf{F}}^{\parallel}_{\mathbf{r}}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}^{\parallel\perp}_{\mathbf{r}'}\right\rangle,\\ G^{(2)}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{k_BT}\int_0^{\Delta t} dt\left\langle \mathcal{Q}\hat{\mathbf{F}}^{\perp}_{\mathbf{r}}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}^{\parallel\parallel}_{\mathbf{r}'}\right\rangle,\\ G^{(3)}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{k_BT}\int_0^{\Delta t} dt\left\langle \mathcal{Q}\hat{\mathbf{F}}^{\perp}_{\mathbf{r}}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}^{\perp\perp}_{\mathbf{r}'}\right\rangle,\end{aligned} \tag{A20}$$

where we have defined

$$\begin{aligned}\hat{\boldsymbol{\sigma}}^{\parallel\parallel} &\equiv \mathbf{t}\cdot\hat{\boldsymbol{\sigma}}\cdot\mathbf{t},\\ \hat{\boldsymbol{\sigma}}^{\parallel\perp} &\equiv \mathbf{t}\cdot\hat{\boldsymbol{\sigma}}\cdot\mathbf{n},\\ \hat{\boldsymbol{\sigma}}^{\perp\perp} &\equiv \mathbf{n}\cdot\hat{\boldsymbol{\sigma}}\cdot\mathbf{n}.\end{aligned} \tag{A21}$$

We may also construct the contractions

$$\begin{aligned}\mathbf{n}^{\alpha}\mathbf{H}^{\alpha\beta\gamma}\mathbf{T}^{\beta\gamma} &= 2H^{(1)},\\ \mathbf{T}^{\alpha\beta}\mathbf{H}^{\alpha\beta\gamma}\mathbf{n}^{\gamma} &= 2H^{(2)},\\ \mathbf{n}^{\alpha}\mathbf{n}^{\beta}\mathbf{H}^{\alpha\beta\gamma}\mathbf{n}^{\gamma} &= H^{(3)}.\end{aligned} \tag{A22}$$

From Eq. (11), these kernels can be expressed as Green-Kubo expressions as follows:

$$\begin{aligned}H^{(1)}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{k_BT}\int_0^{\Delta t} dt\left\langle \mathcal{Q}\hat{\boldsymbol{\sigma}}^{\parallel\perp}_{\mathbf{r}}(t)\mathcal{Q}\hat{\mathbf{F}}^{\parallel}_{\mathbf{r}'}\right\rangle = G^{(1)}_{\mathbf{r}'\mathbf{r}},\\ H^{(2)}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{k_BT}\int_0^{\Delta t} dt\left\langle \left(\mathcal{Q}\hat{\boldsymbol{\sigma}}^{\parallel\parallel}_{\mathbf{r}}(t)\hat{\mathbf{F}}^{\perp}_{\mathbf{r}'}\right\rangle = G^{(2)}_{\mathbf{r}'\mathbf{r}},\\ H^{(3)}_{\mathbf{r}\mathbf{r}'} &= \frac{1}{k_BT}\int_0^{\Delta t} dt\left\langle \mathcal{Q}\hat{\boldsymbol{\sigma}}^{\perp\perp}_{\mathbf{r}}(t)\mathcal{Q}\hat{\mathbf{F}}^{\perp}_{\mathbf{r}'}\right\rangle = G^{(3)}_{\mathbf{r}'\mathbf{r}},\end{aligned} \tag{A23}$$

where the identification of the H kernels with the transpose of the G kernels is due to Onsager reciprocity.

The explicit form of the projected force and stress tensor has been given in Eq. (B17) of Ref. 1 and reproduced here

$$\begin{aligned}\mathcal{Q}\hat{\mathbf{F}}_{\mathbf{r}} &= \hat{\mathbf{F}}_{\mathbf{r}} - \left\langle\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle\\ &\quad - \int d\mathbf{r}'\int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho_{\mathrm{eq}}(\mathbf{r}'))\langle\delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle^{-1}\left\langle\delta\hat{\rho}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle,\\ \mathcal{Q}\hat{\boldsymbol{\sigma}}^{\alpha\beta}_{\mathbf{r}} &= \hat{\boldsymbol{\sigma}}^{\alpha\beta}_{\mathbf{r}} - \left\langle\hat{\boldsymbol{\sigma}}^{\alpha\beta}_{\mathbf{r}}\right\rangle\\ &\quad - \int d\mathbf{r}'\int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho_{\mathrm{eq}}(\mathbf{r}'))\langle\delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle^{-1}\left\langle\delta\hat{\rho}_{\mathbf{r}''}\hat{\boldsymbol{\sigma}}^{\alpha\beta}_{\mathbf{r}}\right\rangle.\end{aligned} \tag{A24}$$

Note that the equilibrium averages involving the tangential component of the force vanish and therefore

$$\mathcal{Q}\hat{\mathbf{F}}_{\mathbf{r}}^{\parallel} = \hat{\mathbf{F}}_{\mathbf{r}}^{\parallel}. \tag{A25}$$

The reason is that for every value of the tangent force within the equilibrium average, there is another value of equal magnitude and opposite sign, leading to a vanishing average. In a similar way, the equilibrium averages involving the shear components of the stress tensor also vanish and therefore

$$\mathcal{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\parallel\perp} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\parallel\perp}. \tag{A26}$$

REFERENCES

[1] D. Camargo, J. A. de la Torre, D. Duque-Zumajo, P. Español, R. Delgado-Buscalioni, and F. Chejne, J. Chem. Phys. **148**, 064107 (2018).
[2] H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics* (Springer, 1982).
[3] J. G. Anero, P. Español, and P. Tarazona, J. Chem. Phys. **139**, 034106 (2013).
[4] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**, 817 (1950).
[5] R. Piccirelli, Phys. Rev. **175**, 77 (1968).
[6] D. Duque-Zumajo, D. Camargo, J. A. de la Torre, F. Chejne, P. Español, "Discrete hydrodynamics near solid planar walls" (unpublished).
[7] D. Duque-Zumajo, J. A. de la Torre, and P. Español, "Slip and non-Markovian effects in nanohydrodynamics" (unpublished).
[8] D. Duque-Zumajo, D. Camargo, J. A. de la Torre, F. Chejne, and P. Español, "Discrete hydrodynamics near solid walls: Slip and non-Markovian effects" (unpublished).
[9] D. Duque-Zumajo, D. Camargo, J. A. de la Torre, F. Chejne, and P. Español, "Space and time locality for discrete hydrodynamics in unconfined fluids" (unpublished).
[10] D. Bedeaux, A. Albano, and P. Mazur, Physica A **82**, 438 (1976).
[11] D. Bedeaux, *Advances in Chemical Physics* (Wiley & Sons, 1986), Vol. LXIV, p. 47.
[12] D. Einzel, P. Panzer, and M. Liu, Phys. Rev. Lett. **64**, 2269 (1990).
[13] P. Sheng, T. Qian, and X. Wang, Int. J. Mod. Phys. B **21**, 4131 (2007).
[14] T. Qian, C. Qiu, and P. Sheng, J. Fluid Mech. **611**, 333–364 (2008).
[15] H. C. Öttinger, J. Non-Newtonian Fluid Mech. **152**, 66 (2008).
[16] L. Sagis, Rev. Mod. Phys. **83**, 1367 (2011).
[17] H. Brenner and V. Ganesan, Phys. Rev. E **61**, 6879 (2000).
[18] L. Bocquet and J.-L. Barrat, Phys. Rev. E **49**, 3079 (1994).
[19] J. Barrat and F. Chiaruttini, Mol. Phys. **101**(11), 1605 (2003).
[20] J. Petravic and P. Harrowell, J. Chem. Phys. **127**, 174706 (2007).
[21] J. Hansen, B. D. Todd, and P. J. Daivis, Phys. Rev. E **84**, 016313 (2011).
[22] S. K. Kannam, B. D. Todd, J. S. Hansen, and P. J. Daivis, J. Chem. Phys. **135**, 144701 (2011).
[23] K. Huang and I. Szlufarska, Phys. Rev. E **89**, 032119 (2014).
[24] B. Ramos-Alvarado, S. Kumar, and G. P. Peterson, Phys. Rev. E **93**, 023101 (2016).
[25] P. Daivis and B. Todd, Processes **6**, 144 (2018).
[26] S. Chen, H. Wang, T. Qian, and P. Sheng, Phys. Rev. E **92**, 043007 (2015).
[27] P. Español, J. de la Torre, and D. Duque-Zumajo, Phys. Rev. E **99**, 022126 (2018).
[28] W. Chen, R. Zhang, and J. Koplik, Phys. Rev. E **89**, 023005 (2014).
[29] A. Popadić, J. H. Walther, P. Koumoutsakos, and M. Praprotnik, New J. Phys. **16**, 082001 (2014).
[30] J.-P. Hansen and I. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1986).
[31] T. Weinhart, A. R. Thornton, S. Luding, and O. Bokhove, Granular Matter **14**, 289 (2012).
[32] P. Tarazona, J. A. Cuesta, and Y. Martinez-Raton, in *Lecture Notes on Physics*, edited by Á. Mulero (Springer Berlin Heidelberg, Berlin, Heidelberg, 2008), Vol. 753, pp. 247–341.
[33] P. Español and A. Donev, J. Chem. Phys. **143**, 234104 (2015).
[34] J. T. Hynes, R. Kapral, and M. Weinberg, J. Chem. Phys. **70**, 1456 (1979).
[35] D. Lesnicki and R. Vuilleumier, J. Chem. Phys. **147**, 094502 (2017).
[36] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, 2001).
[37] B. A. Dalton, K. S. Glavatskiy, P. J. Daivis, B. D. Todd, I. K. Snook, B. A. Dalton, K. S. Glavatskiy, P. J. Daivis, and B. D. Todd, J. Chem. Phys. **139**, 044510 (2013).
[38] B. A. Dalton, K. S. Glavatskiy, and P. J. Daivis, Phys. Rev. E **92**, 012108 (2015).
[39] B. Todd and P. Daivis, *Nonequilibrium Molecular Dynamics* (Cambridge University Press, 2017).