Statistical mechanics derivation of hydrodynamic boundary conditions: the diffusion equation

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Abstract. Considering the example of interacting Brownian particles we present a linear response derivation of the boundary condition for the corresponding hydrodynamic description (the diffusion equation). This requires us to identify a non-analytic structure in a microscopic relaxation kernel connected to the frequency dependent penetration length familiar for diffusive processes, and leads to a microscopic definition of the position where the hydrodynamic boundary condition has to be applied. Corrections to the hydrodynamic limit are obtained and we derive general amplitudes of spatially and temporally long ranged fluctuations in the considered diffusive system.
1. Introduction

The description of dynamical processes in condensed matter greatly simplifies if fluctuations are studied which are slow and smooth compared to the microscopic length and time scales of the system. Then hydrodynamic equations for a small number of fields can be derived, either using rather general phenomenological considerations, or by coarse graining starting from a microscopic statistical mechanics description. In the latter a large number $N$ of particles needs to be handled and the hydrodynamic fields (normally) arise as coarse grained densities of conserved variables $[1]$. The Zwanzig–Mori operator formalism enables one to perform the coarse graining of the microscopic equations of motion using spatially Fourier transformed variables in the limit of vanishing wavevector $q$ (corresponding to large wavelengths $2\pi/q$). Already in 1931, Onsager explained how the microscopic equations in the limit of $q \to 0$ and small frequency lead to the hydrodynamic equations $[2]$. He suggested that in an infinite system a perturbation described by macroscopic hydrodynamic equations decays from its initial value according to the identical dynamical equations as a long–wavelength and small frequency fluctuation around local thermodynamic equilibrium $[3]$. As an important side-product, this correlation functions approach has led to general and exact microscopic expressions for the phenomenological transport coefficients of the hydrodynamic equations (the Green–Kubo relations).

Hydrodynamic equations, which are partial differential equations, require temporal and spatial boundary conditions to give unique solutions; see e.g. the examples in $[4]$. Following Onsager, only the former are understood from microscopic many–body approaches, while, by studying infinite systems, the latter have been neglected. Within the phenomenological approach, simple continuity considerations lead to the required conditions on surfaces, yet their derivation from information about microscopic interactions and molecular parameters still appears desirable. First, this would provide rigorous statistical mechanics definitions of the parameters characterising the boundary condition; second, different conditions (like stick or slip for fluid flow, or flux versus no–flux with or without adsorption of particles at a surface) could be predicted from molecular interactions; and third, generalizations beyond the true hydrodynamic limit (e.g. for finite geometries) would become possible. Only the question about the tangential velocity of a flow along a solid boundary has a long history, which goes back to Maxwell, and, for rarefied gases, is quite well answered in the framework of the Boltzmann equation (Knudsen-layer problem $[5]$). Yet, beyond the dilute limit a fluctuating hydrodynamics calculation by Wolynes $[6]$ has uncovered the subleties arising from back flow patterns (coupling of hydrodynamic modes), and only rather recently there has been the first study of this problem in the microscopic correlation functions approach by Bocquet and Barrat $[7]$. In our study of the simpler system of a single conserved variable which macroscopically obeys a diffusion equation, we follow the approach of Bocquet and Barrat and connect a microscopic linear response calculation to the macroscopic hydrodynamic description via a generalization of Onsager’s regression hypothesis.

On the macroscopic level, the number density $n(r,t)$ of interacting Brownian particles at the space point $r$ and at time $t$ obeys a diffusion equation

$$\partial_t n(r,t) = D \nabla^2 n(r,t),$$

(1)

where $D$ is the (gradient) diffusion coefficient which enters Eq. (1) as a phenomenological transport coefficient; $\partial_t = \partial/\partial t$ denotes a partial time derivative.
Hydrodynamic boundary conditions

and \( \nabla = \partial / \partial r \) a spatial gradient. If the diffusing particles border a solid surface which moves with velocity \( \mathbf{v}(t) \) then the number of particles (per unit area and time) displaced by the surface, \( n \mathbf{v} \), needs to be balanced by a particle flux \( \mathbf{j} \) away from the boundary. As the latter obeys \( \mathbf{j} = -D \nabla n \), the no–influx boundary condition on the solid surface becomes:

\[
\hat{e}_n [n(r,t) \mathbf{v}(t) + D \nabla n(r,t)]_{bd} = 0 ,
\]

(2)

here \( \hat{e}_n \) is a unit vector normal to the surface, whose position is abbreviated as “bd” for boundary.

In sections 2. and 3. of this manuscript, Eq. (2) will be derived up to linear order in \( \mathbf{v} \) by coarse graining the many–body statistical mechanics description of interacting Brownian particles. At first the appropriate microscopic kernel is found (sect. 2.), and then its small \( q \) and \( \omega \) behavior discussed (sect. 3.). The calculation entails the (standard) derivation of Eq. (1) including the Green–Kubo type calculation of \( D \). The solution of Eqs. (1,2) around a spherical object to linear order in the perturbing velocity \( \mathbf{v} \) is summarized in Appendix A for comparison reasons, while Appendix B contains technical material. Section 4. describes an application of our results. The power–law decay of the force experienced by a large sphere moving among the Brownian particles is deduced along with its mean-squared displacement, which exhibits a long time tail.

2. Microscopic approach

2.1. Smoluchowski equation, and notation

The statistical mechanics basis for interacting Brownian particles is given by the Smoluchowski equation, which is a generalized diffusion equation in high-dimensional phase space. It describes the temporal evolution of the many–body probability distribution \( \Psi(\{r_i\}, t) \), which depends on the positions \( r_i \) of all particles, \( i = 1, \ldots, N+1 \), where we consider \( N \) identical bath particles with Brownian diffusion coefficient \( D_i = D_0 \) and one additional tracer with index \( s = N + 1 \) and diffusion coefficient \( D_s \):

\[
\partial_t \Psi = \sum_i D_i \partial_i \cdot (\partial_i - F_i) \Psi .
\]

(3)

Here \( \partial_i = \partial / \partial r_i \), and energies are measured in units of the thermal energy. The particle interactions enter Eq. (2) via the potential forces \( \mathbf{F}_j = -\partial_j V(\{r_i\}) \) resulting from interactions between the bath particles \((V^p)\) and between tracer and bath particles \((V^s)\), \( V = V^p + V^s \). Dynamic effects due to the background medium (hydrodynamic interactions) are neglected at the present stage. To reach the hydrodynamic limit we will take the size of the tracer to become much larger than the bath particle size. For the presentation in the main text, the tracer is assumed to be immobile from the outset, \( D_s = 0 \), and Appendix B verifies that the limit \( D_s \to 0 \) can be taken after the formal manipulations. Summation and indices are from now on always understood to run from 1 to \( N \), i.e., to exclude the index \( s = N + 1 \) for the tracer. To simplify the presentation, we also introduce the radii \( a_s \) and \( a \) of the tracer and the bath particles, respectively. It is however important to realize that we consider arbitrary isotropic short ranged particle interactions, where \( a \) and \( a_s \) may be effective state dependent sizes as e.g. in the case of soft repulsions of the form \( V^p(r = |r_i - r_j|) \propto r^{-12} \).
For the following, we introduce some further notational conventions. It is convenient to work with the backward or adjoint Smoluchowski operator
\[ \Omega \equiv D_0 \sum_i (\partial_i + F_i) \cdot \partial_i , \] (4)
which gives the time evolution of variables \( A(\{ r_i \}) \) on phase space: \( \partial_t A = \Omega A \). It also determines the time evolution of correlation (fluctuation) functions \( \Phi_{AB}(t) = \langle A^* \exp \{ \Omega t \} B \rangle / \langle A^* B \rangle \), which we normalize by their equal time values calculated by canonical averaging with the Gibbs–Boltzmann weight \( \langle ... \rangle \propto \int \prod_{i=1}^{N+1} d r_i \ldots e^{-V} \).

Note that here the tracer-particle interactions enter in full non–linear detail, and that the equilibrium weight is a stationary solution of Eq. (3).

The fluctuating microscopic bath particle density at position \( r \) is given by \( \varrho(r) = \sum_j \delta(r - r_j) \), with spatial Fourier transform, \( \varrho_q = \sum_j \exp \{ i q r_j \} \), where the \( q = 0 \) contribution from the constant bulk density \( n \) will be neglected. The corresponding tracer density fluctuation is given by \( \varrho_s^q = \exp \{ i q r_s \} \). Temporal Fourier decomposition shall be denoted by \( A_\omega = \int_{-\infty}^{\infty} dt \, e^{i \omega t} A(t) \), while the Laplace transformation is used with the convention: \( A(\omega) = \int_0^{\infty} dt \, e^{i \omega t} A(t) \).

2.2. Generalized Onsager regression hypothesis

The connection between the statistical mechanics description on the Smoluchowski level and the macroscopic hydrodynamic picture shall be made by comparing the density fluctuations predicted from both descriptions for the identical given boundary problem in a simple geometry.

In order to use the familiar Smoluchowski operator of Eq. (3), we consider the motion of particles around a spherical object, the tracer. Bath particle \( j \) experiences the short-ranged force \( F^s_j = -\partial_j V^s \) close to it. Moving the tracer, by unspecified external means, with velocity \( v(t) \) induces a particle flux at its surface, which in linear order in \( v \) equals \( j_{bd}(t) = n v(t) \) on the macroscopic level. Deviations of the coarse grained particle density around the tracer \( n(r, t) \) from the bulk value \( n \) would enter in higher order in \( v \) only. The disturbance on the microscopic level, required to induce this applied particle flux thus can be obtained from requiring the non–equilibrium average of the tracer velocity to agree with the macroscopic value up to non–linear corrections:
\[ \langle \partial_t r_s \rangle^{(ne)} = v(t) + \mathcal{O}(v^2) . \] (5)

Adiabatically turning on the applied velocity in the infinite past eliminates initial value contributions in the deviatoric density, \( \delta n(r, t) = n(r, t) - n \), and allows us to use a Fourier decomposition, \( v(t) = \int (d\omega/2\pi) \, e^{-i\omega t} v_\omega \). Linear response theory then connects the density deviation to the given disturbance via a (vector) susceptibility \( \chi(r, t) \). It vanishes for \( t < 0 \) because of causality, and its spatial argument \( r \) is measured from the tracer sphere center. After Fourier transformation, both the macroscopic hydrodynamic result (cf. Appendix A) and the microscopic result (cf. sections 2.3 and 2.4) can be written as
\[ \delta n_{q, \omega} = n v_\omega \cdot \chi_q(\omega) + \mathcal{O}(v^2_\omega) . \] (6)

Now, in the spirit of Onsager’s hypothesis we assume that the microscopic calculation of Eq. (6) reduces to the macroscopic solution for smooth and slow fluctuations, viz. in the limit of small frequencies and wavevectors. Yet, in order to derive hydrodynamic boundary conditions, the coarse graining must be taken...
Hydrodynamic boundary conditions

with respect to the bath particle size \( a \) only, while the tracer size is required to satisfy \( a_s \gg a \). Thus we keep \( a_s \) fixed so that the macroscopic diffusion equation description, while it applies for distances \( r \gg a \) only, nevertheless includes both far field (\( r \gg a_s \)) and near field (\( r \ll a_s \)). The latter case is equivalent to considering the density profile \( \delta n(z,t) \) at a distance \( z \) close to a planar wall obtained formally when taking \( a_s \to \infty \). Although this limit does not provide a faithful representation of a macroscopic boundary as an assembly of atoms, it has the virtue of being the conceptually simplest realization of a hydrodynamic boundary problem.

Two aspects of the described approach are worth mentioning: First, while Eqs. (5,6) are linear in the applied boundary flux, the particle–wall (tracer) interactions are included exactly. Thus on a local length scale the unperturbed equilibrium density variations arise, which somewhat differs from the approach to shear flow past a surface in Ref. [7]. Second, as discussed e.g. by Kadanoff and Martin for the initial value problem [3], a general perturbation to the fluid induces fluctuations in the non–conserved variables, which have to die out before the hydrodynamic description applies. For the present boundary perturbation the same reasoning applies, and thus the hydrodynamic description only holds for large distances, while locally deviations from the hydrodynamic solution need to appear; for rarefied gases these Knudsen–layers effects are familiar [5]. In the present many–body linear response calculation the technical difficulty is connected to coarse graining across the equivalent layer, which has a width connected to the particle size \( a \).

2.3. Linear response calculation

In order to proceed, the perturbation to the Smoluchowski operator \( \Omega \) needs to be found which gives the required velocity of the tracer in Eq. (5). Without hydrodynamic interactions, the perturbation equivalent to a constant solvent velocity, which is felt solely by the tracer, is by inspection

\[
\Delta \Omega = \mathbf{v}(t) \cdot \partial_s .
\]

A standard linear response calculation using its adjoint \( \Delta \Omega^\dagger = -\mathbf{v}(t) \cdot \partial_s \), which acts on the probability density in Eq. (3) [6], gives the resulting deviation in an arbitrary variable \( A \)

\[
\langle \delta A(t) \rangle^{(ne)} \equiv \langle A(t) \rangle^{(ne)} - \langle A(t) \rangle = -\int_{-\infty}^{t} d\tau \, \mathbf{v}(\tau) \cdot \langle F_s e^{\Omega(t-\tau)} A \rangle + \mathcal{O}(v^2) .
\]

Thus, Eq. (5) becomes

\[
\langle \partial_t r_s \rangle^{(ne)} = \langle (\Omega + \Delta \Omega) r_s \rangle^{(ne)} = \langle \mathbf{v}(t) \cdot \partial_s r_s \rangle + \mathcal{O}(D_s/D_0, v^2) .
\]

See Appendix B, for a more careful discussion for finite tracer diffusivities \( D_s > 0 \). As required, the perturbation Eq. (7) gives the average velocity of the tracer, which enters the macroscopic boundary condition Eq. (4).

The linear response formula can also be applied to the microscopic density field \( \rho(\mathbf{r}') \) at a (vector) distance \( \mathbf{r} \) from the tracer center: \( \mathbf{r}' = \mathbf{r}_s + \mathbf{r} \). Its unperturbed equilibrium value is proportional to the familiar tracer-particle pair correlation function [1]:

\[
g^s(\mathbf{r}) = (1/n) \sum_i \langle \delta [\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_s)] \rangle,
\]

which gives the probability of finding bath particles at a distance \( r \) from the center of the tracer. The linear deviation in the density around the tracer induced by the perturbation, Eq. (6), follows
Hydrodynamic boundary conditions

Immediately from Eq. (8), and by comparison with Eq. (6), the required linear response susceptibility is found:

\[ \chi_q(\omega) = -\frac{1}{n} \left\langle F_s \frac{-1}{\Omega + i\omega} \varrho_q^s \varrho_q \right\rangle, \quad \text{or} \]

\[ \chi(r, t) = -\frac{1}{n} \left\langle F_s e^{\Omega t} \varrho(r + r_s) \right\rangle \theta(t), \quad (10) \]

where the step-function \( \theta(t) \) expresses causality.

2.4. Time scale separation

The exact linear response susceptibility varies on rapid microscopic time and length scales but also on smooth and slow ones, which are amenable to a hydrodynamic description. The Zwanzig-Mori projection operator formalism enables one to disentangle these contributions by splitting the resolvent into fast and slow subspaces \([1]\). The resolvent \( R(\omega) = \frac{1}{\Omega + i\omega} \) arises in the Laplace transform of a general correlation function, \( \Phi_{AB}(\omega) = \left\langle A^* R(\omega) B \right\rangle / \left\langle A^* B \right\rangle \), and contains poles which shift to vanishing frequency for smooth fluctuations (\( q \to 0 \)). These so-called hydrodynamic poles are connected with the exact conservation laws of the system, and the Zwanzig-Mori formalism isolates them. In the present situation, where Eq. (3) holds, there are only poles connected with particle number conservation: each particle, including the tracer, is conserved as is the total density, \( \partial_t \varrho_q \propto q \) for \( q \to 0 \). While the more careful calculation in Appendix B takes into account the tracer, here we chose for the slow subspace the one spanned by the total density only. That is, we use the projector \( P = \langle \varrho_q \rangle (NSq)^{-1} \langle \varrho_q^* \rangle \), which is normalized by the equilibrium Brownian particle structure factor \( S_q = \langle \varrho_q^* \varrho_q \rangle / N \) \([1]\). The justification for this simplification is provided by the thermodynamic limit, in which only a non–extensive number of particles actually interacts with the tracer; see below and Appendix B.

The exact identity obtained in the Zwanzig–Mori projection operator formalism \([10]\) gives for a general fluctuation function:

\[ \left\langle A^* R(\omega) B \right\rangle = \left\langle A^* R'(\omega) B \right\rangle + \left\langle A^* (1 + R'(\omega) \Omega) PR(\omega) P(1 + \Omega R'(\omega)) B \right\rangle, \quad (11) \]

where the reduced resolvent describes the fast dynamics decoupled from the slow fluctuations of the conserved density:

\[ R'(\omega) = \frac{-1}{Q \Omega Q + i\omega} Q \quad \text{with} \quad Q = 1 - P. \quad (12) \]

Thus, the coupling of the arbitrary variables \( A, B \) to the slow conserved density is found; explicitly it is obtained when writing out \( PR(\omega)P \) in Eq. (11), and the slow variable couples in with static (i.e. \( \langle A^* \varrho_q \rangle \)) and frequency dependent (i.e. \( \langle A^* R'(\omega) \Omega \varrho_q \rangle \)) overlaps.

In order to apply Eq. (11) to the correlation function in Eq. (10), the (expected) problem arises that it is formed with variables that are not defined in a translationally invariant manner. Translational symmetry is broken by the boundary (i.e. measuring distances from the tracer). On the macroscopic level this could be handled by introducing the appropriate eigenfunctions that satisfy the boundary conditions for the prescribed geometry. Yet, on the microscopic level this would require determining the many–body eigenfunctions of the Smoluchowski operator Eq. (4) for a given force field arising from \( V^s \). Within the framework of fluctuating hydrodynamics Wolynes achieved a related task in a scattering–formalism calculation for the flow...
of a Newtonian fluid past a wall \[ \] . His calculation focused on the non-linear coupling of the hydrodynamic modes and thus could circumvent the study of the local variables close to the boundary. Consequently, he did not determine the boundary position microscopically and instead introduced a short distance cut-off (in his case irrelevant). Because we aim for an exact determination of the boundary condition, we chose the plane-wave decomposition of the density fluctuations which enables one to use Eq. (11), and apply it to the resolvent in a shifted coordinate system

\[
R_q(t) = g_q^s R(t) g_q^s = R(t) \left( 1 + \mathcal{O}(D_s/D_0) \right). \tag{13}
\]

It agrees with the original resolvent only if thermal tracer fluctuations are neglected (cf. Appendix B). In this limit, the Fourier transformed susceptibility becomes

\[-n \chi_q(\omega) = \langle F_q^* R(\omega) g_q \rangle = \langle F_q^* \left[ 1 + R'(\omega) \Omega \right] g_q \rangle \Phi_q(\omega), \tag{14}\]

where we have introduced the tagged force density fluctuation \( F_q^s = F_s g_q^s \) and the (normalized) density correlator \( \Phi_q(\omega) = \langle g_q^s R(\omega) g_q^s \rangle/(NS_0) \). Application of Eq. (11) to the latter gives the familiar expression

\[
\Phi_q(\omega) = \left[ -i\omega - \frac{\langle g_q^s \Omega g_q \rangle}{NS_q} + \frac{\langle g_q^s \Omega R'(\omega) \Omega g_q \rangle}{NS_q} \right]^{-1} \rightarrow \left[ -i\omega + q^2 \frac{D_0}{S_0} \right]^{-1}. \tag{15}\]

The second expression in Eq. (15) is taken in the hydrodynamic limit of small frequencies and wavevectors, where it gives the (transformed) fundamental solution of the diffusion equation Eq. (1). This leads to the known microscopic definition of the gradient diffusion coefficient, \( D = D_0/S_0 \). Here, \( S_0 \) is a normalized compressibility. The result for \( D \) may be called of Green-Kubo type because its apparent static nature originates in an instantaneously decaying associated current.

The frequency independent (or instantaneous) overlap in Eq. (14) can be expressed in terms of the Fourier transform of the non-trivial part, \( h^s(\mathbf{r}) = g^s(\mathbf{r}) - 1 \), of the tracer-particle pair correlation function introduced above, \( \langle F_q^* g_q \rangle = i q n h_q^s \), but little further simplification is possible in the retarded second term. Upon introducing the total force density fluctuation \( F_q = \sum_j j e^{i \mathbf{q} \cdot \mathbf{r}_j} Q \Omega g_q = iQ \sum_j q \cdot F_q \), and the final (still exact) result for \( \chi \) becomes (for \( t > 0 \))

\[
\chi_q(t) = -i q h_q^s \Phi_q(t) - \frac{D_0}{n} \int_0^t d\tau \langle F_q^* R'(t - \tau) \cdot F_q \rangle \Phi_q(\tau). \tag{16}\]

It is written as function of time to clearly present the instantaneous (first term) and retarded coupling of the density fluctuations to the susceptibility. Because of Newton’s third law, the potential force \( F_s \) felt by the tracer can be reexpressed as the negative of the total force exerted by the tracer on all particles; \( F_s = -\partial_i V^s = \sum_i \partial_i V^s \equiv -F_0 \). For the same reason it is opposite equal to the integrated total force; \( F_s = F_q=0 = -F_q=0 = \sum_i \partial_i V_i = -F_0 \). A noteworthy aspect of the (straightforward) calculation in this section concerns the thermodynamic limit which is required in order for the obtained bulk quantities to take their standard values for an unbounded system. For example, the tracer bath particle interactions enter the expression for \( S_q \) (and consequently for \( D \)) via the equilibrium distribution function. Nevertheless, in the thermodynamic limit this correction vanishes because the assumed short-ranged interaction of the bath particles with the tracer decays beyond the distance of a few \( a \), and the bulk of the particles is not affected.
3. Coarse graining and discussion

The exact correlation function, Eq. (14), describes the response of the system to an injected boundary flux of particles on all length scales. In order to derive the hydrodynamic boundary condition, coarse graining is required as discussed in section 2.2. Appendix A collects the results from the macroscopic approach in order to compare them with the small wavevector and frequency limits of the microscopic susceptibility.

3.1. Instantaneous response

In order to familiarize oneself with Eq. (16), it is useful to consider a rapid velocity pulse on the tracer at time \( t_0 \), \( \mathbf{v}(t) = \mathbf{V}\delta(t - t_0) \), and to concentrate on the instantaneous response of the density:

\[
\delta n(\mathbf{r}, t = t_0) = n \mathbf{V} \cdot \chi(\mathbf{r}, t = 0) = n \mathbf{V} \cdot \nabla h^s(\mathbf{r}).
\]

This arises from the first term in Eq. (14), which simplifies because of \( \Phi_q(t = 0) = 1 \), and is determined by the equilibrium density profile of bath particles around the tracer. The inserted flux, \( n \mathbf{V} \), is packed close to the boundary according to the equilibrium fluid structure \( h^s \) of the bath particles. The (Ursell) function \( h^s \) varies between the universal limits, \( h^s = -1 \) for short distances where the hard core volumes of the particles are excluded by the tracer, and \( h^s = 0 \) far away from the tracer. In between, it shows layering over a distance of the order of a few \( a \).

In the hydrodynamic limit, which corresponds to \( a_s \gg a \) here, the present work provides the connection of the position of the boundary to the molecular interaction potential \( V^s \). At a radial distance \( \sigma \) from the tracer center, \( h^s \) varies rapidly and in the limit \( a \rightarrow 0 \) with fixed \( a_s \) and \( r \), may loosely be taken as a step function, \( h^s(\mathbf{r}) = -\theta(\sigma - r) \). The macroscopic sphere asymptotically becomes impenetrable for the bath particles irrespective of the exact interaction potential. The latter however determines the exact boundary position \( \sigma \), and its definition becomes:

\[
h^s_q = -2\pi a^3 f(\sigma a) + \mathcal{O}(\sigma^2) \quad \text{for} \quad a_s \gg a \quad \text{and} \quad qa \ll 1, \quad (17)
\]

where \( f(x) = (\sin x - x \cos x)/x^3 \). Whenever Eq. (17) does not hold, possibly for long ranged forces or wetting situations, we expect Eq. (16) to be violated. Such situations are excluded in the following. A finite (positive or negative) surface excess density enters in the corrections of order \( \sigma^2 \). In the following sections we show that exactly the same structure also appears in the retarded contributions to Eq. (16), and that the boundary position \( \sigma \) thus is a static equilibrium concept (see however Ref. [7] for Newtonian fluid flow).

In the limit of \( a_s \gg a \), the rapid variation of \( h^s \) can be used to define a one-dimensional cut through the density profile, which in the limit \( a_s \rightarrow \infty \) (and consequently \( \sigma \rightarrow \infty \)) would correspond to the situation at a wall \( \mathbb{I} \). With the wall at \( x = \sigma \), and its normal vector pointing along \( \hat{x} \), the wall profile \( h^{sW} \) as function of \( \hat{r} = \mathbf{r} - \sigma \hat{x}, \hat{x} = \hat{r} \cdot \hat{x} \) follows:

\[
h^s(\mathbf{r}) \rightarrow h^{sW}(\hat{x}) + \mathcal{O}(\hat{r}/\sigma) \quad \text{for} \quad \sigma \rightarrow \infty. \quad (18)
\]

It obeys, \( h^{sW}(\hat{x} \rightarrow -\infty) \rightarrow -1 \) and \( h^{sW}(\hat{x} \rightarrow \infty) \rightarrow 0 \), with rapid variations on a length scale of order \( a \) around \( \hat{x} \approx 0 \). Its one-dimensional Fourier transform is given by

\[
h^{sW}_{q_s} = \int_{-\infty}^{\infty} d\hat{x} e^{iq_s\hat{x}} h^{sW}(\hat{x}) = \mathcal{H}_{q_s} - \frac{1}{iq_s} + \mathcal{H}'(1 + \mathcal{O}(q_s a)), \quad (19)
\]
where the constant $H'$ is the surface density excess divided by $n$ and is of order $a$ itself. By shifting the origin to $\bar{x} = 0$ ($x = \sigma$), we eliminated (for simplicity) a phase factor $e^{iq_x \sigma}$ in $h_{q \sigma}^W$, which would prove convenient when keeping track of the wall position.

3.2. Near–field solution

Generically, boundary conditions are formulated when considering the motion in a half space bounded by a planar surface (wall). As discussed above for the instantaneous response, this situation can be realized in Eq. (16) by taking the limit $a_s \to \infty$ and calculating

$$\chi(r = \sigma \hat{x} + \bar{r}, t) = \chi^W(\bar{x}, t) \hat{x} + O(\bar{r}/\sigma)$$

to non–vanishing order. The result $\chi^W(\bar{x}, t)$ describes the motion close to an infinite plane wall or, in general, the near–field solution for non–planar solid surfaces. Only its small wavevector limit is required in the following, and this simplifies because the force exerted on the diffusing particles by the wall (for $a_s \to \infty$) is perpendicular to it:

$$\chi^W_{q x}(\omega) \sim \left[ 1 + i q x D_0 n \frac{\hat{x} \cdot F_0 R(\omega) \hat{x} \cdot F_0}{\omega} \right] \Phi_{q x}(\omega). \quad (20)$$

Here we have used that for vanishing wavevector the reduced resolvent in the relaxation kernel again agrees with the full dynamics [1]. The retardation kernel in Eq. (20) therefore has the familiar Green–Kubo form. If it could be replaced by a constant rate for small frequency, $\langle \hat{x} \cdot F_0 R(\omega \to 0) \hat{x} \cdot F_0 \rangle \to \Gamma$, then for consistency the square bracket would become $[\ldots] \to 1 + O(q)$. Fortunately, in an exact calculation for vanishing concentration of hard Brownian spheres, $n \to 0$, Dieterich and Peschel have shown that

$$i D_0 n \langle \hat{x} \cdot F_0 R(\omega) \hat{x} \cdot F_0 \rangle = \sqrt{-i D_0 \omega} (1 + O(na^3)). \quad (21)$$

In this limit $D = D_0$, and the result of Eqs. (13,20) agrees with the solution of the hydrodynamic equations, Eqs. (1,2), in the considered geometry; see Eq. (A.3). This proves the boundary condition Eq. (2) in the dilute limit of hard spheres [12].

For the general situation of interacting Brownian particles at finite concentrations, no exact calculations of the relaxation kernel in Eq. (20) are known. We proceed by performing a mode coupling approximation [8, 13, 14], where the starting point is the more general expression of Eq. (16) as it captures near– and far–field terms. The conserved density fields are the slow variables and in the lowest pair–fluctuation approximation the overlap of the fluctuating forces with $g_k g_{k'}^* \Phi_k$ needs to be considered. In the small wavevector limit of interest, the memory function becomes identical to the well studied tracer force autocorrelation kernel, and its mode coupling result can be taken from the literature [14].

$$\frac{D_0}{n} \langle F_0 R(t) Q F_0 \rangle \approx D_0 Q \lim_{q \to 0} \int \frac{d^3k}{(2\pi)^3} (kk) \frac{h_{k k} h_{q - k} - k \Phi_k(t)}, \quad (22)$$

where the tracer density fluctuation function does not appear explicitly (it equals 1 because of $D_s = 0$).

The mode coupling approximation of the relaxation kernel can be applied to the wall or near–field problem upon the realization that the forces arise from density fluctuations whose probability depends on the wall distance according to $h_{q \sigma}^W(\bar{x})$ and is

\footnote{It can be expected that this approximation does not give numerically exact hydrodynamic results [13], but Schofield and Oppenheim [16] have argued that this problem can be overcome by systematically taking the overlap with higher order density products into account.}
Hydrodynamic boundary conditions

independent of the parallel coordinates, \( \vec{y} \) and \( \vec{z} \). For the relevant wavevector region \( \vec{q} \), the \( h^k \) in Eq. (22) thus corresponds to

\[
h^k \approx h^W = (2\pi)^2 \delta(\vec{q}) \left[ \frac{h^s}{i q_x} \right],
\]

(23)

where \( \delta(\vec{q}) \) restricts the parallel wavevector to vanish, \( q_y = q_z = 0 \), and the wall profile function \( h^s \) defined in Eq. (19) enters. We find the approximation:

\[
\frac{D_0}{\bar{n}} \langle \hat{x} \cdot F_0 R(\omega) \hat{x} \cdot F_0 \rangle \approx (2\pi)^2 \delta(\vec{q}) \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \left[ \frac{[H^s_{k_x}]^2}{S_{k_x}} \Phi_{k_x}(\omega) \right],
\]

(24)

where in the integrand \( k_y = k_z = 0 \). Importantly, in the hydrodynamic limit \( \omega \to 0 \), the integral converges already for such small \( k_x \ll 1/a \) that the structure functions can be replaced by their homogeneous zero wavevector limits, \( H^s \to 1 \) and \( S_{k_x} \to S_0 \). The latter is the bulk compressibility required to turn the single particle \( D_0 \) into the gradient diffusion constant \( D \). It is thus interesting that the exact one-dimensional result of Eq. (21) in the dilute limit only applies to the present case because the (isolated) particles experience no interactions and thus \( D = D_0 \) in Eq. (24). Because the integration in Eq. (24) is dominated by \( k \ll a \), the density correlator can be replaced by its universal hydrodynamic limit from Eq. (15).

Collecting all terms together and performing the integrations gives the mode coupling approximation

\[
\chi_q(\omega) \approx \hat{x} (2\pi)^2 \delta(\vec{q}) \left\{ 1 + \sqrt{\frac{-i D q_x^2}{\omega}} \left[ \frac{1}{2} + \ldots \right] \right\} \frac{1}{D q_x^2 - i\omega},
\]

(25)

where the term \( \frac{1}{2} \) in the square bracket arises from the considered pair density projections and \( \ldots \) indicate higher order density projections which should be taken into account following an expansion procedure developed by Schofield and Oppenheim [16]. Assuming the series of density projections in the square bracket in Eq. (25) to sum up to one, the comparison with Eq. (A.3) proves the correctness of the boundary condition Eq. (2), now at finite concentrations.

3.3. Far-field solution

While the verification of the boundary condition Eq. (2) is achieved by the calculation of the near-field, it is instructive to also consider the density fluctuations very far away from the spherical boundary. In this limit, both particle sizes \( a \) and \( a_s \) are small compared to the wavelength and the susceptibility in Eq. (16) simplifies to

\[
\chi_q(t) \sim -i \vec{q} \alpha \Phi_q(t) \quad \text{with} \quad \alpha = h^s_0 \frac{D_0}{3n} \int_0^\infty dt \langle F_0(t) \cdot F_0 \rangle,
\]

(26)

for \( q a_s \ll 1 \); where the density correlator takes its hydrodynamic form, \( \Phi_q(t) = \exp(-q^2 D t) \) from Eq. (15). The density profile around a moving tracer rearranges by particle diffusion and thus requires more and more time the larger the involved distances. In the steady case, \( \omega = 0 \), a power law density profile develops

\[
\delta n_{\omega=0}(r) \sim -\frac{\alpha n}{4\pi D} \frac{v_{\omega=0} \cdot \hat{r}}{r^2},
\]

(27)

First, Eq. (22) is transformed to \( r \)-space and then \( h^s(r) \) is analyzed according to Eq. (18). The procedure is checked a posteriori from the convergence of the integral.
as follows from Eqs. (6,15,26) and transformation to r-space. It is of similar nature to the Oseen velocity profile around a colloidal particle in a Newtonian solvent [4], as such long–ranged patterns generally arise in hydrodynamic steady states [17]. In the Brownian particle context, it is well known from calculations in the dilute limit, $n \to 0$ [9, 18, 19], and the amplitude factor $\alpha$ extends those calculations to finite densities.

Interestingly, the expression for $\alpha$ in Eq. (26) holds for arbitrary size ratios $a_s/a$, even beyond the macroscopic hydrodynamic limit, which is obtained for $a_s \gg a$. For dilute hard spheres, the known result $\alpha(n \to 0, a/a_s \to 0) = -2\pi\sigma^3$ (where $\sigma = a_s$) [9, 18] agrees with the expectation from the macroscopic calculation, Eq. (A.2). For finite densities the mode coupling approximation Eq. (22) can be used

$$\alpha \approx h_s^0 - \lim_{\omega \to 0} D_0 \int_0^\infty \frac{dk}{6\pi^2} \frac{k^2 h_s k}{S_k} \Phi_k(\omega).$$

(28)

In the limit of a macroscopic tracer, which becomes impenetrable to the Brownian particles so that $h_s^0(r)$ approaches a step function as argued in Eq. (17), the integration in Eq. (28) already converges for $ka \ll 1$. The density correlator is then given by the hydrodynamic limit and the structure factor equals the compressibility, $S_k = S_0$, so that

$$\alpha \approx -2\pi\sigma^3 \left\{ \frac{2}{3} + \left[ \frac{2}{9} + \ldots \right] \right\}.$$

(29)

The leading contribution $2/3$ arises from the static term, while we may again expect [10] the Green–Kubo expression to sum up to the missing $1/3$ if, extending our pair–density factorization, higher order density fluctuations are included.

### 4. Application to diffusive long time tail

An immediate consequence of the long–ranged structure built by particle diffusion around a macroscopic tracer, are slow time dependent fluctuations in the force the tracer feels. An interesting aspect of these so-called long time tails is that hydrodynamic calculations provide insights into them [3, 20], even in the presence of boundaries [21]. As an application of the above discussion of boundary conditions for the diffusion equation, we study the long time tail in the force autocorrelation function of a tracer diffusing among Brownian particles. This extends the knowledge available at infinite dilution [3, 13, 10].

As a first step, the constitutive equation connecting the force a particle feels to the fluctuations of the conserved variable, the bath density, is required. It follows from the Zwanzig–Mori decomposition as [10]

$$\langle \delta F^{*}_q(\omega) \rangle = \frac{\langle \delta \varrho^*_q(\omega) \rangle}{NS_0} \left( \langle F^{*}_q \varrho_q \rangle + \langle F^{*}_q R'(\omega) \varrho_q \rangle \right) \to i q \frac{\alpha}{S_0} \langle \delta \varrho^*_q(\omega) \rangle,$$

(30)

where the limit in the second part holds for $q \to 0$ and $\omega \to 0$, and the coefficient $\alpha$ was defined in Eq. (26). Therefore, in the hydrodynamic limit, if a density gradient exists, it causes the force field:

$$\langle \delta F_s(r, \omega) \rangle = \frac{\alpha}{S_0} \nabla \langle \delta \varrho(r, \omega) \rangle.$$

(31)

A sphere among the Brownian particles experiences this force density, and if it moves with velocity $\mathbf{v}$, the density fluctuations in its vicinity are described by Eqs. (16). Following, the macroscopic approach to long time tails, and inserting...
these expressions (with obvious definition of the matrix field $\alpha(\mathbf{r}, \omega)$) into Eq. (11) gives the force field around the sphere. The sphere feels the interactions on its surface and thus the total force on it is obtained by averaging over the surface:

$$
\mathbf{F}_{s, \omega} = \frac{n\alpha}{S_0} \mathbf{v}_\omega \int \frac{d^3 f_r}{4\pi} (\mathbf{v}_\omega \cdot \nabla r) \int d^3 s \mathbf{v}_\omega \cdot \alpha(s, \omega) \cdot \nabla r \Phi(r - s, \omega) \bigg|_{r=\sigma},
$$

where $\Phi(\mathbf{r}, \omega) = \frac{1}{4\pi D_\sigma^2 e^{-\kappa r}}$ with $\kappa^2 = -i\omega/D$ follows from Eq. (13). In general this result can not be simplified and e.g. the $\omega = 0$ value, which would be connected to the tracer diffusion coefficient, cannot be found from our hydrodynamic consideration alone. Linear response theory enables one to identify the tracer force autocorrelation function from Eq. (12): $\mathbf{F}_{s, \omega} = -(1/3)\langle \mathbf{F}_s(\omega) \cdot \mathbf{F}_s \rangle \mathbf{v}_\omega$. In the dilute limit, it shows a small frequency anomaly of order $\kappa^3$ and expecting this result at finite densities also, we expand the fundamental solution $\Phi$ of the diffusion equation up to this order. Abbreviating the uninteresting terms this leads to:

$$
\langle \mathbf{F}_s(\omega) \cdot \mathbf{F}_s \rangle = c + c'i\omega + \frac{n\alpha^2}{4\pi D S_0 \sigma^3} \left[ \frac{-i\omega \sigma^2}{D} \right]^{3/2} + \mathcal{O}(\omega^2).
$$

Importantly, the linear term in $\kappa$ vanishes (it would indicate $\langle \mathbf{F}_s(t \to \infty) \cdot \mathbf{F}_s \rangle \propto t^{-3/2}$), and the leading $\omega^{3/2}$ anomaly corresponds to the final power law decay $\langle \mathbf{F}_s(t \to \infty) \cdot \mathbf{F}_s \rangle \sim 3\pi n\alpha^2/[16S_0(\pi D t)^{5/2}]$. As was expected from the spatial long–ranged pattern around the tracer there exists a temporal long time tail whose amplitude is closely connected to the latter. Interestingly, standard mode coupling theory gives different results $[8, 13, 14, 22]$ and requires additional considerations $[23]$. Our result implies that a frequency dependent vertex coupling density modes would be required in order to obtain Eq. (33), which agrees with the known low density results $[3, 4]$ upon accounting for the tracer diffusion by the replacement $D \to D_0 + D_s$ and the identification $\sigma = a + a_s$. The tracer mean squared displacement is connected to the force correlation function via the equation of motion, $\partial_t^2 \langle \Delta r^2(t) \rangle = -2D_s^2 \langle \mathbf{F}_s(t) \cdot \mathbf{F}_s \rangle$, and exhibits a power law approach $\alpha = -\alpha^2 t^{-1/2}$ to the long time diffusion.

5. Conclusions and outlook

We have presented the first statistical mechanics derivation of a hydrodynamic boundary condition for the diffusion equation, including the definition of the macroscopic boundary position from molecular parameters. This has proven surprisingly difficult, because a non–analytic (non-Markovian) structure in the resulting relaxation kernel needed to be identified. Quoting exact low density results and performing a mode coupling approximation, this structure could be established. The $1/\sqrt{\omega}$ anomaly of diffusion close to a wall is connected to the penetration length $\sqrt{D/\omega}$ which arises generically in these situations $[1]$. Thus, we believe the appearance of non–Markovian relaxation kernels is inherent to the statistical mechanics derivation of boundary conditions. Gratifyingly, within the mode coupling approximation it arises from a non–linear coupling of the hydrodynamic modes themselves, and thus, as required for a macroscopic hydrodynamic concept, does not depend on molecular details.

As an application of the derived boundary condition, we calculated the long range density pattern around, the resulting force on, and the mean squared displacement of a tracer sphere moving among the bath particles. Extending results for dilute systems, a generic power law approach (long time tail) to the ultimate diffusion was found in
Hydrodynamic boundary conditions

the motion of the tracer, whose amplitude ($\propto \alpha^2$) we determined for arbitrary tracer size. Interestingly, $\alpha$ may vanish for special interaction parameters, in which case the tracer might be called “invisible”.

Clearly our calculation only presents a first step to determining boundary conditions for hydrodynamic equations. Thus when considering dispersed particles, their hydrodynamic interactions mediated via the solvent should be included. As these are long–ranged, interesting effects may appear. Also the description of the surface should be improved by going beyond the single tracer calculation. Structured or rough surfaces could be modeled, as well as fluctuating ones in order to adress the dynamics close to e.g. membranes. As the Smoluchowski equation is the basis for the dynamics of polymers and general macromolecules, the diffusion of complex molecules close to surfaces also could be analyzed following the presented approach. We hope to address some of these points in the future.

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Appendix A. Solution of the diffusion equation around a sphere

For convenience of comparison with the results obtained in the main text, this abstract summarizes some hydrodynamic expressions. To linear order in the perturbing tracer velocity $v$, it is straightforward to solve the macroscopic Eqs. (1,2) around a sphere with radius $\sigma$ that oscillates with velocity amplitude $v_\omega$. With $\kappa^2 = -i\omega/D$ the square of the inverse skin depth, one obtains

$$ n_\omega(r) = v_\omega \cdot \hat{r} \frac{n \sigma^3 / D}{2 + 2\kappa \sigma + (\kappa \sigma)^2} \frac{1 + \kappa r}{r^2} e^{-\kappa (r-\sigma)}. \quad (A.1) $$

It simplifies to the far–field expression

$$ n_\omega(r) \sim v_\omega \cdot \hat{r} \frac{n \sigma^3}{2D} \frac{1 + \kappa r}{r^2} e^{-\kappa r}, \quad n_{q_\omega} \sim v_\omega \cdot q \frac{2\pi i n \sigma^3}{Dq^2 - i\omega}, \quad (A.2) $$

for a small sphere, $\sigma \to 0$. Close to the sphere, it takes the near–field expression

$$ n_\omega(x) \sim \frac{n}{D} v_\omega e^{-\kappa \bar{x}} \frac{1 + \sqrt{-iDq^2_\omega}/\omega}{Dq^2_\omega - i\omega}, \quad n_{q_\omega} \sim n v_\omega \frac{1 + \sqrt{-iDq^2_\omega}/\omega}{Dq^2_\omega - i\omega}, \quad (A.3) $$

because the sphere degenerates to a plane upon taking the limit $\sigma \to \infty$; here $\bar{x}$ gives the distance ($r = \sigma \bar{x} + \hat{r}$) and the Fourier transformation in Eq. (A.3) is one–dimensional.

Appendix B. Mobile tracer calculation

To simplify the presentation in the main text and to make direct contact with the hydrodynamic calculation, we have worked with a non–fluctuating, macroscopic tracer throughout. This appendix extends the calculations of the main text to a finite tracer mobility $D_s$, and checks that they are indeed recovered by taking the limit $D_s \to 0$. 
Concerning the tracer velocity in Eq. (2); with Eqs. (3,4), and working in linear response approximation, it becomes
\[
\langle \partial_t r_s \rangle^{(\text{ne})} = \langle v \rangle + \langle D_s F_s \rangle^{(\text{ne})} = v - D_s \int_{-\infty}^{t} d\tau \, \langle F_s e^{\Omega(t-\tau)} F_s \rangle. \tag{B.1}
\]
The deviation from the hydrodynamic velocity \( v \) is explicitly of the order \( D_s \) and thus vanishes as required for \( D_s = 0 \).

At finite \( D_s \), the resolvents \( R_{\mathbf{q}} \) and \( R \) in Section 2.4 differ. Further, the tagged particle density now being a dynamic fluctuating variable, it has to be considered as a separate slow mode in the projection in Eqs. (11,12):
\[
P = \varrho_{\mathbf{q}}^* \langle \varrho_{\mathbf{q}}^* + \varrho_{\mathbf{q}} \rangle S_{\mathbf{q}}^{-1} \langle \varrho_{\mathbf{q}}^* - \varrho_{\mathbf{q}} \rangle \frac{n_c^s}{N} \langle \varrho_{\mathbf{q}}^* - \varrho_{\mathbf{q}} \rangle \frac{n_c^s}{N} \langle \varrho_{\mathbf{q}}^* \varrho_{\mathbf{q}}^* \rangle. \tag{B.2}
\]
Here, \( c_s^* = h_s^* / S_{\mathbf{q}} \) is the (tagged) direct correlation function. It is straightforward to check that \( PP = P, P \varrho_{\mathbf{q}} = \varrho_{\mathbf{q}}^* \), and \( P \varrho_{\mathbf{q}}^* = \varrho_{\mathbf{q}}^* \) up to corrections that are smaller by \( (nh_{\mathbf{q}}^*)^2 / (NS_{\mathbf{q}}) \) relative to the leading order. The susceptibility of Eq. (14) is rewritten as
\[
n \chi_{\mathbf{q}}(\omega) = - \left[ \left( \langle F_{\mathbf{q}}^* \varrho_{\mathbf{q}} \rangle - \langle F_{\mathbf{q}}^* R_{\mathbf{q}}^* \Omega_{\mathbf{q}} \varrho_{\mathbf{q}} \rangle \right) \langle \varrho_{\mathbf{q}}^* R_{\mathbf{q}} \varrho_{\mathbf{q}} \rangle / (NS_{\mathbf{q}}) \right]. \tag{B.3}
\]
Hence, exactly the same decomposition of the susceptibility into an instantaneous and a retarded contribution has been achieved as in Eq. (14) of the main text because of the negligible feedback of the tracer onto the bulk. To make contact with the expressions in the main text, a factorization approximation is required because of the tracer motion
\[
\langle \varrho_{\mathbf{q}}^* R_{\mathbf{q}} \varrho_{\mathbf{q}} \rangle = \langle \varrho_{\mathbf{q}}^* \varrho_{\mathbf{q}}^* R_{\mathbf{q}} \varrho_{\mathbf{q}} \rangle \approx NS_{\mathbf{q}} \Phi_{\mathbf{q}}(\omega) \Phi_{\mathbf{q}}^*(\omega), \tag{B.4}
\]
where \( \Phi_{\mathbf{q}}(\omega) \equiv \langle \varrho_{\mathbf{q}}^* R(\omega) \varrho_{\mathbf{q}} \rangle \). The memory function \( \langle F_{\mathbf{q}}^* R_{\mathbf{q}}^* \Omega_{\mathbf{q}} \varrho_{\mathbf{q}} \rangle \) also acquires a contribution from the tracer diffusion. To relevant lowest order in \( q \) it becomes
\[
i D_0 \left( \langle F_{\mathbf{q}}^* R_{\mathbf{q}}^* \mathbf{q} \cdot \mathbf{F}_{\mathbf{q}} \rangle - i D_s \langle F_{\mathbf{q}}^* R_{\mathbf{q}}^* \mathbf{q} \cdot \mathbf{F}_s \varrho_{\mathbf{q}} \rangle \right). \tag{B.5}
\]
The limit \( D_s \to 0 \) recovers the results in the main text, where \( D_s = 0 \) from the outset.

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