Nonlinear macroscopic transport equations in many-body systems from microscopic exclusion processes.

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Abstract. Describing particle transport at the macroscopic or mesoscopic level in non-ideal environments poses fundamental theoretical challenges in domains ranging from inter and intra-cellular transport in biology to diffusion in porous media. Yet, often the nature of the constraints coming from many-body interactions or reflecting a complex and confining environment are better understood and modeled at the microscopic level.

In this paper we investigate the subtle link between microscopic exclusion processes and the mean-field equations that ensue from them in the continuum limit. We derive a generalized nonlinear advection diffusion equation suitable for describing transport in a inhomogeneous medium in the presence of an external field. Furthermore, taking inspiration from a recently introduced exclusion process involving agents with non-zero size, we introduce a modified diffusion equation appropriate for describing transport in a non-ideal fluid of \(d\)-dimensional hard spheres.

We consider applications of our equations to the problem of diffusion to an absorbing sphere in a non-ideal self-crowded fluid and to the problem of gravitational sedimentation. We show that our formalism allows one to recover known results. Moreover, we introduce the notions of point-like and extended crowding, which specify distinct routes for obtaining macroscopic transport equations from microscopic exclusion processes.

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1. Introduction

Diffusive transport is central in many areas of physics, chemistry, biology and soft matter [1-4]. However, while the mathematics of diffusive processes in dilute and simple media is fairly well developed and understood [1], many interesting and relevant diffusive processes take place in strongly non-ideal conditions. These include a wealth of different highly dense media, from non-ideal plasmas [5] to biological membranes [6], media with complex topological structures, including porous media [7-9] and living cells [10, 11] and strongly confining environments [3, 12-17].

Crowding and confinement effects on diffusion-influenced phenomena still pose fundamental yet unanswered questions. Concerning molecular mobility, for example, several computational and experimental indications exist of anomalous diffusion in the cell cytoplasm as a result of amount and type of crowding [18, 19], suggesting that living cells behave much like fractal or otherwise disordered systems [20, 21]. However, strong evidences also exist in favour of normal (Brownian) diffusion, crowding and confinement resulting in this scenario in (often nontrivial) modifications of the diffusion coefficient [10, 22-24]. Another related issue is that of diffusion-limited reactions [25], which are ubiquitous in many domains in biology and chemistry, touching upon problems such as association, folding and stability of proteins [26, 27] and bimolecular reactions in solution [28-32], including enzyme kinetics [33], but also the dynamics of active agents [34]. Many theoretical studies have tackled these and related problems under different angles [16, 26, 30, 33, 35-37]. Nevertheless, a full theoretical comprehension of transport in non-ideal media remains an elusive task, Fick’s law itself and the very notion of effective diffusion coefficient being questionable in a disordered medium [21].

In this paper we consider the subtle link between macroscopic transport equations, such as the diffusion equation, and microscopic processes, modeling the stochastic dynamics of some agents. The purpose of our study is two-fold. On one hand, we wish to understand in greater depth the delicate procedure of obtaining mean-field transport equations from microscopic, agent-based stochastic models, paying special attention to what exactly is lost in going to the continuum. The idea is that sometimes it may prove simpler or more effective to describe a complex transport process (or a simple one occurring in a complex milieu) at the microscopic level. On the contrary, it is sometimes better to deal with macroscopic equations. It is thus important to investigate how the two levels of description interface with each other. On the other hand, as a result of our investigation, we will derive new macroscopic equations that provide useful analytical tools for exploring particle transport in non-ideal fluids in complex environments.

The paper is organized as follows. In section 2, we discuss the general framework of simple exclusion processes (SEPs), which constitute the basic tool of our microscopic description, as well as the process of obtaining mean-field equations from SEPs. In section 3, we move a step forward and consider microscopic exclusion processes involving agents characterized by a finite size, as opposed to standard SEPs. We introduce in particular the notions of point-like and extended crowding and discuss the formalism with reference to the problem of gravitational sedimentation.

We then go on in section 4 to propose, based on a simple analogy, a modified diffusion equation appropriate for describing transport in non-ideal fluids of d-dimensional hard spheres at high densities. The obtained equation allows one to recover a known result for the basic problem of particle flux at a spherical absorbing
boundary in self-crowding media. Finally, a summary of the main results obtained in this paper is drawn in the last section.

2. From microscopic processes to macroscopic equations

Simple exclusion processes are space-discrete, agent-based stochastic processes modeling some kind of transport according to specific rules and bound to the constraint that no two agents can ever occupy the same site. SEPs occupy a central role in non-equilibrium statistical physics \[35, 39\]. While the first theoretical ideas underlying such processes can be traced back to Boltzmann’s works \[40\], SEPs were introduced and widely studied in the 70s as simplified models of one-dimensional transport for phenomena like hopping conductivity \[41\] and kinetics of biopolymerization \[5\]. Along the same lines, the asymmetric exclusion process (ASEP), originally introduced by Spitzer \[42\], has become a paradigm in non-equilibrium statistical physics \[43–45\] and has now found many applications, such as the study of molecular motors \[40\], transport through nano-channels \[47\] and depolymerization of microtubules \[48\].

The most general SEP in one dimension is described by a stochastic jump process on a 1D lattice with inequivalent sites in the presence of a field

\[n_i(k+1) - n_i(k) = z_i^+ n_{i-1}(k)[1 - n_i(k)] + z_i^- n_{i+1}(k)[1 - n_i(k)] - z_i^- n_i(k)[1 - n_{i-1}(k)] - z_i^+ n_i(k)[1 - n_{i+1}(k)]\]  

Eq. (1) is to be regarded as the update rule for a Monte Carlo process, where \(n_i(k)\) is the occupancy of site \(i\) at time \(t = k\Delta t\), which can be either zero or one. The quantities \(z_i^\pm\) are variables which have the value 0 or 1 according to a random number \(\xi_i\) which has a uniform distribution between 0 and 1. By defining the jump probabilities \(q_j^\pm\) (\(j = i, i \pm 1\)) one can formally write:

\[z_i^+ = \theta(\xi_i) - \theta(\xi_i - q_i^+)\]
\[z_i^- = \theta(\xi_i - q_i^-) - \theta(\xi_i - q_i^- - q_i^+)\]
\[z_i^+ = \theta(\xi_i - q_i^- - q_i^-) - \theta(\xi_i - q_i^- - q_i^- - q_i^+)\]
\[z_i^- = \theta(\xi_i - q_i^- - q_i^- - q_i^+) - \theta(\xi_i - 1)\]

where \(\theta(\cdot)\) stands for the Heaviside step function and where we are assuming that \(q_i^- + q_i^+ + q_i^- = 1\). Note that the ordering of appearance of the \(q_j^\pm\) in the above expressions is arbitrary. Equations (2) entail that \((z_j^\pm) = q_j^\pm\), where \((\cdot)\) indicates an average over many values of \(\xi_i\), for a given configuration \(\{n_i\}\). The above process is fully determined by the fields \(q_j^\pm\), specifying the probability of jumping from site \(i\) to site \(i + 1\) (\(q_i^+\)) or to site \(i - 1\) (\(q_i^-\)) in a time interval \(\Delta t\).

A (discrete-time) master equation for the above SEP can be obtained by averaging over many Monte Carlo cycles performed according to rule (1)

\[P_i(k+1) - P_i(k) = q_i^+ [P_{i-1}(k) - P_{i,i-1}(k)] + q_i^- [P_{i+1}(k) - P_{i,i+1}(k)] - q_i^+ [P_{i+1}(k) - P_{i,i+1}(k)] - q_i^- [P_i(k) - P_{i,i-1}(k)]\]  

where we have defined the one-body and two-body site occupancy probabilities

\[P_i(k) = \langle n_i(k) \rangle\]  
\[P_{i,i\pm1}(k) = \langle n_i(k) n_{i\pm1}(k) \rangle\]

Here \(\langle \cdot \rangle\) denotes averages performed over many independent Monte Carlo cycles performed until time \(k\Delta t\) starting from the same initial condition. We emphasize that
the same equation has been derived through a slightly different procedure by Richards in 1977 [41].

2.1. Mean-field equations

With the aim of deriving macroscopic transport equations from the microscopic stochastic process described by eqs. (1), it is customary to assume a mean-field (MF) factorization,

\[ P_{i,k} \equiv \left\langle \langle n_i(k) \rangle \langle n_{i\pm 1}(k) \rangle \right\rangle = P_i(k) P_{i\pm 1}(k) \]  

(5)

With the help of eq. (5), the master equation (3) becomes

\[
P_i(k + 1) - P_i(k) = q_i^+ P_{i-1}(k)[1 - P_i(k)] + q_i^- P_{i+1}(k)[1 - P_i(k)] - q_i^+ P_i(k)[1 - P_{i+1}(k)] - q_i^- P_i(k)[1 - P_{i-1}(k)]
\]  

(6)

Nonlinear mean-field equations for exclusion process of this type have been used since the 70s to investigate one-dimensional transport in solids [49].

Let \( a \) be the lattice spacing and let us define a reversal probability \( \epsilon_i \), such that

\[ q_i^+ = Q_i, \quad q_i^- = Q_i - \epsilon_i \]  

(7)

The condition (7) (with \( \epsilon_i > 0 \)) amounts to considering a field introducing a bias in the positive \( x \) direction. In order to take the continuum limit \( \lim_{a, \Delta t \to 0} P_i(k) = P(x, t) \), we must require

\[ \lim_{a, \Delta t \to 0} \frac{Q_i a^2}{\Delta t} = D(x) \]  

(8a)

\[ \lim_{a, \Delta t \to 0} \frac{\epsilon_i a}{\Delta t} = v(x) \]  

(8b)

Eq. (8a) defines the position-dependent diffusion coefficient, while eq. (8b) defines the field-induced drift velocity. Note that we are assuming that the reversal probability vanishes linearly with \( a \).

With the help of eqs. (7), (8a) and (8b) it is not difficult to see that in the continuum limit eq. (6) yield

\[
\frac{\partial P}{\partial t} = (1 - P) \nabla^2 [D(x)P] + D(x)P \nabla^2 P - \frac{\partial}{\partial x} [v(x) P(1 - P)]
\]  

(9)

where we have explicitly highlighted the fact that both the diffusion coefficient and the drift velocity are position-dependent quantities.

Eq. (9) is a nonlinear advection-diffusion equation, appropriate for describing the continuum limit of a microscopic exclusion process occurring on a lattice of inequivalent sites in the presence of a field. Although it represents the mean-field approximation of a known master equation, we are not aware of any authors stating it in its most general form. It is interesting to note that in the case of equivalent sites, which translates to a constant diffusion coefficient, the diffusive part of eq. (9) becomes linear, i.e. the microscopic exclusion rule is lost in the diffusive part. In the case of zero field, one then simply recovers the ordinary diffusion equation which, as it is widely known, can be derived from a microscopic jump process with no exclusion rules. This curious observation has been first reported by Huber [49]. If both the diffusion coefficient and the drift velocity are constant, eq. (9) reduces to

\[
\frac{\partial P}{\partial t} = D \nabla^2 P - v \frac{\partial}{\partial x} [P(1 - P)]
\]  

(10)
an equation already obtained recently in Ref. \[50\].

Eq. (9) contains the single-particle probability field \( P(x,t) \), which is a number between zero and one. The value \( P = 1 \) should correspond to the maximum density \( \rho_M \) allowed in the system. Thus, a more physical equation can be obtained by introducing the agent density

\[
\rho(x,t) \equiv \rho_M P(x,t) = \frac{\phi_M}{v_1(\sigma/2)} P(x,t)
\]

where

\[
v_1(r) = \frac{(\pi^{1/2}r^d)}{\Gamma(1 + d/2)}
\]

is the volume of a \( d \)-dimensional sphere of radius \( r \) and \( \phi_M \) is the maximum packing fraction for systems of \( d \)-dimensional hard spheres, \( \phi_M = 1 \) (\( d = 1 \)), \( \phi_M = \pi/\sqrt{12} \approx 0.907 \) (\( d = 2 \)) and \( \phi_M = \pi/\sqrt{18} \approx 0.740 \) (\( d = 3 \)) \[51\]. With these definitions, and using a more general vector notation, eq. (9) becomes

\[
\frac{\partial \rho}{\partial t} = \left(1 - \frac{\rho}{\rho_M}\right) \nabla^2 [D(x)\rho] + D(x) \left(\frac{\rho}{\rho_M}\right) \nabla^2 \rho - \nabla \cdot \left[v(x)\rho \left(1 - \frac{\rho}{\rho_M}\right)\right]
\]

This is the first important result of this paper.

### 3. Point like versus extended crowding in one dimension

The MF diffusion-advection equation (9) has been derived from a master equation containing exclusion terms of the type \((1-P_i)\) in the limit of vanishing lattice spacing. This amounts to considering agents of vanishing size in the continuum limit. We term this peculiar situation in the macroscopic world point-like crowding. However, one may argue that considerable microscopic information is lost in going to the continuum limit with point-like agents. Incidentally, this has to be the reason why the mean-field approximation does lose all the memory of the microscopic exclusion constraint and the diffusion equation is recovered for equivalent sites in the absence of a field.

Interestingly, a generalized exclusion process for agents of extended size in one dimension (hard rods) can be found in the literature, termed the \( \ell \)-ASEP \[52\]. The authors derive a mean-field equation, which, in the absence of a field and for equivalent sites, reads

\[
\frac{\partial \rho}{\partial t} = D \nabla^2 \left[\frac{\rho}{1 - \sigma \rho}\right]
\]

where \( \sigma \) is the length of the rods. The nonlinear diffusion equation (14) is most interesting for a number of reasons. First of all, even if it has been derived through an ingenious but complicated change of variables based on a quantitative mapping between the \( \ell \)-ASEP and the zero-range process \[52\], it turns out that it can be regarded as the local-density approximation (LDA) of a simple general property of one-dimensional exclusion processes. As pointed out in 1967 by Lebowitz and Percus \[53\] concerning bulk properties

\[\ldots\] For many purposes, however, adding a finite diameter does not introduce any new complications; it merely requires the replacement in certain expressions of the actual volume per particle \( \rho^{-1} \) by the reduced volume \( \rho^{-1} - \sigma \), i.e. \( \rho \rightarrow \rho/(1 - \sigma \rho) \).

\‡ We emphasize that we use the general terminology of \( d \)-dimensional hard spheres. Obviously, these are hard rods in one dimension and hard disks in two.
Remarkably, by performing the above substitution in Fick’s law, under the local density approximation, \( \rho(x,t) \rightarrow \rho(x,t)/[1-\sigma\rho(x,t)] \), one recovers eq. (14). Extending the terminology of the \( \ell \)-ASEP \[52\], we term this scenario extended-size crowding. Point-like crowding in the mean field approximation corresponds to systems of fully penetrable spheres, while extended-size crowding yields a transport equation suitable for systems of totally impenetrable (hard) spheres.

It is possible to substantiate and further illustrate the above considerations by showing that the transport equations for point-like and extended-size crowding for homogenous systems in a gravitational field allow to recover the appropriate equations of state (EOS) for fully penetrable spheres (FPSs) and totally impenetrable (i.e. hard) spheres (TISs), respectively. Let us consider sedimentation in one dimension. Let \( \rho_p \) and \( \rho_s \) indicate the particle and solvent material densities \[4\], respectively, and \( m^* = (\rho_p - \rho_s)\nu_\sigma \) the buoyant mass of the particles. The appropriate equation for point-like crowding bears in the case of non-zero field the signature of the microscopic exclusion process. Recalling that \( \phi_M = 1 \) in one dimension and thus \( \rho_M = 1/\sigma \) (see eq. (11)), eq. (13) reduces to

\[
\frac{d^2 \rho}{dz^2} + \frac{1}{\ell_g} \frac{d}{dz} [\rho (1-\sigma \rho)] = 0 \tag{15}
\]

Here \( \ell_g = k_B T/m^* g \) is the so-called sedimentation (or gravitational) length and we have taken an upward pointing \( z \)-axis. Eq. (15) can be solved by noting that at equilibrium the osmotic current is exactly balanced by the gravitational one, thus \( J = d\rho/dz + \rho (1-\sigma \rho)/\ell_g = 0 \), which gives

\[
\rho(z) = \frac{1}{\sigma \left(1 + Ae^{z/\ell_g}\right)} \tag{16}
\]

The constant \( A \) is to be determined by imposing the boundary conditions. Usually, this is done by introducing the bulk density \( \rho_0 \), such that

\[
\frac{1}{h} \int_0^h \rho(z) \, dz = \rho_0 \tag{17}
\]

where \( h \) is the height of the initially homogenous suspension. This gives

\[
\rho(z) = \sigma^{-1} \left[1 + \left(\frac{1-e^{-(1-\sigma \rho_0)h/\ell_g}}{e^{\sigma \rho_0 (h/\ell_g)} - 1}\right) e^{z/\ell_g}\right]^{-1} \tag{18}
\]

For \( h \gg \ell_g \) one has that the density at the bottom is exponentially close to the maximum density \( \rho_M = \sigma^{-1} \)

\[
\rho(0) \simeq \frac{1}{\sigma \left(1 + e^{-\sigma \rho_0 (h/\ell_g)}\right)} \tag{19}
\]

In practice, particle settling leaves only supernatant solvent at the top of the cell. Hence we can safely take \( h \rightarrow \infty \), which shows that the fluid attains maximum packing at the bottom of the cell.

The nice thing about this exercise is that we can derive an equation of state (EOS) from the sedimentation profile. In fact, the osmotic pressure \( \Pi \) in the suspension is given by

\[
\frac{\Pi(z)}{k_B T} = \frac{1}{\ell_g} \int_z^\infty \rho(z) \, dz \tag{20}
\]

\[\frac{\Pi}{k_B T} \] is the reduced pressure.
where, accordingly to the above considerations, we have taken the upper integration limit as $h \to \infty$. It is a straightforward calculation to show that the general expression (16) yields, independently of the chosen boundary conditions,

$$\frac{\Pi}{k_B T} = -\sigma^{-1} \log[1 - \sigma \rho]$$

The EOS (21) has a straightforward physical interpretation. In a system of fully penetrable spheres with reduced density $\sigma \rho$, the volume fraction $\phi_p$ occupied by the particles is given by $\phi_p = 1 - \exp(-\sigma \rho)$ \[51\]. Hence, the modified EOS (21) can be obtained from the perfect gas EOS by replacing the reduced density with its expression containing the actual volume fraction. This unveils the meaning of the above modified EOS, featuring the true volume fraction in the right-hand side. At the same time, this also illustrates the notion of point-like crowding.

Summarizing, a point-like microscopic exclusion process such as (6) yields a macroscopic transport equation that describes a fluid of fully penetrable spheres. Therefore, extending this line of reasoning to what we have dubbed the extended-crowding scenario, we expect that the $\ell$-ASEP mean-field equation in non-zero field \[52\] would yield the EOS of a system of hard rods, also known as the Tonk gas \[54\]

$$\frac{\Pi}{k_B T} = \frac{\rho}{1 - \sigma \rho}$$

We shall now prove that this is indeed the case. Inserting the Tonk gas EOS (22) in eq. (20) and differentiating with respect to $z$, one gets

$$J_\sigma = \frac{d\rho}{dz} + \frac{1}{\ell_g} \rho(1 - \sigma \rho)^2 = 0$$

the known LDA equation for sedimentation of hard rods \[55\]. However, the above equation also equals the condition that the total $\ell$-ASEP particle flux $J_\sigma$ vanishes at equilibrium. Indeed, the stationary mean-field equation corresponding to the $\ell$-ASEP reads \[52\],

$$\frac{d^2}{dz^2} \left[ \frac{\rho}{1 - \sigma \rho} \right] + \frac{1}{\ell_g} \frac{d\rho}{dz} = 0$$

which leads to the same expression for the total (constant) particle flux as eq. (23). Hence, the $\ell$-ASEP yields a macroscopic transport equation that describes a gas of hard rods in the local density approximation.

The discussion above which leads to the concept of extended crowding applies to one dimensional systems. Starting from this setting, one can raise the question whether similar arguments might be employed to obtain a modified nonlinear equation accounting for excluded volume effects in the diffusion of hard spheres in two and three dimensions. The following section is devoted to speculating further along this line of reasoning.

4. Excluded volume interactions of finite-size agents in higher dimensions.

In the preceding section we have shown that the point-like crowding scenario leads to the mean-field equation (13) from a standard simple exclusion process at the microscopic level. The extended-crowding generalization consists in endowing agents
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Table 1. The particle conditional pair distribution function $G_{p}$ for stationary ensembles of $d$-dimensional spheres of diameter $\sigma$.

|                | $d = 1$ | $d = 2$ | $d = 3$ |
|----------------|---------|---------|---------|
| Fully penetrable spheres | $1$     | $1$     | $1$     |
| Totally impenetrable spheres | $\frac{1}{1 - \sigma \rho}$ | $a_0 + a_1 \left( \frac{\sigma}{\rho} \right)$ | $b_0 + b_1 \left( \frac{\sigma}{\rho} \right) + b_2 \left( \frac{\sigma}{\rho} \right)^2$ |

with a finite size (hard core). The ensuing exclusion process in one dimension has been termed in the literature the $\ell$-ASEP \[52\].

We have shown that the nonlinear transformation put forward by Lebowitz and Percus in 1967, under the local density approximation, allows one to recover the $\ell$-ASEP mean-field transport equation \[14\] for the evolution of the density of extended rod-like agents in one dimension. Interestingly, it is possible to posit a generalization of such macroscopic transport equation adequate to the mean-field limit of exclusion processes involving extended objects in more than one dimension by borrowing general concepts in the theory of heterogenous media.

With reference to standard definitions of micro-structural descriptors in $d$ dimensions \[51\], we can identify the aforementioned substitution by Lebowitz and Percus as a mapping between certain statistical properties characterizing systems of fully penetrable spheres and totally impenetrable (i.e. hard) spheres. More precisely, let us introduce the so-called conditional pair distribution function (CPDF) $G_{p}(r)$.

Let $r$ denote the distance from the center of some reference particle in a system with bulk density $\rho_0$. Then, by definition $\rho_0 s_1(r) G_{p}(r) dr$ equals the average number of particles in the shell of infinitesimal volume $s_1(r) dr$ around the central particle, given that the volume $v_1(r)$ of the $d$-sphere of radius $r$ is empty of other particle centers. Here

$$s_1(r) = \frac{dv_1(r)}{dr} = \frac{2\pi^{d/2}r^{d-1}}{\Gamma(d/2)}$$ \hspace{1cm} (25)

The CPDF for FPS and TIS systems are reported in Table 1, where one can readily recognize the Lebowitz and Percus substitution as a mapping between the FPS and TIS CPDFs in one dimension. The coefficients appearing in the expressions of $G_{p}(r)$ are given by the following expressions \[51\] for $d = 2$

$$a_0 = \frac{1 + 0.128 \phi}{(1 - \phi)^2}$$ \hspace{1cm} (26a)
$$a_1 = -\frac{0.564 \phi}{(1 - \phi)^2}$$ \hspace{1cm} (26b)

while for $d = 3$ one has

$$b_0 = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}$$ \hspace{1cm} (27a)
$$b_1 = \frac{\phi(3\phi^2 - 4\phi - 3)}{2(1 - \phi)^3}$$ \hspace{1cm} (27b)
$$b_2 = \frac{\phi^2(2 - \phi)}{2(1 - \phi)^3}$$ \hspace{1cm} (27c)

These are the expressions appropriate to the liquid phase below the freezing point, i.e. for $\phi < \phi_f$ ($\phi_f = 0.69$ for $d = 2$ and $\phi_f = 0.494$ for $d = 3$).
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where $\phi = v_1(\sigma/2)\rho$ is the packing fraction, $\sigma$ being the diameter of a $d$-dimensional sphere.

The above discussion suggests a way to generalize the $t$-ASEP \[14\] to describe excluded-volume effects in more than one dimension in the mean-field approximation in a homogeneous medium and zero field. For a spherically symmetric problem we posit

$$\frac{\partial \rho}{\partial t} = D \nabla^2 [\rho G_p(\rho, r)]$$

where we have emphasized that $G_p$ depends explicitly on $r$ (for $d > 1$). Eq. (32) is the second main result of this paper. The coefficients appearing in the expressions for $G_p$ are given by eqs (26a), (26b), (27a), (27b) and (27c) and it is understood that, according to the local density approximation, one should replace $\phi$ with $v_\sigma \rho(r, t)$, where $v_\sigma \equiv v_1(\sigma/2)$ is the volume of one hard $d$-dimensional sphere, so that $G_p$ depends on $r$ both explicitly and implicitly through $\rho(r)$.

4.1. The Smoluchowski problem at finite densities

In order to provide some $a$ posteriori justification for eq. (28), it is instructive to consider how the classical problem of diffusion to an absorbing sphere is modified in a non-ideal fluid. Let us imagine a fixed sink of radius $R_s$ that absorbs hard spheres of radius $\sigma/2$ and bulk density $\rho_0$. The rate $k$ measuring the number of particles absorbed by the sink per unit time equals the total flux into the sink. For ordinary Fickian diffusion, one has the classical result $k = k_s \equiv 4\pi D(R_s + \sigma/2)\rho_0$, known as the Smoluchowski rate \[25\]. This result is indeed the prediction of a two-body problem, i.e. it amounts to considering the absorption of non-interacting, or equivalently fully penetrable, spheres. Thus, it describes the problem in the infinite dilution limit. Eq. (28) can now be employed to repeat the same exercise for hard spheres at finite densities, that is, the Smoluchowski problem with excluded-volume interactions accounted for. One should then solve the following boundary-value problem

$$\nabla^2 [\rho G_p(\phi(r), r)] = 0$$

$$\rho(r = R_s + \sigma/2) = 0$$

$$\lim_{r \to \infty} \rho(r) = \rho_0$$

The rate can be computed readily without really solving the (modified) Laplace equation. From (29a), we have directly

$$\frac{\partial}{\partial r} [\rho G_p(\phi(r), r)] = \frac{k}{4\pi D r^2}$$

where we have defined $\phi(r) = v_\sigma \rho(r)$, so that $\phi = v_\sigma \rho_0$ denotes the bulk packing fraction of the hard spheres. Integrating eq. (30) between $R_s + \sigma/2$ and infinity and taking into account the boundary conditions (29b) and (29c), it is straightforward to obtain

$$\frac{k}{k_s} = G_p(\infty)$$

where $G_p(\infty) \equiv \lim_{r \to \infty} G_p(\phi(r), r)$. In three dimensions, one thus has $k/k_s = b_0(\phi)$, where one can recognize $b_0(\phi)$ as the compressibility $Z(\phi)$ of the hard sphere fluid in the Carnahan-Starling approximation \[56\]. We see that eq. (28) allows one to recover our previous result $k/k_s = Z(\phi)$, obtained in two different ways, by assuming a density-dependent mobility in the diffusion equation \[57\] and from a transport equation derived in the local-density approximation \[58\].
5. Summary and discussion

In this paper we have discussed a general framework allowing to obtain macroscopic transport equation accounting for excluded volume effects in systems of $d$-dimensional hard spheres starting from a microscopic stochastic exclusion processes. The aim of this procedure is to derive mean-field equations suitable for describing transport processes in many-body systems in highly non-ideal conditions. We have identified two strategies for doing so. The first route, termed point-like crowding, leads from a standard simple exclusion process to the mean-field equation (13). For a homogenous medium in the absence of a field this reduces to a simple diffusion equation, which is why we have dubbed this scenario point-like crowding. Only for inequivalent sites and/or in the presence of a field does the microscopic exclusion constraint survives in the mean-field limit. The second strategy, named extended-crowding, takes inspiration from a modified microscopic exclusion process in one dimension involving extended agents, the so-called $\ell$-ASEP [52]. By extending an argument originally put forward by Lebowitz and Percus in 1967, coupled to a local density approximation, we have posited a modified nonlinear diffusion equation suitable for studying in an effective manner transport processes in dense systems of hard spheres, eq. (32). We have shown that this equation allows one to recover recent results obtained for the problem of diffusion to an absorbing sphere in a self-crowded medium. Furthermore, we have brought to the fore an interesting structure underlying the two above strategies for obtaining macroscopic equations from microscopic stochastic processes. While extended crowding is indeed appropriate for diffusion of hard spheres, the continuum limit of point-like crowding exclusion processes is only appropriate for systems of fully penetrable spheres. Therefore, when one takes the continuum limit, all signatures of the microscopic exclusion constraints are lost in the diffusive part of the transport equation.

We note that eq. (28) provides a sensible description of diffusion in a non-ideal fluid in the case where the problem has spherical symmetry. We may ask whether our line of reasoning may be extended to a problem with different or no symmetry. Guided by the observation that $G_p^\infty = Z(\phi)$ for a system of $d$-dimensional hard spheres, we can speculate that a modified equation could be considered, involving the bulk CPDF $G_p^\infty(\phi)$ in the local density approximation,

$$\frac{\partial \rho}{\partial t} = D_0 \nabla^2 \left[ \rho G_p^\infty(\rho) \right]$$

(32)

where again one should understand $\phi \rightarrow v_\sigma \rho(r,t)$ in the expression for the coefficients $a_i(\phi)$ and $b_i(\phi)$. Some justification for the above idea can be gathered by recalling the known equation that one obtains by introducing a density-dependent mobility in the diffusion equation given by the derivative of the osmotic pressure with respect to the density [2], $D(\rho) = D_0 \beta \frac{d\Pi(\rho)}{d\rho} = D_0 Z(\rho)$, namely

$$\frac{\partial \rho}{\partial t} = D_0 \nabla \cdot \left[ Z(\rho) \nabla \rho \right]$$

(33)

where $D_0$ is the bare diffusion coefficient (corresponding to the infinite dilution limit) and $Z(\rho)$ is the compressibility factor. At zero order, where $G_p(\rho) = G_p(\rho_0) = \text{const.}$ and $Z(\rho) = Z(\rho_0) = \text{const.}$ eq. (32) and eq. (33) are the same, as $G_p^\infty(\phi) = Z(\phi)$.

As a last observation, we see that, if we compare eq. (24) with eq. (15), the point-like route to a macroscopic mean-field equation for a homogenous medium bears the signature of the microscopic exclusion mechanism in the advection term. On
the contrary, at least in one dimension, the extended-crowding procedure yields a modified diffusion term, while the term associated with the external field current is left unchanged. The profound meaning of this fact appears still elusive, but it would be certainly interesting to dig further.

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