Dynamics of a suspension of interacting yolk-shell particles

L. E. Sánchez Díaz1, E. C. Cortes-Morales2, X. Li1, Wei-Ren Chen1 and M. Medina-Noyola2

1 Biology and Soft Matter Division, Oak Ridge National Laboratory - Oak Ridge, TN 37831, USA
2 Instituto de Física “Manuel Sandoval Vallarta”, Universidad Autónoma de San Luis Potosí
Álvaro Obregón 64, 78000 San Luis Potosí, SLP, México

received 22 September 2014; accepted in final form 8 December 2014
published online 7 January 2015

PACS 82.70.Dd – Disperse systems; complex fluids: Colloids
PACS 61.20.Lc – Structure of liquids: Time-dependent properties; relaxation

Abstract – In this work we study the self-diffusion properties of a liquid of hollow spherical particles (shells) bearing a smaller solid sphere in their interior (yolks). We model this system using purely repulsive hard-body interactions between all (shell and yolk) particles, but assume the presence of a background ideal solvent such that all the particles execute free Brownian motion between collisions, characterized by short-time self-diffusion coefficients $D_0^s$ for the shells and $D_0^y$ for the yolks. Using a softened version of these interparticle potentials we perform Brownian dynamics simulations to determine the mean squared displacement and intermediate scattering function of the yolk-shell complex. These results can be understood in terms of a set of effective Langevin equations for the $N$ interacting shell particles, pre-averaged over the yolks’ degrees of freedom, from which an approximate self-consistent description of the simulated self-diffusion properties can be derived. Here we compare the theoretical and simulated results between them, and with the results for the same system in the absence of yolks. We find that the yolks, which have no effect on the shell-shell static structure, influence the dynamic properties in a predictable manner, fully captured by the theory.

Copyright © EPLA, 2014

In recent years, there has been a growing interest in designing and manufacturing new materials with nano- and micro-particles having specifically tailored morphologies [1–3], such as yolk-shell particles, in which a hollow shell carries a smaller particle in its interior [1,4]. These nanostructures can be synthesized by a variety of methods [5] for application in various fields such as nanoreactors [4], lithium-ion batteries [6], biomedical imaging [6], catalysis [7], and energy storage devices [6]. One can envision that current efforts to study individual yolk-shell entities with light or neutron scattering techniques [8] will soon be extended to consider liquids, and even crystals or glasses, of strongly interacting yolk-shell particles. Similarly, conventional preparation methods [9] could be employed to produce microemulsion droplets bearing a smaller solid particle inside, to study equilibrium and out-of-equilibrium condensed phases [10] made of such microemulsion yolk-shell droplets. To understand these phases and other self-assembled states [11], however, one needs to understand the dynamic properties of systems of strongly interacting yolk-shell particles in terms of the direct (i.e., conservative) and hydrodynamic interactions among shells and between yolks and their confining shells.

The detailed and simultaneous description of such coupled effects is, of course, a highly involved problem. To make headway, however, we may profit from the ingenious manners to decouple them, developed in similar challenges in colloid science [12,13]. For example, at least for rigid shells, the complex effects of shell-shell hydrodynamic interactions can be taken into account through an effective self-diffusion coefficient $D_0^s$ describing the shells’ short-time Brownian motion [14,15]. For such purposes, the rich phenomenology of the hydrodynamic interactions of the captive yolk with its confining shell [16] could also be modelled as a simple effective free-diffusion process, characterized by another effective (short-time) self-diffusion coefficient $D_0^y$, also amenable to independent experimental determination [16].

Thus, the remaining task is to describe the effects of the direct interactions, for which we may develop or adapt to yolk-shell morphologies the well-established theories and methods proven effective in describing the effects of direct interactions on the structure and dynamics of conventional colloidal dispersions (with hydrodynamic interactions now entering only through the externally provided coefficients $D_0^s$ and $D_0^y$). We have launched a systematic program in
this direction, which starts with a series of Brownian dynamics (BD) simulations on simplified models built upon the assumptions above, and with the development of a self-consistent generalized Langevin equation (SCGLE) theory of yolk-shell colloidal dynamics. The details of the simulations and of the derivation of this theory will be reported separately [17], but the present short communication illustrates the results with the simplest application of these methodologies.

Our simulations are based on the well-known Brownian dynamics algorithm of Ermak and McCammon [18] without hydrodynamic interactions (assumed to be contained only in \( D_0^s \) and \( D_0^y \)). This algorithm consists essentially of the numerical solution of the overdamped version of the 2N stochastic Langevin equations that govern the Brownian motion of the N shells and N yolks, written in terms of the position \( x_i(t) \) and velocity \( v_i(t) \) of the center of mass of the i-th shell particle, and of the position \( y_i(t) \) and velocity \( w_i(t) \) of the center of the i-th yolk particle, as

\[
M_s \frac{dv_i(t)}{dt} = -\zeta_i v_i(t) + \mathbf{f}_i(t) - \sum_{j \neq i} \nabla_i u_{ss}(|x_i(t) - x_j(t)|) - \sum_{j} \nabla_i u_{sy}(|x_i(t) - y_j(t)|) \tag{1}
\]

and

\[
M_y \frac{dw_i(t)}{dt} = -\zeta_y w_i(t) + \mathbf{g}_i(t) - \sum_{j \neq i} \nabla_y u_{ys}(|y_i(t) - y_j(t)|) - \sum_{j} \nabla_y u_{yy}(|y_i(t) - x_j(t)|), \tag{2}
\]

with \( i = 1, 2, \ldots, N \). In these equations, \( \mathbf{f}_i(t) \) and \( \mathbf{g}_i(t) \) are Gaussian white random forces of zero mean, and variance is given by \( \langle \mathbf{f}_i(t)\mathbf{f}_i^*(0) \rangle = 0 \), \( \langle \mathbf{g}_i(t)\mathbf{g}_i^*(0) \rangle = k_BT \zeta_i \delta(t) \delta_{ij} \mathbf{I} \), and \( \langle \mathbf{g}_i(t)\mathbf{g}_j^*(0) \rangle = k_BT \zeta_y \delta(t) \delta_{ij} \mathbf{I} \), with \( i, j = 1, 2, \ldots, N \) and with \( \mathbf{I} \) the 3x3 unit tensor. These equations are coupled together by the mutual direct forces between all the particles, assumed pairwise additive and determined by the radially symmetric pair potentials \( u_{ss}(r), u_{sy}(r), u_{ys}(r) \) and \( u_{yy}(r) \) describing, respectively, the shell-shell, shell-yolk, and yolk-yolk direct interactions. We have used this algorithm in the efficient, low-memory version proposed in ref. [19] to describe, for example, how the mean squared displacement (MSD) \( W(t) = \langle |\Delta \mathbf{R}(t)|^2 \rangle /6 \) and the self-intermediate scattering function (self-ISF) \( F_S(k,t) \equiv \langle \exp[ik \cdot \Delta \mathbf{R}(t)] \rangle \) of tagged yolk-shell particles are influenced by the combined effect of these interactions.

To illustrate the results of this approach, below we shall consider as a first step a model monodisperse colloidal suspensions formed by \( N \) rigid spherical shell particles of outer (inner) diameter \( \sigma_s (\sigma_{in}) \) in a volume \( V \), each of which bears one smaller (“yolk”) rigid particle of diameter \( \sigma_y (< \sigma_s) \) diffusing in its interior. For simplicity, we assume purely repulsive hard-body interactions, such that the yolks only interact with their own shells, \( u_{yy}(r) = 0 \), and that \( u_{ss}(r) \) is infinite for \( r < \sigma_s \) and vanishes for \( r > \sigma_s \), whereas \( u_{ys}(r) \) is infinite for \( r < \sigma_{ys} \) and vanishes for \( r > \sigma_{ys} \equiv (\sigma_{in} - \sigma_y)/2 \). In reality, the BD algorithm above is only defined for systems with continuous pair potentials. Thus, in practice we employ a softened version of these hard-body potentials, as explained in ref. [17].

Regarding our theoretical approach, let us first discuss the limit of infinite dilution, in which one isolated yolk-shell particle diffuses without interacting with other yolk-shell particles. A simple calculation to explain the effect of the yolk on the diffusivity of the shell may then be based on the so-called relaxation-effect method, first recognized by Debye and Hückel [20] and later employed by Onsager [21] in their treatment of ionic conductivity. In our case, the arguments start with Einstein’s relation, \( D_y = k_BT/\zeta_y \), with the friction coefficient \( \zeta_y \) defined by the linear relation \( F = \zeta_y V \) for the drag force when the shell is pulled at constant velocity \( V \). For an empty shell the friction is only caused by the solvent, \( F = \zeta_0^s V \), with \( \zeta_0^s \) determined by the well-known Stokes expression. The fact that it carries a yolk in its interior, however, generates an additional drag force on the shell, \( F = \zeta_0^s V + \Delta \zeta_y V \), so that determining the frictional effects embodied in \( \Delta \zeta_y \) becomes the crucial remaining problem. The determination of \( \Delta \zeta_y \) is analogous to Stokes calculation of \( \zeta_0^s \). Stokes problem involved the solution of the Navier-Stokes equation to describe the hydrodynamic flow past a sphere moving at steady velocity \( V \) [22]. The present calculation of \( \Delta \zeta_y \) requires deriving and solving the equation of motion of the yolk inside the shell (or, more generally, of \( N_y \) yolks inside each shell), and then calculating the corresponding force on the shell.

For this we write the total drag force \( F = \zeta_0^s V + \Delta \zeta_y V \) as

\[
F(t) = \zeta_0^s V(t) - \nabla_r \sum_{1 \leq i \leq N_y} u_{ys}(r_s(t) - r^y_i(t)) \tag{3}
\]

where \( n_y^*(r,t) \) is the local density of yolks at position \( r \), defined as \( n_y^*(r,t) \equiv \int_{V_y} \delta(r - (r^y_i(t) - r_s(t))) \). The time evolution of \( n_y^*(r,t) \) is determined by Fick’s law, which, if the multiple yolks do not interact among themselves (or, equivalently, if \( N_y = 1 \)), leads to

\[
\frac{\partial n_y^*(r,t)}{\partial t} = [\nabla n_y^*(r,t)] \cdot \mathbf{V}(t) + D_y^n \nabla \cdot [n_y^*(r,t) \nabla \ln n_y^*(r,t) + \beta u_{ys}(r)], \tag{4}
\]
where the first term on the r.h.s. is a streaming term due to the fact that the position vector $r$ has its origin in the center of the shell. Under equilibrium conditions $V(t) = V^{eq} = 0$ and $\nabla \ln n^{eq}(r) = 0$, so that

$$n^{eq}(r) = n^{eq}_{0}(r) = N_{0} e^{-\beta u_{ys}(r)} / \int e^{-\beta u_{ys}(r)} dv_{r},$$

and $\int d^{3}r n^{eq}_{0}(r) n^{eq}_{0}(r) = 0$.

In stationary-state conditions, not far from equilibrium, $V(t) \neq V^{eq}$ and $n_{\alpha}(r,t) \neq n^{eq}_{\alpha}(r)$. We may thus write $n^{eq}_{\alpha}(r) = n^{eq}_{0}(r) + \Delta n^{\alpha}_{\alpha}(r)$ and linearize eq. (4) around $n^{eq}(r)$, to solve for $\Delta n^{\alpha}_{\alpha}(r)$. Substituting this solution in eq. (3) allows us to write this equation as

$$F^{ss} = \zeta^{ss} + \Delta \zeta^{s}_{y} \cdot V^{ss},$$

with the friction tensor $\Delta \zeta^{s}_{s}$ given by

$$\Delta \zeta^{s}_{s} = \frac{1}{4\pi D_{y}^{0}} \int d^{3}r \int d^{3}r' [\nabla u_{ys}(r)]^{-1} \nabla n^{eq}_{y}(r') \cdot \nabla n^{eq}_{y}(r).$$

Using the fact that $[\nabla u_{ys}(r)] = \nabla n^{eq}_{y}(r)/n^{eq}_{0}(r)$, and approximating this equation as $\nabla u_{ys}(r) \approx \nabla n^{eq}_{y}(r)/n_{0}$, we can use Fourier transforms to write this expression as

$$\Delta \zeta^{s}_{s} \approx \frac{\zeta^{ss}_{s}}{(2\pi)^{3}n_{0}} \int d^{3}k \frac{n^{eq}_{y}(k)^{2}}{k^{2}} = \zeta^{ss}_{s} \approx \frac{1}{\Delta \zeta^{s}_{s} + \lambda(k) n_{0}} \int d^{3}k \frac{n^{eq}_{y}(k)^{2}}{k^{2}} - \lambda(k).$$

The friction tensor $\Delta \zeta^{s}_{s}$ is diagonal and isotropic, so that $\zeta^{s}_{s} = \Delta \zeta^{s}_{s}$, with

$$\Delta \zeta^{s}_{s} = \frac{\zeta^{ss}_{s}(3\pi)^{3}n_{0}}{\Delta \zeta^{s}_{s} + \lambda(k) n_{0}} \int d^{3}k n^{eq}_{y}(k)^{2}.$$

This result for the scalar $\Delta \zeta^{s}_{s}$ then allows us to determine the total friction coefficient as $\zeta_{s} = \zeta^{ss}_{s} + \Delta \zeta^{s}_{s}$, and the long-time self-diffusion coefficient as $D_{s} = k_{B} T / [\zeta^{ss}_{s} + \Delta \zeta^{s}_{s}]$. However, since the diffusive dynamics of the yolk does not relax instantaneously with respect to the motion of the shell, in the present case we may have to solve the dynamic version of this problem, thus determining a time-dependent friction function $\Delta \zeta^{s}_{s}(t)$, whose time integral is $\Delta \zeta^{s}_{s}$. The hydrodynamic analog is Boussinesq's calculation of a time-dependent hydrodynamic friction function $\zeta(t)$ which incorporates the hydrodynamic memory effect deriving from the non-instantaneous response of the incompressible fluid [22].

The calculation of the time-dependent friction function $\Delta \zeta^{s}_{s}(t)$ not only in the infinite dilution limit is the next task of our theoretical methods. For this, however, a more robust version of the relaxation method must be employed. One possibility is to resort to the well-known dynamical formalism referred to as mode coupling theory (MCT), whose multicomponent version writes the dynamic properties (such as $w(t)$ and $F_{s}(k,t)$) in terms of the short-time parameters $D^{0}_{s}$ and $D^{0}_{y}$ only, and of the static structural properties of the system (i.e., the radial distribution functions or partial static structure factors). In our general program we proceed along these lines, but we employ an alternative (but essentially equivalent) formalism, namely, the SCGLE theory of colloid dynamics [23-28]. This choice originates in the enormous flexibility of this formalism, which has allowed, for example, the development of a quantitative non-equilibrium molecular theory of aging in glass-forming liquids [29].

The application of the SCGLE formalism to the present problem is discussed in detail in ref. [17]. Thus, here we only write the final results of those derivations needed to describe the dynamics of the simulated system above, namely, the following set of four coupled approximate equations. Two of them express $F_{5}(k,t)$ and $F_{5}(k,t) \equiv (1/N) \sum_{j=1}^{N} \xi_{j}(r(k,t)-r_{j}(0))$ (the shell intermediate scattering function) in terms of the time-dependent friction functions $\Delta \zeta^{s}_{s}(t)$ and $\Delta \zeta^{s}_{s}(t)$, which represent the friction effects on a tracer shell particle due to its direct interactions with its own yolk and with the other shells, respectively. In Laplace space these two expressions read

$$F(k, z) = \frac{\zeta(k)}{z + \frac{\zeta(k)}{\pi^{2} \sin(\pi k D_{y}^{0})}},$$

and

$$F_{5}(k, z) = \frac{1}{z + \frac{\zeta(k)}{\pi^{2} \sin(\pi k D_{y}^{0})}}.$$

The other two equations are the self-consistent closure relations for $\Delta \zeta^{s}_{s}(t)$ and $\Delta \zeta^{s}_{s}(t)$, namely,

$$\Delta \zeta^{s}_{s}(t) = \frac{D^{0}_{s} n_{0}}{3(2\pi)^{3}n_{0}} \int d^{3}k [k g_{ys}(k)]^{2} e^{-k^{2} D^{0}_{s} t} F_{5}(k, t),$$

and

$$\Delta \zeta^{s}_{s}(t) = \frac{D^{0}_{s} n_{0}}{3(2\pi)^{3}n_{0}} \int d^{3}k [k S(k) - 1]^{2} F(k, t) F_{5}(k, t).$$

In these equations $S(k)$ is the (shell-shell) static structure factor, $g_{ys}(k)$ is the Fourier transform of $g_{ys}(r) \equiv \exp[-\beta u_{ys}(r)]$, $n_{0} \equiv 1 / \int \exp[-\beta u_{ys}(r)] dv_{r}$, and $n \equiv N / V$. The function $\lambda(k)$ is given by [28]

$$\lambda(k) = 1/[1 + (k/k_{c})^{2}]$$

with $k_{c} = 1.305(2\pi/\sigma)$ being an empirically chosen cutoff wave vector [30].

We have solved eqs. (8)-(11) for our yolk-shell model above, for given static structural properties $g_{ys}(k)$ and $S(k)$, with $S(k)$ provided by the Percus-Yevick [31] approximation with its Verlet-Weisz correction [32]. From this solution, all the collective and self-dynamic properties are determined, including the Verlet-Weisz correction [17]. In what follows we illustrate the solution with the theoretical results for $w(t)$ and $F_{5}(k,t)$, which are compared with the BD simulation data. Let us mention that all the results discussed in this paper correspond to a fixed yolk-shell geometry, in which the thickness ($\sigma_{s} - \sigma_{in}$) of the shell is 5% of the shell's outer diameter, $\sigma_{in}/\sigma_{s} = 0.9$, and in which the yolk's diameter is 0.2
in units of $\sigma_s$, i.e., $\sigma_y/\sigma_s = 0.2$. The results reported below will be expressed using $\sigma_s$ and $\sigma_s^2/D_0^s$ as the units of length and time, respectively.

We begin by analyzing the results in fig. 1 of our BD simulations for the MSD $W(t; \phi, \delta)$ of tagged yolk-shell particles, varying the shell volume fraction $\phi \equiv \pi n \sigma_y^2/6$ and the dynamic asymmetry parameter $\delta \equiv D_0^s/D_0^y$. These results will be compared with the MSD $W^{HS}(t; \phi)$ of the corresponding system of empty shells, equivalent in our model to the MSD of a Brownian hard-sphere liquid at volume fraction $\phi$ [33,34]. Figures 1(a) and (b) contain, respectively, the results for $W(t; \phi, \delta)$ at $\phi = 0$ (freely diffusing yolk-shells) and $\phi = 0.4$ (strongly interacting yolk-shells). Figure 1(a) is intended to illustrate two effects in a simple manner. The first is the effect of yolk-shell interactions, which is illustrated by the comparison of the circles, representing the MSD $W(t; \phi = 0, \delta = 1)$ of freely diffusing yolk-shell particles, and the dotted line, representing the MSD $W_0(t) \equiv D_0^t$ of freely diffusing empty shells. The deviation of the simulation data from $W_0(t)$ is a measure of the additional friction effects upon the displacement of the yolk-shell complex due to the yolk-shell interaction. The solid line that lies near the circles represents the prediction of our SCGLE theory. The first conclusion that we can draw from this comparison is that the SCGLE-predicted deviation of $W(t; \phi = 0, \delta = 1)$ from $W_0(t)$, coincides very satisfactorily with the deviation observed in the BD data.

The second effect illustrated by fig. 1(a) involves the dynamic asymmetry parameter. The next conclusion to draw from the results in this figure is that the deviation of $W(t; \phi = 0, \delta)$ from $W_0(t)$ increases when the dynamic contrast parameter $\delta$ decreases. This is illustrated by the comparison of the BD simulations corresponding to $\delta = 0.2$ (triangles) with the BD data corresponding to $\delta = 1.0$ (circles). This means, for example, that if the interior of the shell becomes more viscous, so that the ratio $\delta$ decreases, then also the overall diffusivity of the yolk-shell particle will decrease. As evidenced by the solid and dashed lines in fig. 1(a), this trend is also predicted by the SCGLE theory and shows good qualitative agreement with the simulation data. In fact, our theory predicts, and the simulations corroborate, that this trend is reversed when one considers the opposite limit, in which $\delta$ is now larger than 1. This trend is best illustrated in the inset of fig. 1(a), which exhibits the measured (circles) and predicted (solid line) dependence on $\delta$ of the scaled long-time self-diffusion coefficient $D^*(\phi, \delta) \equiv D_L/D_0^s$, obtained as $D^*(\phi, \delta) = \lim_{t \to \infty} W(t; \phi, \delta)/D_0^t$. There we can see that the reduction of the mobility $D^*(\phi = 0, \delta)$ from its unit value $D_{HS}^{SS}(\phi = 0) = 1$, in the absence of yolks, may be considerable. For example, for $\delta = 0.2$ we have that $D^*(\phi = 0, \delta) \approx 0.17$. As a reference, a reduction in $D_{HS}^{SS}(\phi)$ of a similar magnitude can also be produced as a result of pure shell-shell interactions, but only at shell volume fractions above 40%, as gathered from the results

![Fig. 1: (Colour on-line) (a) Mean square displacement $W(t; \phi = 0)$ of non-interacting yolk-shell particles, (b) the MSD $W(t; \phi = 0.4)$, and (c) the self-intermediate scattering function $F_S(k = 6.18, t; \phi = 0.4)$ at volume fraction $\phi = 0.4$. For all figures, shell thickness $(\sigma_s - \sigma_y)/2 = 0.05$ (or $\sigma_s = 0.9$) and yolk diameter $\sigma_y = 0.2$. Recall that we take $\sigma_s$, and $\sigma_s^2/D_0^s$ as the time unit. For each figure, circles plot the Brownian dynamics data for the yolk-shell particles, whereas the solid line is the corresponding theoretical prediction of the SCGLE theory with a dynamic asymmetry parameter of $\delta \equiv D_0^y/D_0^s = 1$. In panels (a) and (b) the dotted line represents the MSD $W_0(t; \phi = 0) = D_0^t$ of a freely diffusing empty shell, and in (c) it represents the self-ISF $F^*_S(k, t; \phi = 0) = \exp(-k^2D_0^s t)$ for the same. In (a), the triangles plot the Brownian dynamics data and the dashed line plots the theoretical prediction, both corresponding to $\delta = 0.2$. In the case of (b) and (c), the squares are the simulation data for the empty-shell particles, and the dashed line is the corresponding theoretical prediction of the SCGLE theory with short-time diffusion coefficient $D^*_s = 1$. The inset of (a) shows the long-time self-diffusion $D^*$ as function $\delta$. The insets in panels (b) and (c) are the long-time self-diffusion $D^*$ and $\tau^*$ ($= k^2D_0^s \tau_m$), respectively, both as a function of $\phi$. Symbols and lines for these insets are the same as described in their own main panels. The dot-dashed line in inset (b) is the prediction for $D^*$ using eq. (13), and (c) shows the same prediction for the value of $\tau^*$.

68007-p4
of the inset in fig. 1(b), which discusses the effects of shell-shell interactions.

Let us now study the effects of shell-shell interactions, suppressed in the previous discussion, by analyzing the results of our simulations in fig. 1(b), in which we now fix the dynamic asymmetry parameter at the value \( \delta = 1 \). The circles in this figure represent the BD results for the MSD \( W(t; \phi = 0.4, \delta) \) of yolk-shell particles at a volume fraction \( \phi = 0.4 \). These results are to be compared with the squares, which correspond to the BD results for the MSD \( W^{(4)}(t; \phi = 0.4) \) of a liquid of empty shells (or solid hard spheres) at the same volume fraction and same short-time self-diffusion coefficient \( D_0^* \). The MSD \( W_0(t) = D_0^* t \) of freely diffusing empty shells is also plotted for reference as a dotted line. We observe that the deviation of \( W(t; \phi = 0.4, \delta) \) from \( W^{(4)}(t; \phi = 0.4) \) remains rather similar to the corresponding deviation observed at \( \phi = 0 \) in fig. 1(a) (where \( W^{(4)}(t; \phi = 0) = D_0^* t \)), but now both \( W(t; \phi = 0.4, \delta) \) and \( W^{(4)}(t; \phi = 0.4) \) deviate dramatically from this free-diffusion limit. This means that for this concentration, the mutual friction effects due to shell-shell interactions overwhelm the "internal" friction effects caused by yolk-shell interactions.

From the long-time BD data for \( W(t; \phi = 0.4, \delta) \) and \( W^{(4)}(t; \phi = 0.4) \) in fig. 1(b), we can extract the value of \( D^*(\phi, \delta) \) and \( D^{HS}_0(\phi) \), which represent the mobility of a tracer yolk-shell particle and of an empty shell, respectively. In the inset of fig. 1(b), we plot the values of \( D^*(\phi, \delta) \) and \( D^{HS}_0(\phi) \) (circles and squares, respectively) determined from the corresponding BD results at a few volume fractions. This inset thus summarizes the main trends illustrated by the results in figs. 1(a) and (b), by evidencing that at low volume fractions, the difference between the mobility of a yolk-shell complex and the mobility of an empty shell is determined only by the shell-friction, whereas at higher concentrations it is dominated by the shell-shell interactions. The solid lines in fig. 1(b) represent again the predictions of the SCGLE theory for the properties of the yolk-shell system, whereas the dashed lines are the corresponding predictions for the empty-shell (or hard-sphere) suspension. Once again, the agreement with the simulation results is also quite reasonable for a theory with no adjustable parameters.

Beyond this quantitative observation, however, the theoretical description provides additional insights on the interpretation of the qualitative trends exhibited by the simulation data of the long-time self-diffusion coefficients \( D^*(\phi, \delta) \) and \( D^{HS}_0(\phi) \). For example, it is not difficult to demonstrate that if the shell-shell mutual friction \( \int_0^\infty dt \Delta S^*(\phi, \delta) \) does not depend strongly on the presence or absence of the yolk (which one expects to be the case at high concentrations), then an approximate relationship between \( D^*(\phi, \delta) \) and \( D^{HS}_0(\phi) \) can be derived, namely,

\[
D^*(\phi, \delta) = \frac{D^*_0(\delta) \times D^{HS}_0(\phi)}{D^{HS}_0(\phi) + D^*_0(\delta) [1 - D^{HS}_0(\phi)]},
\]

where \( D^*_0(\delta) \equiv D^*(\phi = 0, \delta) = [1 + \Delta S^*_0(\delta)]^{-1} \), with \( \Delta S^*_0(\delta) \equiv \int_0^\infty dt \Delta S^*(\phi = 0, \delta) \). This expression interpolates \( D^*(\phi, \delta) \) between its exact low- and high-concentration limits \( D^*_0(\delta) \) and \( D^{HS}_0(\phi) \), and the dot-dashed line in the inset of fig. 1(b) is the result of using this approximate expression.

The BD simulations and the SCGLE theory provide other relevant collective and self-diffusion dynamic properties, such as the intermediate scattering functions, specially amenable to determination by dynamic light scattering techniques and adequate index-matching methods. To close this illustrative presentation, let us discuss the BD results in fig. 1(c) for the self-ISF \( F_S(k; \phi = 0.4, \delta = 1) \) (circles), which we compare with the self-ISF \( F^{HS}(k; \phi = 0.4) \) of a liquid of empty shells at the same volume fraction (squares). For reference, we also plot as a dotted line the self-ISF \( F^{HS}_0(k; \phi = 0) \) of freely diffusing empty shells. Here too, the solid and dashed lines correspond to the solution of eqs. (8)–(12) with and without the shell friction term \( \Delta S^*_0(\phi, \delta) \), and comparison again indicates very reasonable agreement with the simulation data.

In this case, the difference between the yolk-shell and empty-shell results can also be expressed more economically in terms of the corresponding \( \alpha \) relaxation times \( \tau_\alpha \), defined by the condition \( F_S(k, \tau_\alpha) = 1/e \) and scaled as \( \tau^* = k^2 D^*_0 \tau_\alpha \). The inset of fig. 1(c) exhibits the theoretical (solid line) and simulated (circles) results for the yolk-shell \( \tau^*(k; \phi, \delta) \) evaluated at \( k = 6.18 \) for \( \delta = 1 \) as a function of \( \phi \). These results may be compared with the theoretical (dashed line) and simulated (squares) results for \( \tau^{HS}_0(k; \phi = 0.4) \), corresponding to the empty-shell suspension, with similar conclusions as in fig. 1(b). In analogy with the relationship in eq. (13), from the SCGLE equations one can also derive an approximate relationship between \( \tau^*(k; \delta) \) and \( \tau^{HS}_0(k; \phi) \), namely, \( \tau^*(k; \phi, \delta) \approx \tau^{HS}_0(k; \phi) + \Delta S^*_0(\delta) \). This prediction of the value of \( \tau^*(k; \phi, \delta) \) has a rather modest quantitative accuracy, as indicated by the dot-dashed line in the inset. Still, it contributes to a simple and correct qualitative understanding of the main features of the properties of the yolk-shell system being studied.

In summary, in this work we have carried out BD simulations and have proposed a statistical mechanical approach for describing the dynamic properties of a complex system, namely, a concentrated suspension of yolk-shell particles. Here we have discussed the simplest illustrative model representation, in which each shell carries only a single yolk, and in which the yolk-shell and shell-shell forces are modeled as purely repulsive, hard-body interactions. This implied an additional simplification, namely, the absence of yolk-yolk direct interactions. These simplifications allowed us to reach a reasonable understanding of the differences between a yolk-shell system and a suspension of empty shell, and of the main trends observed upon the variation of relevant parameters, such as the
short-time dynamic asymmetry parameter $\delta$ or the shell volume fraction $\phi$. The message, however, is that the theoretical approach presented here can be extended to consider other, more complex conditions, such as including more than one yolks per shell and studying the effects of yolk-shell and shell-shell interactions beyond the purely repulsive, hard-core–like interactions considered here.

We close this communication with a reminder that the effects of hydrodynamic interactions must always be taken into account in any practical use of the methodology introduced here. As explained in the introduction, however, this information will be contained in the short-time self-diffusion coefficients $D_0$ and $D_\phi(\phi)$, which are considered here external inputs. A simple illustration of the accuracy of this procedure is provided by the excellent comparison between the experimental data for the ratio $D_T/D_0$ of a hard-sphere suspension, which involves strong hydrodynamic interactions particularly at high concentrations, and its simulated counterpart, which does not involve hydrodynamic interactions (see, for example, fig. 3 of ref. [35]).

***

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences and Engineering Division. This research at the SNS at Oak Ridge National Laboratory was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. This work was also supported by the Consejo Nacional de Ciencia y Tecnología (CONACYT, Mexico), through Grants No. 132540 and No. 182132.

REFERENCES

[1] LOU W. X., ARCHER L. A. and ZHANG Z., *Adv. Mater.*, 20 (2008) 3987.
[2] JOO S. H., PARK J. Y., TSUNG C. K., YAMADA Y., YANG P. D. and SOMORJAI G. A., *Nat. Mater.*, 8 (2009) 126.
[3] YIN D., RIoux R. M., ERDONMEZ C. K., HUGHES S., SOMORJAI G. A. and ALIVISATOS A. P., *Science*, 304 (2004) 711.
[4] KAMATA K., LU Y. and XIA Y. N., *J. Am. Chem. Soc.*, 125 (2003) 2384.
[5] ZHAO Y. and JIANG L., *Adv. Mater.*, 21 (2009) 3621.
[6] LIU J., XIA H., XUE D. F. and LU L., *J. Am. Chem. Soc.*, 131 (2009) 12086.
[7] LI H. X., BIAN Z. F., ZHU J., HUO Y. N., LI H. X. and LU Y. F., *J. Am. Chem. Soc.*, 129 (2007) 8406.
[8] LI X., LIU K.-H., WU B., SANCHEZ-DIAZ L. E., SMITH G. S. and CHEN W.-R., *J. Appl. Crystallogr.*, 46 (2013) 1551.
[9] TEECE J. L. et al., *Soft Matter*, 7 (2011) 1341.
[10] BARTLETT P. et al., *Phys. Rev. E*, 85 (2012) 021404.
[11] OKADA A., NAGAO D., UE NO T., ISHI H. and KONNO M., *Langmuir*, 29 (2013) 9004.
[12] PUSEY P. N., in *Liquids, Freezing and Glass Transition*, edited by HANSEN J. P., LEVESQUE D. and ZINN-JUSTIN J. (Elsevier, Amsterdam) 1991, Chapt. 10.
[13] BARDER J., *J. Phys.: Condens. Matter*, 22 (2010) 363101.
[14] MEDINA-NOYOLA M., *Phys. Rev. Lett.*, 60 (1988) 2705.
[15] BRADY J. F., *J. Fluid Mech.*, 272 (2006) 109.
[16] CERVANTES-MARTINEZ A. E., RAMIREZ-SALTO A., ARMENDA-CALDERON R., OJEDA-Lopez M. A. and ARAUZ-LARA J. L., *Phys. Rev. E*, 83 (2011) 030402(R).
[17] SANCHEZ-DIAZ L. E., CORTESES-MORALES E. C., LI X., CHEN W.-R. and MEDINA-NOYOLA M., in preparation (2014).
[18] ERMAK D. L. and McCAMMON J. A., *J. Chem. Phys.*, 69 (1978) 1352.
[19] DUBEY D., FORD D. C., ELLIS D. E. and SNIRR R. Q., *Mol. Simul.*, 35 (2009) 1084.
[20] ONSAGER L., *Phys. Z.*, 28 (1927) 277.
[21] LANDAU L. D. and LFISHTZ E. M., *Fluid Mechanics* (Pergamon Press, Oxford) 1959.
[22] YEOMANS-REYNA L. and MEDINA-NOYOLA M., *Phys. Rev. E*, 62 (2000) 3382.
[23] YEOMANS-REYNA L. and MEDINA-NOYOLA M., *Phys. Rev. E*, 64 (2001) 066114.
[24] YEOMANS-REYNA L., ACUÑA-CAMPA H., GUEVARA-RODRIGUEZ F. and MEDINA-NOYOLA M., *Phys. Rev. E*, 67 (2003) 021108.
[25] RAMIREZ-GONZALEZ P. E. et al., *Rev. Mex. Fis.*, 53 (2007) 327.
[26] YEOMANS-REYNA L., CHAVEZ-ROJO M., RAMIREZ-GONZALEZ P. E., JUAREZ-MALDONADO R., CHAVEZ-PAEZ M. and MEDINA-NOYOLA M., *Phys. Rev. E*, 76 (2007) 041504.
[27] JUAREZ-MALDONADO R., CHAVEZ-ROJO M., RAMIREZ-GONZALEZ P. E., YEOMANS-REYNA L. and MEDINA-NOYOLA M., *Phys. Rev. E*, 76 (2007) 062502.
[28] SANCHEZ-DIAZ L. E., RAMIREZ-GONZALEZ P. E. and MEDINA-NOYOLA M., *Phys. Rev. E*, 87 (2013) 052306.
[29] LOPEZ-FLORES L., YEOMANS-REYNA L. L. and MEDINA-NOYOLA M., *J. Phys.: Condens. Matter*, 24 (2012) 375107.
[30] PERCUS J. K. and YEVICEK G. J., *Phys. Rev.*, 110 (1957) 1.
[31] VERLET L. and WEIS J.-J., *Phys. Rev. A*, 5 (1972) 939.
[32] DE J. GUEVARA-RODRIGUEZ F. and MEDINA-NOYOLA M., *Phys. Rev. E*, 68 (2003) 011405.
[33] LOPEZ-FLORES L., RUIZ-ESTRADA H., CHAVEZ-PAEZ M. and MEDINA-NOYOLA M., *Phys. Rev. E*, 88 (2013) 042301.
[34] PÉREZ-ÁNGEL G. et al., *Phys. Rev. E*, 83 (2011) 066501(R).