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Extensive study of cage effect and subdiffusion in Pickering emulsions using molecular dynamics simulations

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Abstract : In this work, we aim at an extensive study of the diffusion phenomenon of oil-droplets dispersed in water onto which are strongly adsorbed charged point-like particles (Pickering emulsions). This diffusion that originates from multiple collisions with the molecules of water, is anomalous, due to the presence of relatively strong correlations between the moving oil-droplets. Using Molecular Dynamic simulation, with a pair-potential of Sogami-Ise type, we first observe that the random walkers execute a normal diffusion, at intermediate time, followed by a slow diffusion (subdiffusion) we attribute to the presence of cages, formed by the nearest neighbors (traps). In the cage-regime, we find that the mean-square-displacement increases according to a time-power law, with an anomalous diffusion exponent, α (between 0 and 1). The existence of a cage effect is shown also by computing the velocity auto-correlation function of the random walker. It is found that, in a cage, this function is governed by an underdamped (oscillatory) behavior, for strong densities and surface charges, and low-salt concentration. In the inverse situation, however, we observe that this correlation-function is rather overdamped (non-oscillatory). In the two cases, at large-time, this function fails according to a time-power law, with the exponent $\alpha - 1$.

Keywords : PICKERING EMULSIONS, SOGAMI-ISE POTENTIAL, ANOMALOUS DIFFUSION, CAGE EFFECT, MEAN SQUARE DISPLACEMENT

Introduction

Pickering emulsions are emulsions that are stabilized by solid particles. In fact, the solid particles form a spherical shell and impede coalescence when two droplets approach each other. Pickering emulsifiers irreversibly adsorb at the oil-water interface and require a much higher energy for desorption ($\approx 10^6 - 10^8 k_B T$) as compared to the conventional surfactants ($\approx 7 k_B T$). The emulsifier-free character of Pickering emulsions makes them attractive regarding applications

where the surfactants have detrimental effects, in particular, when contacted with living matter for health and body care applications^[1].

Pickering emulsions have been the focus of considerable research in the past decade due to their properties such as high stability with respect to the coalescence, as well as, due to advances in nanotechnology that allows us to create and characterize the nano-scale structures in new ways. In fact, the colloidal assembly of solid particles within Pickering emulsions can be used as templates for advanced materials such as Janus colloids, composite particles, and colloidosomes.

A Pickering emulsion has a complex structure which presents as a dispersion of droplets of a liquid (dispersed phase) in another (host liquid). Each droplet is surrounded by discrete spherical particles arranged on the surface. If the preparing conditions (such as wettability, charge, concentration, shape and size of particles, as well as, the pH and salt concentration in aqueous phase) are right, the clothed droplets can be considered as "soft-colloids".

Due to the thermal agitation, the clothed droplets experience a (lateral) diffusion with the molecules of the continuous phase. At the beginning, a single clothed droplet normally diffuses, but at large-time, this motion is hampered by the presence of the others, and then, the same clothed droplet executes rather an anomalous diffusion we are interested in. As we shall see below, quantitatively, this anomalous phenomenon mainly depends on the pertinent parameters, such as the surface charge of the droplets, their number density, and the salt-concentration.

In this work, we quantitatively study the anomalous diffusion within Pickering emulsions using the Molecular Dynamics (MD) simulations. The dynamic properties are investigated through the time-evolution of the mean-square-displacement (MSD) combined with the velocity auto-correlation function (VACF). For this purpose, we adopted the Sogami-Ise (SI) pair-potential^[2] between charged clothed droplets. It presents as the sum of a repulsive screened Coulomb potential and an attractive tail.

For the dynamics study, our starting point is a proposition of a relevant dynamic theory, based on the Langevin equation and its generalization (with memory). We then write an integro-differential equation for VACF and its relations with MSD. The exact solution of this equation, with an appropriate choice of the memory-function, enables us to valid the obtained results from MD as a computer experiment.

Pair-potential expression

Consider a suspension of N droplets (soft-colloids) of a liquid that are dispersed in another liquid of different chemical nature. In this study, we restrict ourselves to oil-in-water dispersions, only. The volume of the solution is denoted as V , and the oil-droplet number density as $\rho = N/V$. For simplicity, these oil-droplets are assumed to be monodisperse spheres of common diameter σ . The surface of each oil-droplet is wetted by Z irreversibly adsorbed charged particles of small diameter in comparison with σ . The strong adsorption of the particles rigidifies the surface of the oil-droplets, so they can be viewed as soft spherical colloids (as latex particles in water, for instance) that carry the same charge Ze (macroions). When they are added to the solution, the adsorbed particles are ionized and release small ions (counterions) in the solution. Generally, the colloids are in contact with other free ions resulting from a dissociation of a salt or an electrolyte. It is well-known that the surrounding mobile ions leads to a screening of the Coulomb forces between macroions (oil-droplets).

Beside the screened Coulomb interactions, the macroions experience attractive van der Waals ones, and the thermodynamic properties (phase transitions, structure...) of the system can be described correctly within the framework of the so-called Derjaguin-Landau-Verwey-Overbeek (DLVO) theory^[3]. In the same context, in his seminal paper^[2], I. Sogami used a self-consistent theory combined with a resolution of the Poisson-Boltzmann equation, satisfied by the electric potential created by the macroions (ionized latex

polyballs), for the determination of their associated effective interaction potential. Such a potential involves a short-range (screened) Coulomb repulsion, whose origin is self-evident, in addition to a long-ranged exponential attractive tail.

The expression of the SI potential between charged oil-droplets reads^[2]

$$\frac{U(r)}{k_B T} = l_B \left[\frac{Z \sinh(\kappa \sigma / 2)}{\kappa \sigma / 2} \right]^2 \left[\frac{1 + (\kappa \sigma / 2) \coth(\kappa \sigma / 2)}{r} - \frac{\kappa}{2} \right] e^{-\kappa r} \quad (1)$$

for $r > \sigma$. In this expression, the screening parameter κ is defined by the standard relation

$$\kappa^2 = 4\pi l_B \sum_i \rho_i z_i^2 \quad (2)$$

Here, $l_B = e^2 / \epsilon k_B T$ denotes the Bjerrum length, which is a characteristic length-scale at which the electrostatic interaction between a pair of monovalent ions has magnitude $k_B T$. The length l_B has the value $l_B = 0.7 \text{ nm}$, for water, at room temperature (this length is kept fixed to this value). Throughout this work, the temperature T will be fixed to the value 298 K (room temperature). In the presence of a salt of concentration, C_s , the above formula becomes

$$\kappa^2 = 4\pi l_B (\rho Z^2 + C_s) \quad (3)$$

Figure 1 shows the variation of the reduced SI pair-potential $U(r)/k_B T$, with the dimensionless distance, r/σ , for various values of the salt-concentration. These curves are drawn with parameters: $\rho^* = 0.002$, $Z = 500$ and $\sigma = 5000 \text{ \AA}$.

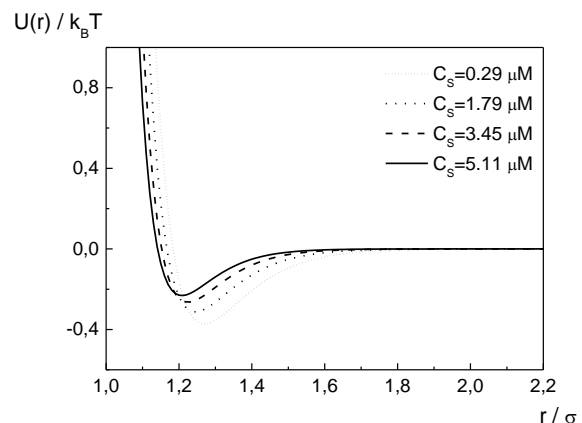


Figure 1: Dimensionless SI pair-potential, $U(r)/k_B T$, versus the dimensionless distance.

Finally, we note that, using this potential, Tata and coworkers^[4] performed Monte Carlo (MC) and Brownian Dynamics simulations, and the obtained results agree well with certain experimental observations^[5,6]. Also Kepler and Fraden^[7] determined the pair-potential of the colloidal particles from measurements of the pair correlation-function of both dilute and moderately concentrated dispersions. Thus, the determined pair-potential can be reproduced by SI potential assuming $C_s = 1.75 \times 10^{21} \text{ m}^{-3}$, as pointed out by Tata and Arora^[8]. The authors argued that the results by Kepler and Fraden supported the counterion-mediated attraction discussed by Sogami.

Results and discussions

Theory:

Normal diffusion: Consider a given clothed oil-droplet, termed tracer, which experiences a normal diffusion, for early times, because of the absence of the correlations. At these small-time-scales, the random walker is not yet trapped in a cage. As we shall below, such a regime will be put in evidence by our computer simulations, for smaller times. The Brownian motion of the tracer can be described by the following phenomenological Langevin equation

$$M \frac{dv(t)}{dt} = -\zeta v(t) + F_s(t) \quad (4)$$

The friction coefficient, ζ , is related to the viscosity of the emulsion, η , and the oil-droplet radius, R , by the classical Stokes relation: $\zeta = 6\pi\eta R$. Of course, the viscosity of the solution depends on the number density of the dispersed oil-droplets, ρ .

Come back to the stochastic force and note that this is considered to be a white noise with

$$\langle F_s(t) \rangle = 0 \quad (5)$$

$$\langle F_s(t) \cdot F_s(0) \rangle = 6k_B T \zeta \delta(t) \quad (6)$$

$$\langle v(0) \cdot F_s(t) \rangle = 0 \quad (7)$$

Now, we are interested in two related physical quantities: *velocity auto-correlation function* (VACF), $\langle v(t) \cdot v(0) \rangle \equiv c_{vv}(t)$, and *mean-square-displacement* (MSD), $\langle [r(t) - r(0)]^2 \rangle \equiv W(t)$. VACF solves the following differential equation [9]

$$\frac{dc_{vv}(t)}{dt} = -\gamma c_{vv}(t) \quad (8)$$

Its solution is simply

$$c_{vv}(t) = \langle v^2 \rangle e^{-\gamma t}, \quad \langle v^2 \rangle = c_{vv}(0) = 3 \frac{k_B T}{M} \quad (9)$$

with the mass weighted friction constant $\gamma = \zeta/M$, called *relaxation rate*.

On the other hand, VACF and MSD are related by [9]

$$W(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 c_{vv}(t_1, t_2) = 2 \int_0^t dt' (t - t') c_{vv}(t') \quad (10)$$

Replacing VACF by its explicit expression (9) in Eq. (10) yields the following time-evolution of MSD [9]

$$W(t) = 6 \frac{k_B T}{M} \left(\frac{e^{-\gamma t} - 1 + \gamma t}{\gamma^2} \right) \quad (11)$$

For times much longer than the inverse relaxation rate, that is for $t \gg \gamma^{-1} \equiv t^*$, MSD grows linearly with time, and we have

$$W(t) = 6Dt, \quad t \gg t^* \quad (12)$$

The linear growth of MSD with time is then reached beyond the characteristic time

$$t^* = \frac{M}{6\pi R \eta(\rho)} \quad (13)$$

This time limit depends only on oil-droplet density through the viscosity $\eta(\rho)$. If, in contrast, $t \ll t^*$, we can approximate $e^{-\gamma t}$ by $1 - \gamma t + \gamma^2 t^2/2$, and find

$$W(t) = \langle v^2 \rangle t^2 = 3 \frac{k_B T}{M} t^2, \quad t \ll t^* \quad (14)$$

which shows that MSD grows as t^2 (ballistic motion).

Anormal diffusion: Now, the raised question is how the tracer moves beyond the relaxation rate, t^* . In this time domain, the tracer (target) feels to be trapped in a cage formed by others clothed oil-droplets (traps), and cannot escape from this cage only after a long-time. As consequence, the presence of the traps makes difficult such a diffusion process, and then, the random walker executes rather a subdiffusion, characterized by an exponent denoted as α .

To discuss the cage effect and the subdiffusion laws, the starting point is a generalized Langevin equation [9],

$$\frac{dv(t)}{dt} = -\gamma v(t) - \int_0^t dt' \kappa(t - t') v(t') + F_s(t) \quad (15)$$

where κ is the memory-function that expresses the friction retardation. We note that this random force $F_s(t)$ satisfies equality (5) and (7), but with the second moment (generalization of Eq. (6))

$$\langle F_s(t) \cdot F_s(0) \rangle = 6Mk_B T [\gamma \delta(t) + \kappa(t)], \quad t > 0 \quad (16)$$

Oscillating regime: In this regime, the random walker is subject to oscillations before it undergoes a subdiffusion process. Therefore, the tracer moves in a harmonic potential resulting from its interactions with the surrounding nearest neighbors. This equivalent to take for the memory-function the following form

$$\kappa(t) = \omega_0^2 \theta(t) \quad (17)$$

The frequency ω_0 must be considered as a phenomenological parameter that depends, of course, on the essential parameters of the problem.

In these conditions, the integro-differential equation (15) writes

$$\frac{dc_{vv}(t)}{dt} = -\gamma c_{vv}(t) - \omega_0^2 \int_0^t dt' c_{vv}(t'). \quad (18)$$

Using Laplace transform, we find that VACF presents three regimes:

- The *underdamped* regime ($\gamma < 2\omega_0$):

$$c_{vv}(t) = \langle v^2 \rangle e^{-\gamma t/2} \left\{ \cos(\widehat{\omega}_0 t) - \frac{\gamma}{2\widehat{\omega}_0} \sin(\widehat{\omega}_0 t) \right\} \quad (19)$$

with the notation: $\widehat{\omega}_0 = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}$.

- The *overdamped* regime ($\gamma > 2\omega_0$):

$$c_{vv}(t) = \langle v^2 \rangle e^{-\gamma t/2} \left\{ \cosh(\widehat{\omega}_0 t) - \frac{\gamma}{2\widehat{\omega}_0} \sinh(\widehat{\omega}_0 t) \right\} \quad (20)$$

with the notation: $\widehat{\omega}_0 = \sqrt{\frac{\gamma^2}{4} - \omega_0^2}$.

- The *critical* regime ($\gamma = 2\omega_0$):

$$c_{vv}(t) = \langle v^2 \rangle e^{-\gamma t/2} \left(1 - \frac{\gamma t}{2} \right) \quad (21)$$

Such a regime separates the oscillating regime and the non-oscillating one.

Using the relation (10) between MSD and VACF, we find that MSD also presents three regimes:

- The *underdamped* regime ($\gamma < 2\omega_0$):

$$W(t) = 6 \frac{k_B T}{M \omega_0^2} \left[1 - e^{-\frac{\gamma t}{2}} \left\{ \cos(\tilde{\omega}_0 t) + \frac{\gamma}{2\tilde{\omega}_0} \sin(\tilde{\omega}_0 t) \right\} \right] \quad (22)$$

- The *overdamped* regime ($\gamma > 2\omega_0$):

$$W(t) = 6 \frac{k_B T}{M \omega_0^2} \left[1 - e^{-\frac{\gamma t}{2}} \left\{ \cosh(\hat{\omega}_0 t) + \frac{\gamma}{2\hat{\omega}_0} \sinh(\hat{\omega}_0 t) \right\} \right] \quad (23)$$

- The *critical* regime ($\gamma = 2\omega_0$):

$$W(t) = 24 \frac{k_B T}{M \gamma^2} \left[1 - e^{-\gamma t/2} \left(1 + \frac{\gamma t}{2} \right) \right] \quad (24)$$

In contrary to the freely diffusing Brownian particle, MSD approaches a plateau value in the limit $t \rightarrow \infty$, independently of the dynamic regime,

$$W(t) = 6 \frac{k_B T}{M \omega_0^2}, \quad t \gg 2\gamma^{-1} \equiv t^{**} \quad (25)$$

Then, this corresponds to the plateau regime where $\alpha_p = 0$.

Subdiffusive regime: Beyond the plateau regime, the random walker executes a slow motion, and the corresponding MSD obeys the law

$$W(t) = \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = 2D_\alpha t^\alpha, \quad (0 < \alpha < 1) \quad (26)$$

The normal diffusion with $W(t) \sim t$ (large-time) corresponds to a vanishing VACF, that is $c_{vv}(t) = 0$ (large-time), whereas $c_{vv}(t) \neq 0$ in the case of an anomalous diffusion. Specifically, $c_{vv}(t) < 0$ corresponds to the subdiffusion (since $\alpha < 1$), and $c_{vv}(t) > 0$ to the superdiffusion (since $\alpha > 1$).

We note that for the determination of the diffusion exponent, α , we shall use relation (26), expressed in log-log scale. This exponent is 1, for normal diffusion regime, 0, for the plateau regime, and between 0 and 1, for the subdiffusive one.

To sum up, we say that we have now all necessary theoretical ingredients for the explanation of the results from our MD simulations. This is the aim of the next section.

Results from MD simulation:

Spirit of MD simulation: Within the framework of MD method for the description of the dynamic properties of Pickering emulsions, the equations of motion are solved in the canonical ensemble using the velocity Verlet algorithm (VA) [10] with the thermostat of Berendsen [11], in order to keep the temperature constant. Periodic boundary conditions are applied to remove the surface effects and simulate an infinite system. In the following, we will use dimensionless units, where the length unit is σ , time in units of $\tau = \sigma\sqrt{(M/\epsilon)}$, $k_B T$ is the energy unit, and $L_0 = N \times (6V/\pi N)^{1/3}$ is the box-size, where V is the volume of simulation box (in periodic conditions). MD simulations were carried out with 1728 particles and the dimensionless time-step for the velocity VA is chosen to be 0.05.

Surface charge effects: In this paragraph, we will look at the influence of the surface charge of the clothed oil-droplets

on their dynamic properties. For the study, the size of the oil-droplets, their reduced number density and the salt-concentration are fixed to the values: $\sigma = 20000 \text{ \AA}$, $\rho^* = 0.0020$ and $C_s = 2.91 \mu M$. Their valence Z is ranged from 1000 to 4500.

Figure 2 shows the log-log plot of the reduced MSD upon dimensionless time, t/τ , for various values of the oil-droplet surface charge. We first remark that, for times less than a (dimensionless) transition time $t_1 \approx 2.483$, which is independent of the surface charge, the curves for different surface charges are superposed, and the random walker experiences a normal diffusion, that is $W(t) = 6Dt$. The reduced normal diffusion coefficient is $D = 14.120$. This simulated normal regime is in perfect agreement with the theoretical predictions relatively to the normal diffusion regime discussed above, eq. (12).

The existence of the normal diffusive regime can be understood as follows. In the intermediate times, the random walkers (oil-droplets) do not feel to be correlated, whatever are the values of their surface charge. For larger times, however, the situation is quite different, and the dynamic of the oil-droplets depends heavily on the surface charge, and MSD behaves rather as $W(t) \sim t^\alpha$, with an average subdiffusion exponent $\alpha_c = 0.418$ (the subscript c is for charge).

In agreement with the theory described above, we remark that the normal diffusion is followed by a transient plateau-like regime, which precedes the subdiffusion one. The existence of this plateau regime is conform with the theoretical eq. (25). This implies the formation of cages, where a given clothed oil-droplet is surrounded by their nearest neighbors. As shown in figure 2, the plateau is more and more pronounced, for strong surface charges. We also remark that the crossover time between the plateau-like regime and the subdiffusion one, t_2 , depends on the value of the surface charge. This means that the moving oil-droplet needs more time to break free of the cage of its nearest neighbors, as the surface charge increases. Physically, for higher surface charges, the available space for the oil-droplets becomes effectively reduced by the volume-excluding, because the repulsion becomes more important. This leads to a slowing down of the diffusion process of the oil-droplets, which stay localized for some time that increases with increasing surface charge. This behavior is reflected in VACFs displayed in figure 3, for the same values of the oil-droplet surface charge. VACFs are characterized by an underdamped (oscillatory) decay, more pronounced, for higher surface charges, in perfect agreement with the theoretical eq. (19). This underdamped feature can be related to the confinement of the particle in the cage formed by its nearest neighbors, and means that the diffusion process is not Markovian, but rather has memory [9]. For low-surface charges, however, we see that VACF is rather an overdamped function, which is conform with the theoretical expression (20). We also observe that, for any value of the surface charge, the tail or the long-time behavior of VACFs, which reflects the diffusional regime of the oil-droplets under consideration, approaches asymptotically zero, from negative values. Therefore, the oil-droplets display a subdiffusion. This negative region indicates that, on average, a displacement of the oil-droplets toward its nearest neighbors is followed by a displacement back toward its initial position. In other words, it reflects the fact that the velocity of the oil-droplets is, on average, reversed by repulsion with the cage of nearest neighbors.

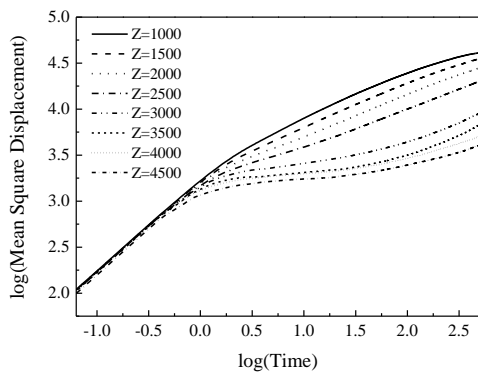


Figure 2 : MSD versus the dimensionless time, t/τ , in log-log scale, for various values of surface charge

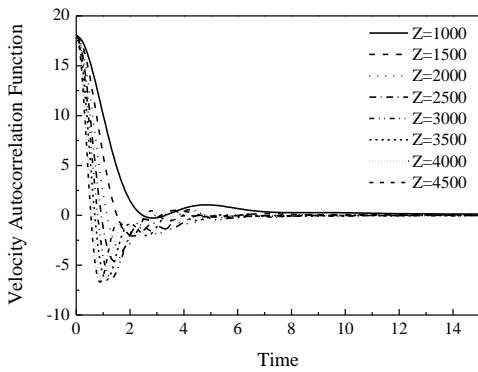


Figure 3: VACF versus the dimensionless time, t/τ , for various values of surface charge

Density effects: To study the influence of the density of the clothed oil-droplets on their dynamics, we keep fixed their surface charge and size, and the salt-concentration to the values: $Z = 2000$, $\sigma = 20000 \text{ \AA}$ and $C_s = 2.91 \mu M$, and vary this density.

In figure 5, we depict the log-log plot of MSD against the dimensionless time, t/τ , for various values of the oil-droplet density. We first remark that for $t < t_1'$, with $t_1' = 1.449$ (reduced transition time), MSDs are straight lines of the same slope, but decrease as the oil-droplet density is increased, in perfect agreement with the theoretical formula (13). Then, the random walker follows a normal Brownian diffusion, whose MSD is $W(t) = 6D(\rho)t$, for $t < t_1'$. Here D is the usual diffusion constant.

Second, for $t > t_1'$, we assist to a cage effect, where MSDs are very sensitive to the variation of the oil-droplet density, and exhibit a subdiffusive behavior, with an average subdiffusion exponent $\alpha_d = 0.432$ (the subscript d is for density). Before, MSDs exhibit a plateau regime that becomes more and more pronounced. The existence of such a regime agrees well with the theoretical formula (25).

The subdiffusive behavior evoked above is clearly shown in figure 6 representing the variation of VACFs upon the reduced time, t/τ , for different values of the oil-droplet density. From these plots, we see that the negative region of VACFs becomes larger as the oil-droplet density increases. In particular, we observe that VACF is underdamped (oscillatory)

for stronger densities, and overdamped for lower ones, in perfect agreement with theoretical formulae (19) and (20), respectively. In addition, the same plots indicate that VACFs tails approach asymptotically zero, from negative values. This means that the oil-droplets undergo a subdiffusion.

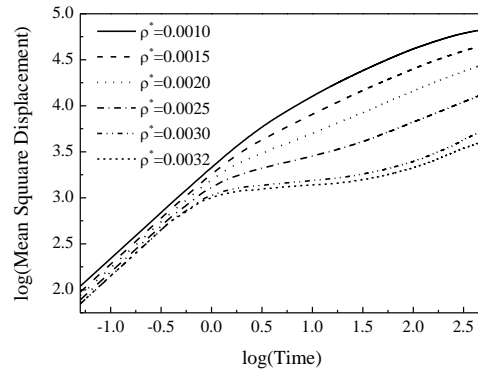


Figure 4: MSD versus the dimensionless time, t/τ , in log-log scale, for various values of the oil-droplet density

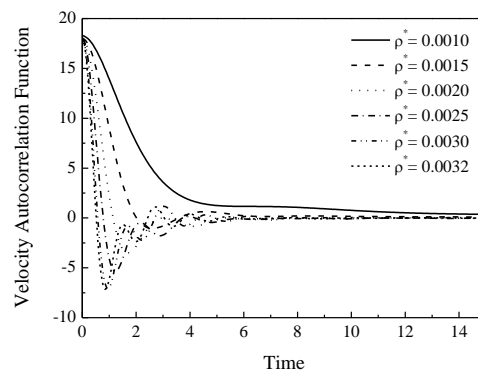


Figure 5: VACF versus the dimensionless time, t/τ , for various values of the oil-droplet density

Salt-concentration effects: Now, we fix the surface charge, size and reduced number density of the oil-droplets to the values: $Z = 500$, $\sigma = 5000 \text{ \AA}$ and $\rho^* = 0.0020$, and vary progressively the salt-concentration, C_s . The aim is to quantify the effects of this concentration on the diffusion process executed by a given clothed oil-droplet.

We represent in figure 8 the log-log plot of MSD upon the dimensionless time, t/τ , for various values of the salt-concentration. We first observe that, for $t < t_1''$, with $t_1'' = 1.439$ (reduced transition time), MSDs increase linearly with time, and have practically the same slope, whatever is the value of the salt-concentration. This means that the tracer experiences a normal Brownian diffusion, whose MSD is $W(t) = 6Dt$, for $t < t_1''$, with the (reduced) normal diffusion coefficient $D = 14.186$, in perfect agreement with the theoretical equation (13).

Second, for larger times ($t > t_1''$), MSDs become very sensitive to the variation of the salt-concentration, and present a subdiffusive behavior, due to the cage effects, with an average subdiffusion exponent $\alpha_s = 0.467$ (the subscript s is for salt).

Before this regime is attenuated, MSDs exhibit a plateau, which is more and more pronounced, rather for low salt-concentrations. The existence of such a regime is in perfect agreement with the theoretical formula (25).

The subdiffusive character of the random walker is also shown in figure 9 that represents VACFs versus the reduced time, t/τ , for many values of the salt-concentration. These curves are underdamped (oscillatory), for low salt-concentrations, and overdamped (non-oscillatory), for high salt-concentrations, before they reach a negative region of VACFs that becomes more and more pronounced, as the salt-concentration is decreased. The existence of underdamped and overdamped behaviors is conform with the theoretical formulae (19) and (20). Thus, the cage effect is more important, decreases with increasing salt-concentration (mutual interactions between charged oil-droplets are drastically diminished). Also, the curves show that VACFs tails approach asymptotically zero, from negative values. This indicates that the oil-droplets experience a subdiffusion.

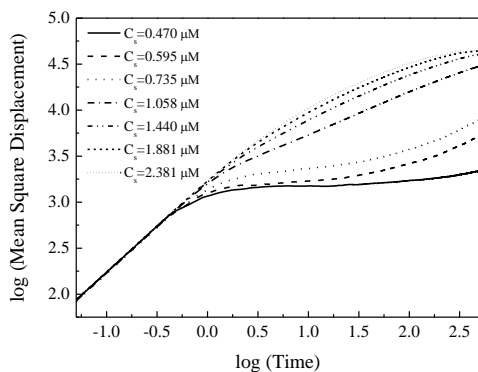


Figure 6: MSD versus the dimensionless time, t/τ , in log-log scale, for various values of the salt concentration

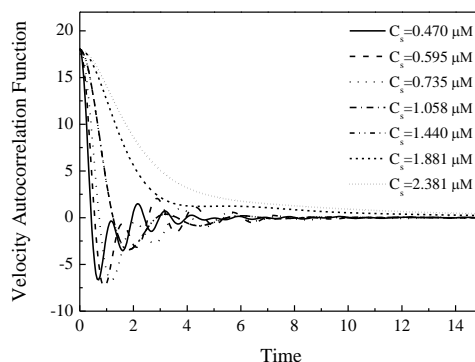


Figure 7: VACF versus the dimensionless time, t/τ , for various values of the salt concentration

Conclusion

In this work, we focus on a dynamic problem that is related to the so-called Pickering emulsions. We are interested in how the stabilization process is accomplished in time. During this process, the clothed oil-droplets execute a diffusion motion we are interested in. Contrary to the diffusion in homogeneous media, we find that, using MD simulations, the oil-droplets experience rather a slow motion, due to the complex structure of the Pickering emulsions. The origin of this anomalous diffusion, observed in many areas of science, is the existence of cages, made of nearest neighbors (traps) surrounding the random walker (target). To validate our MD simulation data, we proposed a memory diffusion theory that is based essentially on a generalized Langevin equation. We found that the results from MD simulations agree well with the predictions of this theory.

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