



Lecture on the anomalous diffusion in Condensed Matter Physics

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Abstract: Diffusion is a natural or artificial process that governs many phenomena in nature. The most known diffusion is the Brownian or normal motion, where the mean-square-displacement of the tracer (diffusive particle among others) increases as the square-root of time. It is not the case, however, for complex systems, where the diffusion is rather *slow*, because at small-scales, these media present an heterogenous structure. This kind of slow motion is called *subdiffusion*, where the associated mean-square-displacement increases in time, with a non trivial exponent, α , whose value is between 0 and 1. In this review paper, we report on new trends dealt with the study of the anomalous diffusion in Condensed Matter Physics. The study is achieved using a theoretical approach that is based on a *Generalized Langevin Equation*. As particular crowded systems, we choose the so-called Pickering emulsions (oil-in-water), and we are interested in how the dispersed droplets (protected by small solid charged nanoparticles) can diffuse in the continuous phase (water). Dynamic study is accomplished through the mean-square-displacement and the velocity-autocorrelation-function. Finally, a comparison with *Molecular Dynamics* data is made.

Keywords: COMPLEX SYSTEMS, ANOMALOUS DIFFUSION, GENERALIZED LANGEVIN EQUATIONS, MEAN-SQUARE-DISPLACEMENT, VELOCITY-AUTOCORRELATION-FUNCTION, MOLECULAR DYNAMICS SIMULATION.

I. Introduction

The anomalous diffusion in various fields of science (physics, chemistry, biology, ecology...) has received much attention from a theoretical and experimental point of view. In fact, such a diffusion

appears in heterogeneous, disordered, fractal, colloidal and polymer systems, and in general, it produces within the complex systems containing entities that move on different scale-times. In opposition to the normal or Brownian diffusion, the anomalous diffusion is slower, due to an extreme difficulty that a particle (*tracer*) moves in a complex structure. This kind of diffusion is usually referred to as *subdiffusion*, and it is characterized by a mean-square-displacement (MSD) that behaves as: $W(t) \equiv \langle (\mathbf{x}(t) - \mathbf{x}(0))^2 \rangle = 2D_\alpha t^\alpha$, with $0 < \alpha < 1$. This large-time behavior then deviates from the linear dependence on time found for the Brownian motion^[1-3]. In expression above, $\mathbf{x}(t)$, represents the time-position of the random walker, and the generalized diffusion coefficient, D_α , also called "fractional diffusion coefficient", is expressed in $\text{length}^2/\text{time}^\alpha$ unit.

We emphasize that the subdiffusion is a feature of the crowded systems, where the trajectories of their mobile constituents are strongly correlated. Notice that the above scaling relation is valid for large-times, that is beyond some characteristic time depending on the specific details of the diffusion process and the structure of the host medium. In general, a particle is said to be subdiffusive if the condition $W(t)/t \rightarrow 0$, for $t \rightarrow +\infty$, is satisfied (very slow diffusion). This explains why the anomalous exponent, α , must be in the interval $0 < \alpha < 1$.

It is noted that the subdiffusive transport appears in a variety of systems, such as the random-walk in fractal structures^[2], fractional-time Brownian motion^[4], living systems^[5], charge carrier transport in amorphous semiconductors^[6,7], NMR diffusometry on percolation structures^[8], and the motion of a colloid in a polymer network^[9]. For example, for diffusion in fractal structures, $\alpha = 2/d_w$, where $d_w > 2$ is the *walk-dimension* ($d_w = 2d_f/d_s$, where d_f and d_s are the fractal and spectral dimensions, respectively), and for the fractional-time Brownian motion, $\alpha = 2H$, where H is the Hurst index. Examples of enhanced diffusion ($\alpha > 1$) include tracer particles in vortex arrays in a rotating flow^[10], layered velocity fields^[11], and Richardson diffusion^[12]. The case $1 < \alpha < 2$ refers to *superdiffusion* (turbulent plasmas, Levy-flights, transport in polymers), $\alpha = 2$, to ballistic diffusion (optical traps), and $\alpha = 3$, to Richardson diffusion (atmospheric turbulence). The subdiffusion or superdiffusion exponent, α , is not a universal quantity, but mainly depends on the pertinent parameters that control the phenomenon. As we shall see below, for the subdiffusion of the clothed droplets of Pickering emulsions, this exponent shall depend on their size, density and surface charge, and the salt-concentration.

Anomalous diffusion is a subject which has been extensively studied, especially in the past decade by using the so-called Generalized Langevin Equation (GLE) (with memory)^[13,14-19]. The last has been introduced by Kubo^[20], as a generalization of the standard Langevin equation describing the Brownian or normal diffusion. Another useful approach to the anomalous diffusion is based on the fractional diffusion equation^[21-23], fractional Fokker–Planck equation^[21,24], generalized Chapman-Kolmogorov equation^[25] and fractional generalized Langevin equation^[26,27].

In their seminal paper, Mainardi and Pironi^[28] had introduced a fractional Langevin equation taking into account the retarding effects due to hydrodynamic backflow and showed that it is a particular case of GLE. These equations can be analyzed by using the properties and asymptotic behaviors of Mittag-Leffler (M-L) functions^[29-41].

For the reader, an exhaustive list of other important developments of the subject can be found in Ref. [42].

In this paper, we show how GLE can be applied to study the sub-diffusion phenomenon within particular complex systems which are Pickering emulsions (PEs)^[43,44], and compare results from this equation to Molecular Dynamics (MD) data^[45]. This computational method was introduced by Alder and Wainwright^[46], in order to study the structure and dynamics of liquids.

PEs are dispersions presenting, very often, as oil-in-water (O/W), water-in-oil (W/O) or double emulsion water-oil-water (W/O/W). These dispersions are stabilized by an addition of small solid (organic or inorganic) particles that act as emulsifiers, instead of the surfactant molecules^[47-50]. These particles that act as *emulsifiers* are of nanometric size, while the stabilized droplets are as small as few micrometers diameter. The stabilization of larger droplets (few millimeters diameter) is possible as well, using micron-sized solid particles. The stabilization of the dispersed droplets within PEs is ensured by a strong adsorption of the solid nanoparticles at their surfaces. In contrary to surfactants, where the adsorption is rather dynamic (reversible), that of the charged solidparticles is irreversible and sufficiently strong, with a very high adsorption energy, between $k_B T$ and $10^8 k_B T$, where $k_B T$ is the thermal energy. Here, k_B is the Boltzmann's constant and T is the bath temperature. Of course, such an energy mainly depends on the value of the wetting (or contact) angle and the droplet-radius^[50].

The anchoring of the solid particles emanates from a partial wetting of the surface of the charged solid particles by water and oil.

Due to their remarkable properties, such as high stability with respect to coalescence and their recent use in nanotechnology leading to the creation and the characterization of the nano-scale structures in new ways, PEs have been the subject of many studies, both from experimental and theoretical point of views. In addition, they can serve as templates for the advanced materials^[51,52], as Janus colloids^[53], composite particles^[54-61] and colloidosomes^[62-64].

PEs are heterogenous liquids which present as a dispersion of droplets of some liquid (dispersed phase) in another one (continuous phase). The two liquids are not chemically and physically compatible. By a mechanical mixing of the emulsion, each droplet becomes surrounded by discrete nanoparticles arranged on its surface. For the study of PEs, the clothed droplets can be regarded as charged soft-colloids^[65]. These charged droplets are subject to an anomalous diffusion as observed by MD simulations^[45], and we are interested in how they really move using a GLE approach. The dynamics of these droplets are studied through two main quantities, which are MSD and the velocity-autocorrelation-function (VACF). As we shall see below, for an appropriate choice of the *memory-function*, the solutions to GLE express themselves in terms of M-L functions.

The remaining of the presentation proceeds as follows. In the first section, we present a general dynamic theory, based on a GLE. A comparison between the results from this theory with MD data is the aim of the third section. Finally, some concluding remarks are drawn in the last section.

II. Dynamic theory

Consider a given particle, termed tracer or random walker, which executes a diffusion movement in the host medium. The raised question is how this random walker diffuses in the host medium, beyond some characteristic time we will precise below. In this time-regime, the random walker (target) feels to be trapped in a cage formed by the surrounding particles (traps), and then, it cannot escape from this cage, except after a long-time. We denote by N_c , the average-number of traps around the considered random walker. Consequently, the presence of the traps makes difficult such a diffusion process, and then, the random walker executes rather a subdiffusion, characterized by an anomalous exponent, α . The latter depends essentially on the nature of the random process and that of the host medium.

The basic dynamic quantities of our interest are MSD, $\langle (\mathbf{x}(t) - \mathbf{x}(0))^2 \rangle \equiv W(t)$, and VACF, $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \equiv c_{vv}(t)$. They are related by

$$W(t) = 2 \int_{t_0}^t dt' (t - t') c_{vv}(t'), \quad c_{vv}(t) = \frac{1}{2} \frac{d^2 W(t)}{dt^2} \quad (1)$$

To investigate quantitatively the cage effect and the subdiffusion phenomenon, the starting point is a GLE developed in the past by Kubo^[20] and by Zwanzig^[66]. Then, GLE describing the motion of the random walker reads

$$m \frac{d\mathbf{v}(t)}{dt} = -m \int_0^t dt' \gamma(t - t') \mathbf{v}(t') + \boldsymbol{\xi}(t) \quad (2)$$

Here, $\gamma(t)$ is the memory-function that expresses a retardation to friction. The random force, $\boldsymbol{\xi}(t)$, satisfies

$$\langle \boldsymbol{\xi}(t) \rangle = \mathbf{0}, \quad \langle \boldsymbol{\xi}(t) \cdot \boldsymbol{\xi}(0) \rangle = m k_B T \gamma(t) \quad (3)$$

For viscous colloidal solutions, the particle acceleration vanishes, and in this case, GLE equation reads

$$-m \mathbf{v}_0 \delta(t) = -m \int_0^t dt' \gamma(t - t') \mathbf{v}(t') + \boldsymbol{\xi}(t) \quad (4)$$

where $\mathbf{v}_0 = |\mathbf{v}_0| = \sqrt{2k_B T/m}$ is the initial velocity of the tracer and the stochastic force, $\boldsymbol{\xi}(t)$, also satisfies relations (3).

Assume, now, that the memory-function has the form

$$\gamma(t) = \gamma_0 \delta(t) + \frac{\gamma_\alpha}{\Gamma(1-\alpha)} t^{-\alpha} \quad (0 < \alpha < 1) \quad (5)$$

Here, γ_0 and γ_α are two positive constants, $\Gamma(x)$ is the *Euler gamma function* and $\delta(t)$ represents the Dirac-distribution. Using the Laplace-transform techniques together with relations (3), we find that MSD and VACF, in the non-inertial regime, are given by

$$W(t) = 2 \frac{k_B T}{m\gamma_0} t E_{1-\alpha,2} \left(-\left(\frac{t}{\tau}\right)^{1-\alpha} \right) \quad (6)$$

$$c_{vv}(t) = \frac{k_B T}{m\gamma_0} \frac{d^2}{dt^2} \left[t E_{1-\alpha,2} \left(-\left(\frac{t}{\tau}\right)^{1-\alpha} \right) \theta(t) \right] \quad (7)$$

with the Heaviside step-function, $\theta(x)$. In these expressions, $E_{\sigma,\tau}(x)$ denotes the *two-parameter M-L function* [29]. There, $\tau = (\gamma_0/\gamma_\alpha)^{1/(1-\alpha)}$ is a time-scale.

For small-times, in comparison with the characteristic one, τ , MSD and VACF behave, respectively, as

$$W(t) = 2D_0 t \quad (t \ll \tau) \quad (8)$$

$$c_{vv}(t) = D_0 \delta(t) \quad (t \ll \tau) \quad (9)$$

Then, at these time-scales, the random walker executes a Brownian (normal) diffusion, with the usual diffusion coefficient, $D_0 = k_B T/m\gamma_0$. For large-times, compared to τ , we find

$$W(t) = 2D_\alpha t^\alpha \quad (t \gg \tau) \quad (10)$$

$$c_{vv}(t) = \alpha(\alpha - 1)D_\alpha t^\alpha \quad (t \gg \tau) \quad (11)$$

with

$$D_\alpha = \frac{D_0}{\Gamma(\alpha+1)} \quad (12)$$

which denotes the generalized diffusion coefficient.

III. Comparison with MD simulations

For the description of the dynamic properties of PEs, using MD method, the equations of motion are solved in the canonical ensemble using the *Velocity Verlet Algorithm (VVA)* [67], with the *Thermostat of Berendsen* [68], in order to keep the temperature constant. In addition, periodic boundary conditions are applied to remove the surface effects and simulate an infinite emulsion. In the following, it will be convenient to use dimensionless units, where the length unit is σ , time in units of $\tau = \sigma\sqrt{M/\varepsilon}$, where M is the oil-droplet mass and ε is the depth of the interaction potential, $k_B T$ is the energy unit, and $L_0 = N \times (6V/\pi N)^{1/3}$ is the box-size, where N is the number of the clothed oil-droplets, and V is the volume of simulation box (in periodic conditions). MD simulations [45] were carried out with 1728 oil-droplets and the dimensionless time-step for VVA is chosen to be 0.05. The last typical value of step-time is that usually adopted in studying the colloidal solutions from MD simulations.

Discussion on dynamics of PEs was made [45] varying the pertinent factors, as the surface charge of oil-droplets, and their density and the concentration of the added salt.

Charge effects

The first goal was the quantification of the influence of the charge carried by the oil-droplets on their dynamic properties [45]. The size of the oil-droplets, their reduced number density and the salt-concentration were fixed to the values: $\sigma = 20000 \text{ \AA}$, $\rho^* = 0.0020$ and $c_s = 2.91 \text{ \mu M}$. But the valence, Z , was varied from 1000 to 4500.

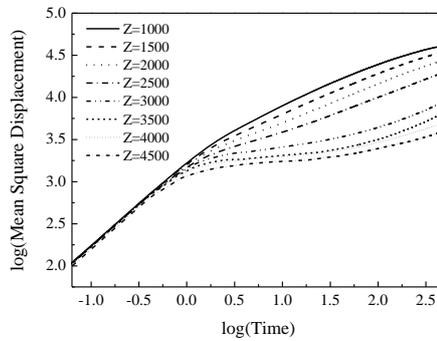


Figure 1: MSD versus dimensionless time, t/τ , in log-log scale, for various values of the oil-droplet surface charge, with the fixed parameters: $\sigma = 20000 \text{ \AA}$, $\rho^* = 0.0020$ and $c_s = 2.91 \text{ \mu M}$.

Figure 1 shows the log-log plot of the reduced MSD upon dimensionless time, t/τ , for various values of the surface charge. Such a figure clearly shows the existence of two time-regimes. For early times, the random walker executes a normal diffusion, independently of the value of the surface charge. This agrees with the theoretical behavior, relation (8). Above some known characteristic time, it executes rather a subdiffusion, and MSD behaves as $W(t) \sim D_\alpha t^\alpha$, with an average subdiffusion exponent $\alpha_c = 0.418$. This result is in perfect agreement with the theoretical behavior, relation (10). As already shown [45], both anomalous diffusion exponent, α , and fractional diffusion coefficient, D_α , decrease progressively with the surface charge. As the later is augmented, the correlations between the oil-droplets become stronger, and consequently, one assists to a slow dynamic.

Figure 2 indicates the time-variation of VACF, for the same values of the surface charge. The abrupt increase of this function, at small-times, can be explained by formula (9) replacing the Dirac-distribution $\delta(t)$ by a very narrow Gaussian function, that is: $\delta(t) \rightarrow (2\pi\sigma)^{-1/2} \exp(-t^2/2\sigma)$, with a very small time-scale σ . For large-times, VACF goes to zero, in agreement with theoretical formula, relation (11).

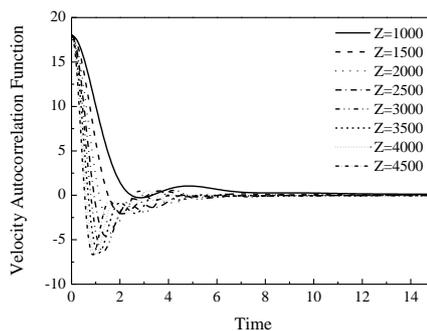


Figure 2: VACF versus dimensionless time, t/τ , in log-log scale, for various values of the oil-droplet surface charge, with the fixed parameters: $\sigma = 20000 \text{ \AA}$, $\rho^* = 0.0020$ and $c_s = 2.91 \text{ \mu M}$.

Density effects

The second goal was the study of the influence of the density of the clothed oil-droplets on their dynamics [45], fixing their surface charge and size, and the salt-concentration to the values: $Z =$

2000, $\sigma = 20000 \text{ \AA}$ and $c_s = 2.91 \text{ \mu M}$.

Figure 3 shows the log-log plot of MSD, versus dimensionless time, t/τ , for various values of the droplet-density. As above, this MSD exhibits two time-regimes: normal, with a density-dependent diffusion coefficient, and subdiffusive, with an average subdiffusion exponent, $\alpha_d = 0.432$. This is in good agreement with the theoretical formulae (8) and (10).

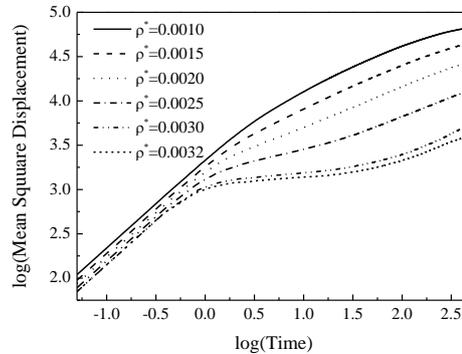


Figure 3: MSD versus dimensionless time, t/τ , in log-log scale, for various values of the oil-droplet density, with the fixed parameters: $Z = 2000$, $\sigma = 20000 \text{ \AA}$ and $c_s = 2.91 \text{ \mu M}$.

Figure 4 indicates the variation of VACF upon time, for the same parameters as before. The time-behavior of this dynamic property agrees well with the theoretical predictions, relations (9) and (11).

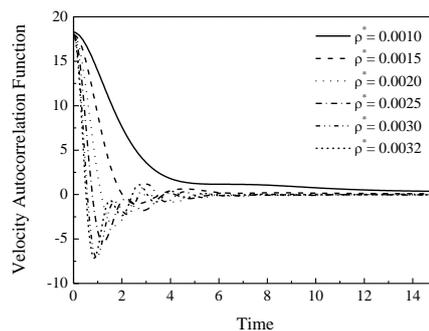


Figure 4: VACF versus dimensionless time, t/τ , in log-log scale, for various values of the oil-droplet density, with the fixed parameters: $Z = 2000$, $\sigma = 20000 \text{ \AA}$ and $c_s = 2.91 \text{ \mu M}$.

Salt-concentration effects

A quantitative investigation of the effects of the salt-concentration, c_s , on the oil-droplets dynamics was achieved in Ref. [45], fixing the remaining parameters to the values: $Z = 500$, $\sigma = 5000 \text{ \AA}$, and $\rho^* = 0.0020$.

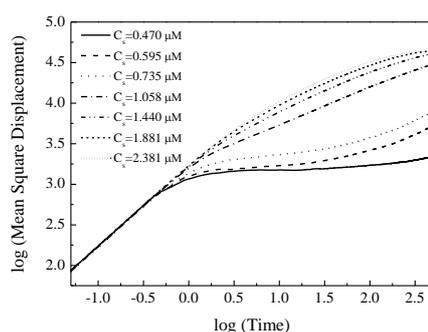


Figure 5: MSD versus dimensionless time, t/τ , in log-log scale, for various values of the salt-concentration, with fixed parameters: $Z = 500$, $\sigma = 5000 \text{ \AA}$ and $\rho^* = 0.0020$.

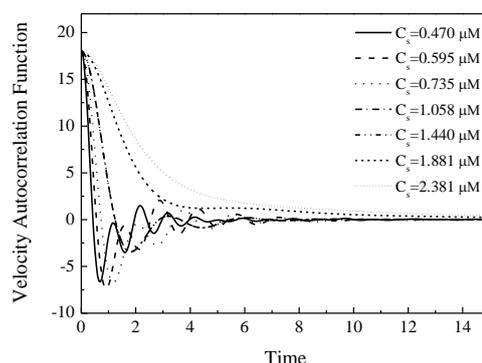


Figure 6: VACF versus the dimensionless time, t/τ , in log-log scale, for various values of the salt-concentration, with fixed parameters: $Z = 500$, $\sigma = 5000 \text{ \AA}$ and $\rho^* = 0.0020$.

Figures 5 and 6 show the time-variation of MSD and VACF, respectively. Also, in this case, MD data are in good agreement with theory, relations (8) to (11). In particular, at large-time, MSD exhibits a subdiffusive behavior with an average exponent $\alpha_s = 0.467$.

III. Conclusion

In this presentation, we focus on a quantitative dynamic study of the subdiffusion phenomenon within crowded systems, as Pickering emulsions, which are stabilized by a strong irreversible adsorption of charged solid nanoparticles on the surface of the dispersed oil-droplets.

As we have shown above, the subdiffusion with complex systems may be approached well using a non-inertial generalized Langevin equation. Dynamic properties were studied through two important physical quantities, which are MSD and VACF. This equation was solved exactly with an appropriate choice of the memory-function, whose solution is expressed in terms of Mittag-Leffler functions.

For Pickering emulsions, it was demonstrated that the diffusion of a given oil-droplet is normal, at short-time, and subdiffusive, at large-time, with an anomalous exponent between 0 and 1, and the theoretical predictions were found to be in perfect agreement with very recent MD simulations^[10].

An important question to ask is how particles that are embedded on the surface of a crowded system, can diffuse in time. Such a question was ensured in the case of fluid or polymerized membranes^[69] and the oil-droplets of a Pickering emulsion^[70]. The main result is that, the random walker executes a subdiffusion, at short-time, followed by a saturation regime, at infinite time.

Finally, it will be interesting to extend these extensive dynamic studies to the situation where the diffusing particles have arbitrary shapes and forms.

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