

Research Article

A Model for the Stability of a TiO_2 Dispersion

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A computational study of a colloidal dispersion stabilized with grafted polymer layers is presented here as a model for white, water-based paints. The interaction model includes repulsive, three-body interactions and attractive van der Waals forces. The electrostatic interactions are also studied. Stability criteria can be established for the dispersion, such as the thickness of the adsorbed polymer layers, and the quality of the solvent. Using implicit solvent molecular dynamics calculations, the spatial distribution of the pigments is obtained through the calculation of the radial distribution functions. The results show that the solvent quality and the thickness of the grafted polymer layer are key variables in the stability of the dispersion. Additionally, a structural phase transition is predicted, which is driven by the pigment concentration in the dispersion. It is argued that the predictions of this work are useful guidelines in the design of paints and coatings of current industrial interest.

1. Introduction

Colloidal dispersions are complex fluids composed of one or more dispersed phases immersed in a continuous phase (solvent). A full statistical mechanical description of such a system is a nontrivial challenge because of the disparity of scales between the colloidal particles and the solvent molecules [1]. These dispersions play a very important role in contemporary societies, as they are present in fields ranging from biological systems to industrial applications. A typical example of a colloidal dispersion is a water-based, architectural paint, which is the system one should have in mind for this work.

The existence of fluctuating electric dipoles among the atoms that make up the colloidal particles leads to the appearance of an attractive interaction between them, known as the van der Waals (vdW) interaction, which is however, short ranged. If no repulsive forces were present, the vdW attraction would drive particles to come close together, leading to the instability of the dispersion [2]. Alternatively, a stable colloidal dispersion is that in which colloids are homogeneously dispersed in the solvent. There are 2 popular mechanisms that help prevent irreversible colloidal instability. One is through steric effects; the other is by means of

electrostatic charges present on the colloids surfaces [1]. The present work deals primarily with the former and considers that all particles are covered with a layer formed by adsorbed polymers. When the particles come close to each other, the polymers that constitute the layers start to overlap, which in turn reduces the number of available spatial configurations for them and therefore their entropy. This process gives rise to an effective repulsion between colloidal particles, which can be enough to stabilize the dispersion.

The purpose of this research is, on the one hand, to study the physicochemical processes involved in the dispersion stability through grafted polymer layers, using an analytical mean-field theory, complemented with molecular dynamics computer simulations. On the other hand, one would like to predict the behavior of colloidal dispersions by means of calculations of the thermodynamic and structural properties that characterize the type of complex fluids of present interest, and in doing so, assess the advantages of developing models for paints and coatings [3]. Two original contributions are presented in this work: on the one hand, the incorporation of a mean-field model of steric stability to a molecular simulation code that predicts colloidal stability through the evolution of the radial distribution function. Charge stabilized colloids are prevalent in aqueous systems and are dealt

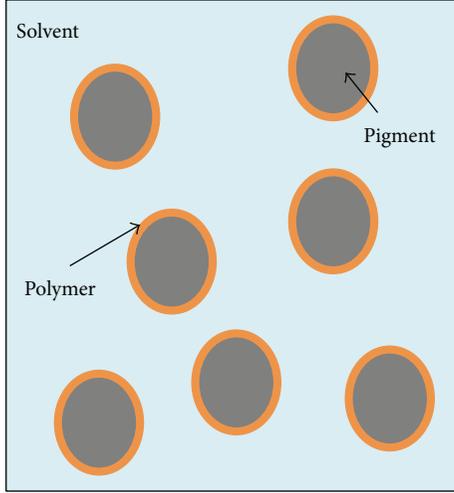


FIGURE 1: Model colloidal dispersion used in the present work. The particles represent the pigments, which are coated with a layer of polymer-grafted chains, immersed in a solvent.

with also in this work. On the other hand, a structural phase transition is found for this mean-field model for the first time, which can drive a stable colloidal dispersion to an unstable state through relatively small changes in the pressure.

This paper is organized as follows. In the next section, the interaction model is introduced in detail followed, in Section 3, by the presentation of the colloidal stability criterion. Section 4 is devoted to the details pertaining to the molecular dynamics simulations and the calculation and analysis of the radial distribution functions of the colloidal particles, which are central for this work. The electrostatic interactions, which are of paramount importance for real-life paints and coatings design, are incorporated in Section 5. A structural phase transition driven by the pigment concentration is predicted to occur, as shown in Section 6, and finally the conclusions of this work are laid out in Section 7.

2. Model

The starting point is the mean-field theory proposed by Zhulina et al. [4]. Let us begin by considering a dispersion in which each colloidal particle surface is covered with a certain number of linear, electrically neutral polymers; see Figure 1. In principle, one should start by taking into account all partial interactions, such as polymer-polymer, colloid-colloid, and polymer-colloid, and in each case, between 2, 3, and more particles. Notice that there is also the interaction of each of these constituents with the solvent and of the solvent with itself. Determining all these interactions exactly is, of course, impossible with the tools available today. Nonetheless, one can take advantage of appropriate approximate methods, such as mean-field theories [5]. In the present context, this means that we shall consider the interaction of a colloidal particle with the rest of other colloids as a whole and, equivalently, the interaction between polymer chains and

colloids with polymer [4]. Therefore, the total interaction is written as follows:

$$U_T = U_A + U_P + U_{LJR}, \quad (1)$$

where U_A corresponds to the attractive vdW colloid-colloid interaction, which decays as $1/r^2$ as a function of the relative distance between the centers of mass of a given pair of particles, r , for distances smaller than the colloidal particles radius. U_P is a repulsive contribution that arises from polymer-polymer steric interactions. Since this term has an opposite sign to that of the first, it should be possible to prevent colloid instability through the competition between those 2 terms. Zhulina and coworkers [4] have developed an effective mean-field theory for this scenario, assuming the area that a polymer chain occupies on a particle surface (σ) is larger than the square of a monomer's size (a), performing then a virial expansion of the thermodynamic potential in terms of the monomer concentration. Colloids collision times are sufficiently long so that polymer configurations can adjust and reach equilibrium after the collision so that equilibrium statistical mechanics can be applied. An additional assumption is that the distance separating the colloids surfaces is smaller than their size, so that the surfaces can be considered planar. The last term in (1) has been added in this work to introduce the excluded volume effect, and it is a Lennard-Jones type of repulsion given by $U_{LJR}(r) = 1/r^{50}$. I chose the exponent arbitrarily equal to 50 (rather than the usual 12) simply to ensure that the interaction was strongly repulsive when surfaces came into contact with one another, since such term was absent in the original mean-field formulation [4]. Lastly, it is shown that electrostatic interactions can be important to improve the stability of the colloidal dispersion [1, 6].

The polymer interaction U_P in (1) is made up of two terms, an elastic term of entropic origin [7] and a volume interaction. The former is obtained from the Gaussian approximation for a linear polymer chain composed of N monomers of size a each [7]. The total contribution of the polymer interactions, U_P , to the full interaction of (1) can be expressed [4] as $U_P = \Delta F_0^\theta \Psi(\beta, r)$, where ΔF_0^θ is the free energy of a free polymer layer at the θ -temperature. The function $\Psi(\beta, r)$, which depends on the quality of the solvent, β , and the relative position between the surfaces of colloids, r , are given by [4]:

$$\begin{aligned} \Psi(\beta, r) &= -2 \left(\beta^2 + \alpha^2 + \frac{4\beta\alpha^3}{3\pi} \right) + 2u^2 r^2 \\ &\quad - \frac{8}{3\pi} \left[2\beta^3 r - 2\beta \left(\frac{3u^2}{2} - 1 \right) r^3 + (u^2 - 1)^{3/2} r^4 \right], \end{aligned} \quad (2)$$

where α is the temperature-dependent, polymer layer dilation coefficient, and u is a variable that obeys the following identity (for full details see [4]):

$$\frac{1}{r^2} + \frac{4\beta}{\pi r} = \frac{2}{\pi} \left[(u^2 - 1)^{1/2} + u^2 \sin^{-1} \left(\frac{1}{u} \right) \right], \quad (3)$$

which for u larger than 1 can be linearized. Under this approximation, and neglecting terms of order r^3 and larger, I obtain the following expression for the full interaction in (1):

$$U_T = \Delta F_0^\theta \left[\left(2\beta^2 - 2\alpha^2 - \frac{8\beta\alpha^3}{3\pi} \right) + \frac{\pi\beta}{r} + \frac{\pi^2}{12r^2} (1 - \gamma) \right] + U_{LJR}. \quad (4)$$

The first term in parentheses is a position-independent constant which does not change once the temperature is fixed. An additional constant, γ , has been introduced [4]:

$$\gamma = \frac{A}{96\pi k_B T w} \left(\frac{\sigma}{Na^2} \right)^3, \quad (5)$$

where w is the third virial coefficient, A is Hamaker's constant for the polymer-solvent system, and N is the degree of polymerization of the grafted polymers. The origin of the term proportional to γ in (4) is the attractive vdW interaction between colloidal particles, U_A , which for planar surfaces (of equal radius R) and for relative distances smaller than the colloids size is given by [2]

$$U_A = -\frac{A}{12} \frac{R}{(2H)^2}, \quad (6)$$

where $2H$ is the distance separating two neighboring colloidal surfaces. Equation (4) is the central potential on which this work is based. Figure 2 shows its position dependence for various values of β or, equivalently, for different temperatures, and for two values of the constant γ in (5).

By inspection of (4), it is clear that the constant γ determines whether the full potential has an attractive contribution (when $\gamma > 1$) or if it is totally repulsive (if $\gamma < 1$). Therefore, it is important to determine the effect that each parameter in (5) has on the stability conditions of our model colloidal dispersion. First, I investigate the effect that the degree of polymerization, N , has on the force that can be derived from the potential in (4), given by the following expression:

$$F = -\frac{dU}{dr} = \frac{\pi\beta}{r^2} + \frac{\pi^2}{6r^3} (1 - \gamma). \quad (7)$$

In deriving (7), the contribution from the Lennard-Jones repulsive term, $U_{LJR}(r)$, has been neglected since its contribution is important only when colloids are very close to each other, which occurs for small values of N . One recognizes in (7) that the force between pigments becomes more repulsive as the solvent quality β is increased, as expected. The influence of the grafting polymer density or of the type of solvent can be studied from the influence of constant γ (see (5)) on the force, (7). Figure 3 was obtained from (7) for increasing degrees of polymerization and shows that a limiting value for the repulsive force at large N is obtained. This trend has been fully corroborated by experiments that measure the force between polymer-coated particles; see for example, [8].

3. Colloidal Dispersion Stability Criterion

The curves in Figure 2 show a maximum for the case when $\gamma > 1$, $U_{\max}(r_{\max}^1)$, localized at certain position r_{\max}^1 , and given by

$$U_{\max}(r_{\max}^1) = \frac{3\beta^2}{\gamma - 1} \Delta F_0^\theta, \quad (8)$$

which is proportional to the quality of the solvent and to the free energy of the unperturbed polymer layer at the theta temperature. This maximum in the potential creates a barrier, which can be seen in Figure 2 for $\gamma > 1$; as long as this barrier is much larger than the thermal energy, $k_B T$, the colloidal dispersion will be kinetically stable [9]. Using typical values for the parameters entering into ΔF_0^θ (polymerization degree $N = 55$; total number of grafted chains per colloid $m = 500$; average area of polymer chain on the colloid surface $\sigma = 7000 \text{ \AA}^2$; monomer size $a = 5 \text{ \AA}$; average thickness of polymer layer at theta temperature $H_0^\theta = 500 \text{ \AA}$) for a good quality solvent ($\beta = 1$), at room temperature, I obtain a value for the ratio of the potential in (8) over $k_B T$ of about 10^4 (see [4]), which means that the colloidal dispersion is stable [2]. This analysis leads us to a stability criterion, expressed by the following condition:

$$\frac{U_{\max}(r_{\max}^1)}{\Delta F_0^\theta} = \frac{3\beta^2}{\gamma - 1} > 1. \quad (9)$$

This is a testable prediction. In what follows, I carry out a molecular dynamics computer simulation study of a model colloidal dispersion, where the motion of the colloidal particles is obtained from the solution of Newton's second law for the force derived from the full potential in (4).

4. Molecular Dynamics Simulations of Colloidal Dispersions

The purpose of molecular dynamics simulations is the prediction of values of thermodynamic and structural properties, among others, obtained from averages over the trajectories of the particles in the system, in phase space [10]. It has been shown before how, for example, molecular dynamics simulations are very helpful in understanding and predicting the behavior of polymers of industrial interest in different solvents [11]. Also, molecular simulation can be a powerful tool in the design of new molecules with certain tailored functionality [12]. The primordial interest here is the calculation of structural properties of a system like that depicted in Figure 1. I start by solving the equation of motion using the velocity Verlet integration algorithm [10] for the potential in (4), using a cubic simulation box (or varying volume to fix the desired particle concentration) with 896 particles with periodic boundary conditions applied on each face of the box. Reduced units are used throughout, at room temperature unless stated otherwise. The solvent is included implicitly through the choice of the Hamaker constant. The simulations are performed at constant particle number, volume, and

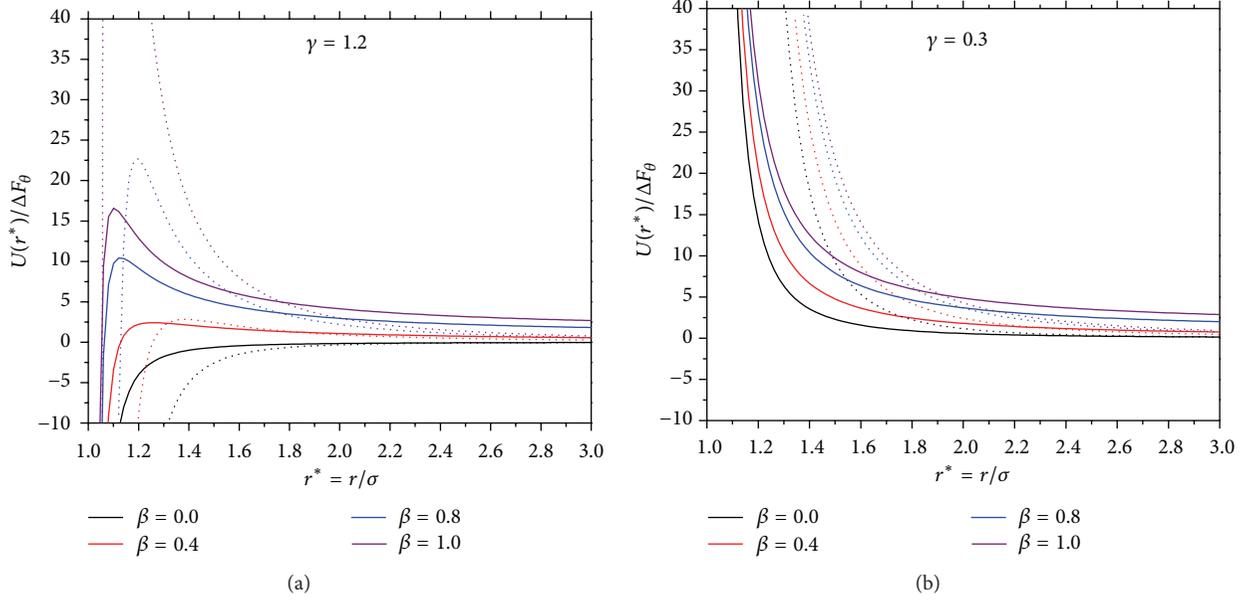


FIGURE 2: Full interaction potential (4) for pigments coated with a polymer layer, as a function of the solvent quality (β) and the γ constant (see (5)). The axes are shown in adimensional units. Full lines represent the potential, while dotted lines are the corresponding forces.

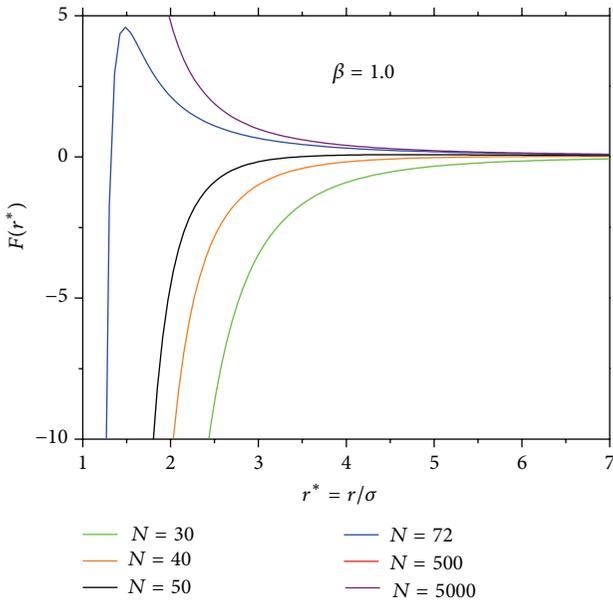


FIGURE 3: Force between colloidal particles with grafted polymer chains of various degrees of polymerization, N . The axes have been normalized appropriately so that they are dimensionless. The curves were obtained from (7), for $\beta = 1.0$. The curves for $N = 500$ and $N = 5000$ are indistinguishable.

temperature, that is, using the canonical ensemble. At least 2×10^5 integration cycles were performed during the production phase of the molecular dynamics simulations, with 3×10^4 cycles for the equilibrium phase. The time step was chosen as $t = 0.007t_{LJ}$, where t_{LJ} is the time step in the Lennard-Jones units [10].

One of the key quantities used to characterize the stability of our model dispersion is through the calculation of the radial distribution function (rdf), usually represented as $g(r)$. The information provided by the rdf helps one determine the relative spatial organization of the molecules in a fluid with three-dimensional symmetry [10]. It is directly evaluated from the dynamics that at each integration time, the number of particles in a shell with radii between r and $r + \Delta r$, that is, $\Delta N(r, r + \Delta r)$, is calculated and normalized by the density of particles, ρ , and the volume of the shell to give

$$g(r) = \frac{\Delta N(r, r + \Delta r)}{(4\pi/3) \rho [(r + \Delta r)^3 - r^3]}. \quad (10)$$

Knowledge of the rdf allows one to determine the influence that the various parameters entering the potential in (4) have on the spatial distribution of the colloidal particles, or in other words, on the stability of the dispersion. One of the variables that play a key role in the present model is the parameter β , which is negative for poor solvents, zero for a theta solvent, and positive for solvents of good quality [4]. In Figure 4, we see the $g(r)$ for a model colloidal dispersion at three different values of increasing solvent quality. They represent a dispersion of polystyrene in water at room temperature, for which the Hamaker constant is $A = 10^{-20}$ J [13].

The first maximum that appears in Figure 4 is displaced to larger values of the relative distance from the centers of mass of the polystyrene particles as the solvent quality is increased, which is in agreement with the expected result. This means that the relative separating distance between colloids has been increased; that is, the dispersion has become more stable as the solvent quality has been increased. One can then conclude that since the solvent quality depends on temperature and on the thermodynamic stiffness of the polymer chains (Kuhn's

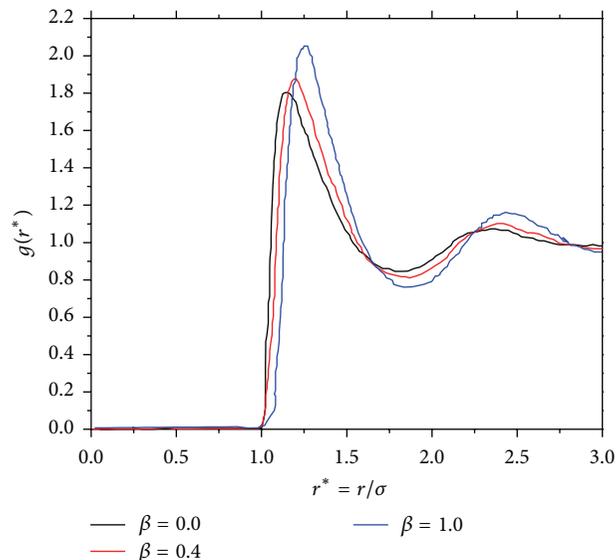


FIGURE 4: Radial distribution functions obtained from molecular dynamics simulations at three different values of the solvent quality, β . The symbol σ represents the size of the colloidal particles. See text for details.

parameter [4]), then increasing these variables would lead to an improvement in the stability of the dispersion. There are, however, additional factors one can control to increase the stability of the dispersion. One of them is the thickness of the polymer layer grafted to the surface of the particles, H , since the thicker this layer is, the more difficult it becomes for the surfaces of the colloids to come into contact with one another thus preventing the attractive vdW interaction to dominate and flocculate the dispersion. This hypothesis was tested with the calculation of the rdf for various thicknesses of the polymer layer, and the results are shown in Figure 5.

Different sets of simulations were carried out for thicknesses of the polymer layer coating the surface of the colloids, ranging from 100 Å up to 800 Å. The resulting rdf for each case are shown in Figure 5, where one notices how the largest maximum in each curve is displaced to larger values of the relative distance between polystyrene particles centers, which indicates that as the polymer layer thickness is increased, the polystyrene dispersion becomes more stable. There are other factors that are expected to enhance colloidal stability, such as temperature, the polymer grafting density, and polymerization degree. However, these factors are already included in the definition of the constant γ (see (5)). Recalling that the potential in (4) acquires an attractive term whenever $\gamma > 1$, then one must seek ways to keep $\gamma < 1$ which means, for example, lowering the Hamaker constant (which is tantamount to choosing a different solvent or an alternative coating for the colloidal surface) and increasing the temperature, the polymerization degree, or the polymer grafting density. Notice also that γ is inversely proportional to ω , the third virial coefficient; that is, three-body interactions contribute directly to the stability of the dispersion.

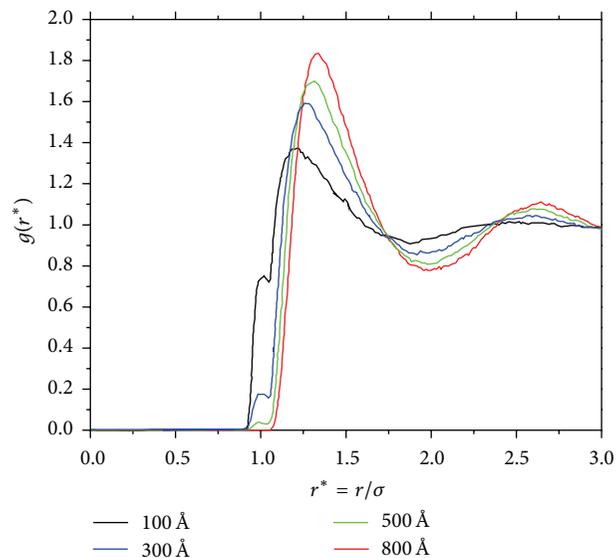


FIGURE 5: Radial distribution function for the model colloidal dispersion, obtained from molecular dynamics simulations using the same set of parameters used for Figure 4, except for the value of the polymer layer thickness, at the theta temperature. The first maximum value is displaced to larger values of the dimensionless r^* as the thickness is increased from left to right: 100 Å (black), 300 Å (blue), 500 Å (green), and 800 Å (red).

The effect of the TiO_2 pigment coating can be investigated also by means of the Hamaker constant [14]. Doing so is important for the particular application of the dispersion one has in mind, for example, in paints, to graft certain kinds of dispersants on the pigment surfaces so that the paints are more stable [12], or to ensure the whiteness of the paint [15], to name just some examples. This can be accomplished through an appropriate combination of the Hamaker constants for the pigment-solvent (A_{12}), with the coating substances, also for the particular solvent chosen (A_{13} , A_{14} , etc.), that is, a mixing rule such as $A_{123} = (A_{12}A_{13})^{1/2}$ [2]. The rdf of a dispersion of TiO_2 pigments with and without a SiO_2 + polystyrene (PS) coating in water is shown in Figure 6.

We see in Figure 6 that the dispersion of uncoated titania is unstable at the theta temperature (red line) since a large maximum appears in the rdf when the relative distance between the centers of mass of the pigment particles is equal to their diameter; that is, the particles are touching. However, when the pigments are coated, the maximum is displaced to larger relative distances (blue line) and the dispersion becomes stable. Therefore, the potential in (4) has enough flexibility to allow one to test various scenarios of practical importance. In the blue line in Figure 6, the calculations were performed for titania particles coated with SiO_2 because many commercial grade TiO_2 pigments used for architectural paints are coated precisely with SiO_2 [15]. Most commercial architectural paints include of course latex particles, which would require the present model to account for colloidal particles of at least two different types, pigment, and latex particles. However, as shown in Figure 6, this can easily be done with a single particle type simply by introducing

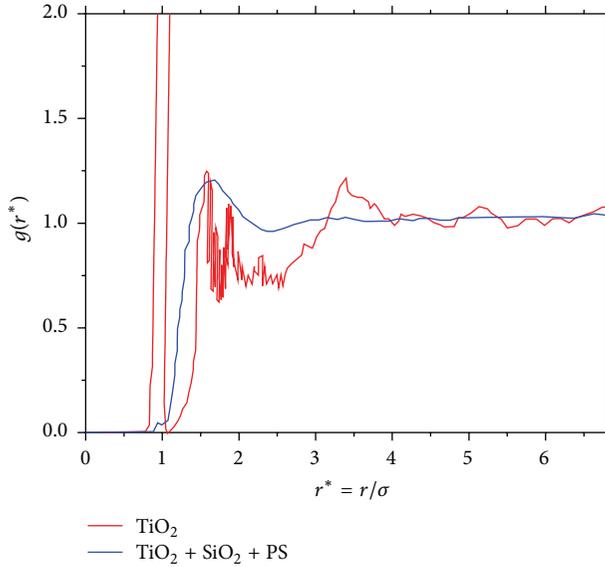


FIGURE 6: Radial distribution functions for a model water based paint with bare TiO_2 pigments (red line) and with the same pigments coated with a layer of silica and polystyrene ($\text{TiO}_2 + \text{SiO}_2 + \text{PS}$, blue line).

an appropriate mixing rule for the type of coating one wants to design, having in hand the required Hamaker constant. For the particular case shown in Figure 6, polystyrene was chosen as a generic latex particle. The case of water soluble, adsorbed polymers such as PEG has been discussed in [12]. As a final word on the rdf shown in Figures 4–6, one notices that the second peak is always weak. This is due to the fact that the dispersion has only very short range order, as seen by the interactions displayed in (4).

5. Influence of the Electrostatic Interaction

Two of the most popular methods for colloidal stabilization are the steric method, exemplified in the previous sections, and the electrostatic one [1]. It is known also [15] that when TiO_2 is used as a pigment in paints and coatings, it is usually coated with oxides such as alumina and silica which, when immersed in a polar solvent such as water, acquire electric charges on the surface [15]. These charges in turn induce polarization of the charges on the grafted polymer chains, and they are immersed in an aqueous medium. Under these conditions, the electrostatic interaction is screened, with a range typically given by the Debye length [2, 16]. It is not the purpose of this work to study the conditions of stability that arise when the competing interactions are the attractive vdW and repulsive electrostatic interactions, since the DLVO model is well suited for that [17]. The objective here is merely to illustrate how the present model can be adapted to include factors such as the electrostatic environment to yield useful predictions for the stability of paints and coatings. Let us start by considering the screened

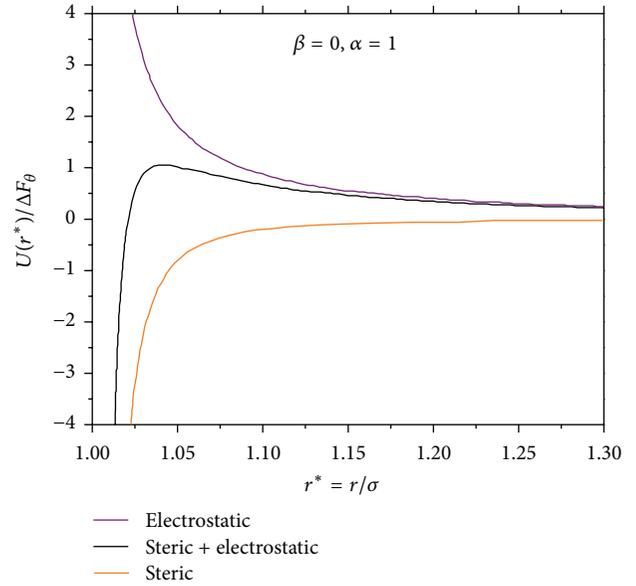


FIGURE 7: Modification of the interaction potential when a repulsive electrostatic term is added. The top (purple) line represents the purely electrostatic repulsion, while the lowest (orange) line corresponds to the nonelectrostatic potential, which is attractive when $\beta = 0$. The black line is the potential that contains both contributions.

electrostatic Yukawa potential [2], given by the following expression:

$$U_{\text{elec}}(r) = \frac{(Z_{\text{effec}}e)^2 \exp[-\kappa_D r]}{(4\pi\epsilon_0\epsilon_r)r}; \quad r > \sigma_{\text{colloid}}, \quad (11)$$

where Z_{effec} is the effective charge on the surface of the pigments, in terms of the fundamental electron charge, e . For the present purposes, I shall consider $Z_{\text{effec}} = 100$ [18]. The constant κ_D is the inverse of the Debye length, which shall be considered to be equal to 20 nm, as in typical aqueous paints [15]. Finally, $\epsilon_0\epsilon_r$ is the medium permittivity, and I shall use the values appropriate for water at room temperature. Equation (11) is added to the interaction potential (4) and new set of molecular dynamics simulations are then carried out. For simplicity and to test the influence of the electrostatics, only the case of a theta solvent is considered, that is, $\beta = 0$.

Figure 7 shows how the interaction potential is modified by the influence of the screened electrostatic interaction, which as seen in the figure, leads to the appearance of a potential barrier that arises from the competition of the vdW attraction and the electrostatic repulsion. The bare Coulomb repulsion and the steric potential, which is purely attractive for this choice of parameters (with $\beta = 0$), are included also in the figure for comparison.

With the potential given by the addition of the screened electrostatic interaction (11) and the steric potential (4), new molecular dynamics simulations were carried out, for a theta solvent ($\beta = 0$) at room temperature, using the same values of the parameters involved in the calculation of the potential

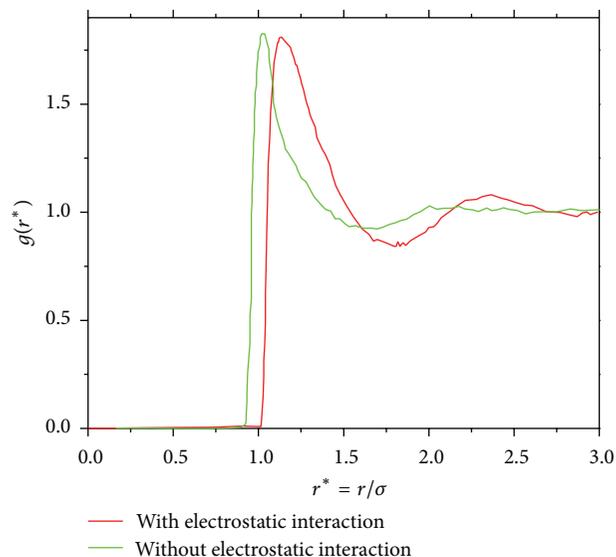


FIGURE 8: Radial distribution function for a system with electrostatic interaction (red line) and without it (green line). Inclusion of electrostatics leads to a repulsion between colloids, which displaces the first maximum to larger relative distances. See text for details.

in Figure 7, which yield $\gamma = 1.05$. Once equilibrium was reached, the rdf was calculated and compared with the rdf of the system without electrostatic interactions. Both results are shown in Figure 8.

The rdf of the system of particles that contains the electrostatic interaction is seen to have its first maximum at a larger relative position between the centers of mass of the colloids than the neutral system. One should keep in mind that the neutral system corresponds to the case of a theta solvent, which is why it is not as stable as it would be expected to be if the quality of the solvent was better.

6. Order-Disorder Phase Transition

In this section, I shall present the evolution of the colloidal dispersion as a model for paints and coatings, when the pigment concentration is increased. Similar studies have shown that a structural phase transition occurs as a function of particle concentration [19]. It is important to determine the conditions under which such a transition takes place, if it does occur. The analysis of the previous sections has shown that raising the temperature lowers the value of γ , that in turn, makes the dispersion more stable while increasing the solvent quality, at the same time. Moreover, we know that for compressible fluids, increasing the concentration leads to an increase in the fluid's pressure; hence, one would like to know if the fluid undergoes any fundamental transformation when the pigment concentration and the temperature are the control variables. I have performed such study through molecular dynamics simulations and, once equilibrium has been reached, calculated the fraction of total number of particles that are closer than a certain distance apart (in this case, when their relative distance is $r^* \leq 0.1$ in reduced units).

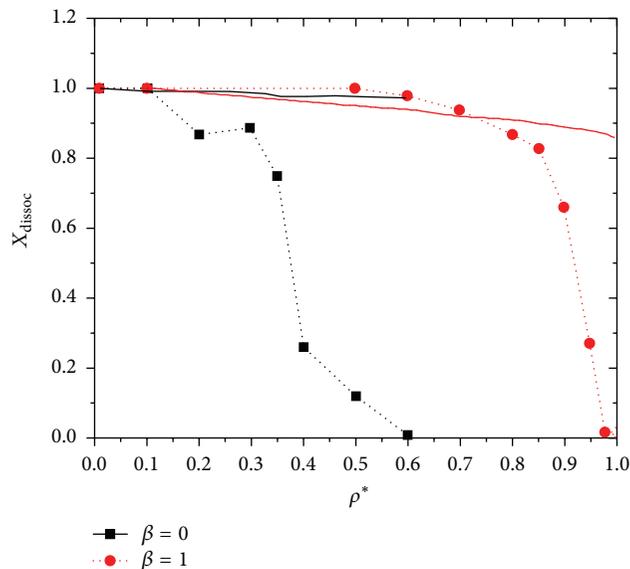


FIGURE 9: Fraction of dissociated colloidal particles (X_{dissoc}) as a function of the total colloid concentration, ρ^* in adimensional units, for two values of the solvent quality (β). The parameters used in the simulation are the same as in the Figure 8 (nonelectrostatic case). The lines are only guides for the eye. The colored lines indicate the total energy of the system, normalized by the particle number, in each case. See text for details.

The fraction of particles that are dissociated, namely, those that are not closer to each other than a distance equal to, or smaller than $r^* = 0.1$, X_{dissoc} , is obtained from the ratio of the number of particles that do not associate over the total particle number. In a well-dispersed system, $X_{\text{dissoc}} \approx 1$ since most particles are separated from one another, whereas when $X_{\text{dissoc}} \approx 0$, most particles have formed aggregates. Therefore, X_{dissoc} plays the role of an order parameter. In Figure 9, we see the evolution of this order parameter as a function of pigment concentration, for two different values of the solvent quality.

It is evident that a transition occurs between a “disordered” state, at low pigment concentration where all or most of the particles are dissociated, to a more “ordered” state where particles form clusters. The term “ordered” is used here only to imply that particles are associated spatially by their relative distance; however, it does not imply that a certain spatial symmetry exists, as it does in crystalline solids. In that sense, Figure 9 is a phase diagram of the model colloidal dispersion under study. The rdf between the ordered and disordered states differ in that the position of the first peak is displaced to smaller distances for the ordered state, due to the aggregation of particles. I have also calculated the total energy of the system as the pigment concentration is increased, and, as the results present in the color lines in Figure 9 demonstrate, there is no discontinuity in the energy when the system goes from fully disordered (stable dispersion) to completely “ordered” (unstable dispersion). Thus, the transition we have found belongs to the so-called “second order” type [13]. There is a small decrease in the normalized energy as the pigment concentration is increased, but this is

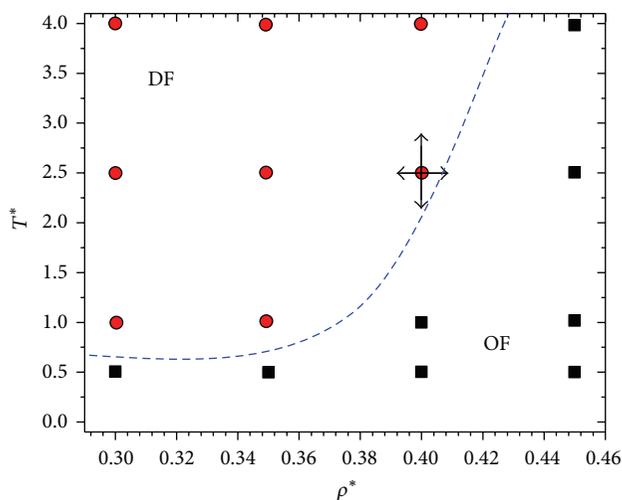


FIGURE 10: Phase diagram of the model colloidal dispersion obtained from molecular dynamics simulations. OF and DF represent ordered (flocculated) and disordered (stable) dispersion, respectively. The dashed line delineates the border between those two phases. The perpendicular arrows illustrate the behavior of the colloidal dispersion when it is close to the boundary between phases.

simply the consequence of having less configurational space available for particles to move, hence their kinetic energy is somewhat reduced.

The phase transition that the colloid dispersion undergoes as a function of pigment concentration can be driven, for example, by an increase in the hydrostatic pressure, but when that happens, other thermodynamic conditions may also change, like the temperature. It is important then to find out how the structural properties of the dispersion are modified as the temperature changes. Using the molecular dynamics simulation data to determine when the majority (more than 50% of the total) of the particles are associated, I have constructed the phase diagram shown in Figure 10. In it, the black squares represent “ordered” states, that is, those where most particles form clusters, while red circles represent dissociated, stable states. The dotted line indicates where the transition from an ordered fluid (OF) to a disordered fluid (DF) occurs, as the temperature and pigment concentration are increased.

Let us take the point marked with the perpendicular arrows in Figure 10, as an arbitrary reference. If the chosen point is close to the boundary between phases, as in the example in the figure, a relatively small increment in concentration (driven, e.g., by the external pressure) can take the dispersion from a stable (DF) to an unstable (OF) state. However, if starting at the same point while keeping the concentration fixed one raises the temperature, the system stays disordered, or kinetically stable. Sengupta and coworkers [20] have found similar trends by means of the Monte Carlo simulations for binary mixtures in two dimensions; however, the results shown in Figure 10 are, to the best of my knowledge, the first time a transition of this type has been reported for fluids composed of a single particle type. As to the origin of

transition, the likely candidate is the increased translational entropy the particles acquire as the temperature is raised.

7. Conclusions

The work reported here shows that the stability of a colloidal dispersion, such as a water-based paint or coating, can be understood as arising from the competition between the reduction in entropy when the polymer layers that coat the pigments come close to each other, and the monomer interactions of the polymer chains when compressed. This compression gives rise to three-body repulsive interactions, which in turn make the dispersion more stable. It was shown also how one can control certain parameters to improve the stability of the dispersion, such as the thickness of the polymer layer, the degree of polymerization of the grafted chains, the solvent quality, and the pigment surface coating. Molecular dynamics computer simulations proved to be a useful tool, not only for the prediction of conditions of colloidal stability but also as a guide to choose and control variables to yield a desired condition. Additionally, molecular dynamics simulations are essentially exact [10], which means that their predictions can go beyond mean-field theory.

Lastly, it was shown that an order-disorder phase transition occurs in the model fluid under consideration, which can turn a stable dispersion into an unstable one when relatively small changes in external conditions such as the hydrostatic pressure (which changes the pigment concentration) take place. Implementing the model presented here is straightforward and the molecular simulations required can be performed on a modern laptop in a relatively small amount of time, yielding useful guidelines before embarking on expensive laboratory tests, with minimal information required beforehand, such as knowledge of the appropriate Hamaker constants, for example. This work is a stepping-stone towards the construction of more sophisticated models for the stability of paints and coatings.

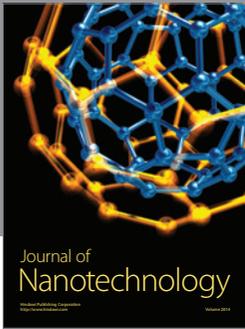
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