Scaling Properties in the Adsorption of Ionic Polymeric Surfactants on Generic Nanoparticles of Metallic Oxides by Mesoscopic Simulation

Estela Mayoral and Eduardo Nahmad-Achar

Abstract We study the scaling of adsorption isotherms of polyacrylic dispersants on generic surfaces of metallic oxides *XnOm* as a function of the number of monomeric units, using Electrostatic Dissipative Particle Dynamics simulations. The simulations show how the scaling properties in these systems emerge and how the isotherms rescale to a universal curve, reproducing reported experimental results. The critical exponent for these systems is also obtained, in perfect agreement with the scaling theory of de Gennes. Some important applications are mentioned.

1 Introduction

Polyelectrolyte solutions have properties quite different from those observed in solutions of uncharged polymers, and their behaviour is less well known (de Gennes 1976; Odijk 1979; Dobrynin et al. 1995). In particular, the scaling of some quantities could present a different behaviour and so atypical scaling exponents could be found. In most cases, the statistical properties of these interesting systems cannot be obtained analytically because of the long-range Coulombic repulsion produced by the presence of small mobile counterions in the bulk, which interact both with the charge in the polymer and with one another. The use of simulation methodologies have shown, however, to be a promising tool in the study of very complex systems (Fermeglia and Pricl 2007).

E. Mayoral (✉)
Departamento de Física, Instituto Nacional de Investigaciones Nucleares, ININ, Km. 36.5,
Carretera México-Toluca, 52750 La Marquesa , Estado de México, Mexico
e-mail: estela.mayoral@inin.gob.mx

E. Nahmad-Achar
Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, UNAM,
Apartado Postal 70-543, 04510 México D. F., Mexico
e-mail: nahmad@nucleares.unam.mx

L. Di G. Sigalotti et al. (eds.), *Computational and Experimental Fluid Mechanics with Applications to Physics, Engineering and the Environment*, Environmental Science and Engineering,
DOI:10.1007/978-3-319-00191-3_30,

In our case of study, the presence of big charged molecules (such as polymers) and small ones (like counterions and solvents) involving different length and time scales, makes an electrostatic mesoscopic approach a good alternative. One of these mesoscopic approaches is *Dissipative Particle Dynamics* (DPD), which is a Langevin dynamics approximation where the fluid is represented by virtual interacting particles through three forces: conservative, random, and dissipative. The conservative force includes repulsive and electrostatic interactions, and determines the equilibrium state of the system, whereas the dissipative and random forces act as a thermostat and allow transport properties, preserving the thermodynamic equilibrium. The electrostatic interactions in DPD simulations were first incorporated by Groot (2003), who solved the electrostatic field locally on a lattice. An alternative way to solve the electrostatic problem in DPD was developed later on by González-Melchor et al. (2006), where the calculation of the electrostatic interactions employs the standard Ewald sum method and, in order to prevent the artificial ionic pair formation, charge distributions are included on the DPD particles.

In this work, we study using electrostatic mesoscopic dissipative particle dynamics simulations, the adsorption of dispersants onto pigments and show the resulting density profiles, the adsorption isotherms, and their scaling properties.

2 Mesoscopic Approach

One of the main problems in many industrial and academic areas is that the systems of interest are often constituted by many particles of different length scales, interacting in different time scales. In order to simplify the study of these systems, in the early 1990 s Hoogerbrugge and Koelman (1992) introduced a mesoscopic simulation technique. This is known as Dissipative Particle Dynamics (DPD) and is a coarse-graining approach, which consists of representing complex molecules as soft spherical beads interacting through a simple pair-wise potential, and thermally equilibrated through hydrodynamics (Groot and Warren 1997). In this formalism, the beads obey Newton's equations of motion

$$\frac{d\boldsymbol{r}_i}{dt} = \boldsymbol{v}_i, \qquad \frac{d\boldsymbol{v}_i}{dt} = \boldsymbol{f}_i, \tag{1}$$

where $\boldsymbol{r}_i$ and $\boldsymbol{v}_i$ are the position and the velocity of the ith particle, respectively, and the force $\boldsymbol{f}_i$ is given by three components:

$$\boldsymbol{f}_i = \sum_j \left(\boldsymbol{f}^C{}_{ij} + \boldsymbol{f}^D{}_{ij} + \boldsymbol{f}^R{}_{ij} \right), \tag{2}$$

corresponding to the conservative, dissipative, and random contributions, respectively. The sum runs over all neighbouring particles within a certain distance R_c. The conservative force $\boldsymbol{f}^C$ derives from a soft interaction potential and there is no hard-core divergence as in the case of a Lennard-Jones potential, thus providing a more efficient scheme of integration; it has the form

$$\boldsymbol{f}^{C}{}_{ij} = a_{ij}\,\omega^{C}(\boldsymbol{r}_{ij})\,\frac{\boldsymbol{r}_{ij}}{|\boldsymbol{r}_{ij}|}\,. \tag{3}$$

When we need to introduce a more complex molecule, such as a polymer, we use beads joined by springs, so we also have an extra spring force given by $\boldsymbol{f}^{S}{}_{ij} = k\,\boldsymbol{r}_{ij}$ if i is connected to j. The dissipative $\boldsymbol{f}^{D}$ and random $\boldsymbol{f}^{R}$ standard DPD forces are given by

$$\boldsymbol{f}^{D}_{ij} = -\gamma\,\omega^{D}(\boldsymbol{r}_{ij})\,\frac{(\boldsymbol{r}_{ij}\cdot\boldsymbol{v}_{ij})\,\boldsymbol{r}_{ij}}{|\boldsymbol{r}_{ij}|^{2}}, \tag{4}$$

and

$$\boldsymbol{f}^{R}{}_{ij} = -\sigma\,\omega^{R}(\boldsymbol{r}_{ij})\,\frac{\theta_{ij}}{\delta_t^{1/2}}\,\frac{\boldsymbol{r}_{ij}}{|\boldsymbol{r}_{ij}|}\,. \tag{5}$$

Here, δ_t is the time step, $\boldsymbol{v}_{ij} = \boldsymbol{v}_i - \boldsymbol{v}_j$ is the relative particle velocity, θ_{ij} is a random Gaussian number with zero mean and unit variance, γ and σ are the dissipation and noise strengths, respectively, while $\omega^{C}(\boldsymbol{r}_{ij}),\ \omega^{D}(\boldsymbol{r}_{ij})$, and $\omega^{R}(\boldsymbol{r}_{ij})$ are dimensionless weight functions. Not all these quantities are independent: some of them are related through the fluctuation-dissipation theorem (Español and Warren 1995) by $\gamma = \sigma^2/2\kappa_B T$ and $\omega^{D}(\boldsymbol{r}_{ij}) = [\omega^{R}(\boldsymbol{r}_{ij})]^{1/2}$, with κ_B being the Boltzmann constant and T the temperature.

The methodology used in our mesoscopic simulations and, specifically, the electrostatic DPD methodology, is briefly described in the following subsection.

2.1 Mesoscopic Simulation: Electrostatic Dissipative Particle Dynamics

We consider in our study an ionic polymeric dispersant, for example polyacrylic acid (*PAA*) or a salt derived from it, in water and in the presence of substrate particles which we assume to be metallic oxides, such as TiO_2, Al_2O_3, CeO_2, etc. We map the polymer chain into beads which we call *DPD beads* as shown by the label *A*—in Fig. 1. Each DPD bead has a volume $v_{DPD} = 90$ Å^3 and radius $r_{DPD} = 2.78$ Å, which correspond to the volume of three water molecules. We can represent a *PAA* chain by N_{DPD} beads of carboxylate monomeric units joined by springs with some spring constant k. In this case $N_{DPD} = v_{mon}N/v_{DPD}$, where v_{mon} is the volume of a carboxylate monomeric unit and N is the number of monomeric units in the chain.

As was mentioned in the Introduction, here we replace the point charge at the centre of the DPD particle by a charge distribution throughout the particle. This is in order to avoid the formation of artificial clusters from oppositely charged ions. Groot (2003) solved the problem by calculating the electrostatic field on a grid.

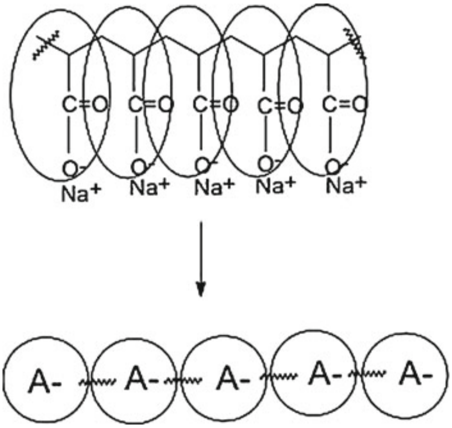

Fig. 1 Mesoscopic identification for a polyelectrolyte such as the sodium salt of *PAA*

The algorithm is known as the particle-particle-particle mesh (PPPM) algorithm. In González-Melchor et al. (2006), we solved this problem by combining the standard method with charge distributions on particles, adapting the standard Ewald method to DPD particles. In the present work, we use the latter method because the Ewald sum technique is the most employed route to calculate electrostatic interactions in microscopic molecular simulations. We take, as in González-Melchor et al. (2006)

$$\omega^C(r) = \omega^R(r) = \omega^D(r)^{1/2} = \omega(r), \tag{6}$$

with

$$\omega(r) = \begin{cases} 1 - r/R_c & : \quad r \le R_c, \\ 0 & : \quad r > R_c, \end{cases} \tag{7}$$

where R_c is the cut-off distance, here assumed to be 6.46 Å (the simulation characteristic length). We also take $\sigma = 3\,\mathrm{kg\,m\,s^{-3/2}}$. We represent the PAA^{N-} with N DPD beads, each one having $v_{mon} = 90$ Å^3 and bonded by a spring with $k = 100$. The Na^+ ions were simulated by one DPD bead each with charge 1^+, and three water molecules per neutral DPD particle. These values reproduce the isothermic compressibility of water in standard conditions. All other quantities, including k, are dimensionless quantities given in reduced units. This is accomplished as follows: since we keep $T = const$ in our simulations, we may take $\kappa_B T = 1$ as the unit of energy; the distance r is measured in units of R_c, i.e., $r^* = r/R_c$; the force has therefore no units as $[E]/[r^*] = [1]$, and neither does k; the density is given as the number of molecules per unit volume and has no units, and the *mass* does not ever enter into the model. Since the force is dimensionless so is the time. The integration time step is taken to be $\Delta t^* = 0.02$ and the total average density is $\rho^* = 3$ (i.e., three water molecules per DPD particle; one may also see that it has the unit of mass as being defined by the mass of a DPD particle with three water molecules).

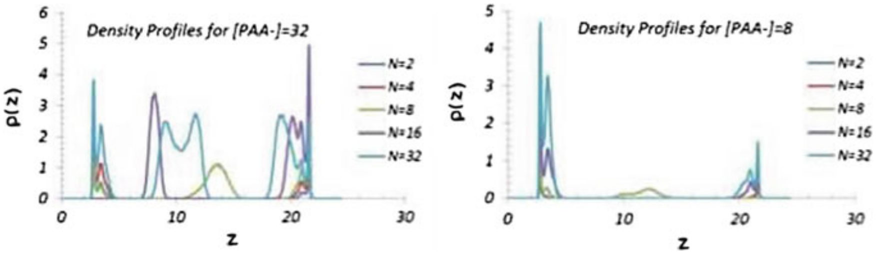

Fig. 2 Density profiles for $[PAA] = 32$ (*left*) and 8 (*right*)

3 Results and Discussion

3.1 Results for Adsorption Isotherms

The DPD electrostatic simulations were performed using our mesoscopic model as described in the last section, in order to obtain the adsorption isotherms for $[PAA^{N-}][Na^{+}]_N$ on generic surfaces of metallic oxides $XnOm$ at a basic pH. The length of the *PAA*-DPD molecule was varied as $N = 2, 4, 8, 16$, and 32 DPD particle units. The repulsive constants a_{ij} in the DPD model were set to $a_{W-PAA^-} = 100$, $a_{W-Na^+} = 100$, $a_{W-H_2O} = 100$, $a_{H_2O-PAA^-} = 82$, $a_{H_2O-Na^+} = 25$, and $a_{PAA^- -Na^+} = 25$. These values can be obtained from solubility parameters, and a more refined calculation can be made by using activity coefficients (cf. Mayoral and Nahmad-Achar 2012).

The resulting density profiles $\rho(z)$, describing the spatial organization of the molecules as a function of one of the spatial coordinates, are shown in Fig. 2 for two different concentrations of the polyelectrolyte, namely $[PAA] = 32$ and $[PAA] = 8$. They show that larger molecules tend to adsorb at the edges of the box (which represent the metallic substrate), and remain less in the aqueous medium (in between the box walls), where smaller molecules can be found.

To obtain the adsorption isotherms we calculate the amount of polyelectrolyte Γ carried by the particle, by integrating the density profile according to

$$\Gamma = \int_0^{L_z} [\rho(z) - \rho_{bulk}]\, dz, \tag{8}$$

where L_z is the width of the first adsorbed layer and ρ_{bulk} the bulk density. Figure 3 shows the number Γ_{mol} of *PAA*-molecules adsorbed on a TiO_2 surface *vs.* the number Γ^b_{mol} of non-adsorbed molecules, by considering a single adsorbed layer. As expected, the saturation on the surface is reached earlier for larger molecules.

However, we may easily renormalize these curves by plotting the number of independently adsorbed DPD beads Γ_{DPD} *vs.* non-adsorbed DPD beads Γ^b_{DPD}, using $N\, \Gamma_{mol} = \Gamma_{DPD}$. The behaviour will then be that of a universal isotherm conformed

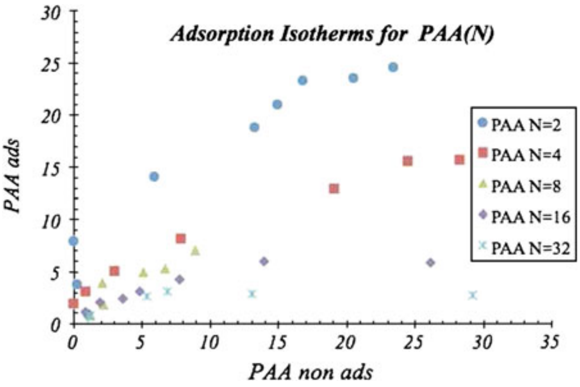

Fig. 3 Adsorption isotherms for *PAA* on a TiO_2 surface for different *N*

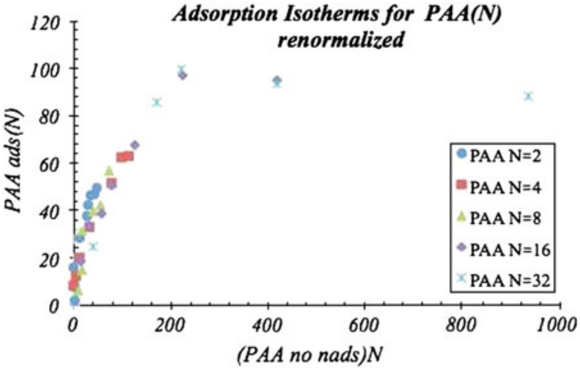

Fig. 4 Universal adsorption isotherm for *PAA* on a TiO_2 surface, renormalized

by the contribution of all sizes, as shown in Fig. 4. Assuming that only one layer is adsorbed on the surface (the self similar region) and that all adsorption positions are equivalent, we can extract the maximum concentration at equilibrium and the adsorption-desorption constant for each isotherm, which is given by the Langmuir isotherm. The dynamic equilibrium is given by $A+N \Leftrightarrow AN$ with velocity constants K_a for the adsorption and K_d for the desorption. The expression for this kind of adsorption model, in the case of *neutral* species, is given by the Langmuir isotherm expressed by

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_M} + \frac{1}{\Gamma_M K C}, \tag{9}$$

where $K = K_a/K_d$ and C is the concentration in the bulk (Γ^b). Γ is the adsorbed quantity and Γ_M is the maximum adsorbed quantity. The linear fit for this isotherm is shown in Fig. 5, and is given by $1/\Gamma_M = 0.0094$ and $1/(\Gamma_M K) = 0.5432$, from which $\Gamma_M = 106.38\, PAA_{DPD}$ and $K = 0.0173$.

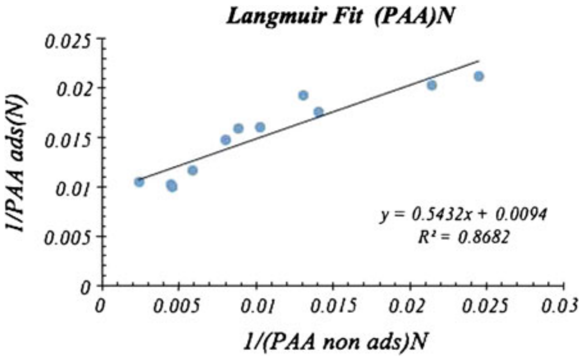

Fig. 5 Langmuir fit for the adsorption isotherms of *PAA* on TiO_2

Table 1 Scaling for Γ_{max} as a function of N

$\ln N$	$\ln \Gamma_{max}$
0.6931	3.3077
1.3863	2.8134
2.0794	2.4581
2.7726	1.5626
3.4657	1.1907

3.2 Scaling for Γ_{max}

In the light of these results, it is interesting to study the behaviour of Γ_{max} with N. We can do this, once more, via DPD electrostatic simulations. Γ_{max} is obtained by fitting each isotherm in Fig. 3 with the Langmuir model, which we have shown to be adequate (*vide supra*). Table 1 shows the results for the fit in each case. When we plot Γ_{max} *versus* N we obtain the behaviour shown in Fig. 6 and the scaling function is $\Gamma_{max} \propto N^{-0.79} \simeq N^{-4/5}$. This result is in perfect agreement with de Gennes et al. (1976).

The scaling theory in the weak adsorption regime indicates that in the flat plateau, i.e., at maximum saturation

$$\gamma_p \sim N^{1/5}, \tag{10}$$

where γ_p is the number of monomers adsorbed in the flat plateau, $\gamma_p = \Gamma_{max} N$. Equation (10) then implies $\Gamma_{max} \sim N^{-4/5} = N^{-0.8}$, which agrees very well with our result. It is interesting that the renormalized behaviour adjusts itself to the scaling model in the weak adsorption regime, *even though we are dealing here with charged molecules*.

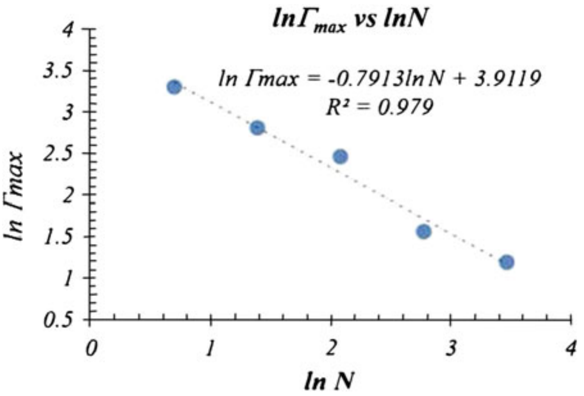

Fig. 6 Scaling of Γ_{max} with N

4 A Simple Application to Colloid Stability

Since *PAA* and its salt derivatives tend to be very hydrophilic, the adsorbed segments will see the substrate as a flat surface when in a good solvent. If R is the effective radius of the substrate particle and $R_g = a_f N^{\nu}$ is the radius of gyration of the polymer chain, with ${a_f}^3$ proportional to the Flory volume, the flat surface regime is given, according to the *loops and tails* model, by $R > a_f\, N^{3/5}$ (Aubouy et al. 1993; Aubouy and Raphaël 1998). Lately, and in order to improve the performance properties of coatings, CeO_2 and Al_2O_3 nanoparticles have been used in their formulations (Mayoral et al. 2012). For these we have $R_{CeO_2} \simeq 10\,\text{nm}$ and $R_{Al_2O_3} \simeq 20\,\text{nm}$ which would give, for *PAA* and its salt derivatives, $N < 400$ ($Mw < 40{,}000$ gr/mol) for CeO_2 and $N < 1{,}250$ ($Mw < 125{,}000$ gr/mol) for Al_2O_3. This accommodates even the higher molecular weight dispersants, so that a flat substrate approximation is appropriate in our mesoscopic approach.

Let us consider a small particle of diameter $d_1 = 2r_1$ and area a_1, and a larger particle with diameter $d_2 = 2r_2 > d_1$ and area $a_2 > a_1$, to be stabilized in an aqueous medium. We know from the previous section that the number of monomers adsorbed in the flat plateau is $\gamma_p = \Gamma_{max} N$, with these quantities scaling as $\gamma_p \sim N^{1/5}$ and $\Gamma_{max} \sim N^{-4/5}$.

Γ_{max} is the number of chains of size N per unit area needed in order to cover satisfactorily some amount, say 1 mol, of material. If we want to cover a surface of area a_1, then $c = a_1 \Gamma_{max,1}$ chains are needed. Now suppose that the weight of one monomeric unit is 1 unit of mass, then $a_1 \Gamma_{max,1}[chains] = a_1 \Gamma_{max,1} N_1 = a_1 \gamma_{p,1}$ and for the same amount of material but with area a_2, we will require $a_2 \Gamma_{max,2}[chains] = a_2 \gamma_{p,2}$. If κ is the amount of mass needed to cover the surface of particles of diameter $2r_1$ divided by the mass of dispersant necessary to cover the surface of particles of diameter $2r_2$, then

$$\kappa = a_1\gamma_{p,1}/a_2\gamma_{p,2} = (a_1 N_1^{1/5})/(a_2 N_2^{1/5}), \tag{11}$$

or

$$\kappa = (r_2/r_1)\,(N_1/N_2)^{1/5}. \tag{12}$$

We can make use of this expression to analyze two interesting cases:

Case 1. If we want to use the same amount of dispersant, taking dispersants with different lengths N_1 and N_2 and having the same chemistry, $\kappa = 1$ and $1 = (r_1/r_2)\,(N_1/N_2)^{1/5}$, that is $N_1 = (r_1/r_2)^5 N_2$. We would then need a dispersant with a very small degree of polymerization compared with N_2 for $r_1 << r_2$. In this case the smallest and the best dispersant will be $N_1 = 1$ (monomeric dispersant), in agreement with the results of Goicochea et al. (2009). If, on the other hand, $(r_1/r_2)^5 << 1$, a change in the chemistry of the dispersant would be a better option.

Case 2. In the limit of a flat approximation, we can consider $N = (R/a_f)^{5/3}$ and have $\kappa = (r_2/r_1)\,[(r_1/r_2)^{5/3}]^{1/5} = (r_2/r_1)^{2/3}$. For Al_2O_3 nanoparticles as compared to ordinary TiO_2 particles used in coatings, for example, we have $R_{TiO_2} \simeq 125\,\text{nm}$ and $R_{Al_2O_3} \simeq 20\,\text{nm}$, and so $\kappa = (125/20)^{2/3} = 3.3993$. Comparing this result to an estimation based on purely geometric arguments (Mayoral et al. 2012), where 6.25 times the dispersant amount was needed for Al_2O_3-nanoparticles, we observe that by choosing a dispersant with an adequate length N we would need a much smaller quantity.

5 Conclusions

Langmuir isotherms were calculated for polyacrylate dispersants adsorbed on metallic oxides, while their scaling properties as a function of the number of monomeric dispersant units were obtained via DPD-simulations. The critical exponent for the renormalized isotherms was obtained, and this agrees perfectly well with the scaling theory of de Gennes et al. (1976), even though polyelectrolytes are being considered.

The results presented here suggest a methodology for estimating the amount of dispersant necessary in different scenarios and for a better choice of the appropriate dispersants. The particular case of the stabilization of metallic nanoparticles is interesting, as their inclusion in many formulations to improve performance properties is presently a major area of research. Problems arise because the dimensions of the nanoparticles and polymeric dispersants are similar, and because of the large total surface area to be covered. However, excessive amounts of any surfactant will cause the property degradation of the material, and new especially designed surfactants circumvent the need for large quantities. Here it was shown that our simulation results improve upon the experimental values obtained by Mayoral et al. (2012).

Acknowledgments This work was partially supported by DGAPA-UNAM (under project IN102811). Valuable support in computing resources was obtained from DGTIC-UNAM.

References

Aubouy M, di Meglio J, Raphaël E (1993) Irreversible adsorption of a polymer melt on a colloidal particle. Europhys Lett 24:87–92

Aubouy M, Raphaël E (1998) Scaling description of a colloidal particle clothed with polymers. Macromolecules 31:4357–4363

Dobrynin AV, Colby RH, Rubinstein M (1995) Scaling theory of polyelectrolyte solutions. Macromoleules 28:1859–1871

Español P, Warren PB (1995) Statistical mechanics of dissipative particle dynamics. Europhys Lett 30:191–196

Fermeglia M, Pricl S (2007) Multiscale modeling for polymer systems of industrial interest. Prog Org Coat 58:187–199

de Gennes PG, Pincus P, Velasco RM, Brochard F (1976) Remarks on polyelectrolyte conformation. Journal de Physique 37:1461–1473

de Gennes PG (1976) Scaling theory of polymer adsorption. Le Journal de Physique 37:1445–1452

Goicochea AG, Nahmad-Achar E, Pérez E (2009) Colloidal stability dependence on polymer adsorption through disjoining pressure isotherms. Langmuir 25:3529–3537

González-Melchor M, Mayoral E, Velázquez ME, Alejandre J (2006) Electrostatic interactions in dissipative particle dynamics using Ewald sums. J Chem Phys 125:224107

Groot RD, Warren PB (1997) Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. J Chem Phys 107:4423–4435

Groot RD (2003) Electrostatic interactions in dissipative particle dynamics–simulation of polyelectrolytes and anionic surfactants. J Chem Phys 118:11265

Hoogerbrugge PJ, Koelman JMVA (1992) Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics. Europhys Lett 19:155–160

Mayoral E, Nahmad-Achar E (2012) Study of interfacial tension between an organic solvent and aqueous electrolyte solutions using electrostatic dissipative particle dynamics simulations. J Chem Phys 137:194701

Mayoral E, Nahmad-Achar E, Rodriguez J (2012) Diameter rules demand: nanoparticle dispersant adsorption and effects evaluated. Eur Coat J 12(2012):84–88

Odijk T (1979) Possible scaling relations for semidilute polyelectro-lytesolution. Macromolecules 12:688–693