SUPPORTING INFORMATION

Electrodynamics of soft multilayered particles dispersions: Dielectric permittivity and dynamic mobility.

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Impact of the particle volume fraction on the dielectric permittivity and dynamic mobility

The dependence of the dielectric increment $\Delta\varepsilon'(\omega)$ on frequency $\omega/2\pi$ is displayed in Figure S1A for various values of particle volume fractions ϕ while keeping the hard core radius a constant. The variation of ϕ is performed under the condition $a + d_1 + d_2 + \kappa^{-1} < b$ in order to avoid the overlapping of polymeric segments and electric double layers of two neighboring particles. All the other parameters are fixed and are reported in the caption of Figure S1. Figure S1B represents the corresponding variations of the dielectric loss $\varepsilon''(\omega)$. Let us first consider the low frequency regime, *i.e.* $\omega/2\pi < 10^3$ s^{-1}. $\Delta\varepsilon'(\omega)$ increases with increasing ϕ from 0.01 to 0.2 and then decreases upon further increase of ϕ from 0.2 to 0.5. In order to understand the mechanism responsible for this apparent non-monotonous variation of $\Delta\varepsilon'(\omega)$ with ϕ, we report in Figure S1C the quantity $\Delta\varepsilon'(\omega \to 0)$ as a function of ϕ. For very diluted dispersions of particles ($\phi << 1$), a permittivity closed to 0 is obtained, as expected. In this situation, the dispersion contains a large amount of medium compared to that of solids. As a result, the α-relaxation process taking place around the few particles in the solution does not significantly impacts the overall dielectric response of the suspension. $\Delta\varepsilon'(\omega \to 0)$ then increases with increasing ϕ up to a critical value ($\phi = 0.2$) and drastically drops upon further increase of ϕ. The initial increase in the magnitude of $\Delta\varepsilon'(\omega \to 0)$ is simply due to the increasing amount of fixed charges in the dispersion. The drop in the magnitude of

$\Delta\varepsilon'(\omega \to 0)$ observed for large ϕ has been discussed in detail in previous work.[1, 2] As explained in the main text, the α–relaxation results from the establishment of an accumulation of neutral electrolyte on one side of the particle and a depletion of neutral electrolyte on the other side. For sufficiently large ϕ (in our case $\phi > 0.2$), the α–relaxation is reduced by the overlap of polarization regions of adjacent particles. Now consider frequencies $\omega/2\pi > \omega_{MW}/2\pi \approx 3.10^7$ s^{-1}. $\Delta\varepsilon'(\omega)$ decreases upon increase of ϕ. At such high frequencies, ions do not have time to migrate/diffuse in response to the applied electric field. The polarization is then mainly governed by the mismatch between permittivity of the dispersing medium ($\varepsilon_r = 78.4$) and that of the hard core of the particle ($\varepsilon_p = 2$). Because ε_p is much smaller than ε_r, the dielectric permittivity decreases with increasing ϕ.

From Figure S1A and B, it is shown that ω_α increases upon increase of ϕ. Let us comment on this. In the situation of diluted dispersions, the establishment of a concentration gradient leads to the diffusion of counterions from one side of the particle to the other with a the characteristic diffusion length. With increasing ϕ, the distance between two neighboring particles is reduced and becomes lower than a. The counterions then diffuse from one particle to the other and the characteristic diffusion length of that process decreases with increasing ϕ. The smaller this characteristic length, the larger is ω_α.

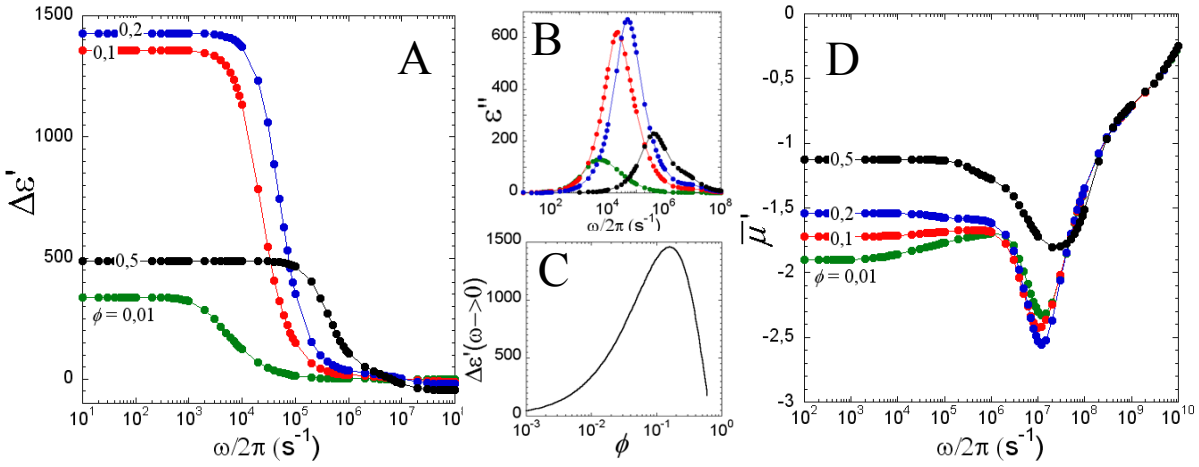

Figure S1. Variations of dielectric increment $\Delta\varepsilon'$ (panel A) and dielectric loss ε'' (panel B) as a function of field frequency $\omega/2\pi$ for various particle volume fractions ϕ (indicated). (Panel C) Variations of the magnitude of $\Delta\varepsilon'(\omega \to 0)$ as a function of ϕ. (Panel D) Variations of dimensionless dynamic mobility $\overline{\mu}'$ as a function of $\omega/2\pi$ for various ϕ (indicated). Other parameters if not indicated in Table 1 (main text): $c^* = 1$mM ; $\lambda_2^0 d_2 = 1$; $\beta_1 = \beta_1^H = 5$; ρ_2^0 / F =-10mM ; d_1 =20nm ; d_2 =5nm ; a =300nm ; $\alpha_1 = \alpha_2 \to 0$; z =1 .

Note that ω_{MWO} does not depend on ϕ. Indeed, the Debye length κ^{-1}, *i.e.* the characteristic length scale defining the MWO relaxation frequency, remains constant upon increase of ϕ (we excluded the overlapping of the electric double layers of neighboring particles).

The counterparts of Figure S1A for the dynamic mobility are given in Figure S1D. Figure S1D shows a decrease in magnitude of $\overline{\mu}'(\omega)$ and a slight increase in the characteristic frequency of inertial relaxation with increasing ϕ. This negative contribution results from increasing particle – particle hydrodynamic interactions that tend to hinder the motion of the particles.

Verification of the outcome of the numerical code presented in this work

In the limiting case where there is only one homogeneous polymeric layer surrounding the particle core surface, we tested our numerical results with those obtained by Ahualli *et al.*[1] For the sake of illustration, Figure S2 displays the dependence of the dielectric permittivity ε' and dielectric loss ε'' on frequency $\omega/2\pi$ as obtained from our numerical procedure under the conditions adopted in Figure 11 in reference [1]. Our results quantitatively agree with those obtained by Ahualli *et al*.

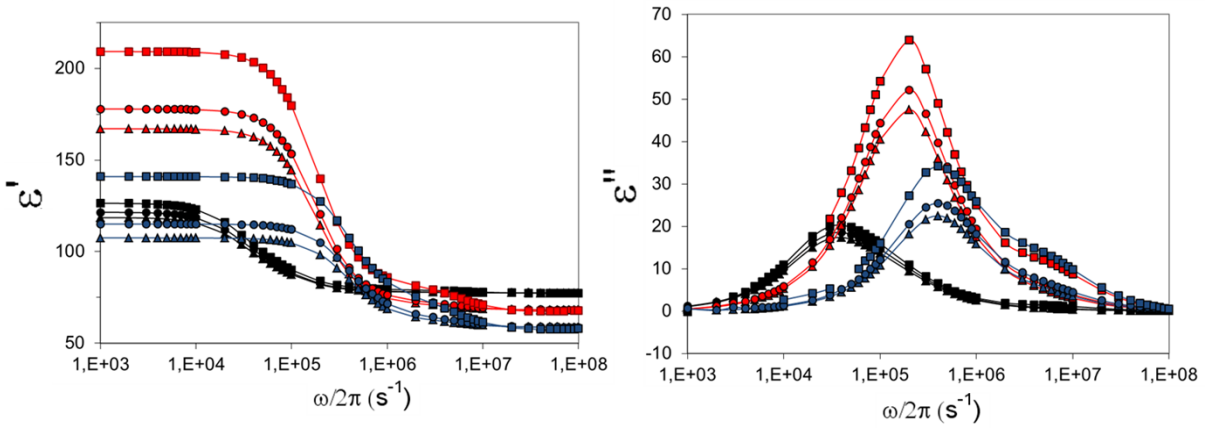

Figure S2. Variations of dielectric permittivity ε' and dielectric loss ε'' as a function of field frequency $\omega/2\pi$ for various particle volume fractions ϕ = 0.01 (black), ϕ = 0.1 (red), ϕ = 0.2 (blue) and various friction parameters $\lambda_1^0 a = 1$ (squares), $\lambda_1^0 a = 10$ (circles) and $\lambda_1^0 a = 1$ (triangles). The particles consist of a hard core covered by a unique homogeneous polymer layer. Other parameters: c^* = 1mM ; d_1=50nm ; a =100nm ; $\alpha_1 \to 0$; z =1, total charge of the hard core = 1.67 10^{-15}C ; total charge of the polymer layer = 1.4 10^{-15}C ; ε_p = 4.5, density ρ_p = 2200 kg m^{-3}.

Figures S3 and S4

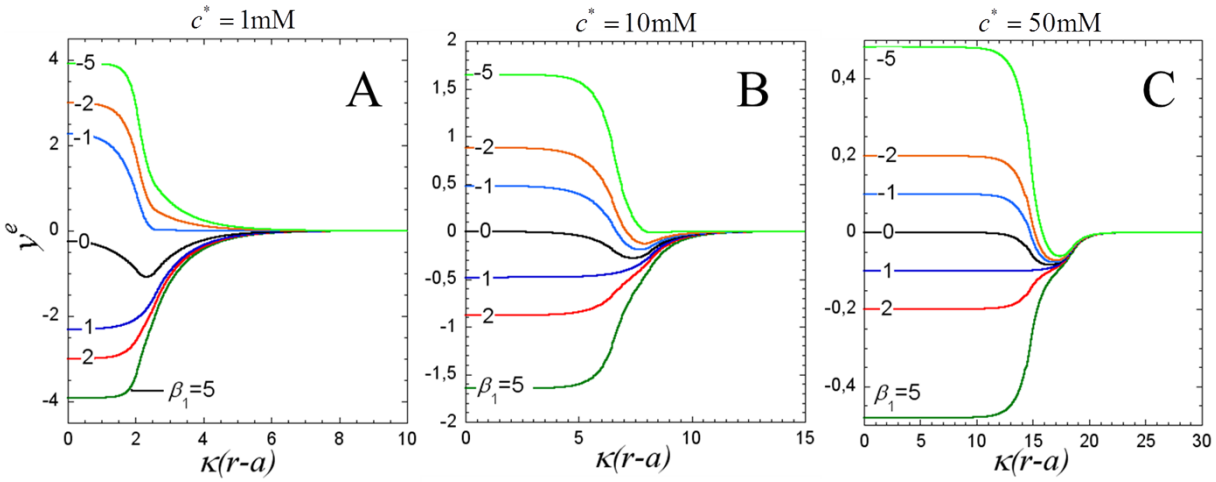

Figure S3. Dimensionless potential distribution from the core surface of the particle to the bulk solution under conditions of Figure 2 (main text) with various β_1 (indicated) and c^* = 1 mM (panel A), c^* = 10 mM (panel B) and c^* = 20 mM (panel C). The outer layer is marked by the bump observed in the situation $\beta_1 = 0$.

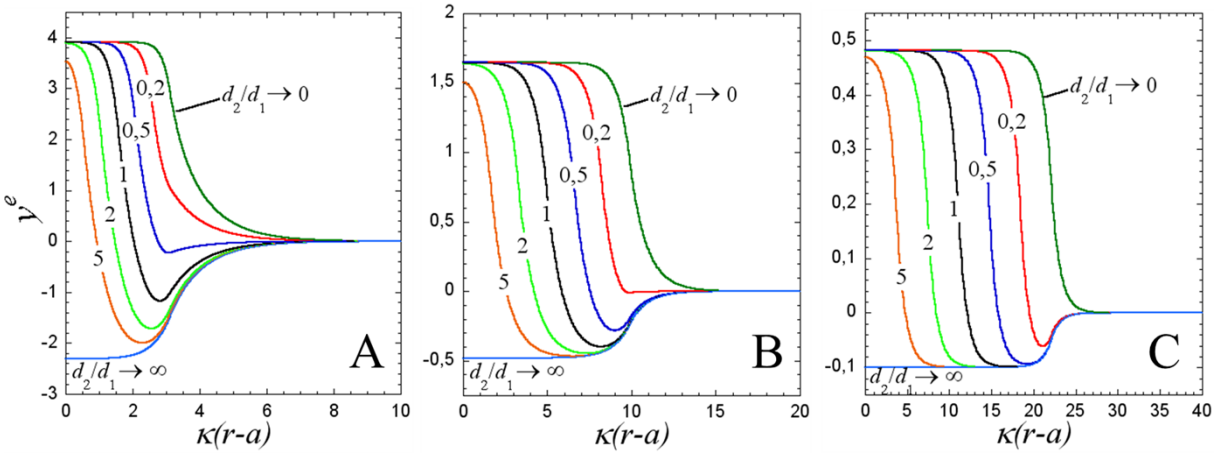

Figure S4. Dimensionless potential distribution from the core surface of the particle to the bulk solution under conditions of Figure 5 (main text) with various d_2 / d_1 (indicated) and c^* = 1 mM (panel A), c^* = 10 mM (panel B) and c^* = 20 mM (panel C).

References

1. S. Ahualli, M. L. Jiménez, F. Carrique and A. V. Delgado, *Langmuir*, 2009, 25, 1986-1997.
2. F. Carrique, *Journal of Chemical Physics*, 2003, 118, 1945-1956.