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# Field-induced clearing in sphere-sphere and rod-sphere binary mixtures of charged colloidal particles

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Binary mixtures of larger and smaller colloids having charges of equal sign display unusual response to low-frequency electric fields. We show here that the previously reported negative torque acting on rodlike particles when in presence of a sea of smaller particles is accompanied by a field-induced clearing of the suspension. Measurements of transmitted intensity performed on mixtures of large (dilute) and small (semidilute) spherical particles indicate that such a clearing effect is universal and due to an anisotropic $E^2$-dependent redistribution of the small spheres around the large ones. We interpret this behavior as resulting from $O(E^2)$ electro-osmotic flows whose magnitude is greatly enhanced by the presence of the small particles.

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The extremely rich behavior of charged colloidal particles in electric fields is rooted in the concurrence of a large variety of hydrodynamic, electrodynamic, and diffusive processes taking place at various time and length scales. Diverse and unexpected phenomena are frequently reported, such as those related to electro-osmotic effects in the proximity of surfaces [1,2] or those related to nonlinear electrokinetic response [3]. In this Rapid Communication we show the intimate relation of two counterintuitive field-induced effects observed in rod-sphere and sphere-sphere binary mixtures of charged colloids: the previously described negative electric torque acting on rods surrounded by smaller spheres [4] and the field-induced transparency in mixtures of larger and smaller spheres. Both phenomena are nonlinear in the electric field $E$ and depend on a field-induced redistribution of the small nanosized particles around the larger ones. The observations coherently combine with the basics of the so-called "standard electrokinetic model" [5] when extended with concepts of nonlinear electrokinetics [3,6,7].

About a decade ago, we have proposed the electric birefringence spectroscopy (EBS) of dispersions of nonspherical particles as a mean to directly access the frequency dependence of the electric polarizability of charged colloids [8]. In EBS we measure the dc component of the birefringence $\Delta n = n_{\parallel} - n_{\perp}$ as a function of the frequency $\nu$ of the ac field applied to the cell. $n_{\parallel}(n_{\perp})$ is the refractive index for light polarized along (perpendicularly) to $E$. $\Delta n$ reflects the stationary component of the orientational distribution of the particles and is proportional to the dc component of the torque $\sigma$ acting on them. The results are expressed through the Kerr coefficient $B(\nu) = \Delta n / \lambda E^2$, which embodies the notion that $\sigma(\nu)$ is, in the low-field regime here explored, proportional to $E^2$. For all experiments in this Rapid Communication, the wavelength of light $\lambda = 633$ nm. In previous papers [9,10], we showed that in the MHz, "Maxwell-Wagner," regime, where diffusive processes and hydrodynamic flows can be neglected, $\sigma$ is directly proportional to the real part of the anisotropy of the polarizability $\Delta\alpha' = \alpha'_a - \alpha'_b$, where $\alpha'_a$ and $\alpha'_b$ are the real part of the polarizability along the long and short particle axes, respectively. More complex has always appeared the behavior in the sub-MHz regime around the so-called "$\alpha$ relaxation" [5], wherein diffusion and convection cannot be neglected. We have recently observed, in this regime, intriguing and unexpected behavior of the torque when rodlike particles are immersed in a sea of smaller spherical particles charged of the same sign [4]. When in this environment, at frequencies below the inverse of the diffusive time of the smaller particles across

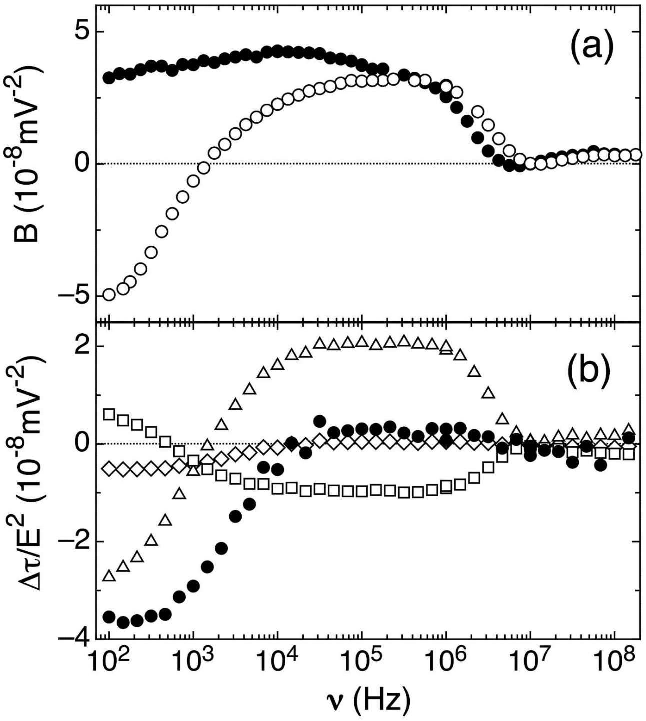

FIG. 1. (a) Kerr coefficient $B$ vs electric field frequency $\nu$. Full dots: PTFE. Empty dots: PTFE+P20 mixture. (b) Electric-field-induced turbidity variations $\Delta\tau/E^2$ vs $\nu$ in a PTFE+P20 mixture, measured for perpendicular polarization ($\tau_{\perp}$, squares) and for parallel polarization ($\tau_{\parallel}$, triangles). Diamonds: $\Delta\bar{\tau}/E^2$. Dots: $\Delta\bar{\tau}/E^2$ magnified seven times. For all data $\phi_{\mathrm{PTFE}} = 10^{-3}$, $\phi_{\mathrm{SP}} = 10^{-2}$, and ionic strength 0.5 mM KCl.

the larger ones, the torque becomes negative, favoring the alignment of the *short* axis of the particle along the field. This is shown in Fig. 1(a), where we plot $B(\nu)$ vs $\nu$ in a mixture of polytetrafluoroethylene (PTFE) rodlike particles (semiaxes 240 and 80 nm, volume fraction $\phi_{\mathrm{PTFE}}=10^{-3}$), either by itself or mixed with smaller, "secondary" particles (SPs), in this case polystyrene particles of radius $R=20$ nm (P20) and $\phi_{\mathrm{SP}}=10^{-2}$. As the frequency is decreased, $B(\nu)$ of the mixtures turns negative, indicating that the PTFE particles align preferentially perpendicular to $E$, a condition that cannot be explained in terms of coupling of electric dipoles [4], and should thus be interpreted in terms of other mechanisms.

To acquire better insight into the structure of the system, we have studied the effects of $E$ on the light scattering cross section of PTFE+SP dispersions. Specifically, through measurements of electric transmitted light intensity (ETLI), we have determined the optical turbidity $\tau$ via the extinction equation $I=I_0\exp(-\tau L)$ in solutions under the effect of an ac electric field. $I_0$ is the incident intensity, $L$ is the length of the cell, and $I$ is the dc component of the transmitted intensity while the field is applied. The polarization of the incident light is either parallel or perpendicular to $E$, yielding $\tau_\parallel$ and $\tau_\perp$. Both quantities are proportional to the total scattering cross section and depend on the optical polarizability of the particles and hence on their orientational distribution. This is shown in Fig. 1(b), where we plot the difference $\Delta\tau$ between $\tau_{\parallel,\perp}(\nu)$ and $\tau_0$, the turbidity in zero field. Since $\Delta\tau$ is found to be proportional to $E^2$ for both polarizations and all frequencies, we plot values normalized to $E^2$. The fact that $\tau_\perp > \tau_\parallel$ confirms the orientational anomaly at low frequency, with particles preferentially oriented perpendicular to $E$. However, the orientational behavior of PTFE does not account for the whole observed ETLI of mixtures. Indeed, from optical modeling we expect, for any cylindrically symmetric distribution of PTFE particles, $\bar{\tau}\equiv(\tau_\parallel+2\tau_\perp)/3\simeq\tau_0$, an equality perfectly verified in dilute PTFE dispersions. In the mixtures we instead find $\bar{\tau}(\nu)<\tau_0$, indicating an overall clearing of the dispersion. We find $\Delta\bar{\tau}=\bar{\tau}-\tau_0$ to be proportional to $\phi_{\mathrm{PTFE}}$ while showing a more complicated monotonically increasing dependence on $\phi_{\mathrm{SP}}$, a behavior analogous to what was previously found for $B(\nu)$ [4]. These findings indicate that a significant field induced redistribution of the spherical particles around each PTFE rods takes place in the same frequency range where the orientational anomaly is found, suggesting the two phenomena to be related. The characteristic frequency $\nu_{mix}\simeq 5$ kHz for these effects is quite low, about 30 times lower than the expected $\alpha$-relaxation frequency $\nu_\alpha$, the slowest electrokinetic effect for charged particles in simple electrolyte solutions. $\nu_\alpha$ marks the "concentration polarization," an accumulation and depletion of neutral electrolyte (counterions *and* coions) that asymmetrically affect the Debye length $\lambda_D$ and charge distribution on the two sides of the particle [5]. $\nu_\alpha\sim D/R^2$, where $R$ is the particle size and $D$ is a mean ionic diffusion coefficient depending on the diffusivity of both coions and counterions and dominated by the slowest of the two [11]. The value of $\nu_{mix}$ is instead compatible with $D_{\mathrm{SP}}/R^2$, i.e., to the diffusion time of the SP around a PTFE rod (here $R$ is the rod mean size). Could $\nu_{mix}$ indeed reflect a process analogous to the concentration polarization where the small negatively charged spheres act similarly to coions? To test this hypothesis and to seek a generalization of the observed phenomena, we performed experiments in mixtures of large and small spheres.

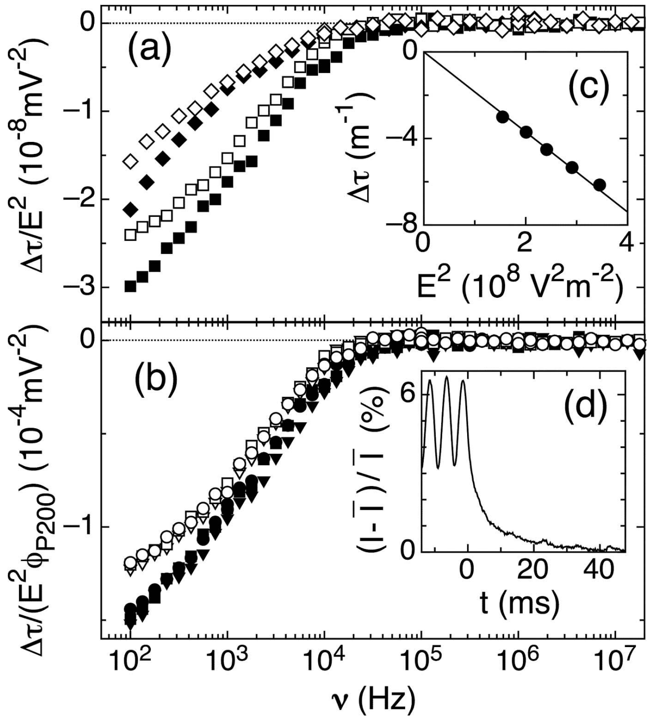

FIG. 2. [(a) and (b)] Field-induced clearing coefficient (a) $\Delta\tau/E^2$ and (b) $\Delta\tau/(E^2\phi_{\mathrm{P200}})$ vs electric field frequency $\nu$ in mixtures of large and small spheres. Full (empty) symbols indicate perpendicular (parallel) polarization. In (a) P200+P20 (diamonds), P200+P30 (squares), and $\phi_{\mathrm{P200}}=2\times10^{-4}$. In (b) P200+P30 mixtures with various $\phi_{\mathrm{P200}}$. $\phi_{\mathrm{P200}}=3\times10^{-4}$ (dots), $\phi_{\mathrm{P200}}=2\times10^{-4}$ (squares), and $\phi_{\mathrm{P200}}=10^{-4}$ (triangles). (c) Turbidity variation $\Delta\tau$ vs $E^2$ for a P200+P30 mixture. (d) Relative variation in the transmitted intensity $I$ for a mixture of P200+P30. $\bar{I}$ indicates the value of $I$ when no field is applied. $E=24$ V mm$^{-1}$ for $t<0$, while $E=0$ for $t>0$. In (c) and (d) $\nu=100$ Hz and $\phi_{\mathrm{P200}}=2\times10^{-4}$. In all panels $\phi_{\mathrm{SP}}=10^{-2}$.

Figure 2 shows ETLI measurements in mixtures of polystyrene spheres of dilute 200 nm radius particles (P200) and either P20 or P30 ($R=30$ nm). Remarkably, even in this case, we find a counterintuitive field-induced clearing, which is observed for both polarizations ($\tau_{\parallel,\perp}<\tau_0$), at frequencies $\nu<\nu_{mix}\simeq 3-5$ kHz. Since the effect is proportional to $E^2$ [see Fig. 2(c)], in the figure we plot the field-induced clearing coefficient $\Delta\tau/E^2$. The clearing is anisotropic, being $\tau_\perp<\tau_\parallel$. Both $\tau_\parallel(\nu)$ and $\tau_\perp(\nu)$ scale proportionally to $\phi_{\mathrm{P200}}$ [see Fig. 2(b)], while the $\phi_{\mathrm{SP}}$ dependence appears more complex.

The observation of a clearing effect in mixtures of spheres, where no orientational effect is possible, unequivocally indicates that the application of low-frequency electric fields induce repulsive interactions between P200 and SP and thus a depletion layer of SP around the P200. Indeed, in the frame of the virial expansion of the equation of state of binary colloidal dispersions [12], the decrease in the scattered intensity implies, in our condition, a negative (repulsive)

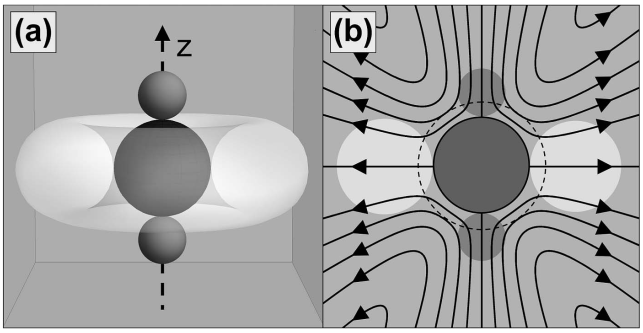

FIG. 3. $O(E^2)$ perturbations around a P200: (a) diagram of $\delta\phi_2$ used to quantitatively match the scattering data in Fig. 2(b) for $\nu = 100$ Hz and $E = 15$ V mm$^{-1}$. $\delta\phi_2$ is positive within two spherical volumes of radius 100 nm symmetric along $E$ and negative within an equatorial toroidal region having section equal to that of the P200. Gray levels indicate the resulting refractive index $n$: toroid ($n = 1.335$), background ($n = 1.336$), enhanced spherical volumes ($n = 1.337$), and P200 ($n = 1.59$). (b) $O(E^2)$ solvent flows around the P200 drawn according to the equations in Refs. [13,14]. The dashed line qualitatively indicates the SP exclusion shell.

P200-SP cross term. The data also indicate that such interaction, and hence the depletion layer, is anisotropic. The shape of the SP depletion layer can be quantified by analyzing the data in Fig. 2 to determine $\phi_{SP}(\mathbf{r})$, the local value of $\phi_{SP}$ at a distance $\mathbf{r}$ from the center of each P200. By symmetry we expect $\phi_{SP}(\mathbf{r},E) = \phi_{SP}(E=0) + \delta\phi_1(\mathbf{r}) + \delta\phi_2(\mathbf{r})$, where $\delta\phi_1(\delta\phi_2)$ is the $O(E)(O(E^2))$ local variation in $\phi_{SP}$, hence necessarily odd (even) along the $z \parallel E$ coordinate and cylindrically symmetric around $E$. Because of its odd symmetry, even when relevant, $\delta\phi_1(\mathbf{r})$ yield negligible variations to the light scattered by P200, as it can be shown by simple evaluations. ETLI experiments enable instead to quantitatively evaluate $\delta\phi_2(\mathbf{r})$ once simplifying assumptions on its shape, already constrained by symmetry, are made. By assuming that SP concentration around each P200 is incremented within spherical regions along $E$ and decreased within a toroidal volume as sketched in Fig. 3, we can reproduce, by calculations in the Rayleigh-Gans scattering regime, the observed low-frequency values of $\Delta\tau/\tau_0$ for both polarizations. An estimate of the size of the modulations in $\delta\phi_2(\mathbf{r})$ is obtained by studying the "recovery" time $t_{ETLI}$ necessary for the scattering anomaly to diffuse away after $E$ is switched off [at $t=0$ in Fig. 2(d)]. We find $t_{\text{ETLI}} \approx 6$ ms, corresponding to SP diffusion over $\sim 350$ nm. On this basis, we held the inner diameter of the toroid equal to that of P200 and found we could match the data by setting the radius of accumulation spheres $\approx 100$ nm and the level of SP depletion and accumulation to 20% and 50%, respectively.

The field-induced arrangement of SP deduced from ETLI data cannot be justified in terms of purely electric interactions. Indeed, induced dipole-induced dipole forces are in this case way too weak and have a much higher characteristic frequency, in the MHz Maxwell-Wagner regime. The SP distribution sketched in Fig. 3(a) can instead be understood as consequences of $O(E^2)$ electro-osmotic flows around the large particles, qualitatively drawn in Fig. 3(b). Electro-osmotic flows are generated by the electric force acting on the charged fluid within the electric double layer (EDL) [5]. Unperturbed, symmetric EDLs yield polar $O(E)$ Stokes flows around centrosymmetric particles. $O(E)$ electric polarization breaks the symmetry of the EDL thus giving way to $O(E^2)$ terms in the flow field of magnitude related to the nature and amplitude of the asymmetries in the EDL. For this reason, the $\nu$ dependence of $O(E^2)$ flows is expected to reflect the $\alpha$ and Maxwell-Wagner polarization processes. $O(E^2)$ flows have been recently studied in the frame of "induced-charge electro-osmosis" models, treating uncharged, highly polarizable particles in simple electrolytes [15], a condition, rather different from ours, where $O(E^2)$ flows dominate even at low fields. Much less is known about $O(E^2)$ electro-osmosis around low dielectric charged colloids since in this case its effects are normally masked by the linear term. The available theoretical model [13,14] predicts the $O(E^2)$ flows sketched in Fig. 3(b), explicitly computable on the basis of zeta potential and ionic strength. We expect SP to be generally dragged along the solvent flow lines except when the flow runs too closely to the large particles surface, where SP are excluded because of steric and electrostatic repulsions. Such exclusion shell, pictured in Fig. 3(b) by a dashed line, is larger than the EDL, and hence the SP are stopped outside the region where the electro-osmotic flows are the strongest, thus accumulating and depleting around the P200 as observed. However, to explain the onset of the depleted toroid in the measured 1 ms characteristic time, a large fluid velocity is required, much larger (up to 1000 times) than what is expected by the theory in Refs. [13,14] for standard particles in simple electrolytes. The fact that such enhanced flow appears at $\nu < \nu_{mix}$ suggests a crucial role of SP in greatly perturbing the EDL of the larger particles and setting the bases for large $O(E^2)$ electro-osmotic flows.

Parallel considerations enable interpreting the perpendicular orientation of rodlike particles as another consequence of SP enhanced $O(E^2)$ electro-osmotic flows around the large particles. Indeed, at low frequency, the torque on charged rodlike particles is not limited to the purely electric coupling $\sigma_E$ between $E$ and induced dipole but includes relevant contribution from electrohydrodynamic effects [16]: $\sigma = \sigma_E + \sigma_H$, $\sigma_H = \int_\Sigma \mathbf{r} \times f(\mathbf{r}) d\Sigma$, where $f(\mathbf{r})$ is the viscous force acting on the surface $\Sigma$ of the particle. The flow fields generating $f(\mathbf{r})$ are in turn due to electro-osmosis. $O(E)$ flows around centrosymmetric particles produce no torque [4]. In turn, $O(E^2)$ electro-osmotic flows yield nonvanishing $\sigma_H(\nu)$. $\sigma_H(\nu)$ has been explicitly calculated for uncharged metallic spheroidal particles within the frame of induced-charge electro-osmosis [17] and by numerical evaluation of the nonlinearized electrokinetic model for charged rodlike particles [18]. While $\sigma_E$ is expected to be generally positive, computation in [18] clearly indicate that $\sigma_H$ can be either positive or negative, depending on the charge distribution in and around the polarized EDL. In the Maxwell-Wagner regime the polarization entails only a displacement of counterions in the EDL and typically yields a small and negative $\sigma_H$. As the frequency is lowered toward $\nu_\alpha$, the ionic concentration polarization further modifies the structure of the EDL, giving rise to negative $\sigma_H$ values when slowly diffusing coions are present [18]. For colloids in simple electrolytic solution, $\nu_\alpha$ is expected to be the lowest characteristic frequency of $\sigma_H$. The appearance of a largely negative $\sigma_H$ in the mixtures at $\nu_{mix} \leqslant \nu_\alpha$ again suggests that in these systems a new electrokinetic process involving SP is present.

All data here presented coherently point to the following scenario. As $E$ is turned on, SP accumulate, by mobility mismatch, on one side of the larger PTFE or P200 particles while depleting on the other side ($\delta\phi_1 \neq 0$). This polar accumulation undetected by ETLI because of symmetry continues until it is compensated at $\nu < \nu_{mix}$ by diffusion of SP across the larger particles, in close analogy with the accumulation of coions for $\nu < \nu_\alpha$. We envision such "colloidal concentration polarization" as the only possible $O(E)$ electrokinetic process having the correct characteristic frequency and potentiality to greatly affect the structure of the EDL and hence making electro-osmosis asymmetric, for example, through overlapping EDLs and percolative electro-osmotic paths. We interpret our data as consequences of SP colloidal concentration polarization—yet to be directly observed—whose effect on the EDL of the large particles yields largely enhanced nonlinear electro-osmotic flows around them. At $\nu < \nu_{mix}$, such flows could have the amplitude required to account for the observed $O(E^2)$ depletion of the smaller spheres around the large ones and for the observed large negative $O(E^2)$ hydrodynamic torque on the rodlike particles.

The counterintuitive field-induced negative orientation and clearing of binary mixtures of colloids are examples of the complex behavior of charged colloids due to linear and nonlinear electro-osmotic flows. Results in this Rapid Communication extend the realm of electro-osmotic colloidal phenomena from the already reported behavior of charged $\mu m$ sized particles in the proximity of surfaces to the behavior and interparticle interactions of bulk mixtures of nanocolloids.

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