Anisotropic electrostatic and elastic interactions of charged colloidal spheres

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Charged systems where ions, DNA, proteins and/or charged colloidal particles are dispersed in an isotropic fluid, are found in a range of prominent materials and biological systems. However, generally the role of the host material dielectric anisotropy in charged colloidal materials is ignored, despite frequent relevance in defining colloidal self-assembly, biological function and out-of-equilibrium behaviour. In this work, we formulate and experimentally demonstrate anisotropic electrostatic interactions in a system of charged colloidal particles in a nematic electrolyte. Experimentally, charged dumpling-shaped near-spherical colloidal particles are used as a model system of charged colloidal particles in a nematic medium, demonstrating anisotropic elastic and electrostatic effective pair interactions for colloidal surface charges tunable from neutral to high. Theoretically, we derive asymptotic expressions for (i) the anisotropic electrostatic potential on the single-particle level and (ii) the effective pair interaction in the system, under the assumption of spherical charged particles in a uniform nematic director field. The analytical expressions for the pair interactions are compared with experiments, demonstrating good qualitative agreement within an experimentally accessible parameter range. More generally, our work extends the traditional Derjaguin-Landau-Verwey-Overbeek (DLVO) theory for charge-stabilised colloidal suspensions in isotropic solvents, to dielectric anisotropic host media with orientational elasticity.

Highly charged biopolymers like DNA and filamentous actin are just two of many examples of biological relevance of electrostatic interactions that are screened by counterions under physiological conditions. In soft condensed matter, similar effects allow for exploiting electrostatic interactions between particles in defining colloidal self-organized superstructures that they can form and, even more importantly, enabling the very existence of metastable colloidal systems. The celebrated theory of Derjaguin, Landau, Verwey and Overbeek (DLVO)1,2 is a paradigm for interactions in charge-stabilised colloids. The theory combines an attractive dispersion (London-van der Waals) interaction which is, assuming additivity, counterbalanced by a screened electrostatic pair interaction \( \Phi_E(d) \) due to the (bare) mean-field ion-ion and ion-particle Coulomb interaction and the ion entropy,

\[
\frac{\Phi_E(d)}{k_BT} = Z^2 \lambda_B \left( \exp \left( \frac{a}{\lambda_D} \right) \right)^2 \exp \left( -\frac{d}{\lambda_D} \right),
\]

with \( k_BT \) the thermal energy, \( Z \) the number of elementary charges \( e \) on the particle surface, \( \lambda_B \) the Bjerrum length, \( a \) the particle radius, \( \lambda_D \) the (isotropic) Debye screening length and \( d \) the center-to-center particle distance. This theory has been rigorously experimentally tested, and despite its limitations, its appeal lies in its simplicity of capturing the essential effects in a wide range of systems. Historically, the DLVO theory predicts why particle charge and the salt concentration (tunable via \( \lambda_D \)), can prevent or stimulate colloid coagulation, due to the balance between electrostatic repulsion and attractive dispersion interaction.2 Later, the electrostatic part of the DLVO theory turned out to be useful in describing the short-range liquid order in scattering,3 for direct measurements of the pair interactions6–7, performing or comparing with simulations8–9, to investigate the effects of external fields10–12 and predicting phase behaviour, such as demixing13,14 and crystallisation15–17. Moreover, DLVO theory has been applied to other fields than colloidal science, such as ion transport18 and biology19–21.

The electrostatic part of the DLVO theory — in the original formulation — is formally valid (only) within the mean-field approximation for homogeneously-charged spherical particles dispersed in isotropic solvents in the limit of low electrostatic potentials and negligible double layer overlap.22,23 However, major effort was performed in overcoming these assumptions. The concept of charge renormalisation24,25 was, for example, introduced to overcome the limitation of low electrostatic potentials by including non-linear effects. Furthermore, analytical and numerical extensions have been made to include many-body effects26–29, charge regulation30–33, fluctuations34–36, ion-specific dispersion interactions37, nonadditivity38, and a zoo of so-called “non-DLVO

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forces"\textsuperscript{39}, to just name a few, although this might lead to loss of transparency of the original simple theory.

On the other hand, the host material anisotropy in DLVO interactions is a novel open challenge, centred at the question, how electrostatic screening is changed when the medium is characterised by a dielectric tensor, rather than a dielectric constant, such as for isotropic solvents. A major example of such controllable anisotropic materials are liquid crystals (LCs), where the anisotropy is described by one dielectric coefficient along the primary dielectric tensor axis -also called director- and a second dielectric coefficient in the perpendicular direction. Spatially dependent dielectric anisotropy also occurs sometimes in isotropic liquids, for example, near solid-water interfaces\textsuperscript{40,41}. For a hypothetical, everywhere radial director around a colloidal sphere, only the dielectric tensor components projected in the radial direction contribute, and hence the Bjerrum length and consequently the Debye screening length are renormalised with a constant, and one can just use the standard (isotropic) DLVO form as given in Eq. (1). However, a completely different situation arises when the director configuration around the particle does not have the same symmetry as the particle itself. The simplest non-trivial example would be a constant director field along the \(z\) axis surrounding a spherical particle, and in this case the screening will become direction dependent, as we shall see in this paper. Furthermore, as it is the more usual case in anisotropic nematic media with dispersed particles\textsuperscript{42–62}, the director field is usually spatially dependent and varies in space due to various geometry, surface effects, and external field, leading to rich and diverse elasticity-mediated anisotropic inter-particle interactions. Multipole expansions have been used to describe elasticity-mediated colloidal interactions in liquid crystals, drawing parallels to electrostatic interactions\textsuperscript{63–74}. In general, elasticity-mediated interactions in LCs are accompanied by screened electrostatic and dispersive (London-van der Waals)\textsuperscript{75}, however, the previous studies of such colloidal systems with LC hosts were done for highly anisotropic rod- and disc-shaped particles, so that the role of the anisotropy of colloidal particles and that of the LC medium was not separated from the effects due to particle’s shape anisotropy and so far explored while probing phase behavior and self-assembly of colloidal superstructures\textsuperscript{76–78}.

In this paper, we explore anisotropic colloidal interaction in electrostatically screened near-spherical charged colloids, to develop a generalised understanding of electrostatic interactions in colloids, subjected to and determined by the material dielectric anisotropy profiles. Experimentally and theoretically, we use so-called charged dumpling particles (with almost spherical shape) as a charged colloidal model system, because they can become appreciably charged in a simple liquid crystal (LC) such as 5CB, with weak enough elastic interaction that allows competition with the electrostatic forces. We generalise the DLVO theory for the anisotropic screening and calcu-
lute the effective pair interaction under the assumption that elastic, dispersive and electrostatic interactions are additive, just like in DLVO theory. Furthermore, the electrostatic part is treated within linear screening theory in combination with a far-field multipole expansion approach, on the same level as typically elastic interactions are treated. Finally, we compare the theoretically calculated interactions with experiments, finding good qualitative agreement.

RESULTS

Charged colloidal dumpling particles dispersed in a nematic electrolyte as model system

As our charged colloidal model system, we use particles (Fig. 1c) of “dumpling-like” shape. Their rough shape and overall dimensions are close to those of a sphere with a diameter \(2a = 1 \mu m\). Colloidal dumplings were dispersed in 5CB at low concentration (< 1000 ppm) to obtain well-separated colloidal particles. In Figs. 1a, b, d, and e we show microscopy images of a single colloidal dumpling. The colloidal dumplings have homeotropic anchoring on their surfaces and the symmetry of resulting director distortions \(\mathbf{n}(r)\) around particles (Fig. 1f) is of the “quadrupolar” type, with an encircling half-integer disclination loop (“Saturn ring”). The in-plane diffusion of the colloidal dumplings due to Brownian motion (Figs. S8a,b, see SI) is anisotropic with respect to \(\mathbf{n}_0\) with diffusion coefficients \(D_{\parallel}/D_{\perp}=1.49-1.54\) (Fig. S8c, see SI), and this is close to theoretical predictions for spheres, \(D_{\parallel}/D_{\perp} = 1.72\) with possible discrepancy explained by the irregular shape. We used charged and uncharged particles in our experiments. The number of elementary charges on the particles surface \(Z=50-350\) was determined using their electrophoretic motion between two in-plane electrodes placed perpendicular to \(\mathbf{n}_0\) in a planar nematic cell. Charged particles were moving along \(\mathbf{n}_0\) towards a negative electrode when a DC electric field was applied between electrodes. The velocity of the particles depends on their charge and the strength of electric field. The displacement of particles was tracked using video microscopy, which allows us to estimate the effective charge \(Ze\), from the balance of the Stokes viscous drag force and the electric force. To probe only the electrostatic pair interactions between charged colloidal dumplings, we measured their pair interactions in the isotropic phase of 5CB, where the contribution due to LC elastic forces is eliminated. When brought nearby with the help of optical tweezers, colloidal dumbplings repel from each other with a potential \(\Phi_E\) of tens of \(k_BT\). The effective charge number \(Z\) and Debye screening length \(\lambda_D\) can be also extracted from experimental pair interactions (Fig. 1h) using Eq. (1). The effective charge numbers obtained by electrophoretic measurements (Fig. 1g) were in a good agreement with values obtained from electrostatic interaction potential (Fig. 1h). The Debye screening lengths obtained from fitting the interaction potentials were within the range of \(\lambda_D=300-1000\) nm measured for 5CB samples in our experiments using impedance spectroscopy.

Due to the effective elastic nature of the anisotropic liquid crystal host, also uncharged colloidal particles interact via anisotropic elastic interactions, which for our dumpling particles are of quadrupolar symmetry with elastic interaction potential \(\Phi_{LC}(d,\theta)\) (Fig. 2).

\[
\Phi_{LC}(d,\theta) = \frac{16}{9} \pi K c^2 \frac{9 - 90 \cos^2 \theta + 105 \cos^4 \theta}{d^5},
\]

where \(d\) is the center-to-center separation. Note, that the potential falls off as \(1/d^5\), and depends on the angle \(\theta\) between the uniform far-field \(\mathbf{n}_0\) and \(d\) which makes it strongly anisotropic, with the attraction direction at \(\approx 40-50^\circ\) (Fig. 2b). We can extract the elastic pair potential (Fig. 2d) from a single particle released due to Brownian motion (Fig. 2c) and based on the elasticity measurements (using the single elastic constant \(K = 8 \cdot 10^{-12}\) N), we find for our system that \(c = 0.1 - 0.2 \mu m^3\).

Electrostatic potential of single charged colloidal sphere in an anisotropic dielectric

Electrostatic interactions between charged particles are conditioned by the profile of the electrostatic potential surrounding the particles. This quantity exhibits anisotropic screening as it is directly determined by the anisotropy of the host medium. We calculate this anisotropic electrostatic potential in the mean-field approach by using the Poisson-Boltzmann equation for the
Fig. 3 Anisotropic electrostatic potential \( k_B T \phi(r)/e \) for charged spherical colloidal particle in anisotropic dielectric host. a and b Potential for large (isotropic) Debye screening length and \( c \), d short Debye screening length, with uniform director host \( c = 0 \) (along \( z \) direction) and with quadrupolar director material anisotropy \( (c \neq 0) \). e, f Electrostatic potential along selected directions from the particle centre, at constant angle \( \theta \) with respect to the \( z \) axis. Full lines correspond to uniform and dashed lines to quadrupolar material anisotropy \( c = 0.2 \, \mu m^3 \). The grey line is the isotropic electrostatic potential line. g Anisotropic Debye screening length \( \lambda_D(\theta) \) relative to the isotropic screening length \( \lambda_D^0 \), in different directions, which gives the decay length at fixed angle for sufficiently large distance for the uniform and quadrupolar distorted director field. For numerical parameters, we take particle radius \( a = 0.5 \, \mu m \) with constant charge \( Z = 50 \) in a nematic electrolyte with dielectric properties \( \epsilon_\perp = 6, \epsilon_\parallel = 19 \) and \( \bar{\epsilon} = 10 \).

electrostatic potential in the nematic host with fixed director field \( \mathbf{n}(r) \) surrounding the particle (see SI),
\[
\partial_i [\epsilon_{ij}(r) \partial_j \phi(r)]/\bar{\epsilon} = \kappa^2 \sinh[\phi(r)], \quad (r > a), \tag{3}
\]
where \( k_B T \phi(r)/e \) is the electrostatic potential, \( \bar{\epsilon} \) is the rotationally averaged dielectric constant of the nematic medium, and \( \kappa^{-2} = \lambda_D^0 \) the isotropic Debye screening length used as a “reference” decay length. Note that in the above, we assume that the dumpling particles can be approximated as spherical, have constant-charge boundary conditions with total homogeneously distributed charge \( Ze \), and that the far-field director surrounding the particle has cylindrical symmetry. The host material anisotropy is given by the dielectric tensor as: 
\[
\epsilon_{ij}(r) = \epsilon_{\perp} \delta_{ij} + \Delta \epsilon n_j(r)n_i(r),
\]
with \( \Delta \epsilon = \epsilon_{\parallel} - \epsilon_{\perp} \) the dielectric anisotropy difference between dielectric tensor components projected parallel to the director \( \epsilon_{\parallel} \) and perpendicular to the director \( \epsilon_{\perp} \). We take -in accordance with our experiments- that ions cannot penetrate the particle with dielectric constant \( \epsilon_p = 2 \), hence inside the particle one has to solve the Laplace equation,
\[
\nabla^2 \phi(r) = 0, \quad (r < a). \tag{4}
\]
The anisotropic electrostatic potential [Eqs. (3) and (4)] is numerically calculated using COMSOL Multiphysics software exploiting the cylindrical symmetry, with the results shown in Fig. 3. We show results for two material anisotropic regimes, one with uniform director field \( \mathbf{n} = \mathbf{e}_z \) and second -the realistic one for our experiments- a director field with elastic quadrupole distortion \( \mathbf{n} = [\mathbf{e}_z + (2cZp/r^5)\mathbf{e}_p]/[\mathbf{e}_z + (2cZp/r^5)\mathbf{e}_p] \) (as shown in Fig. 1f), with \( c \) the quadrupole strength. The quadrupole is derived from a multipolar expansion for the Saturn-ring configuration.81

For the uniform director field (Fig. 3a) and the Debye screening length larger than particle size, the diffuse screening cloud has a prolate-spheroidal like shape with the long axis coinciding with the \( z \) axis, whereas upon considering the full quadrupolar distortion, we see that the electric potential profile (i.e. the double layer) gets distorted close to the region of the Saturn ring defect (Fig. 3b), but again evolves to the prolate-spheroid shape further away from the particle. Fig. 3c shows the electrostatic potential along selected directions from the particle at constant angle \( \theta \) with respect to the \( z \) axis,
that can be compared to the isotropic electrostatic potential, showing a similar magnitude. In Figs. 3d-f, the electrostatic potential for the regime of Debye screening length smaller than the particle size is shown for uniform director (Fig. 3d) and quadrupolar director (Fig. 3e); electrostatic potential variation along constant $\theta$ is shown in Fig. 3f. At these short Debye lengths, the electrostatic potential inside the particle becomes strongly inhomogeneous and although the ions are closer to the particle, the electrostatic potential is still strongly anisotropic.

In order to obtain more insights on the shape of the anisotropic electrostatic potential, we derive an analytical expression in the following two steps. (i) First of all, we map the ion impenetrable charged sphere with radius $a$ and surface charge density $\sigma$, on an ion-penetrable spherical shell with radius $R$ and surface charge density $\sigma_S$. Having described the particle by a singular charge distribution, we obtain an integral expression of the electrostatic potential as a convolution of the singular surface charge distribution and the Green’s function of the anisotropic Debye-Hückel (DH) differential operator in the limit of uniform director fields, defined by the operator inverse, 

$$G(r,r') = -4\pi \left[ (\epsilon_{ij}/\epsilon) \partial_i \partial_j - \kappa^2 \right]^{-1} \delta(r-r'). \quad (5)$$

The salt-dependent parameters $\alpha = \sigma_S/\sigma > 1$ and $\gamma = R/a < 1$ can be determined using a fit to the numerically obtained surface potential. By fitting only the surface potential, it is found that the integral expression is practically numerically exact for $r > a$ in a wide range of salt concentrations, see the SI. (ii) Using the integral representation, we perform a multipole expansion of the electrostatic potential, to capture the far-field behaviour. The result is (see SI),

$$\phi(r) = \frac{\alpha^2 Z \lambda_B}{\sqrt{\epsilon^2 \epsilon/\epsilon}} \left[ G_m(r) + \frac{(\gamma a)^2}{6} G_q(r) \right. \left. + \frac{(\gamma a)^4}{120} G_h(r) + \ldots \right], \quad (6)$$

with multipolar basis functions $G_i(r)$ ($i = m, q, h, \ldots$) defined by linear combinations of partial derivatives of Eq. (5), see the SI for the expressions. The higher-order multipoles become more important at higher salt concentrations (smaller $\lambda_D^I$), and also the parameters $\alpha$ and $\gamma$ depend on $a/\lambda_D^I$.

As is usual for multipole expansions, Eq. (6) fails at short distances, but at large enough $r = |r|$ it captures the proper angle dependence, given that enough multipoles are taken into account (see the SI). For example, up until hexadecapolar order, Eq. (6) is numerical exact up until $a/\lambda_D^I \sim 2$ (5% deviation), while at higher salt concentrations truncation at the hexadecapolar order turns out to be not sufficient. As an example, for $a/\lambda_D^I \sim 5$, we see even asymptotically far from the particle that the deviation is $10-60\%$ depending on the angle with the director, see the SI. Finally, $Z$ is the actual charge number for $|\phi(r)| \ll 1$, but for high electrostatic potentials $Z$ should be interpreted as a renormalised charge density, similar to what is known in “isotropic” charged colloids.

At low salt concentrations, or at sufficiently large $r$ at fixed $\theta$, Eq. (6) reduces to

$$\phi(r) = \alpha^2 Z \lambda_B(\theta) \frac{\exp[-r/\lambda_D(\theta)]}{r}, \quad (7)$$

with angle-dependent Bjerrum length,

$$\lambda_B(\theta) = \frac{\bar{\epsilon}}{\sqrt{\epsilon_\perp (\epsilon_\parallel - \Delta \epsilon \cos^2 \theta)}}, \quad (8)$$

and angle-dependent Debye screening length

$$\lambda_D(\theta) = \sqrt{\frac{\epsilon_\perp \epsilon_\parallel}{\epsilon_\parallel - \Delta \epsilon \cos^2 \theta}}, \quad (9)$$

with for $\Delta \epsilon > 0$ ($\Delta \epsilon < 0$) a maximum (minimum) at $\sqrt{\epsilon_\perp/\bar{\epsilon}}$ and a minimum (maximum) at $\sqrt{\epsilon_\parallel/\bar{\epsilon}}$. Note that $\lambda_D(\theta)/\lambda_D^I \neq \lambda_B(\theta)/\lambda_B^I$, as one would maybe naively think based on $\lambda_D^I = (8\pi \lambda_B^I \rho_S)^{-1/2}$. We plotted Eq. (9) in Fig. 3g for $\Delta \epsilon > 0$, and from this the shape of the double layer can be understood. Would we have had taken $\Delta \epsilon < 0$ the double layer would have had an oblate-spheroidal shape.

Eq. (7) reveals that for fixed $\theta$ and varying $r$, the anisotropic $\lambda_B(\theta)$ is the decay length sufficiently far from the particle, and $\lambda_D(\theta)$ should therefore rightfully be treated as an anisotropic Debye screening length. This is not only the decay length for the uniform director case, but also for the quadrupolar-distorted (Saturn ring) case at large enough distances where the director distortions are small. Moreover, not only the decay length becomes angle dependent, but also the prefactor of the distance-dependent part. However, one has to include the higher order terms from Eq. (6) to correctly account for this, see the SI. The fact that this prefactor becomes angle-dependent is not new. It occurs, for example, also for anisotropic particles in isotropic solvents, and the asymptotic angle dependence is quantified by the so-called anisotropy function. It has been determined for disks and rods, and ion-penetrable spheroidal particles. The anisotropy function is, however, not a useful concept here: the radial part does not trivially factorise from the angle-dependent part, because the anisotropy is here caused by the medium and not by the particle shape. Moreover, we note that the persistence of the anisotropy at infinity also occurs for charge-screened particles with an anisotropic shape in an isotropic medium.

Finally, we evaluate the salt-dependent renormalisation parameters $\alpha$ and $\gamma$ for some values of $a/\lambda_D^I$. The salt-dependent factors $\alpha$ and $\gamma$ can be found by a fit of the numerically obtained surface potential from finite-element calculations, and we performed this procedure for a few values of $a/\lambda_D$ (more information in SI).
**Anisotropic electrostatic and elastic pair interactions**

Charged colloidal dumplings interact in the nematic LC (Fig. 4a), both via anisotropic electrostatic and elastic interactions, each with a different anisotropic profile. Generally, the electrostatic interaction is repulsive, whereas the nematic elastic interaction has regions (directions) of attraction and regions of repulsion. If the charge of the particles is high enough, the electrostatic repulsion can counterbalance the elastic attraction at any angle, and the two colloidal particles bounce around each other without getting into the full contact (Fig. 4b). Polar plots (Fig. 4b) and histograms of center-to-center distance between particles (Fig. 4c) show that the steady-state separation is \( d \approx 5 \mu m \) for \( \theta \approx 90^\circ \) and \( d \approx 6 \mu m \) for \( 0^\circ \) or \( 180^\circ \). This difference in the steady-state separation depends on the position of the two particles relative to the far field director, which can result from the anisotropy in the charge distribution around colloidal dumplings (Fig. 3). Histograms of an angle \( \theta \) show that there were two preferred orientations for \( d \), at \( \approx 50^\circ \) and \( \approx 140^\circ \) (Fig. 4b,d), which indicate equilibrium distance and orientation of particles resulting from a competition of anisotropic elastic attraction and electrostatic repulsion, as we shall explore theoretically below. Contributions to the asymmetry could also result from the non-spherically symmetric shape of the particles and their orientation change with respect to \( \mathbf{n}_0 \) when interacting. On the other hand, if the electric charge at the dumpling surface is sufficiently small, the elastic attraction is dominant and two colloidal particles attract and get to the full contact as elastic quadrupoles (Figs. 4e-g) similar to colloidal dumplings without charge (see Fig. 2).

The effective pair interaction between anisotropic charged colloids is determined theoretically, by splitting — in the spirit of the DLVO theory — the total interaction potential \( \Phi(d, \theta) \), as the sum of screened electrostatic

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**Table I. Renormalised parameters for spherical-shell method.**

| \( \alpha/\lambda_D \) | \( \gamma \) | \( \alpha \) |
|--------------------------|-------------|-------------|
| 0.1                      | 1           | 1           |
| 0.5                      | 1           | 1.06        |
| 1                        | 0.99        | 1.2         |
| 2                        | 0.988       | 1.43        |
| 5                        | 0.9662      | 2.0614      |

**Fig. 4 Pair interactions of charged dumpling particles in a nematic LC.**

(a) Bright-field micrograph of two interacting colloidal dumplings. (b) Polar plot of a separation depending on an angle \( \theta \) for two charged particles drifting around each other after being brought nearby and released from an optical traps; particles do not come to the direct contact at any angle. Colour shows the time with respect to colour scale. c Histogram showing the preferred separations between two highly charged particles. d Histogram showing the preferred angle \( \theta \) for a pair of two highly charged particles. e Trajectory of interactions between two weakly charged particles. f Polar plot of a separation depending on an angle \( \theta \) for two weakly charged particles; particles come to the direct contact at \( 45^\circ-60^\circ \). g Time dependence of separation corresponding to e and f.
\( \Phi_E(d, \theta), \) van der Waals \( \Phi_{vdW}(d) \) and, because we are in a nematic host, the nematic elastic interactions \( \Phi_{LC}(d, \theta), \)

\[
\Phi(d, \theta) = \Phi_E(d, \theta) + \Phi_{vdW}(d) + \Phi_{LC}(d, \theta). \tag{10}
\]

The van der Waals interaction can be derived using Hamaker-de Boer theory,

\[
\Phi_{vdW}(d) = -\frac{A_H}{3} \left[ \frac{a^2}{d^2} - \frac{a^2}{d^2} + \frac{1}{2} \ln \left( 1 - \frac{4a^2}{d^2} \right) \right], \tag{11}
\]

which fails at center-to-center distances close to contact \( (d \approx 2a) \) where the (quantum-mechanical) Born repulsion becomes important, and for large \( d \) where relativistic effects become important. For this interaction, the anisotropy enters only the Hamaker constant, but not in the coordinate-dependent part of the expression, assuming the non-relativistic limit\(^{89}\). Finally, the elastic interaction \( \Phi_{LC}(d, \theta) \) is given by the quadrupolar far-field expression Eq. (2).

The main challenging contribution to determine is the anisotropic screened electrostatic interaction \( \Phi_E(d, \theta) \), which we determine from the asymptotic expression of the electrostatic potential [Eq. (6)] within the linear superposition approximation (for full derivation see SI). The anisotropic screened electrostatic interaction reads

\[
\frac{\Phi_E(d, \theta)}{k_B T} = \frac{\alpha^2 \gamma^2 Z^2 \lambda_D^4}{\sqrt{\varepsilon_\parallel^2 \varepsilon_\perp^2 / \varepsilon^2}} \left[ G_m(d, \theta) + \frac{(\alpha a)^2}{3} G_q(d, \theta) + \frac{2}{45} (\alpha a)^4 G_h(d, \theta) + \ldots \right]. \tag{12}
\]

now treated on the same level of (multipolar) approximation as the elastic interactions, where \( G_{m,q,h}(d, \theta) \), \( \alpha \) and \( \gamma \) are the same as the ones derived for the single-particle case, see Eq. (6). Note also, that in the limit of low salt concentration, only the monopole term is relevant and the above equation reduces to the anisotropic Yukawa form

\[
\frac{\Phi_E(d, \theta)}{k_B T} = \alpha^2 \gamma^2 Z^2 \lambda_B^4 \exp \left[ \frac{-d/\lambda_D(\theta)}{d_D} \right], \tag{13}
\]

which is reminiscent of the well-known standard isotropic DLVO potential Eq. (1).

In Fig. 5a we show the total analytically calculated interaction potential for parameters, in qualitative range of our experiments. The position of a local minimum of several \( k_B T s \) is found at \( \theta \sim 55^\circ \), which is in good qualitative agreement with experiments (Fig. 2d). In Fig. 5b we show the contributions of the anisotropic electrostatic effective interaction, in Fig. 5c the elastic interaction and in Fig. 5d the van der Waals interaction. The van der Waals interaction is of shortest range, and does not contribute significantly to the total interaction potential, whereas elastic and screened electrostatic potentials clearly compete, and it is their detailed balance that determines the overall inter-particle potential. Finally, note that if we had used the isotropic DLVO potential to calculate the total potential (and using same material parameters), the predicted local minimum would shift to angles \( \sim 20^\circ \), which underlines the clear role of the electrostatic anisotropy.

The total interaction potential Eq. (10) exhibits a range of possible qualitatively different inter-particle interaction regimes, as we show in Fig. 6, which depends on the particle charge \( Z \) and the host electrolyte screening length \( \lambda_D^\parallel \) (salt concentration). Notably, we calculate the total regimes for a smaller elastic interaction \( c = 0.02 \, \mu m^3 \) as in our experiments \( (c \sim 0.2 \, \mu m^3) \), which makes the anisotropic electrostatic DLVO-type interaction of more similar magnitude as the nematic elasticity at the reported particle charges, which are lower than

![Fig. 5 Analytically calculated total effective interaction potential for a spherical particle in nematic electrolyte.](image)
the one chosen in Fig. 5. We want to stress, however, that the electrostatics is based on a far-field multipole expansion in combination with the linear-superposition approximation, hence our theory underestimates the repulsions when the double layers of the particles overlap at sufficiently high salinity and low particle separations, see Fig. S5 in the SI, as is also common in isotropic DLVO theory\textsuperscript{22}, not to mention because of the currently unknown non-additive effects between elasticity and electrostatics, or close-approach elastic effects.

In Figs. 6a-c we show the situation when the screening length is larger than the particle size. For low enough charges a global minimum located at approximately 49° is separated from a shallow local minimum with depth \( \sim 0.001 \ k_B T \). Both local and global minimum disappear when the particle charge is increased (Figs. 6b and c), and the interaction potential is repulsive for all distances and directions. For Debye lengths similar to the particle size, we see that higher charges are needed to overcome the attractive elastic interaction. Indeed at the same particle charge, but smaller screening length (Fig. 6d), the electrostatic interaction is too weak to overcome the elastic interaction, resulting in a purely attractive direction in the interaction potential. Such a situation is reminiscent of what we observed experimentally (but for different exact parameters) in Fig. 4f,g, where a low charge results in particle coagulation. When increasing \( Z \) further, again a local minimum emerges (Fig. 6e) that is deeper than the low-screening case. The depth of this minimum becomes smaller when \( Z \) increases even further (Fig. 6f).

The trend that deeper attractive minima can be attained for larger salt concentrations, but that higher charges are needed, is something that we also see for double layers smaller than the particle size (Figs. 6g-i). When comparing Fig. 6 with Fig. 5 we see that increasing the strength of elastic interaction at the expense of higher \( Z \), also gives rise to deeper attractive minima.
DISCUSSION

Summarising, we introduced a screened electrostatic colloidal model system that can become appreciably charged in a nematic liquid crystal, with particles of almost spherical shape. Theoretically, we discussed that dielectric anisotropy of the colloidal host, given in nematic fluids by the director field, gives rise to anisotropic screening of the electrostatic potential when there is a mismatch between the nematic and particle symmetry, and in turn, also to the electrostatic effective pair interaction. In our system of nematic colloids, the screened electrostatic interaction is inherently combined with effective nematic elastic interactions, which leads to different interaction regimes where particles are: (i) repelled for all distances and angles, (ii) are subjected to a weak local minima of $\leq 1k_B T$ such that they can still move due to thermal fluctuations and (iii) are dominated by the elastic interactions with distinct attractive and repulsive directions. In our experiments we have observed regimes (ii) and (iii), whereas to access for regime (i) we would need to achieve even higher particle charges and/or more deionised samples.

We have shown, within an experimentally accessible parameter range, that even effectively spherical particles exhibit strongly anisotropic electrostatic interactions in LCs. Experimental results indicate that both elastic and electrostatic interactions of charged particles in a nematic LCs are relatively long-ranged and anisotropic with respect to the director, so that the colloidal behaviour depends on their interplay. While charging could be controlled from neutral to hundreds of elementary effective charges per single particle, we could show that the interparticle forces could be dominated by elasticity or by electrostatics in the two limiting regimes, with both elastic and electrostatic interactions being highly anisotropic. While we focused on thermotropic nematics with accessible range of host medium’s Debye screening lengths in the range 300-1000 nm and on colloidal particles with the accessible range of surface charges (0-350)e, our findings do indicate a plethora of colloidal behaviour arising from the interplay of electrostatic and elastic interactions with salient anisotropic features, consistent with theoretical modelling.

This study can be in future extended further by exploiting the elasticity and electrostatics interplay for lyotropic water-based LC colloidal systems where Debye screening lengths can be much shorter, on the order of several nanometers, as well as highly deionized LCs that potentially could allow for accessing the range of Debye screening lengths from several nanometers to 10 microns. As shown in Fig. 6 tuning the screening length can change the relative position of a local minimum in the effective pair potential. Moreover, we note that lyotropic systems, might have additional features that our theory does not explore yet, being often a five-component mixture (an isotropic solvent such as water, liquid-crystal particles, cations, anions, and the larger colloidal particles), compared to the thermotropic four-component suspension in this paper (liquid crystal, cations, anions and colloidal particles). Note that lyotropic systems can also have a dielectric anisotropy that couples the director with electrostatics, just as in the thermotropic systems under consideration here. Furthermore, when the liquid-crystal lyotropic particles are smaller colloidal (nano)particles, we envisage tuning of the dielectric, elastic and possibly flexoelectric properties of the nematic host medium by changing the particle functionality. Tuning of elastic properties by charged nanoparticles as function of particle charge and salt concentration, has already been explored theoretically. Moreover, lyotropic systems can be made active, as opposed to the molecular thermotropic nematic building blocks, giving rise to possibly new unexplored hydrodynamic-electrokinetic active processes, which may be interesting also in a biological setting.

From the standpoint of view of particle designs, these studies could be extended to patchy particles with different density or even signs of charges, potentially allowing for different electrostatic multipoles, whereas as our study showed homogeneously charged spheres only give rise to even anisotropic Yukawa multipoles. Furthermore, while highly anisotropic disc- and rod-shaped particles have been studied already, there is a considerable range of possibilities in defining colloidal behaviour also by the particle shape and surface treatment for different boundary conditions for the LC director at colloidal surfaces.

As further main theoretical results, we derived asymptotic theoretical expressions for the electrostatic potential and the resulting pair interaction for homogeneous director configurations, which highlights not only an anisotropy in the screening length, but also in the prefactor, where the latter also occurs for anisotropic particles in isotropic solvents. Both anisotropies together predict that local minima in the total pair potential are shifted in terms of equilibrium angle compared to an isotropic electrostatic interaction, in line with our experimental observations. Finally, one obvious extension to the theory is to numerically investigate the effect of close distances between particles and relaxing the requirement of additivity in the pair potential by coupling the full Landau-de Gennes theory in terms of the tensor order parameter with electrostatics. We will explore this in future work.

More generally, our work contributes to the generalisation and extension of the DLVO interactions to ubiquitous anisotropic soft matter systems, such as complex fluids and anisotropic colloids. While nematic colloids formed by a thermotropic LC host and near-spherical colloidal inclusions provide validation of our theoretical findings, the concepts introduced here can be applied in biological contexts of highly structured biological cell interior and membranes, active matter systems with the additional forms of anisotropy stemming from activity, lyotropic LCs with varying degrees of orientational and partial positional ordering, ionic fluids, and so on. While
the experiments and model focused on even anisotropic Yukawa multipoles formed by like-charged spherical particles, future studies can extend our concepts to odd anisotropic Yukawa multipoles via a heterogeneous surface charge distribution or non-spherical particle shape on the electrostatic side of the spectrum, and to elastic monopoles through hexadecapoles and higher-order multipoles on the elastic side. It will be of interest to consider further the effects of various topological defects on counterion distributions, the role of flexoelectricity and surface polarisation, surface anchoring effects, as well as how similar concepts work in LC mesophases with different point group symmetries and partial positional ordering. Overall, our findings will contribute to the soft matter toolkit for forming colloidal composite materials with pre-engineered structure and composition of the constituent building blocks.

METHODS

Materials and Techniques

The dumpling colloidal particles were prepared using the hydrothermal synthesis method as reported earlier. The chemical ingredients used for synthesis, ytterbium nitrate hexahydrate (Yb(NO$_3$)$_3$·6H$_2$O), yttrium nitrate hexahydrate (Y(NO$_3$)$_3$·6H$_2$O), erbium nitrate pentahydrate (Er(NO$_3$)$_3$·5H$_2$O), and sodium fluoride (NaF) were all purchased from Sigma Aldrich. Octanoic acid (OA) was purchased from Acros Organics. In a typical synthesis, 130 mg of Y(NO$_3$)$_3$, 40 mg of Yb(NO$_3$)$_3$ and 10 mg of Er(NO$_3$)$_3$ were mixed with 10 ml of deionised water and 13.5 ml of ethanol. After forming a clear transparent solution, 0.35 g of NaOH and 1.83 g of OA were added into the above solution and kept stirring at 50°C for 30 min. Then 9 ml of 0.2 M NaF solution in deionised water was added dropwise to the above solution and stirred continuously for 30 min at 50°C. The mixture was transferred to a 40 ml Teflon-lined autoclave and kept in an oven for 200°C for 7h. After the reaction, the autoclave was allowed to cool down to room temperature naturally. The particles precipitated at the bottom of the reaction vessel were collected by centrifugation and washed with ethanol and deionised water in sequence and finally dispersed in 2.5 ml of cyclohexane. The reaction yields OA as a precipitate. To induce positive surface charges, the particles were dispersed in 5 ml of cyclohexane. The reaction yields OA as a precipitate.

Calculation of electrostatic potential

In order to calculate the electrostatic potential in an anisotropic dielectric medium, we start from Gauss’ law, which is given inside a spherical particle with radius $a$ due to the absence of free charges by,

$$\nabla \cdot \mathbf{D}(r) = 0, \quad (r < a),$$

with $\mathbf{D}(r) = \varepsilon_0 \varepsilon_r \mathbf{E}(r)$ the displacement field expressed in terms of the vacuum permittivity $\varepsilon_0$, particle dielectric constant $\varepsilon_r$, and electric field $\mathbf{E}(r)$. Outside the particle, in the nematic, we have ions with number densities $\rho_{\pm}(r)$, and hence the Gauss law reads (in SI units),

$$\nabla \cdot \mathbf{D}(r) = \varepsilon [\rho_+ (r) - \rho_- (r)], \quad (r > a),$$

where now, $\mathbf{D}(r) = \varepsilon_0 \varepsilon_e \mathbf{E}(r)$, with $\varepsilon(r)$ the (symmetric) dielectric tensor. We can express the electric field in terms of the electrostatic potential $k_B T \phi(r)/e$, and using the result that within the mean-field approximation the ion densities are Boltzmann distributed, we find Eqs. (3) and (4) of the main text, solved numerically with COMSOL Multiphysics under the assumption of a constant
charge density $\varepsilon \sigma$. In the SI, we derive Eqs. (3) and (4) also from a free energy approach.

For $|\phi(\mathbf{r})| \ll 1$ and a constant dielectric tensor, Eq. (3) simplifies to

$$\nabla^2 \phi(\mathbf{r}) = 0, \quad (r < a),$$

$$\left[(\varepsilon_{ij}/\varepsilon)\partial_i\partial_j - \kappa^2\right] \phi(\mathbf{r}) = 0, \quad (r > a),$$

to be matched by the boundary condition,

$$\nu_i \left[\varepsilon_{ij}\partial_j \phi(\mathbf{r})|_{r=a^+} - \varepsilon_p \partial_i \phi(\mathbf{r})|_{r=a^-}\right]/\varepsilon = 4\pi \lambda_B^i \sigma,$$

with $\nu$ an outward pointing unit normal vector. To obtain analytical solutions, is however difficult, because of the different symmetry inside the particle, compared to outside the particle, which prevents us to find a closed-form expression for $\phi(\mathbf{r})$, while satisfying the constant-charge Neumann boundary condition. We can, however, find a very accurate analytical approximation used in the main text, for which we will sketch the approach here, and leave the details of the calculations for the SI.

The most important step in finding an analytical solution is to observe that an approximate solution can be found by solving the auxiliary problem of an ion-impenetrable charged shell with surface charge density $\varepsilon \sigma_S$ and radius $R$,

$$\left[(\varepsilon_{ij}/\varepsilon)\partial_i\partial_j - \kappa^2\right] \phi(\mathbf{r}) = -4\pi \lambda_B^i \sigma S \delta(r-R),$$

where $\sigma_S$ and $R$ need to be fitted to the numerically obtained electrostatic potential. Then, it turns out that

$$\phi(\mathbf{r})|_{r\geq a} \approx \phi(\mathbf{r})|_{r\geq a}. \quad (20)$$

In general, and especially at high salt concentrations, $R \neq a$ and $\sigma_S \neq \sigma$, except in the limit where $\kappa \to 0$. The advantage of the auxiliary problem is that the solution has a closed-form expression with only a double integral left to be evaluated, in terms of the analytically known anisotropic DH Green’s function $G(\mathbf{r}, \mathbf{r}')$, defined by

$$\left[(\varepsilon_{ij}/\varepsilon)\partial_i\partial_j - \kappa^2\right] G(\mathbf{r}, \mathbf{r}') = -4\pi \delta(\mathbf{r} - \mathbf{r}'). \quad (21)$$

Hence, we only have to determine the parameters $\gamma = R/a$ and $\alpha = \sigma_S/\sigma$ based on a two-parameter fit of the numerically obtained surface potential, to get the electrostatic potential everywhere outside the particle. The resulting integral expression of $\phi(\mathbf{r})$ turns out to be almost indistinguishable from the real $\phi(\mathbf{r})$, see the SI for comparative figures. Evaluating a double integral is computationally less expensive than solving the (linearised) PB equation, but the real value of the integral representation comes when calculating pair interactions (see next subsection).

Moreover, the integral expression gives analytical insight. It is now possible to perform a multipole expansion, because we have an integral representation of the electrostatic potential outside the particle, as a convolution of a singular charge distribution with the anisotropic DH Green’s function. Performing this expansion, the remaining double integrals can be evaluated to find that the decay length is given by Eq. (9). As is common with multipole expansions, they fail at short distances from the particle, as can be seen from the comparative figures supplied in the SI, but still capturing the correct angle dependence for sufficiently large distances.

**Calculation of the screened electrostatic pair interaction potential**

Within linear screening theory $|\phi(\mathbf{r})| \ll 1$, ion entropy terms do not contribute to the effective pair potential, and hence it is given by

$$\Phi_E/k_B T = \frac{1}{2} \int d\mathbf{r} q(\mathbf{r}) \phi(\mathbf{r}) - 2U^\text{self}_{k_B T}, \quad (22)$$

with $q(\mathbf{r}) = \sum_{i=1,2} \sigma \delta(|\mathbf{r} - \mathbf{R}_i| - a)$, with $\mathbf{R}_1$ and $\mathbf{R}_2$ the centre-of-mass position of particle 1 and 2, respectively, and $U^\text{self}_{k_B T}$ is the self energy of a single particle. Now $\phi(\mathbf{r})$ is the dimensionless electrostatic potential of the two-body problem. Using the linear superposition approximation (LSA), which entails that the two-body electrostatic potential is given by the sum of the single-particle electrostatic potentials of the two particles, gives the DLVO expression Eq. (1) if one uses the stress-tensor method$^{23}$. However, applying the LSA directly to Eq. (22) gives the wrong result, because it inappropriately accounts for ion-exclusion from the hard core of one particle caused by the double layer of the other particle, which is a curious peculiarity of the free energy energy route to pair interactions in the theory of charged colloids$^{82}$.

Using the spherical-shell renormalisation method, on the other hand, we find that the effective pair potential can be approximated as

$$\Phi_E/k_B T \approx \int d\mathbf{r} q_S(\mathbf{r}) \varphi_{2S}(\mathbf{r}) - 2U^\text{self}_{k_B T}. \quad (23)$$

Here $q_S(\mathbf{r}) = \sum_{i=1,2} \sigma_S \delta(|\mathbf{r} - \mathbf{R}_i| - R)$ is the charged distribution of two ion-impenetrable charged shells, with the same centre-of-mass positions as the spherical particles. Note that singular-charge distributions have an infinite self energy $U^\text{self}_{k_B T}$ that we have to subtract in Eq. (23) by using an appropriate regularisation procedure. For example, one way is by giving the shells a finite thickness, and taking the thickness in the final step of the calculation to zero. It can straightforwardly be shown that the two-shell electrostatic potential is simply $\varphi_{2S}(\mathbf{r}) = \sum_{i=1,2} \varphi(\mathbf{r} - \mathbf{R}_i)$. Therefore, the real benefit of this method is that Eq. (23) is determined by the same $\alpha$ and $\gamma$ that are determined from the single-particle problem. This method resembles how the electrostatic part of the DLVO expression can be obtained by solving the auxiliary problem of a spherical shell or a point charge, accounting properly for ion-hard core exclusions, although
The point/shell charge value together with the ions contained within \( r < a \) equal the charge on the particle, see for a more detailed discussion the Appendix in Ref. \(^{82}\) for the shell calculation and Section 2.6 in Ref. \(^{91}\) for the point-charge method. Unfortunately, a similar method to determine \( \sigma_2 \) does not apply here, since \( \phi(r) \) is inhomogeneous for \( r < a \) when the particle is dispersed in an anisotropic dielectric medium, which therefore requires a numerical fit. However, using the shell method does give the correct expression within LSA via a free energy route.

Furthermore, the DLVO theory is just the first-order term in a complicated series expansion, where the higher-order terms become more important in the case of high salt concentrations and strong double layer overlap beyond the LSA\(^2\). We can therefore expect that Eq. (23) becomes progressively more inaccurate at high salt concentrations and strong double layer overlaps\(^{23}\). Indeed, comparing with numerical calculations, we show in the SI that this is indeed the case.

To evaluate Eq. (23) one has to perform four integrals numerically, which is computationally less expensive than solving the (three-dimensional) PB equation followed by a stress tensor or free-energy integration. To progress further, one can perform again a multipole expansion, but this time of the pair potential from the shell method, to obtain an analytically tractable expression that gives more insight in the physics of the effective pair interaction in anisotropic media. See the main text Eq. (12), and the SI for the derivation of the multipole expansion, as well as comparison with numerical calculations of the full nonlinear theory (but at low charges). Second, we choose to use the multipolar expansion in the main text because we want to treat the screened electrostatic interaction on the same footing as the elastic interaction, which is given on the level of a multipolar expansion as well.

**DATA AVAILABILITY**

All data are available from the authors upon reasonable request.

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**AUTHOR CONTRIBUTIONS**

J. C. E. performed the numerical and analytical theoretical calculations under the supervision of M. R.; B. S. and H. M. performed experiments and analyzed experimental data under supervision of I. I. S. All authors contributed in writing and discussing the manuscript.

**COMPETING INTERESTS**

The authors declare no competing interests.