I will discuss here several aspects of liquid crystal colloids:

- orientational ordering of liquid crystal around colloidal particles (including defects, density, order parameter, and biaxiality maps).
- host-mediated interactions between these particles (elastic and depletion-like).

In this work we use large-scale computer simulations (molecular dynamics). I will also explain advantages and disadvantages of using this technique to study colloidal systems.
What are nematic colloids?

A `good' model for a conventional colloidal system is a mixture of spherical particles of different sizes. Particles of each type have the same size; different types have incomparable sizes: a typical colloidal system has ratio of the order mcm/A. The difference in scales often allows to treat small particles (i.e. host system) phenomenologically, without going into molecular details, and consider interaction and dynamics of bigger particles `mediated' by small particles.

If particles of a host fluid have anisotropic shape and are, on average, aligned along some axis (called a director, \( n \)) then the host liquid has long-range orientational ordering. Note, that translational ordering is still short-ranged (i.e. it is still a liquid, not a solid). In this case the host liquid forms a nematic phase, the simplest of the liquid crystals mesophases, and we call the colloidal system a liquid crystal colloid.
What differs liquid crystal colloids from usual colloidal systems? Why do we consider them separately from ordinary colloids? There are several reasons for doing this.

Any text-book on liquid crystals (e.g. P.G.De Gennes, J.P.Prost ‘Physics of Liquid Crystals’) mentions that orientational ordering of liquid crystals is long ranged. If we distort average molecular orientation (the director $n$) then this distortion vanishes on the scale much larger than the molecular scale. In the elastic theory this distance is infinite. If we take into account thermal fluctuations of the director, the distortions become negligible when their amplitude is comparable to the amplitude of the thermal fluctuations of the director.

In addition, elastic deformations of the director are anisotropic, i.e. one needs different amount of energy to create different type of the deformation (splay, bend, or twist). This implies that interactions of colloidal particles due to elastic forces can be anisotropic.
Defects

Satellite defect (hyperbolic hedgehog) Saturn-ring defect with a disclination ring

Possible director configurations induced by a spherical droplet with homeotropic boundary conditions in a nematic with total topological charge of zero.

• Interactions between the particles are anisotropic
• Defect type defines symmetry of interaction (dipolar, quadrupolar)


Long-range elastic interaction is not the end of the story. Director field is a vector field. Colloidal particles provide some orientation of this field at the particle surface. Sufficiently strong homeotropic anchoring of the director (that is, normal to the particle surface) induces a radial point (hedgehog) defect with topological charge +1. If the director field is uniform far from the particle, i.e. the total topological charge of the whole system is zero, then an additional defect must be created to compensate the radial hedgehog.

Several types of defects can arise in this case. The first is a hyperbolic hedgehog with a topological charge −1, called dipolar or satellite defect. The second is quadrupolar or Saturn-ring defect, i.e. −1/2 strength disclination ring that encircles the spherical particle. The dipole configuration is stable for the micrometer-sized particles (or droplets) usually realized experimentally; the Saturn-ring configuration appears when the droplet size is reduced.

Since the far director field around the particles can be of dipolar or quadrupolar symmetry, the long-range interactions can be of dipolar or quadrupolar type. This will depend on the boundary conditions on the particle surface and the size of the particles.
Example: Multiple Emulsion

(a) Microscope image of a nematic multiple emulsion
(b) A chain of water droplets under high magnification,
(c) A nematic drop containing a single water droplet.


Everything above can be observed in multiple emulsions, when the water droplets (1-5mcm) are dispersed in a nematic liquid crystal host with a small amount of a surfactant added to stabilize the interface. The nematic LC is usually a much larger drop (50mcm) in a continuous water phase (multiple emulsion).

When two or more small water droplets cohabit the same nematic drop, they form linear chains. The effect is driven by nematic host – the chains break and colloidal droplets disperse upon warming the sample to the isotropic phase. Therefore, anisotropic LC induces an attractive interaction to cause the chaining (dipole-dipole interaction) as well as a short-range repulsive interaction. The defects in the host fluid prevent contact and give rise to the long-range anisotropic attractive interaction between the droplets [P. Poulin, H. Stark, T.C. Lubensky, D.A. Weitz, Science, 1997].
Chaining

Two water droplets with normal boundary conditions

Several water droplets suspended in an aligned nematic

Additional long-range forces can induce ordering in suspended droplets


Here is more detailed optical microscope picture using crossed polarizers of two water droplets with normal boundary conditions suspended in an aligned liquid crystal. The droplets are aligned along the alignment axis of the liquid crystal which is along the horizontal axis. The director of each dipole, defined by the direction from the center of the droplet to the core of the compensating defect, is the same. This leads to the presence of a hyperbolic hedgehog between the particles. The separation between the particle is a few tenths of a micrometer.

Optical microscope picture of several water droplets suspended in an aligned liquid crystal. The droplets form a long chain that is aligned along the alignment axis of the liquid crystal, which is along the horizontal axis.
Another example of nematic colloids is a **soft solid**, discovered recently. If we increase concentration of the colloidal particles (particle volume fraction $f \sim 20\%$), we will observe a colloid-liquid-crystal composite. At room temperature it is sufficiently rigid to slice with a knife and engrave. Note, that this suspension without liquid crystal is an easily pourable liquid, as is 5CB in its nematic phase. The mixture at room temperature is a birefringent waxy solid with significant storage modulus [S.P. Meeker, W.C.K. Poon, J. Crain, E.M. Terentjev, Phys. Rev. E, 2000].

Stages in the formation of the composite morphology (a) The isotropic dispersion: the colloidal particles are dispersed homogeneously in the isotropic phase of 5CB. (b) The kinetic mechanism by which the particle network is formed: at the isotropic-nematic transition the colloidal particles are expelled from the emergent nematic droplets (grey regions). The mixture therefore separates into pure (particle-free) nematic domains separated by (particle-rich) isotropic regions. The nematic domains continue to grow until the network morphology is fully developed. The final result, (c), is therefore largely determined by the phase transition kinetics of the liquid crystal.

The storage modulus of this composite is anomalously high and cannot easily be deduced from the known properties of the parent compounds.
Descriptions of the host fluid

**Elastic theory** (Frank free energy):
1. The defect core is treated as an isotropic inclusion with some unknown free energy
2. The liquid crystalline phase is treated as uniaxial
3. Order parameter and density are constant

**Full order tensor** (Landau-de Gennes free energy):
1. Density is constant
2. No depletion-like interactions

**Molecular Dynamics simulation**: takes into account almost everything

There are several ways to describe liquid crystal host:

**Elastic theory**
- predicts stability of defects and enables to calculate elastic part of colloidal interactions analytically.
- neglects defect core structure, treats nematic liquid crystal as uniaxial even in the core region, ignores variation of order parameter and density.

**Full order tensor description**
- provides order parameter/biaxiality maps of the defect core; takes into account some non-linear effects
- no density variation and depletion-like forces.

**Molecular dynamics**
- takes into account density variation near the particle surface and in the core region (important for lyotropic LCs) and depletion-like interactions between particles.
- limitation on the system size (small colloidal particles).

In this work we used molecular dynamics simulation. We used domain decomposition algorithm which allows to simulate trajectories of several million particles in a reasonable time.
The systems consist of 8,000-1,000,000 mesogens.


Several words about the potential we used. Host liquid (nematic liquid crystal) was modeled as a sea of ellipsoids interacting through the soft repulsive potential. For a given temperature \((T = 1.0 \text{ in dimensionless units})\) this can be thought as hard ellipsoids of elongation \(e = 3\).

The interaction of molecules with colloidal particles and walls was given by a shifted Lennard-Jones repulsion potential between their centers. This interaction potential results in strong homotopic anchoring of the liquid crystal molecules, normal to the particle surface or to the wall.

Due to long-range director distortions around the colloidal particles we used systems of 8,000 – 1,000,000 particles.
To begin with, we consider single spherical particle and study liquid crystal ordering and defect structures around this colloidal particle.

For all studied radii (R = 3-15) the ring defect appears immediately after equilibration of the system starting from the isotropic phase. This type of the defect is energetically more favorable for the chosen (small) droplet sizes.

A typical director map one can see that the ring defect does not have very long director distortions. Its core region is located very close to the droplet surface and the director distortion vanishes very quickly in the liquid crystal bulk. This is in agreement with quadrupolar nature of the defect. This type of the defect can be studied using comparatively small number of particles = small simulation boxes.

The order parameter map in general reflects the typical structure of the core: the center of the core has lower order than the bulk and the core region extends over a few molecular length.
From the typical density map one can see that profiles that avoid disclination have an oscillating structure near the particle surface that is typical for a liquid-wall interface. The profiles that cross the disclination ring do not have these oscillations. The difference is due to partial melting of the liquid crystal in the disclination core region, as well as change in the orientation of the liquid crystal molecules. We will come back to the density profile later, when we consider depletion interactions between the particles.
Satellite Defect

In case of satellite defect director distortion extends much further than that of the ring defect. This reflects the dipolar symmetry of the director distribution. Therefore, to study satellite defect, one needs very large systems. Another reason for using such a big system is that satellite defect is stable only for large particles (R ~ 15).

The order-parameter map shows that the core region is elongated and the region occupied by the disclination core is quite large. It will be difficult to describe this defect as a point with some definitive core region. The density maps show that, in this case, the density oscillations are not affected by the presence of the defect.
Both the satellite and ring defects are at least metastable for $R=15$ (recently was shown that there is a first-order transition between these defects [R.Yamamoto, Phys.Rev.Lett., 2001]). Once particular defect is realized in the system, it is stable over the scale that is accessible to our simulations. However, the satellite defect is not stable for smaller droplets. Indeed, we observed a rapid transition (several thousands MD steps) of the satellite defect to the ring defect for $R < 15$).

For small particles, equilibrating the configuration with satellite defect we observed that it evolves into an off-center ring defect. The ring moved slowly toward an equatorial position. In principle, one might observe the same type of transition in the opposite direction, for droplet sizes large enough to stabilize the satellite defect. This is still unreachable for the system sizes we explore here.
What happens if we have elongated particles? The situation becomes even more complicated. On the list of problems one has to clarify are:

- The nematic ordering around the particle, including possible topological defects;
- The type and strength of the orientational coupling between the particle and its aligned molecular environment;

As we already know, the answer to the first question is known for spherical particles. However, due to the loss of azimuthal symmetry, there are no studies of the nematic ordering around elongated particles even in the framework of the elastic theory.

The answer to the second question is also not know. The results of the theory only indicate that, depending on the type and strength of anchoring, the equilibrium position of the particle may be either parallel or perpendicular to the liquid crystal director [S.V.Burylov and Y.L.Raikher, Phys. Rev. E, 1994].
Here a slice in the $y$-$z$ plane is shown, for different tilt angles of the rod. It is clear that the director distribution around the rod is not axially symmetric. In principle, the configuration with axial symmetry is also possible, when the rod is along the $z$ axis. However, we were not able to observe it in our simulations even when distorted isotropic configurations containing the colloidal particle were compressed to the ordered nematic state. This method, in principle, gives the lowest free-energy configurations in an unbiased way.

As rod rotates, the director field becomes less and less frustrated and finally we have a stable orientation of the rod perpendicular to the director.
Elastic Torque

Here torque on the rod vs rod tilt angle is shown. Positive torque corresponds to the situation when the liquid crystal host tends to align the rod perpendicular to the director far from the particle (which is along the z axis). Two cases are shown, when the rod is far from the wall, in the middle of the cell (squares) and close to the wall (circles). Triangles represent the depletion force on the particle, when it is close to the wall.

The dependence of the torque on the rod is far from the sin(2θ) proposed by Burylov and Raikher. Moreover, the torque is not equal to zero at θ = 0, because of the symmetry braking.
From the measurement of the torque on the particle we saw that the equilibrium position of it is perpendicular to the director far-field. Therefore, here we consider the situation when the particle is normal to the director in more detail. It is effectively a two-dimensional case, because of the transnational symmetry along the symmetry axis of the particle.

The same topological arguments are applicable as in the case of a spherical particle: one can have a disclination line of strength \(-1\), or a pair of disclination lines of strength \(-1/2\).

However, from the energetic point of view, the situation is different. For the elongated particle, both defects are disclination lines. The elastic energy per unit length associated with a disclination of strength \(m\) is \(\pi K m^2 \ln(R/r)\), where \(R\) is the size of the sample and \(r\) is a lower cutoff radius (the core size). This means that the energy of a pair of \(-1/2\) disclinations is always smaller than that of a single \(-1\) disclination. Therefore, one can expect that the pair of \(-1/2\) disclinations will always be a stable configuration. In principle, the \(-1\) defect can still form a metastable state [see more detailed discussion in: J.Fukuda and H.Yokoyama, Eur.Phys.J.E, 2001; M.Tasinkevych, N.M.Silvestre, P.Patricio, and M.M.Telo da Gama, to be published, 2002].

In our MD simulations we observed only a pair of \(-1/2\) defects.
I will continue with particle-particle interactions. We already know that long particles tend to orient perpendicular to the director. Therefore, here we consider interaction of two long rods which are aligned perpendicular to the director and parallel to each other. We also know the defect configuration: each particle has two $-1/2$ disclination lines. Therefore, we expect quadrupolar interaction between the particles.
Density oscillations near the particles immediately tell us that we will have an oscillating depletion-like contribution to the total interparticle force. Moreover, for small separations (several molecular length) this contribution is dominating and should not depend on the direction of the particle-particle separation vector, since liquid crystal molecules in between the particles are aligned parallel to the separation vector.

For larger separations we shall observe non-linear elastic interactions since the position of the defects may change. For even larger separations, when depletion force are small, we shall recover quadrupolar interaction.
If one assumes that the final distribution of the director is a superposition of the director fields around particles (large particle-particle separations, linear elastic theory) then the effective interaction reads

\[ F = 6\pi K (r^4 + R^4)/d^4 \left( 1 - 2\sin^2 2\alpha \right) \]

The effective elastic interaction between colloidal particles decays as \( d^4 \) is strongly anisotropic: repulsive if particles approach each other horizontally or vertically (\( \alpha = 0, 90\text{deg} \)), and attractive for intermediate oblique orientations (e.g. \( \alpha = 45 \)).
Finally, here is the inter-particle force (component parallel to the center-center vector) as a function of the center-center separation distance. Positive (negative) values correspond to the repulsion (attraction) between the particles. It is clear that for the size of the colloidal particles we use the depletion force is much bigger than the elastic force, this is why all three curves are almost on the top of each other. Inset shows the force curve for larger distances, the differences are relatively small, but can be still seen.

We expect that bigger particles will give more distinct dependence on the orientation of the center-center vector (elastic force scales as $R^4$).
To check if we observe the elastic force, we measured the force perpendicular to the center-center vector. There is no depletion contribution to this component of the force, and if it is non-zero it is elastic by nature. Indeed, as we can see from the plot, for $\alpha = 45$ deg this component of the force has negative value. In case of $\alpha = 0$ the force is zero. However, as I already mentioned, there are non-linear effects, and for small separations defects change their positions, breaking the symmetry, which can be seen from the small increase of the force near the separation $d = 8$. 

A component of the force perpendicular to the center-center vector. Colloidal radius: $R = 3$. 

Tangential Component

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Nonlinear Effects

Here we present how the director structure and position of the defects changes with the change of the separation between the particles. If we have 2 particles then in total there are 4 disclinations lines. However, when the particles merge, two defects annihilate to conserve the total topological charge of the system. Before the annihilation, the defects to change their position relative to the particles. At these separations we have nonlinear effects, which can modify the quadrupolar interaction between the particles. Indeed, in the framework of the elastic theory it was shown that this nonlinearity can lead to the repulsion of the particles, which might prevent their coalescence [M.Tasinkevych, N.M.Silvestre, P.Patricio, and M.M.Telo da Gama, to be published, 2002].
Conclusions

Spherical particles

- Two types of defects: satellite of strength $-1$ and Saturn ring of strength $-1/2$.
- Complex defect core structure (biaxial with density modulation).
- Rapid transition of the satellite to Saturn ring defect via off-center ring defect.

Elongated particles

- Orient perpendicular to the director.
- Two $-1/2$ strength defect lines.
- Nonlinear effects (change in the position of defects) for small separations influence inter-particle interaction.
- Depletion interaction dominates for the MD accessible particle sizes.
- Elastic forces can be measured from the transverse component of the force.
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