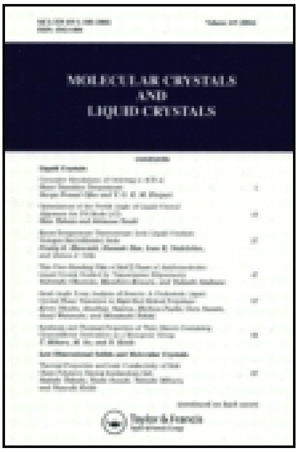


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# Temperature and Confinement Effect on Interparticle Force in Nematic Colloids

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# Temperature and Confinement Effect on Interparticle Force in Nematic Colloids

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*We experimentally studied the interparticle force between two colloidal particles with point defects in a nematic liquid crystal. The force* F *at various temperatures was measured using optical tweezers and with a free release method. The effective elastic constant was evaluated from* F *using electrostatic analogy of nematic field. At respective temperatures, that is in good agreement with the splay constant obtained by dielectric measurement. The dependence of* F *on cell thicknesses was also studied in a wedge-type cell. In a thinner cell, the magnitude of* F *becomes smaller, and* F *becomes short-ranged.*

**Keywords** Colloidal particle; confinement effect; electrostatic analogy; interparticle force; nematic liquid crystal



## 1. Introduction

The specific interaction between colloidal particles in structural fluids such as liquid crystals [1–3] has recently attracted attentions of researchers. When a colloidal particle with strong homeotropic surface anchoring is dispersed in a nematic liquid crystal (NLC), the particle itself becomes a topological defect of orientational order in nematic medium (radial hedgehog). Moreover, an additional point defect (hyperbolic hedgehog) spontaneously appears near the particle to minimize the orientational deformation of the whole NLC [1–6]. This type of a particle-defect pair is often called a "*dipole*". Owing to the long-ranged and anisotropic nature of the orientational order in an NLC, the interaction between colloidal particles in an NLC is also long-ranged and anisotropic.

According to the electrostatic analogy for a nematic field [3], a particle in dipole configuration exhibits the interaction of dipolar nature. When two particle-defect pairs are aligned collinearly parallel to the uniform director field, the interparticle force $F$ for same size particles (radius $a$) is theoretically given by [3]

$$F = -\frac{24\pi K\alpha^2 a^4}{R^4} + \frac{480\pi K\beta^2 a^6}{R^6}, \tag{1}$$

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where $R$ is the center-to-center distance between the particles, $K$ is the elastic constant of the NLC (one-constant approximation), $\alpha$ is the dipolar constant ($\alpha = 2.04$), and $\beta$ is the quadrupolar constant ($\beta = 0.72$). Since the contribution of quadrupolar term to the total force is expected to be relatively small [3,4], $F$ is attractive and proportional to $R^{-4}$.

In this paper, we studied the dependence of $F$ on temperature and thickness of a cell. Although there are many experimental studies on interparticle forces in NLCs [7–12], the dependence of $F$ on temperature has not been reported except ref. [13]. In this study, we discussed the dependence of $F$ on temperature quantitatively by comparing the effective elastic constant evaluated from experimental data using Eq. (1) with the elastic constants of an NLC measured by dielectric method. For confinement effect, the interparticle force in a confined NLC has been reported experimentally and theoretically [14–16]. However, the experimental study was limited to the case of particles with quadrupole nature in a homeotropic cell. We studied the influence of cell thickness on $F$ between the particles in dipole configuration in a homogeneous cell for the first time.

## 2. Experiment

In experiments, we dispersed polystyrene latex particles with radius $a = 2.55 \pm 0.1\,\mu m$ (Magsphere Inc.) in low refractive NLCs, MJ032358 and MLC-2082 (MERCK). This enables us to trap the particles by optical tweezers stably in any direction. Since the Nematic-Isotropic phase transition temperature of MLC-2082 is 37.2°C, this NLC was used for the measurement of temperature dependence. For the measurement of cell-thickness dependence, MJ032358 was used for its large value of $F$. The particles were coated with octadecyldimethyl (3-trimethoxysilypropyl) ammonium chloride (DMOAP) to promote homeotropic anchoring at their surfaces. The mixture of the particles and the NLC was injected into a cell. The surfaces of the cell were spin-coated with polyimide and were rubbed unidirectionally to attain the homogeneous alignment of the NLC in a cell. For the measurement of temperature dependence, the thickness of the NLC sample was fixed to about 20 μm. For the measurement of thickness dependence, we used a wedge-type cell. The thickness of the NLC sample can be varied from 6 to 40 μm by changing the position of the particles in the cell using optical tweezers.

We used a Nd:$YVO_4$ laser (Spectra Physics, wavelength: 1064 nm) for dual beam optical tweezers. The beam was introduced to an inverted fluorescence microscope (TE2000U, Nikon) and focused by a 100× oil immersion objective lens (Nikon Plan Flour, NA 1.30). The position of one laser spot was varied by two Galvano mirrors (Model 6450, Cambridge Technology Inc.), and the other tweezers is fixed.

### 2.1. *Free Release Experiment*

In this method, we evaluated the interparticle force $F$ between two particles in a nematic host by simply observing their motions under a microscope. When we placed two particles at a certain separation, they approached each other along the far-field director. The observed time evolution of the interparticle distance $R$ is shown in Figure 1. From Figure 1, we evaluated the approaching speed $v$ at respective $R$. The interparticle force $F$ was evaluated from the Stokes law, as $F = 3\pi\eta_{\|}av$ [7].

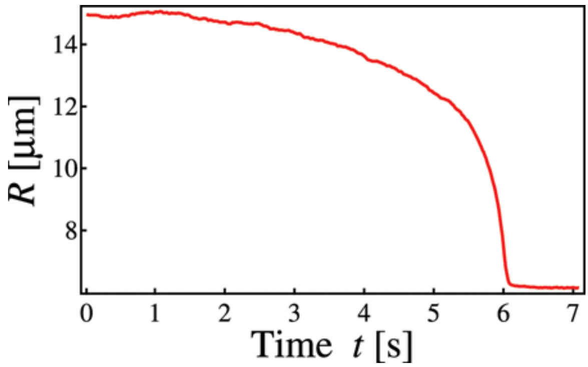


**Figure 1.** Time evolution of interparticle distance $R$ obtained by free release measurement. (Figure appears in color online.)

Here, $\eta_{\parallel}$ is the viscosity parallel to the director and is measured the viscosity $\eta_{\parallel}$ by separate experiment explained below [17].

The local viscosity was obtained from the Brownian motion of a single particle. We calculated the time evolution of the mean square displacement of the center position of the particle from the microscope image. The diffusion coefficient of a Brownian particle along director, $D_{\parallel}$, is given by the Stokes-Einstein relation as $D_{\parallel} = k_B T / 6\pi\eta_{\parallel} a$ [17], where $k_B$ is the Boltzmann constant and $T$ is the temperature. Figure 2 shows the dependence of the mean square displacement of a particle along the director $\Delta_{\parallel}^2$ on the elapsed time $t$. Since $\Delta_{\parallel}^2$ is theoretically given as $\Delta_{\parallel}^2 = 2D_{\parallel}t$, the slope of the best-fitted line in Figure 2 is $2D_{\parallel}$. With use of the Stokes-Einstein relation, we obtained $\eta_{\parallel} = 0.0176$ [Pa · s]. We evaluated the force $F$ from the approaching speed $v$ and the viscosity $\eta_{\parallel}$.

### 2.2. *Dual Beam Optical Tweezing Measurement*

We used a dual beam optical tweezers to measure the interparticle force. One beam was fixed to measure the displacement of the trapped particle in order to calculate $F$

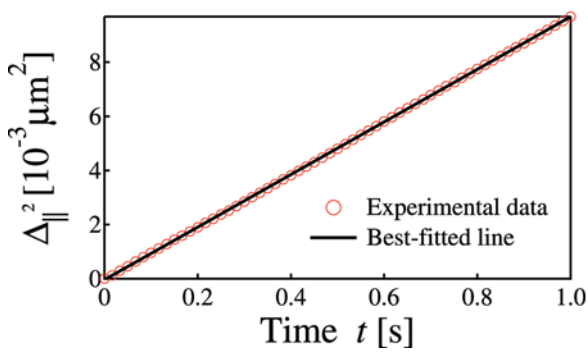


**Figure 2.** Time evolution of the mean square displacement $\Delta_{\parallel}^2$. The slope of the best-fitted line drawn as a solid line is $2D_{\parallel}$, where $D_{\parallel}$ is the diffusion coefficient parallel to director. (Figure appears in color online.)

[12,18]. The distance $R$ was varied along the direction parallel to the far-field director by scanning the other beam as slowly as 50 nm/s. In order to evaluate the force, we measured the spatial profile of the optical trapping potential beforehand by observing the thermal motion of a particle and evaluated a "spring constant" of the optical trapping potential. We calculated the force $F$ from the spring constant and the displacement of the particle trapped by the fixed beam.

### 2.3. *Dielectric Measurement*

The elastic constants of MLC-2082 were measured by dielectric measurement [19]. We measured a capacitance of a liquid crystal cell (electrode area $S$ is 16 mm$^2$ and thickness $L$ is 20 μm) with homogeneous alignment by an LF impedance analyzer (4192A, Hewlett-Packard).

The splay ($K_1$) and bend ($K_3$) elastic constants were obtained by the bias electric field dependence of the permittivity. Figure 3 shows the dependence of the capacitance $C$ on the bias voltage $V$. When a high voltage $V$ is applied to the cell, $C$ is theoretically given by

$$\frac{C}{C_\perp} \cong \gamma + 1 - \frac{2\gamma}{\pi}(1+\gamma)^{\frac{1}{2}}\frac{V_C}{V}\int_0^1 \left(\frac{1+\chi\varphi^2}{1+\gamma\varphi^2}\right)^{\frac{1}{2}} d\varphi, \tag{2}$$

where $\gamma$, $\chi$ are constants and $V_C$ is the threshold voltage of Freedericksz transition. They are respectively defined as

$$\gamma = S\Delta\varepsilon / C_\perp L, \tag{3}$$

$$\chi = K_3/K_1 - 1, \tag{4}$$

$$V_C = \pi(K_1/\Delta\varepsilon)^{\frac{1}{2}}, \tag{5}$$

where $\Delta\varepsilon$ is the dielectric anisotropy ($=\varepsilon_{//}-\varepsilon_\perp$), and $C_\perp$ is the capacitance of the cell with homogeneous alignment. According to Eq. (2), when we plotted the dependence

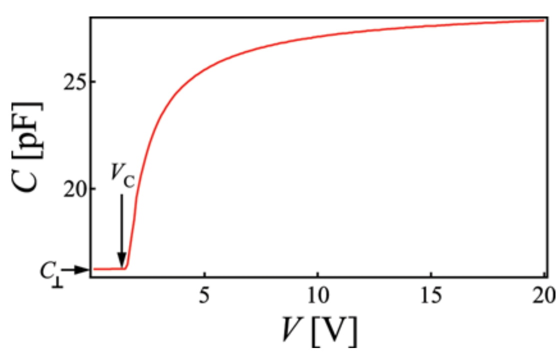


**Figure 3.** Dependence of the capacitance $C$ on the bias voltage $V$. The capacitance of the cell with homogeneous alignment is $C_\perp = 16.18$pF. The threshold voltage of Freedericksz transition is $V_C = 1.58$ V. (Figure appears in color online.)

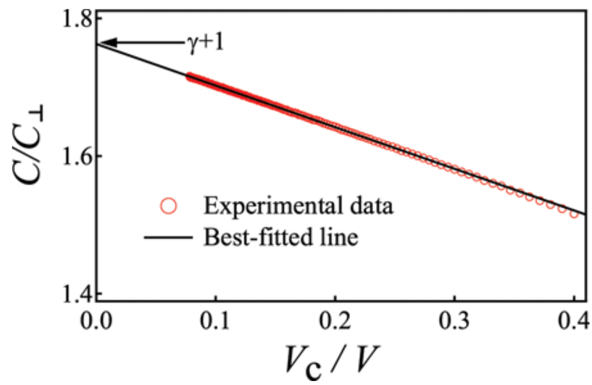


**Figure 4.** Dependence of $C/C_{\perp}$ on $V_C/V$. $C/C_{\perp}$ is almost proportional to $V_C/V$ (Eq. (2)). (Figure appears in color online.)

of $C/C_{\perp}$ on $V_C/V$ as shown in Figure 4, $\gamma+1$ is obtained from the interception of Figure 4. Moreover, $\Delta\varepsilon$ is obtained from Eq. (3), and $\chi$ is determined from the slope of Figure 4. We evaluated $K_1$ from Eq. (5), and $K_3$ from Eq. (4).

## 3. Results and Discussion

### 3.1. *Temperature Dependence of Interparticle Force*

The dependence of $F$ on the interparticle distance $R$ obtained by optical tweezers and free release method at 25°C are shown in Figure 5. In both force curves, $F$ at large $R$ is found to follow the theoretical dependence of $F=-A/R^4$ ($A$: constant). On the other hand, $F$ at small $R$ deviates from the theoretical force curve. The deviation, which is not our focus in this paper, has been discussed and explained by the short-range repulsive force caused by deformation of a point defect between particles [10].

For the magnitude of $F$, they are largely different for the two methods. In the free-release method, we assume that the viscosity is independent of $R$ and equals

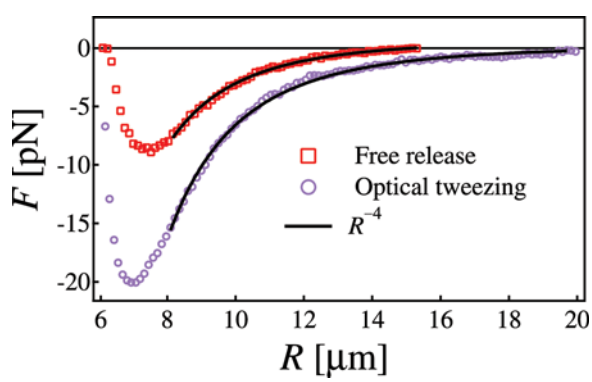


**Figure 5.** Dependence of interparticle force $F$ on the interparticle distance $R$ obtained by two methods at 25°C. The solid line shows the dependence predicted by Eq. (1) of $R^{-4}$. (Figure appears in color online.)

to that obtained from the Brownian motion. However, for small $R$, the orientation of the liquid crystal between the particles differs from that for large $R$. Therefore, the effective viscosity for small $R$ will be different from that used in calculation. We also assume that the interparticle force equals to the frictional force. The velocity of a particle increases for short $R$, and the system is no longer stationary. In addition, the nematic host cannot escape quickly from the region between the particles. This hydrodynamic effect seriously affects the obtained interparticle force in the free release method. On the other hand, in the optical tweezers method, the results obtained are free from the viscosity or the hydrodynamic effect. Therefore, the optical tweezers method seems to be more reliable than the free-release method.

We studied the dependence of interparticle force $F$ on temperature for MLC-2082. Since the constant $A$ is theoretically given by $A = 24\pi K\alpha^2 a^4$ from the Eq. (1), the effective elastic constant $K$ can be evaluated at respective temperatures and are shown in Figure 6. In Figure 6, we also plotted the splay $K_1$ and the bend elastic constant $K_3$ obtained by dielectric measurement at respective temperatures. The discrepancy between $K$ values is due to the hydrodynamic effect in the free-release method, as mentioned above. The effective elastic constant $K$ obtained by optical tweezing measurement is found to be close to $K_1$. This seems to be reasonable because the main deformation around a particle with dipole configuration is splay one.

### 3.2. *Confinement Effect on Interparticle Force*

We studied the dependence of $F$ on $R$ for MJ032358 in a homogeneous cell with various thicknesses $L$ as shown in Figure 7. The force $F$ was measured with dual-beam optical tweezers. Although the force curves are qualitatively similar to each other, the magnitude of $F$ at the same $R$ decreases with decrease of $L$. For large thickness $L = 20$, 30, and 38 µm (the force curves for $L = 30$ and 38 µm are not shown in Figure 7 for clarity), $F$ at large $R$ exhibits the power law of $|F| \propto R^{-4}$. We obtained the exponent $\beta$ assuming that power law $|F| \propto R^{\beta}$ at the distance $R > 8$ µm and shown

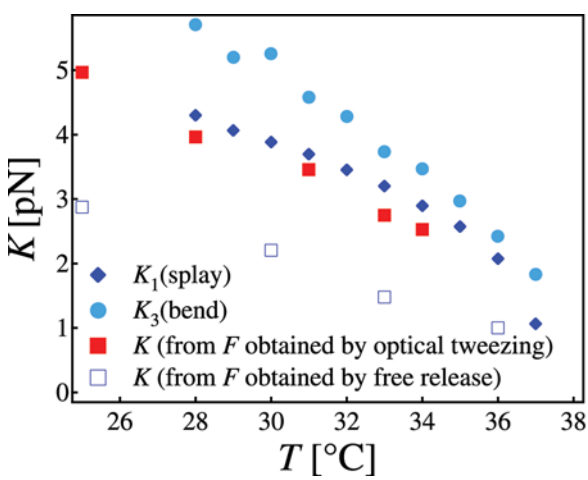


**Figure 6.** Dependence of the elastic constant $K$ of MLC-2082 on temperature $T$. $K_1$ and $K_3$ were measured by dielectric method. (Figure appears in color online.)

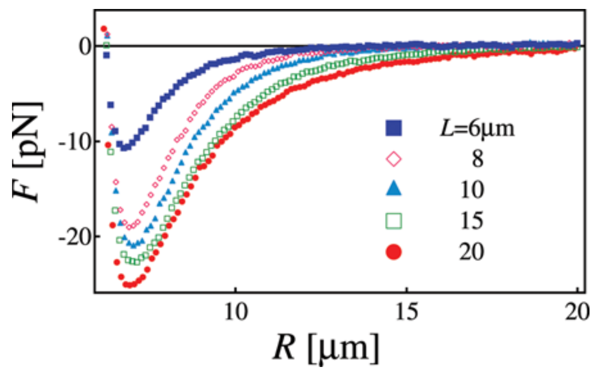


**Figure 7.** Dependence of the interparticle force $F$ on the interparticle distance $R$ for MJ032358 confined in the cells with various thicknesses $L$.

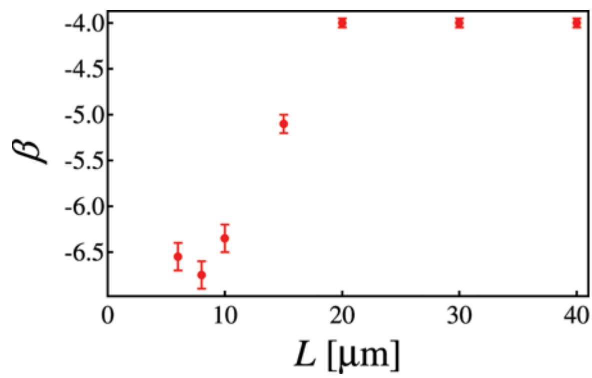


**Figure 8.** Dependence of the exponent $\beta$ on the cell thickness $L$. $\beta$ monotonically decreases from $-4$ to $-6.5$ with decreasing $L$ from 20 to 6 μm. (Figure appears in color online.)

in Figure 8. The exponent $\beta$ monotonically decreases from $-4$ to $-6.5$ with decreasing $L$ from 20 to 6 μm. The behavior that $F$ becomes more short ranged in thinner cells is qualitatively in agreement with that for quadrupolar particles in a homeotropic cell [14].

## 4. Conclusions

We studied the interparticle force between two colloidal particles with hyperbolic hedgehog defects in a nematic liquid crystal. The dependence of the interparticle force on interparticle distance in a thick cell follows a power law which has been predicted theoretically. From the magnitude of the force, the effective elastic constant was evaluated and compared with the splay and bend elastic constants. The effective constant obtained by optical tweezing measurement is found to be close to the splay constant at various temperatures. The effect of confinement in a thin cell on the interparticle force was also studied using a wedge-type cell. The force at the same distance becomes smaller and more short-ranged in a thinner cell.

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