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Matsuyama Akihiko, Kato Tadaya

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Discontinuous elongation of nematic gels by a magnetic field

Akihiko Matsuyama and Tadaya Kato
Department of Chemistry for Materials, Faculty of Engineering, Mie University, Tsu Mie 514-8507, Japan
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The effects of a magnetic field on the swelling of a nematic gel immersed in a low molecular weight liquid crystal solvent are examined by using a mean field theory. The nematic-isotropic (paranematic) phase transition temperature of the gel and the solvent is controlled by the external field. As a result of an anisotropic coupling between the gel and solvent, the shape of the gel is discontinuously (or continuously) elongated with increasing the strength of the external field. We examine the condition for a first- and second-order volume phase transition of the gel under a magnetic field.

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Liquid crystalline (LC) gels have attracted a considerable attention in recent years due to their anisotropic mechanical, electrical, and optical properties [1,2]. These properties are induced by the coupling between shape change and orientational (nematic) ordering. The controls of the nematic ordering by mechanical stress and magnetic (or electric) fields are particularly important in dynamical and static properties of the LC gels. Moreover, when a LC gel are immersed in a low molecular weight liquid crystal solvent, deformations of the gel can be induced by applied electric field because a rearrangement of the LC solvent transmits to the gel [3]. The theoretical studies on phase behaviors of LC gels have been accomplished for nematic gels immersed in isotropic solvents and in nematogens in the absence of the external field [4–7]. It is now important to consider phase behaviors and molecular shape of a gel immersed in a LC solvent under a magnetic field.

Some authors considered theoretically the influence of a magnetic field on a nematic-isotropic transition temperature of pure nematogens [8,9], phase behaviors in solutions of rodlike polymers [10], phase diagrams of polymer-liquid crystal mixtures [11], and orientations of nematic elastomers [12]. Recently, we examined the effect of the magnetic field on the swelling of a nematic gel immersed in an isotropic solvent [13] and showed that the nematic ordering of the gel by applied magnetic field causes a discontinuous condensation of the gel.

In this Rapid Communication we theoretically study the swelling of a nematic gel immersed in a LC solvent under a magnetic (or electric) field by using a mean field theory. We show that the gel causes a discontinuous (or continuous) elongation with increasing the strength of the external field due to the anisotropic coupling between the gel and LC solvent.

Consider a main-chain liquid crystalline polymer gel dissolved in a low molecular weight liquid crystal. Our theory can be quite general for side-chain liquid crystalline polymer gels in the frame work of our mean field approximations. Let \( n \) be the number of segments on a subchain between crosslinks and \( n_0 \) be the axial ratio of the LC solvent. The repeating unit on the subchain consists of a rigid mesogen with the axial ratio \( n_m \) and a flexible spacer which has the number \( n_s \) of segments. The total number of segments on the subchain is given by \( n = (n_m + n_s)t \), where \( t \) is the number of repeating units. Let \( N_s \) and \( N_0 \) be the number of the subchains and solvents inside the gel, respectively. Then the volume fraction of the gel is given by \( \phi = a^3 n N_s / V \), where \( a^3 \) is the volume of a unit segment, \( V = a^3 N \) is the volume of the gel, \( N_s = n N_s / N_0 \) shows the total number of unit cells, and \( R^3 = V / N_s \) is the volume per a subchain. The volume fraction of the mesogen is given by \( \phi_m = a^3 n_m N_s / V \). The fraction of spacer segments is \( \phi_s = p \phi_m \).

To derive the value of the equilibrium concentration \( \phi \), we consider thermodynamics of our systems. The free energy of the LC gel can be given by

\[
F = F_{el} + F_{mix} + F_{nem} + F_{ext}. \tag{1}
\]

The first term shows the elastic free energy due to the deformation of the gel. Let \( R_1 \) be the length of the gel along the direction \( z \) of the orienting field and \( R_p \) be the length along the perpendicular direction \( (R^2 = R_z^2 + R_p^2) \). Combining the classical elastic free energy obtained by Flory [14] with the freely jointed rod model [15], the elastic free energy is given as a function of \( \phi \) and an orientational order parameter \( S_m \) of the mesogen [6,13],

\[
\beta F_{el} / N_1 = \frac{3}{n A} \left[ \left( \frac{\phi}{n A} \right)^{1/3} + \frac{\phi}{3} \ln A - \phi \left( 1 - \frac{2}{3} \ln \sqrt{n} \phi \right) \right]. \tag{2}
\]

where \( A = (1 + 2 S_m)(1 - S_m)^2 \). The elongation of the gel is measured by \( R_z / R_0 \),

\[
R_z / R_0 = \left[ \frac{1 + 2 S_m}{\sqrt{n} \phi (1 - S_m)} \right]^{1/3}. \tag{3}
\]

where \( R_0 = a \sqrt{n} \). When \( S_m = 0 \), Eq. (2) results in the elastic free energy for an isotropic swelling [14]. The second term \( F_{mix} \) in Eq. (1) shows the free energy for an isotropic mixing of a gel with a solvent molecule and is given by the Flory-Huggins theory [14].
\[
\beta F_{\text{mix}}^{\alpha}/N_i = \frac{(1-\phi)}{n_0} \ln(1-\phi) + \chi(1-\phi)\phi_s, \tag{4}
\]

where \(\chi\) shows the isotropic (Flory-Huggins) interaction parameter between a nematogen and a spacer segment. Here we assume that the LC solvent is a good solvent for the mesogen on the subchain. The third term \(F_{\text{nom}}\) in Eq. (1) shows the free energy for nematic ordering. To describe the nematic ordering of mesogens and LC solvents, we take into account the orientational-dependent (Maier-Saupe) interactions [15,17]. We consider three coupling terms of the anisotropic interactions. Let \(\nu_{mm}\) be the orientational dependent (Maier-Saupe) interactions between the mesogens, \(\nu_{m0}\) be that between the mesogen and the solvent, and \(\nu_{00}\) be that between the solvents. The nematic free energy is given by

\[
\frac{\beta F_{\text{nem}}^{\alpha}/N_i}{n_0} = \sum_{i=m,0} \phi_i \int f_i(\theta) \ln 4\pi f_i(\theta) d\Omega - \frac{1}{2} \nu_{mm} \phi_m^2 S_m^2 - \nu_{m0} (1-\phi) S_m S_0 - \frac{1}{2} \nu_{00} (1-\phi)^2 S_0^2, \tag{5}
\]

where \(d\Omega = 2\pi \sin \theta d\theta\), \(\theta\) is the angle between a nematogen and a director of the orienting field. The \(f_i(\theta) (i=m,0)\) shows the orientational distribution functions of the mesogen \((m)\) and that of the nematogen \((0)\), respectively. In the numerical calculations, we set \(\nu_{00} = \nu (=U_u/k_B T)[17]\) for a simplicity. The orientational order parameter \(S_m\) is given by \(S_m = \int f_m(\cos \theta) f_m(\theta) d\Omega\), where \(f_m(\cos \theta) = \frac{1}{3} \cos^2 \theta - 1/3\). The last term \(F_{\text{exy}}\) in Eq. (1) shows the free energy changes due to an external field. Let \(\Delta \chi_m = \chi_\parallel - \chi_\perp\) be a diamagnetic anisotropy of the mesogen and \(\Delta \chi_0 = \chi_\parallel - \chi_\parallel\) be a diamagnetic anisotropy of the solvent. When a magnetic field \(\mathbf{H}\) is applied to the system, the free energy is given by

\[
\beta F_{\text{exy}}^{\alpha}/N_i = -\phi_m \int \beta \Delta \chi_m (\mathbf{n} \cdot \mathbf{H})^2 f_m(\theta) d\Omega \]

\[
- (1-\phi) \int \beta \Delta \chi_0 (\mathbf{l} \cdot \mathbf{H})^2 f_0(\theta) d\Omega, \tag{6}
\]

where \(\mathbf{n}\) and \(\mathbf{l}\) are the unit orientation vector of the mesogen and that of the solvent, respectively. We here define two dimensionless parameters of the external field as \(h_m = \beta \Delta \chi_m H^2\) and \(h_0 = \beta \Delta \chi_0 H^2\). In this paper we set \(h = h_0 (=h_m) > 0\) and define the reduced magnetic field \(\epsilon = h / h_0\) in terms of a critical magnetic field \(h_c\) for the pure LC solvent.

The orientational distribution function \(f_m(\theta)\) of the mesogen and \(f_0(\theta)\) of the LC solvent are determined by free energy (1) with respect to these functions under the normalization conditions \(\int f_i(\theta) d\Omega = 1\). This leads to the self-consistency equation for two orientational parameters: \(S_i = I_i[\eta_i]/I_0[\eta_i]\), where

\[
\eta_m = n_m \left[ \nu_{mm} \phi_m S_m + \nu_{m0} (1-\phi) S_0 + \frac{2}{3} h_m - B(\phi, S_m) \right], \tag{7}
\]

FIG. 1. Phase diagram on the temperature-concentration plane for the gel of \(n_m = 2.5\). The reduced external field \(\epsilon\) is varied.

\[
B(\phi, S_m) = \frac{3}{n \phi_m} \left[ \left( \phi/n_A \right)^{1/3} - \phi \right] S_m(1-S_m). \tag{8}
\]

\[
\eta_m = n_m \left[ \nu_{m0} \phi_m S_m + \nu_{00} S_0(1-\phi) + \frac{2}{3} h_0 \right], \tag{9}
\]

and the function \(I_i[\eta_i]\) is defined as

\[
I_i[\eta_i] = \int_0^1 [P_2(\cos \theta)]^{q \exp[\eta_i P_2(\cos \theta)]} d(\cos \theta). \tag{10}
\]

The chemical potential \(\mu_0(\phi, S_m, S_0)\) of the LC solvent inside the gel can be calculated by \(\mu_0 = (\partial F/\partial N_0)_{N, \epsilon}\) and the chemical potential \(\mu_s(\eta_s)\) of the pure LC solvent outside the gel is given by substituting \(\phi = 0\) into \(\mu_s(\phi, S_m, S_0)\). The orientational order parameter \(S_m\) of the LC solvent outside the gel is determined by the self-consistent equation \(S_b = I_b[\eta_b]/I_0[\eta_b]\), where \(\eta_b = n_b(\nu_0 S_b + 2 h_0/3)\).

The equilibrium concentration \(\phi\) of the gel can be determined from the balance among the LC solvent existing outside and inside the gel [13].

\[
\mu_0(\phi, S_m, S_0) = \mu_0(\phi, S_m, S_0). \tag{11}
\]

Here we have two characteristic nemat-s isotropic transition (NIT) temperatures: One is the NIT temperature \(T_{N,N}^{\text{NIT}} = n_0 U_u/(4.54 k_B)\) of the pure LC solvent outside the gels, and the other is the temperature \(T_{N,N}^{\text{NIT}}\) of the gels. In the following calculations, we set \(n_0 = 2, n_s = 2, t = 20, \nu/\chi = 6\) for a typical example [13].

Figure 1 shows the phase diagram on the temperature-concentration plane for the gel of \(n_m = 2.5\) \(T_{N,N}^{\text{NIT}} = 1.09\). The value \(\epsilon\) of the reduced external field is varied. When \(\epsilon = 0\), for high temperatures of \(T > T_{N,N}^{\text{NIT}}\), the gel and LC solvent are both in an isotropic state. With decreasing temperature, the swelling curve of the gel has a kink at \(T_{N,N}^{\text{NIT}}\), where
the LC solvent outside the gel becomes a nematic phase (see Fig. 2). At further decreasing temperature, the isotropic gel is condensed (or the volume fraction of the gel is increased), and the NIT takes place at \( T_{NI}^G \) where the gel and the LC solvent inside the gel become a nematic phase. The condensed-isotropic gel is discontinuously transformed into a swollen-nematic gel at \( T_{NI} \). The dotted lines show the two phase coexistence between the nematic \((N)\) and isotropic \((I)\) (or paranematic \((pN)\)) gels. It is important to emphasize that, for a LC gel immersed in an isotropic solvent, the isotropic gel is discontinuously transformed into the condensed nematic state at \( T_{NI}^G \) as temperature decreases because the free energy is minimized by the condensation (phase separation) rather than the swelling of the gel [5,13,18]. As the strength of the external field increases, the phase transitions move to higher temperatures and critical points (closed circles) appear on the phase diagram. The orientational order parameters are shown in Fig. 2 for various values of the external field \( \epsilon \). The solid curve refers to the orientational order parameter \( S_b \) of the pure LC solvent outside the gel, the dash-dotted line shows the order parameter \( S_0 \) of the LC solvent inside the gel, and the dotted curve shows the order parameter \( S_m \) of the mesogen on the gel. For a finite \( \epsilon \), the nematic phase transforms into the paranematic phase with field induced order as increasing temperature. The nematic-paranematic transition (NPT) temperature \( T_{NP}^G (T_{NP}^L) \) of the gel (LC solvent) moves to higher temperatures with increasing \( \epsilon \). The critical field appears at \( \epsilon = 1 (h_c = 0.04) \) for the LC solvent outside the gel and at \( \epsilon = 1.25 \) for the gel. At \( T_{NP}^L \), the condensed gel corresponds to the paranematic phase with a weak orientational order and the swollen gel corresponds to the nematic state where the gel and solvent molecules are highly oriented. The swelling of the nematic gel needs to nematic ordering of the solvent molecules.

Figure 3 shows the phase diagram on the temperature-concentration plane for the gel of \( n_m = 4 \) (\( T_{NI}^G / T_{NI}^L = 0.96 \)) for various values of the \( \epsilon \). When \( \epsilon = 0 \), for high temperatures of \( T > T_{NP}^G \), the gel and LC solvent are both in an isotropic state. As temperature decreases, the isotropic gel is discontinuously collapsed into the nematic state at \( T_{NI}^G \) (see Fig. 4). At further decreasing temperature, the nematic gel is swelled and the swelling curve of the gel has a kink at \( T_{NI} \). As increasing \( \epsilon \) the discontinuity in the volume of the gel diminishes at \( \epsilon = 0.6 \). The critical magnetic field appears at \( \epsilon = 1 (h_c = 0.03) \) for both the gel and LC solvent. At a given

**FIG. 2.** Temperature dependence of the orientational order parameters for various values of the reduced external field \( \epsilon \) with \( n_m = 2.5 \).

**FIG. 3.** Phase diagram on the temperature-concentration plane for the gel of \( n_m = 4 \). The reduced external field \( \epsilon \) is varied.

**FIG. 4.** Temperature dependence of the orientational order parameters for various values of the reduced external field \( \epsilon \) with \( n_m = 4 \).
temperature between \( T_{NI} \) and \( T_{N\ell} \), the gel is swelled with a weak external field. As shown in Fig. 4, as increasing the strength of the external field, the NPT temperature \( T_{NP} \) of the LC solvent moves to higher temperatures but the \( T_{N\ell} \) of the gel is almost constant. When \( \epsilon = 0.6 \) these two NPT temperatures become the same, but it still shows the first-order phase transition. For \( \epsilon = 1 \), the critical temperature appears

and the three order parameters are continuously changed with temperature.

Figure 5 shows the elongation \( R_z / R_0 \) for the gel of \( n_m = 2.5 \) plotted against the reduced external field \( \epsilon \) for various temperatures. When \( T < T_{N\ell} \), the nematic gel is elongated along the orienting field and the value of the length \( R_z \) is slowly increased with \( \epsilon \). When \( T_{N\ell} < T < T_c (= 0.98 T_{NI}) \), the gel is discontinuously elongated by applied magnetic field and transformed from the condensed-paranematic state into the swollen-nematic state. For the case of a LC gel immersed in an isotropic solvent, the length \( R_z \) is discontinuously decreased with increasing the strength of the magnetic field because the nematic ordering induced by the external field causes a condensation of the gel [13]. The nematic ordering of not only the gel but also of the LC solvent is central importance to elongating and swelling of the nematic gel by applied magnetic field. The anisotropic expansion of the nematic gel is induced by the strong anisotropic coupling between the gel and LC solvent under the external field. The discontinuity in the length \( R_z \) diminishes with increasing temperature until the critical temperature \( T_c \).

To summarize, we have predicted different phase diagrams of a nematic gel immersed in a nematogen under a magnetic (or electric) field and showed that the nematic gel is discontinuously (or continuously) elongated with increasing the strength of the external field. We hope that such discontinuity in the gel will provide new electrical and optical properties by magnetic and electric fields.