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Volume phase transitions of smectic gels

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We present a mean-field theory to describe volume phase transitions of side-chain liquid crystalline (LC) gels, accompanied by isotropic-nematic-smectic-*A* phase transitions. Three different uniaxial nematic phases (N_1, N_2, and N_3) and smectic-*A* phases (S_1, S_2, and S_3) are defined by using orientational order parameter S_m of side-chain liquid crystals (mesogens), S_b of semiflexible backbone chains, and a translational order parameter σ for a smectic-*A* phase. We derive the free energy for smectic-*A* phases of side-chain LC gels dissolved in an isotropic solvent and examine the swelling curve of the LC gel, the orientational order parameters, and the deformation of the LC gel as a function of temperature. We find that the LC gel discontinuously changes the volume at an isotropic-nematic, an isotropic-smectic-*A*, and a nematic-smectic-*A* phase transition.

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I. INTRODUCTION

Swelling behavior of a liquid crystalline (LC) gel dissolved in a solvent molecule has been the subject of many theoretical and experimental studies. A liquid crystalline ordering such as a nematic and a smectic ordering can be a major cause in the shape change of LC elastomers [1–5]. Recent experimental studies [6–11] have demonstrated that a nematic ordering can take place the first-order volume phase transition of nematic gels. These volume changes are induced by changing temperature and applied electric fields [12–16]. The experimental swelling curves have been theoretically described in the context of Flory and Maier-Saupe models [9,17–19].

When we consider a nematic phase of LC gels or LC polymers, there are three possible types of the nematic phase, which was first considered by Wang and Warner [20]. The three nematic phases can be defined by two orientational order parameters: one is S_m of nematogenic side-chains (mesogens) and the other is S_b of a semiflexible backbone chain. When one order parameter is positive, the other can be positive or negative. Figure 1 shows three principal uniaxial nematic phases for a side-chain LC polymer. The N_1 phase ($S_m>0$ and $S_b<0$) is defined as that the mesogens are aligned along to the ordering direction (z) and the backbone chain is perpendicular to the mesogens. The N_2 phase ($S_m<0$ and $S_b>0$) is defined as that the backbone chain is aligned along to the ordering direction z and the mesogens are perpendicular to the backbone chain. The third N_3 phase is defined by $S_m>0$ and $S_b>0$, where the backbone and mesogens are oriented to the ordering direction z. In the N_1 phase, the backbone chain adopts an oblate shape. In the N_2 and N_3 phases, a prolate shape of the backbone is obtained. The identification of these nematic phases has been based on an examination of the shape of the backbone chain using x-ray diffraction [21,22] and neutron scattering [23,24]. The N_2 phase is unusual because the side chains are not aligned with the director (z axis). Such a polymer requires both mesogenic side groups and a mesogenic rigid-backbone chain [25,26], where the backbone chain and side groups simultaneously and independently are ordered. Recently, we have presented a mean-field theory to describe these nematic phases (N_1, N_2, and N_3) for a side-chain LC gel dissolved in an isotropic solvent and predicted volume phase transitions [27].

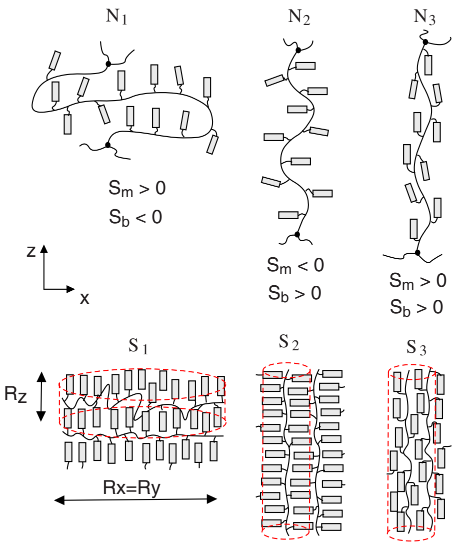

FIG. 1. (Color online) Schematic representations of three nematic and smectic-*A* phases for side-chain liquid crystalline gels. Depending on two orientational order parameters, one is the S_m of nematogenic side chains (mesogens) and the other is the S_b of semiflexible backbone chain, we can define a nematic N_1 phase with $S_m>0$ and $S_b<0$, a N_2 phase with $S_m<0$ and $S_b>0$, and a N_3 phase with $S_m>0$ and $S_b>0$. In the N_1 phase, the backbone chain adopts an oblate shape. When these nematic domains are stacked into a smectic-*A* phase, three different smectic-*A* phases appear, depending on the value of the orientational order parameters S_m and S_b. In the S_1 phase, the backbone chain is distributed on the *x*-*y* plane, which is perpendicular to a nematic director. In the S_2 and S_3 phases, the backbone chain has a prolate shape within a layer of a smectic-*A* phase.

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When these nematic domains are stacked into a smectic layer, we can expect three possible types of the smectic-*A* phase depending on the value of the orientational order parameters S_m and S_b. As shown in Fig. 1, the S_1 phase shows a smectic-*A* phase with $S_m > 0$ and $S_b < 0$. The backbone chain between crosslinking points has an oblate shape within a smectic-*A* phase. The S_2 phase shows a smectic-*A* phase with $S_m < 0$ and $S_b > 0$ and the S_3 phase shows a smectic-*A* phase with $S_m > 0$ and $S_b > 0$. In the S_2 and S_3 phases, the backbone chain has an prolate shape within a smectic layer. When temperature decreases, we can expect nematic (N_1)-smectic-*A* (S_1) phase transition (N_1S_1), N_2S_2, etc.

These anisotropic deformations of smectic gels are strongly dependent on the chemical structures of networks, such as side-chain or main-chain liquid crystalline elastomers and interactions between a backbone chain and a side chain. Moreover, isotropic-smectic and nematic-smectic phase transitions may be a major cause of the volume changes of liquid crystalline gels. There is no experimental evidence about volume phase transitions of smectic gels dissolved in isotropic solvent molecules, although it is worth giving a first attempt to understand the relations between the volume changes and the liquid crystalline phase transitions stated above paragraph. Recently Adams and Warner (AW) [28] presented the elastic free energy of smectic elastomers and confirmed some experimentally observed elastic behavior such as stress-strain curves of smectic-*A* elastomers. However, the AW model cannot describe the phase transitions such as isotropic-smectic and smectic-nematic ones because it does not include order parameters for nematic and smectic-*A* phases. To describe the volume phase transitions of smectic gels, we have to take into account these order parameters in the elastic free energy of smectic gels because the order parameters continuously or discontinuously change through the phase transitions. The elastic free energy including the orientational order parameter has been presented by Warner and Terentjev [1] for nematic elastomers, known as neoclassical rubber theory. However, there is no attempt for elastic free energy including the translational order parameter of a smectic-*A* phase at least a mean-field level.

In this paper we derive the elastic free energy as a function of deformations of smectic gels, orientational order parameters, and a translational order parameter of a smectic-*A* phase. We extend the previous model for the nematic phases (N_1, N_2, and N_3) [27] to the smectic-*A* phases (S_1, S_2, and S_3) of a LC gel and we construct the free energy of smectic gels dissolved in isotropic solvent molecules. In the next section, we derive the elastic free energy of the smectic-*A* gel and the free energy of the LC gel. In Sec. III, we obtain the equilibrium values of the order parameters and the chemical potential of a solvent molecule inside the LC gel. In the Sec. IV, we show some numerical results. We find that isotropic-smectic-*A* and nematic-smectic-*A* phase transitions induce volume phase transitions of the LC gels.

II. FREE ENERGY OF LIQUID CRYSTALLINE GELS

We consider a side-chain liquid crystalline polymer gel, consisting of a semiflexible backbone chain and LC side chains (mesogens), dissolved in a solvent. Let n be the number of segments on a side-chain LC polymer between crosslink points. The repeating unit on the side-chain LC polymer consists of a mesogen with the axial ratio n_m and a backbone chain which has the number n_b of segments. We here assume that all segments (backbone chain and side group) to be the same width, which is taken as the unit length a. Then the total number of units of length in a repeating unit is n_m+n_b and the total number of segments on the side-chain LC polymer is given by $n=(n_m+n_b)t$, where t is the number of repeating units. Let N_g and N_0 be the numbers of the side-chain LC polymers and solvent molecules inside the gel, respectively.

The volume fraction of the gel dissolved in a solvent is given by

$$\phi_g = a^3 n N_g / V, \tag{1}$$

where a^3 is the volume of an unit segment, $V=a^3N_t$ is the volume of the gel, and $N_t(=nN_g+N_0)$ shows the total number of segments including polymers and solvent molecules. The volume of the gel is also given by $V=N_gR_xR_yR_z$, where R_i is the distance along the $i(=x,y,z)$ axis between crosslink points of the gel. The volume fraction of the mesogen is given by

$$\phi_m = a^3 n_m t N_g / V = w\phi_g, \tag{2}$$

where $w \equiv n_m/(n_m+n_s)$ is the fraction of mesogen segments. The volume fraction ϕ_b of the backbone chain is given by $\phi_b=(1-w)\phi_g$ and we have $\phi_b+\phi_m=\phi_g$.

To derive the equilibrium volume fraction ϕ_g of the gel, we consider thermodynamics of our systems. The free energy of the LC gel can be given by

$$F = F_{el} + F_{mix} + F_{nem} + F_{sm}, \tag{3}$$

where the first term F_{el} shows the elastic free energy due to the strain of a liquid crystalline gel, the second term shows the free energy of mixing of a gel with a solvent molecule, the third term corresponds to a nematic ordering of the gel, and the last term shows the free energy of smectic ordering. When $F_{el}=0$, the free energy F results in that of the bulk solution of a LC gel without deformations. In the following sections, we derive the four free energies.

A. Elastic free energy

The first term F_{el} shows the elastic free energy due to the deformation of a gel, which shows an isotropic state, nematic, and smectic-*A* phase. This free energy consists of three terms

$$F_{el} = F_{el,1} + F_{el,2} + F_{el,3}, \tag{4}$$

where the first term shows the elastic free energy due to the deformation of nematic gels [1,29,30]. The second term is the pairing of functions at the ends of the chain in the formation of networks, which is given by Flory's elastic theory [31,32]. The last term corresponds to the layer compressibility of smectic-*A* gels. In the following we introduce the three terms.

We first briefly introduce the elastic free energy ($F_{el,1}$) for nematic polymers. This term is given by the deformation of backbone chains of the LC gel and then it can be given by applying the classical rubber theory to nematic elastomer [1]. Let $\mathbf{R}$ be the end-to-end distance of a backbone polymer and $N(=n_b t)$ be the total number of segments on a backbone chain. In uniaxial polymers, the mean-square end-to-end distance is given by

$$\langle \mathbf{R}_i \cdot \mathbf{R}_j \rangle = \frac{1}{3}\ell_{ij} L, \tag{5}$$

where the effective step lengths form a tensor ℓ_{ij} and $L=aN$ is the contour length of the chain. Here, we take that a nematic director is along the z axis. In uniaxial polymers, mean-square sizes in the plane perpendicular to director $\mathbf{n}$ are identical: $R_x=R_y$. For such nematic polymers, we here consider for the step length ℓ_{ij} of a freely jointed nematic polymer chain. Using Eq. (5), the step length is given by

$$\ell_{ij} = \frac{3a}{N}\sum_{i,j}^{N}\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle, \tag{6}$$

where $\mathbf{u}$ is the unit vector along the bond vector of a segment. In the freely jointed model, there is no correlation between the different bonds and then we have $\mathbf{u}_i \cdot \mathbf{u}_j = u_i^2 \delta_{ij}$. The coordinate projections in the frame where the director is along z give $u_z = \cos\,\theta$, $u_y = \sin\,\theta$, and $u_x = \sin\,\theta$, where θ is the angle between the bond and the z direction. This means that the backbone chain describes a random walk with step lengths $a\cos\,\theta$ in the z direction and $a\sin\,\theta$ in the xy plane. Then, from Eqs. (5) and (6), the spontaneous mean-square radius $\mathbf{R}_s = (R_{x0}, R_{x0}, R_{z0})$ of the backbone chain in a nematic phase along the z axis and the perpendicular direction are given by

$$R_{z0}^2 = \frac{1}{3}\ell_{\parallel} L = a^2 N \langle \cos^2\,\theta \rangle = R_0^2 (1 + 2S_b), \tag{7}$$

$$R_{x0}^2 = \frac{1}{3}\ell_{\perp} L = a^2 N \langle \sin^2\,\theta \rangle = R_0^2 (1 - S_b), \tag{8}$$

respectively, where $\ell_{\perp}$ and $\ell_{\parallel}$ are the effective step lengths in the directions parallel and perpendicular to the director and we have used the nematic order parameter $S_b = (3/2)\langle \cos^2\,\theta \rangle - 1/2$ of the backbone chain. In the nematic phase the spontaneous radius depends on the order parameter. In an isotropic phase, $S_b = 0$, the spontaneous radius of the chain results in $R_0 = a\sqrt{N}$. The reference state of the deformation strains is given by the spontaneous radius $\mathbf{R}_s$ of the chain. When a chain of the spontaneous radius $\mathbf{R}_s$ as a reference state is transformed to $\mathbf{R} = \hat{\lambda}\mathbf{R}_s$ by a strain, the deformation tensor $\hat{\lambda}$ is given by

$$\hat{\lambda} = \begin{pmatrix} \lambda_{xx} & 0 & 0 \\ 0 & \lambda_{yy} & 0 \\ 0 & 0 & \lambda_{zz} \end{pmatrix}, \tag{9}$$

where the deformation of the gel is characterized by the principal ratios

$$\lambda_{zz} \equiv R_z / R_{z0} = R_z / (R_0 \sqrt{1 + 2S_b}), \tag{10}$$

$$\lambda_{xx} = \lambda_{yy} \equiv R_x / R_{x0} = R_x / (R_0 \sqrt{1 - S_b}). \tag{11}$$

The number of configurations of the polymer chain, connected two crosslinks separated by a distance $\mathbf{R}$ in the nematic network, is proportional to the anisotropic Gaussian distribution

$$p(\mathbf{R}) \propto \exp\left[-\frac{3}{2L} R_i \ell_{ij}^{-1} R_j\right] = \exp\left[-\frac{3R_x^2}{2\ell_{\perp} L} - \frac{3R_y^2}{2\ell_{\perp} L} - \frac{3R_z^2}{2\ell_{\parallel} L}\right]. \tag{12}$$

Then the elastic entropy of the polymer chain is given by

$$S_1(\mathbf{R}) = k_B T \ln p(\mathbf{R}). \tag{13}$$

Using the deformation λ_{ii}, Eq. (13) can be written as

$$S_1(\mathbf{R}) = -\frac{k_B}{2}[\lambda_{xx}^2 + \lambda_{yy}^2 + \lambda_{zz}^2]. \tag{14}$$

Then the entropy change due to the deformation from the initial spontaneous state $\mathbf{R}_s$ to the current state $\mathbf{R}$ is given by

$$\Delta S_1 = S_1(\mathbf{R}) - S_1(\mathbf{R}_s) = -\frac{k_B}{2}[\lambda_{xx}^2 + \lambda_{yy}^2 + \lambda_{zz}^2 - 3]. \tag{15}$$

The elastic free energy $F_{el,1}$ due to the deformation of the gel, consisting of N_g backbone chain, is given by

$$F_{el,1} = -N_g T \Delta S_1 = \frac{k_B T N_g}{2}[\lambda_{xx}^2 + \lambda_{yy}^2 + \lambda_{zz}^2 - 3]. \tag{16}$$

Equation (16) is the free energy of a deformed rubber, where λ_{ii} is diagonal with no shear deformations, known as a neoclassical rubber theory for uniaxial extension [1]. Note that the anisotropic of the backbone chain resides in the factor λ_{ii}, which is given by the orientational order parameters [Eqs. (10) and (11)].

Another additional term in the elastic free energy is given by the pairing of functions occurring at the ends of the chain. According to the Flory elastic theory [31,32], the probability of occurrence of a configuration in which ξ pairs of reactive sites are suitably situated for combination to take place is proportional to $(\delta V / V)^{\xi}$, where δV is the volume within which one junction must occur relative to its reaction partner and $V(=R_x R_y R_z)$ is the volume of the polymer chain, depending on $\mathbf{R}$. The entropy of the pairing is given by

$$S_2(\mathbf{R}) = -k_B \xi \ln[\delta V / V(\mathbf{R})]. \tag{17}$$

Then the entropy change due to the deformation from the initial spontaneous state $\mathbf{R}_s$ to the current state $\mathbf{R}$ is given by

$$\Delta S_2 = S_2(\mathbf{R}) - S_2(\mathbf{R}_s) = k_B \xi \ln(\lambda_{xx}\lambda_{yy}\lambda_{zz}). \tag{18}$$

For a perfect network of functionality ξ (or mean functionality), the total number N_g of the chains, consisting of the gel, is $N_g = \xi J/2$, where J is the number of junctions on the gel. Then the free energy change due to the dispersion of the embedded junctions is given by

$$F_{el,2} = -N_g T \Delta S_2 = -k_B T N_g (2/J) \ln(\lambda_{xx}\lambda_{yy}\lambda_{zz}). \tag{19}$$

Elastic free energies $F_{el,1}$ and $F_{el,2}$ do not include the deformation of a smectic phase. We here take into account

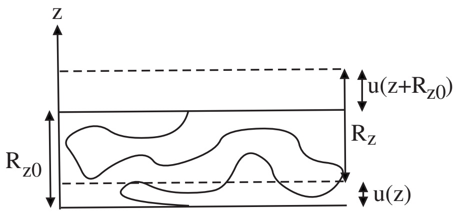

FIG. 2. Layer displacement $u(z)$ for a smectic-A phase.

the layer compressibility for a smectic-A (S_m-A) phase [28,33,34]. The smectic-A phase of the gel is characterized by a density (or volume fraction) modulation along a z direction to the layers

$$\phi_g(\mathbf{r}) = \phi_g[1 + \sigma \cos(q_0(z + u(\mathbf{r}))\ ], \tag{20}$$

where ϕ_g is the mean value, q_0 is the periodicity wave number, and $u(\mathbf{r})$ is the layer displacement or an arbitrary phase [35]. In an isotropic and a nematic phase, $\sigma=0$. Then, for the natural choice of a order parameter of S_m-A phases is σ, which is defined as the amplitude of a one dimensional density wave along z axis. To take into account both σ and $u(\mathbf{r})$, it is convenient to define the complex order parameter [35]

$$\psi(\mathbf{r}) = \sigma \exp[iq_0 u(\mathbf{r})], \tag{21}$$

where σ generally depends on a position, however, we assume that σ is constant in the mean-field level. The complex order parameter varies from place to place and then we have to add gradient terms which express the tendency for the S_m-A phase to be homogeneous. Such free energy of the displacements is given by [33–35]

$$F_{el,3} = B\left|\frac{\partial \psi}{\partial z}\right|^2, \tag{22}$$

where B is the layer compressibility and we neglect the layer bending caused by a splay deformation: $|\partial\psi/\partial x|^2 + |\partial\psi/\partial y|^2$. As schematically shown in Fig. 2, the polymer chain is confined into the smectic layer of the length R_{z0} and the dimensionless wave number of the S_m-A phase is given by $q_0 = 2\pi/(R_{z0}/a)$. The length R_z is $R_z = u(z+R_{z0}) - u(z) + R_{z0}$ and so the layer displacement is given by

$$\partial u/\partial z = (R_z - R_{z0})/R_{z0} = \lambda_{zz} - 1. \tag{23}$$

The layer compressibility for a smectic-A phase is given by

$$\begin{aligned} F_{el,3} &= B\left|\frac{\partial \psi}{\partial z}\right|\left|\frac{\partial \psi^*}{\partial z}\right| = B\sigma^2 q^2\left(\frac{\partial u(z)}{\partial z}\right)^2 \\ &= B\sigma^2\left(\frac{2\pi}{R_{z0}/a}\right)^2(\lambda_{zz}-1)^2 = \frac{4\pi^2 B\sigma^2}{n_b t(1+2S_b)}(\lambda_{zz}-1)^2, \end{aligned} \tag{24}$$

where ψ^* denotes complex conjugate.

Then the elastic free energy for a LC gel, which shows isotropic, nematic, and S_m-A phases, is given by the sum of the three terms

$$\begin{aligned} \beta F_{el} &= \beta(F_{el,1} + F_{el,2} + F_{el,3}) \\ &= N_g\left[\frac{1}{2}(\lambda_{xx}^2 + \lambda_{yy}^2 + \lambda_{zz}^2 - 3)\right. \\ &\quad \left. - (2/J)\ln(\lambda_{xx}\lambda_{yy}\lambda_{zz}) + B_1(\lambda_{zz} - 1)^2\right], \end{aligned} \tag{25}$$

where $\lambda_{xx} = \lambda_{yy}$ for an uniaxial deformation. We also find the dimensionless layer compression modulus

$$B_1 \equiv \frac{b\sigma^2}{n_b t(1+2S_b)}, \tag{26}$$

where $\beta \equiv 1/k_BT$, T is the absolute temperature, and k_B is the Boltzmann constant. The $b \equiv 4\pi^2 B/\mu$ is the reduced layer compression modulus per a chain and $\mu = N_g k_B T$ is the shear modulus. Note that the dimensionless layer compression modulus B_1 depends on the order parameters S_b and σ.

Adams and Warner [28] derived the elastic free energy of smectic elastomers for the deformation of stretching parallel to the layer normal, including the deformation λ_{zx} of z dimension by layer rotation. The shear λ_{zx} starts at a threshold and lead to torques when the deformation λ_{zz} increases. Equation (25) can correctly describe the deformation without torques. The free energy obtained by Adams and Warner does not include the order parameters S_b and σ and so it is impossible to describe phase transitions such as isotropic-nematic, isotropic-smectic, and nematic-smectic phase transitions. We emphasize that Eq. (25) can be used for liquid crystalline phase transitions. When the values of S_b and σ are nonzero, Eq. (25) results in AW's elastic free energy with $\lambda_{zx}=0$, omitting the term $F_{el,2}$. The neoclassical nematic rubber theory does not take into account the term $F_{el,2}$. If we consider isotropic volume changes of the gel, we may need this term. However, the free energy $F_{el,2}$ is not an essential part for liquid crystalline elastomers because it corresponds to the pairing of functions. When $S=0$ and $\sigma=0$, Eq. (25) results in the elastic free energy for isotropic deformations, which were derived by Flory [31].

The volume fraction ϕ_g of the gel is given by

$$\phi_g = \frac{a^3 n}{R_z R_x^2} = \frac{1}{c_1\sqrt{A}\lambda_{zz}\lambda_{xx}^2}, \tag{27}$$

where we define

$$A \equiv (1+2S_b)(1-S_b)^2 \tag{28}$$

and

$$c_1 \equiv (n_b t)^{1.5}/n. \tag{29}$$

Using Eq. (27), the elastic free energy [Eq. (25)] can be expressed as

$$\begin{aligned} \beta F_{el}/N_t = \frac{\phi_g}{n}&\left[\frac{1}{c_1\sqrt{A}\phi_g\lambda_{zz}} + \frac{1}{2}\lambda_{zz}^2 - \frac{3}{2} + \frac{2}{J}\ln(c_1\sqrt{A}\phi_g)\right. \\ &\left. + B_1(\lambda_{zz}-1)^2\right]. \end{aligned} \tag{30}$$

Because the strain tensor λ_{ij}, in Eqs. (10) and (11), is a function of the orientational order parameter S_b, it is convenient to use the deformation (κ_i), related to the isotropic Gaussian chain, as

$$\kappa_z \equiv R_z/R_0, \tag{31}$$

$$\kappa_x \equiv R_x/R_0 = R_y/R_0. \tag{32}$$

Using κ_z, the volume fraction is given by

$$\phi_g = 1/(c_1 \kappa_z \kappa_x^2), \tag{33}$$

and then Eqs. (10) and (11) are rewritten as

$$\lambda_{zz} = (1 + 2S_b)^{-1/2} \kappa_z, \tag{34}$$

$$\lambda_{xx} = (1 - S_b)^{-1/2} (c_1 \phi_g \kappa_z)^{-1/2}. \tag{35}$$

Substituting Eqs. (34) and (35) into Eq. (25), the elastic free energy can be expressed as

$$\beta F_{el}/N_t = \frac{\phi_g}{n}\left[\frac{1}{c_1 \phi_g (1 - S_b)\kappa_z} + \frac{\kappa_z^2}{2(1 + 2S_b)} - \frac{3}{2} + \frac{2}{J}\ln(c_1 \phi_g \sqrt{A}) + B_1\left(\frac{\kappa_z}{\sqrt{1 + 2S_b}} - 1\right)^2\right]. \tag{36}$$

In this section we derive the elastic free energy of the LC gels due to the deformation. In the following sections, we obtain the bulk free energy for isotropic, nematic, and smectic-*A* phases.

B. Mixing free energy

The second term F_{mix} in Eq. (3) shows the free energy for an isotropic mixing of a gel with a solvent molecule. According to the Flory-Huggins theory [36], this free energy is given by

$$\beta F_{mix}/N_t = (1 - \phi_g)\ln(1 - \phi_g) + \chi \phi_g (1 - \phi_g), \tag{37}$$

where χ shows the isotropic (Flory-Huggins) interaction parameter between a gel and a solvent molecule. In this paper we take $\chi = 0$, where the solvent molecule is a good solvent for the gel.

C. Nematic free energy

The third term F_{nem} in Eq. (3) shows the free energy for nematic ordering. To describe the nematic behaviors, we take into account the orientational-dependent (Maier-Saupe) interactions [27,35,37]. We consider three coupling terms of the anisotropic interactions. Let ν_{mm} be the orientational dependent (Maier-Saupe) interactions between the mesogens, ν_{mb} be that between the mesogen and the backbone, and ν_{bb} be that between the backbone chains. Then, the nematic free energy is given by

$$\beta F_{nem}/N_t = \frac{\phi_m}{n_m}\int f_m(\theta)\ln 4\pi f_m(\theta) d\Omega + \frac{\phi_b}{n_b}\int f_b(\theta)\ln 4\pi f_b(\theta) d\Omega - \frac{1}{2}\nu_{mm}\phi_m^2 S_m^2 - \nu_{mb}\phi_m\phi_b S_m S_b - \frac{1}{2}\nu_{bb}\phi_b^2 S_b^2, \tag{38}$$

where $d\Omega \equiv 2\pi \sin\theta d\theta$, with θ is the angle between the liquid crystalline molecules and the director of the orienting field. When $\nu_{mb} > 0$, the mesogen prefers along align backbone chain. When $\nu_{mb} < 0$, the mesogen prefers to be perpendicular to backbone chain. The $f_m(\theta)$ and $f_b(\theta)$ show the orientational distribution functions of the mesogen and that of the backbone chain, respectively. The orientational order parameter S_m of the mesogen is given by

$$S_m = \int P_2(\cos\theta) f_m(\theta) d\Omega, \tag{39}$$

and the orientational order parameter S_b of the backbone chain is given by

$$S_b = \int P_2(\cos\theta) f_b(\theta) d\Omega, \tag{40}$$

where $P_2(\cos\theta) \equiv 3(\cos^2\theta - 1/3)/2$.

D. Smectic free energy

The last term F_{sm} in Eq. (3) shows the free energy for smectic-*A* ordering. To describe smectic-*A* phases, we here assume that the centers of gravity of mesogens are periodically placed along $\tilde{z}(\equiv z/n_m)$ axis. Based on the McMillan's free energy for a smectic-*A* phase [38,39], it is given by

$$\beta F_{sm}/N_t = \frac{\phi_m}{n_m}\int_0^1 f(\tilde{z})\ln f(\tilde{z}) d\tilde{z} - \frac{1}{2}\gamma \phi_m^2 (S_m \sigma)^2, \tag{41}$$

where the first term shows the entropy change due to a smectic ordering and $f(\tilde{z})$ is the distribution function for molecular position along $\tilde{z}$ axis. In inhomogeneous systems, the volume fraction of the segments on the gel is given by $\phi_g(\tilde{z})$ as a function of a position $\tilde{z}$. Using the distribution function $f(\tilde{z})$, it is given by $\phi_g(\tilde{z}) = \phi_g f(\tilde{z})$, where ϕ_g is the mean volume fraction of the gel. When the system is positionally homogeneous, we have $f(\tilde{z}) = 1$ and Eqs. (41) and (21) become zero. The distribution function is consistent with Eq. (20). The parameter γ shows the dimensionless interaction parameter between mesogens for a smectic ordering and can vary between 0 and 2 [38]. Using the distribution function $f(\tilde{z})$, the scalar order parameter σ in Eq. (21) for a smectic-*A* phase can be calculated by

$$\sigma = \int_0^1 \cos(2\pi\tilde{z}) f(\tilde{z}) d\tilde{z}. \tag{42}$$

When $\sigma = 0$, the complex order parameter becomes zero.

In the original McMillan's model for a smectic-*A* phase, the order parameter for the smectic-*A* phase is given by $\langle P_2[\cos(\theta)]\cos(2\pi\tilde{z})\rangle$. In Eq. (41), we here used the simplification of the McMillan theory obtained by decoupling the mixed order parameter: $\langle P_2[\cos(\theta)]\cos(2\pi\tilde{z})\rangle = S_m\sigma$. It has been reported that the decoupled model for the smectic-*A* phase is in quantitative agreement with the original McMillan's theory [40]. In the next section, we derive the deformation κ_z, the order parameters (S_m, S_b, σ), and the volume fraction ϕ_g of the gel in a thermal equilibrium.

III. EQUILIBRIUM SWELLING OF LIQUID CRYSTALLINE GELS

A. Equilibrium value of λ_{zz}

The equilibrium value of the elongation λ_{zz} is determined by $(\partial F/\partial\lambda_{zz})_{\{\phi_g,S_m,S_b,\sigma\}}=0$ or equivalently $(\partial F/\partial\kappa_z)_{\{\phi_g,S_m,S_b,\sigma\}}=0$. This yields

$$\lambda_{zz}-\frac{1}{c_1\sqrt{A}\phi_g\lambda_{zz}^2}+2B_1(\lambda_{zz}-1)=0. \tag{43}$$

Substituting Eq. (27) into Eq. (43), we obtain

$$\lambda_{xx}^2=[\lambda_{zz}^3(1+2B_1)-2B_1\lambda_{zz}^2], \tag{44}$$

and the volume fraction of the gel is given as a function of λ_{zz} or κ_z,

$$\phi_g=\frac{1}{c_1\sqrt{A}[\lambda_{zz}^3(1+2B_1)-2B_1\lambda_{zz}^2]}. \tag{45}$$

When $\sigma=0$, or $B_1=0$, Eq. (43) yields the deformations of nematic gels [27]

$$\kappa_z=\left[\frac{1+2S_b}{c_1\phi_g(1-S_b)}\right]^{1/3} \tag{46}$$

and

$$\kappa_x=\left[\frac{1-S_b}{c_1^2\phi_g^2(1+2S_b)}\right]^{1/6}. \tag{47}$$

Apparently, when $S_b=0$, or in an isotropic phase, we have $\kappa_z=\kappa_x=(c_1\phi_g)^{-1/3}(\equiv\kappa_{iso})$ for an isotropic deformation.

B. Equilibrium value of orientational order parameters

The orientational distribution functions $f_m(\theta)$ of the mesogen and $f_b(\theta)$ of the backbone chain are determined by the free energy (3) with respect to these functions:

$$[\delta F/\delta f_b(\theta)]_{[f_m,f(z),\phi_g,\kappa_z]}=0, \tag{48}$$

$$[\delta F/\delta f_m(\theta)]_{[f_b,f(z),\phi_g,\kappa_z]}=0, \tag{49}$$

with the normalization conditions

$$\int f_i(\theta)d\Omega=1,$$

$$i=m,b. \tag{50}$$

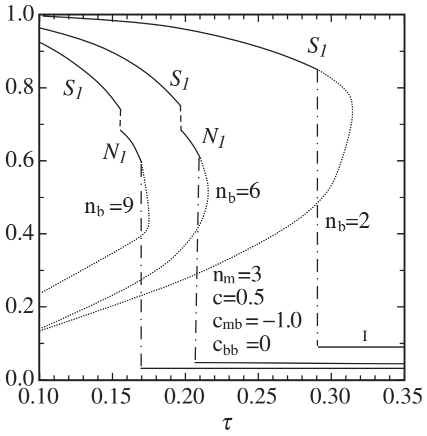

FIG. 3. Swelling curve of the gel on the $\tau-\phi_g$ plane for $t=10$, $b=1$, $n_m=3$, $c=0.5$, $c_{mb}=-1$, and $c_{bb}=0$. The value of n_b is changed.

These lead to the orientational distribution function

$$f_b(\theta)=\frac{1}{Z_b}\exp[\Gamma_b P_2(\cos\theta)], \tag{51}$$

$$\Gamma_b\equiv n_b(\nu_{bb}\phi_b S_b+\nu_{mb}\phi_m S_m-D_1/\phi_b) \tag{52}$$

for the backbone chain, where the D_1 and the required derivatives are shown in the Appendix and

$$f_m(\theta)=\frac{1}{Z_m}\exp[\Gamma_m P_2(\cos\theta)], \tag{53}$$

$$\Gamma_m\equiv n_m[\nu_{mm}\phi_m S_m(1+c\sigma^2)+\nu_{mb}\phi_b S_b] \tag{54}$$

for the mesogen, where $c\equiv\gamma/\nu_{mm}$ and the constants Z_i $(i=m,b)$ are determined by the normalization condition (50). From Eqs. (50), (51), and (53) we obtain

$$Z_i=4\pi I_0[\Gamma_i], \tag{55}$$

where the function $I_0[\Gamma_i]$ is defined as

$$I_q[\Gamma_i]\equiv\int_0^1[P_2(\cos\theta)]^q\exp[\Gamma_i P_2(\cos\theta)]d(\cos\theta), \tag{56}$$

where $q=0,1,2,\ldots$. Substituting Eq. (53) into Eq. (39), the orientational order parameter for the mesogen is determined by the self-consistency equation

$$S_m=I_1[\Gamma_m]/I_0[\Gamma_m]. \tag{57}$$

Similarly, using Eqs. (51) and (40), we derive the orientational order parameter for the backbone chain

$$S_b=I_1[\Gamma_b]/I_0[\Gamma_b]. \tag{58}$$

The values of Γ_b [Eq. (52)] and Γ_m [Eq. (54)] show the strength of a nematic field for a backbone chain and a mesogen, respectively. The larger values of Γ_i [or $I_0(\Gamma_i)$] correspond to the lower free energy [see Eq. (66)]. It is worth to give brief explanations of the underlying physics. For example, when $\nu_{bb}=0$, namely, there is no anisotropic interaction between backbone chains, the nematic phase is dominated by the nematic field (Γ_m) of mesogens. Then when $\nu_{bb}=0$, $\nu_{mb}>0$, and $\nu_{mm}>0$, the value of Γ_m becomes larger when $S_m>0$ and $S_b>0$. This corresponds to that the N_3 phase becomes stable in an equilibrium state (see Fig. 5). On the other hand, when $\nu_{bb}=0$, $\nu_{mb}<0$, and $\nu_{mm}>0$, the value of Γ_m becomes larger when $S_m>0$ and $S_b<0$ due to the term $\nu_{mb}S_b$ in Eq. (54). This corresponds to that the N_1 phase becomes stable in an equilibrium state (see Fig. 3). When $\nu_{bb}>0$, $\nu_{mb}>0$, and $\nu_{mm}>0$, it is easy to understand that the N_3 phase becomes stable. When $\nu_{bb}>0$, "$\nu_{mb}<0$," and $\nu_{mm}>0$, the two nematic fields Γ_b and Γ_m compensate. For example, when the value of n_b is smaller than n_m, the nematic field (Γ_m) of a mesogen dominates the system. We then have $S_m > 0$ and $S_b < 0$ (N_1 phase). For larger n_b, however, the nematic field (Γ_b) of the backbone chain becomes dominant and we then have $S_m < 0$ and $S_b > 0$, which corresponds to the N_2 phase (see Fig. 7). The value of ν_{bb}, the sign of ν_{mb}, and the length n_m (or n_b) are important to determine the anisotropic phases of the LC gel.

C. Equilibrium value of translational order parameter

The smectic distribution function $f(\tilde{z})$ of the mesogen is determined by the free energy (3) with respect to this function:

$$[\delta F/\delta f(\tilde{z})]_{(f_m,f_b,\phi_g,\kappa_z)} = 0, \tag{59}$$

with the normalization condition

$$\int_0^1 f(\tilde{z}) d\tilde{z} = 1. \tag{60}$$

We then obtain

$$f(z) = \frac{1}{W_0}\exp\{\ \Lambda_m \cos(2\pi\tilde{z})]\}, \tag{61}$$

where

$$\Lambda_m \equiv n_m(\gamma\phi_m S_m^2 - D_2)\sigma, \tag{62}$$

$$D_2 \equiv \frac{2b}{(n_m t)(n_b t)(1+2S_b)}\left[\frac{\kappa_z}{\sqrt{1+2S_b}} - 1\right]^2. \tag{63}$$

The constant W_0 can be determined by Eq. (60) as

$$W_q[\Lambda_m] = \int_0^1 [\cos(2\pi\tilde{z})]^q \exp[\Lambda_m \cos(2\pi\tilde{z})] d\tilde{z}, \tag{64}$$

where $q=0,1,\ldots$. Substituting Eq. (61) into Eq. (42), we obtain the self-consistency equation for σ,

$$\sigma = W_1[\Lambda_m]/W_0[\Lambda_m]. \tag{65}$$

The values of Λ_m [Eq. (62)] show the strength of a smectic field. The larger values of Λ_m (or W_0) correspond to the lower free energy [see Eq. (67)]. On increasing the value of Λ_m, we have direct isotropic-smectic-*A* phase transitions without nematic phases (see Figs. 3 and 5). The equilibrium values of three order parameters, S_m, S_b, and σ, are determined by numerically solving the three coupled Eqs. (57), (58), and (65) as a function of temperature and the volume fraction of a gel.

D. Equilibrium swelling

Substituting Eqs. (51) and (53) into Eq. (38), the nematic free energy is given by

$$\beta F_{nem}/N_t = \frac{1}{2}\nu_{mm}\phi_m^2 S_m^2(1+2c\sigma^2) + \nu_{mb}\phi_m\phi_b S_m S_b + \frac{1}{2}\nu_{bb}\phi_b^2 S_b^2 - \frac{\phi_m}{n_m}\ln I_0[\Gamma_m] - \frac{\phi_b}{n_b}\ln I_0[\Gamma_b] - S_b D_1. \tag{66}$$

Using the distribution function (61), the smectic free energy (41) can be rewritten by

$$\beta F_{sm}/N_t = \frac{1}{2}\gamma\phi_m^2(S_m\sigma)^2 - \phi_m D_2\sigma^2 - \frac{\phi_m}{n_m}\ln W_0. \tag{67}$$

Then the equilibrium free energy (3) is given by the sum of Eqs. (36), (37), (66), and (67). The chemical potential μ_0 of the solvent inside the gel is given by

$$\begin{aligned}\beta(\mu_0 - \mu_0^\circ) &= \beta(\partial F/\partial N_0)_{N_g} = f - \phi_g(\partial f/\partial\phi_g)\\ &= \frac{1}{n}\left[\frac{1}{c_1(1-S_b)\kappa_z} - \frac{\phi_g}{J}\right] + \ln(1-\phi_g) + \phi_g + \chi\phi_g^2\\ &\quad + \frac{1}{2}\nu_{mm}S_m^2\phi_m^2 + \nu_{mb}S_m S_b\phi_m\phi_b + \frac{1}{2}\nu_{bb}S_b^2\phi_b^2\\ &\quad + \frac{3}{2}\gamma(S_m\sigma)^2\phi_m^2,\end{aligned} \tag{68}$$

where $f \equiv \beta F/N_t$ and μ_0° shows the chemical potential of pure solvents outside the gel. When $\sigma=0$, Eq. (68) results in the chemical potential for nematic gels [27].

The equilibrium volume fraction ϕ_g of the gel can be determined from the balance among the solvents existing outside and inside the gel

$$\mu_0(\kappa_z, S_m, S_b, \sigma, \phi_g) - \mu_0^\circ = 0, \tag{69}$$

where the deformation κ_z is related ϕ_g through Eqs. (34) and (45). When the osmotic pressure ($\beta\Pi \equiv \beta(\mu_0^\circ - \mu_0)$) plotted against ϕ_g contains van der Waals loops, where stability conditions are determined by using the Maxwell construction, the equilibrium concentration ϕ_g can be obtained by $\Pi=0$. The region $(\partial\Pi/\partial\phi_g)_T < 0$ corresponds to unstable spinodal regions.

IV. VOLUME PHASE TRANSITIONS

In this section, we show some numerical results of the volume phase transitions and deformation of side-chain LC gels. We here set $J=4$ for a tetrafunctional network and the reduced temperature $\tau = 4.54 n_m/\nu_{mm}$ and define the anisotropic interaction parameters

$$c_{bb} \equiv \nu_{bb}/\nu_{mm}, \tag{70}$$

$$c_{mb} \equiv \nu_{mb}/\nu_{mm}, \tag{71}$$

$$c \equiv \gamma/\nu_{mm}, \tag{72}$$

where c_{bb}, c_{mb}, and c are constants. When $c_{bb}=0$, the backbone chain is sufficiently flexible and does not orient in the constituent pure state. When the backbone chain is a semiflexible LC polymer, we can take $c_{bb}>0$. The c_{mb} shows the nematic interaction parameter between a mesogen and a backbone chain. The larger values of the anisotropic parameter c_{mb} show the stronger attractive interactions between the backbone chain and mesogen. When $c_{mb}>0$, the backbone chain favors to be parallel to the mesogen and when $c_{mb}<0$, the backbone chain favors to be perpendicular to the mesogen. The constant $c(>)0$ shows the smectic interaction parameter between mesogens or McMillan's parameter for a smectic-*A* phase. These parameters are of order of thermal energy because the interactions considered here essentially come from van der Waals interaction. Then we assume that these parameters are of order of 1. In this paper, we take $\chi=0$ (a good solvent condition) in Eq. (37) to emphasize the "volume phase transitions induced by liquid crystalline ordering." The parameter χ controls the swelling of LC gels in an isotopic phase. If we add another nematic parameter $\alpha(\equiv\nu_{mm}/\chi)$, we can describe swelling curves of LC gels in an isotropic phase, which is induced by the polymer-solvent interaction, namely, χ parameter [41]. In this paper ϕ_g keep constant in an isotropic phase because of $\chi=0$. The parameter α has been discussed in phase separations of mixtures of a polymer and a liquid crystal [39].

We first consider the behaviors of the side-chain LC gel in the absence of the attractive interaction between backbone chains, $c_{bb}=0$, which means that the nematic ordering is forbidden in the constituent pure flexible backbone chain. In this case, the backbone chain interacts only with mesogens through the interaction parameter c_{mb}. Depending on the sign of the c_{mb}, we can expect variety of the phase transitions. Figure 3 shows the phase diagram (swelling curve) on the reduced-temperature (τ)-volume fraction (ϕ_g) plane of the side-chain LC gel with $t=10$, $b=1$, $n_m=3$, $c=0.5$, $c_{mb}=-1$, and $c_{bb}=0$. The value of n_b is changed. Solid curves show the stable swelling curves of the gel and dotted curves correspond to the unstable regions. The dash-dotted lines indicate the first-order volume phase transition of the gels. At higher temperature, the gel is swollen and is in an isotropic state. On decreasing temperature, we have the first-order phase transition from an expanded gel to a condensed state. When $n_b=2$, the condensed gel has the smectic-*A* (S_1) phase. The transition temperature decreases with increasing n_b because of no coupling between backbone chains ($c_{bb}=0$). For longer backbone chains, $n_b=6,9$, we find the isotropic-nematic (N_1) phase transition (IN_1) at a higher temperature. On decreasing temperature, we have a discontinuous N_1 to S_1 phase transitions (N_1S_1). When n_b is small, the mesogens are densely packed at low temperature and then we have the direct IS_1 transition. On increasing n_b, the nematic phase appears since the smectic phase is diluted with long backbone chains.

Figure 4(a) shows the orientational order parameters S_m, S_b, and the translational order parameter σ, plotted against the reduced temperature τ for $n_b=6$ in Fig. 3. The dotted curves correspond to the unstable regions. At high temperature, the swollen gel is in an isotropic state with $S_m=0$, $S_b=0$, and $\sigma=0$. On decreasing temperature, we find the first-order phase transition from an isotropic to a nematic N_1 phase, where we have $S_m>0$, $S_b<0$, and $\sigma=0$. Further decreasing temperature, the smectic order parameter σ jumps from zero to a finite value and the smectic S_1 phase appears, where we have $S_m>0$, $S_b<0$, and $\sigma>0$. Figure 4(b) shows the deformations κ_z/κ_{iso} and κ_x/κ_{iso} of the gel [Eq. (43)] plotted against the reduced temperature τ for $n_b=6$ in Fig. 3. The value of κ_z is normalized by the deformation κ_{iso} in the isotropic phase. In the N_1 phase, we have $\kappa_x/\kappa_{iso}>1$ and $\kappa_z/\kappa_{iso}<1$ and the gel is condensed and has an oblate shape as shown in Fig. 1. The mesogens are parallel to the nematic director (*z* axis) and the backbone chains are randomly distributed on the *x*-*y* plane. When the N_1S_1 phase transition takes place, the value of κ_x/κ_{iso} jumps and the volume of the gel is discontinuously changed. In the smectic-*A* phase, the gel is strongly deformed by the jumps of the order parameter σ. From Eq. (46), we see that the value of κ_z decreases with decreasing temperature because the value of S_b is negative and decreases with decreasing temperature in the N_1 and S_1 phases.

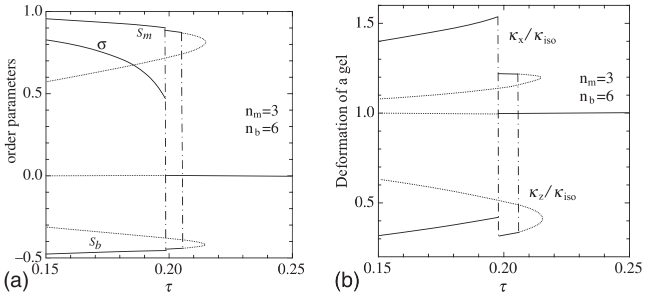

FIG. 4. (a) Order parameters S_m, S_b, and σ and (b) the deformations κ_z/κ_{iso} and κ_x/κ_{iso} of the gel, corresponding to $n_b=6$ in Fig. 3, plotted against the reduced temperature (τ).

Figure 5 shows the phase diagram (swelling curve) on the reduced-temperature (τ)-volume fraction (ϕ_g) plane of the side-chain LC gel with $t=10$, $b=1$, $n_m=3$, $c=0.5$, $c_{mb}=1$, and $c_{bb}=0$. The value of n_b is changed from 2 to 9. The solid lines correspond to the stable swelling curve and the dotted lines show the unstable regions. The dash-dotted lines indicate the first-order phase transition between two phases. When $c_{mb}=1$, the mesogens tend to be parallel to the backbone chain. For $n_b=2$, or a short backbone chain, we have the first-order phase transition between an isotropic and a

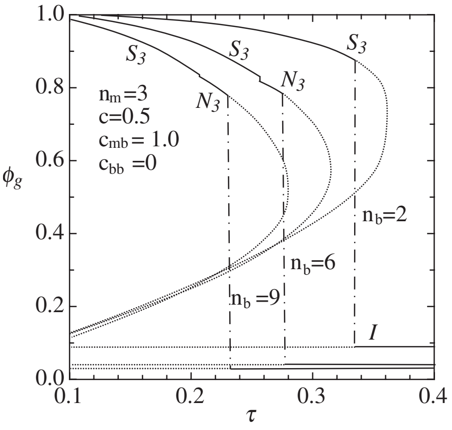

FIG. 5. Swelling curve of the gel on the $\tau-\phi_g$ plane for $t=10$, $b=1$, $n_m=3$, $c=0.5$, $c_{mb}=1$, and $c_{bb}=0$. The value of n_b is changed.

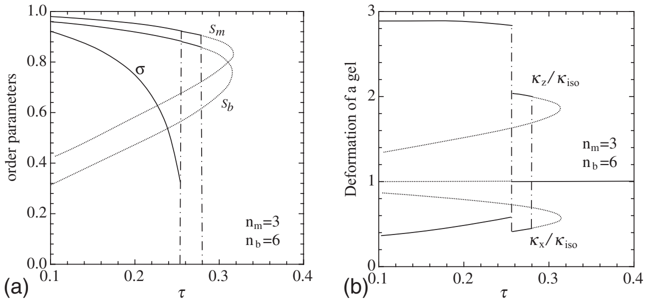

FIG. 6. (a) Order parameters S_m, S_b, and σ and (b) the deformations κ_z/κ_{iso} and κ_x/κ_{iso} of the gel, corresponding to $n_b=6$ in Fig. 5, plotted against the reduced temperature (τ).

smectic S_3 phase of the gel. For long backbone chains, $n_b=6,9$, we find the two phase transitions. One is the isotropic-nematic $N_3(IN_3)$ phase transition at a high temperature, where the gel is discontinuously collapsed with decreasing temperature. The other is the nematic N_3–smectic $S_3(N_3S_3)$ phase transition at lower temperature. The IN_3 and N_3S_3 phase-transition temperatures shift to lower temperature with increasing n_b.

Figure 6(a) shows the order parameters plotted against the reduced temperature for $n_b=6$ in Fig. 5. The dotted curves show the unstable regions. On decreasing temperature, the IN_3 phase transition takes place at $\tau=0.28$, where we have $S_b>0$ and $S_m>0$ and the mesogens align parallel to the backbone chain. Further decreasing temperature, the smectic order appears at $\tau=0.25$ and we have the S_3 phase with $S_b>0$, $S_m>0$, and $\sigma>0$. As shown in Fig. 5, the volume of the gel discontinuously changes at the N_3S_3 phase transition. Figure 6(b) shows the deformation (κ_z/κ_{iso}) of the gel plotted against the reduced temperature for $n_b=6$ in Fig. 5. In the N_3 and S_3 phases, we have $\kappa_z/\kappa_{iso}>1$ and $\kappa_x/\kappa_{iso}<1$, where the gel is condensed along the parallel to the nematic director and the backbone chain has a prolate shape.

To understand the qualitative behaviors of the results, we here expand the term $\ln(1-\phi_g)$ in Eq. (68) in power series of ϕ_g and Eq. (69) approximately is given by

$$\frac{1}{c_1\sqrt{A}\lambda_{zz}\phi_g^2}-\frac{1}{J\phi_g}-\frac{n\phi_g}{3}=n\left[\frac{1}{2}-\chi-Y(S_m,S_b,\sigma)\right], \tag{73}$$

where we define

$$Y(S_m,S_b,\sigma)\equiv\frac{1}{2}\nu_{mm}w^2S_m^2(1+3c\sigma^2)+\nu_{mb}w(1-w)S_mS_b+\frac{1}{2}\nu_{bb}(1-w)^2S_b^2, \tag{74}$$

and the value of Y increases with increasing order parameters. When ϕ_g is large, or condensed nematic or smectic phases, the third term of Eq. (73) balances with the right-hand side and we obtain

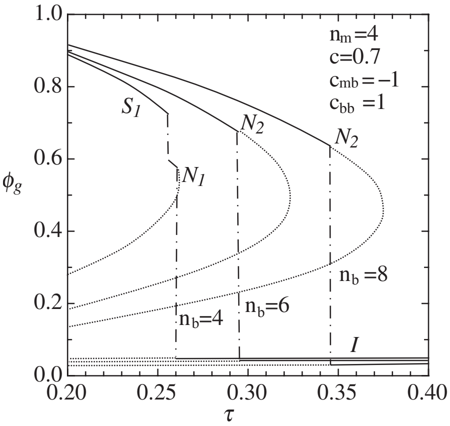

FIG. 7. Swelling curve of the gel on the $\tau-\phi_g$ plane for $t=10$, $b=1$, $n_m=4$, $c=0.7$, $c_{mb}=-1$, and $c_{bb}=1$. The value of n_b is changed.

$$\phi_g\approx Y+\chi-\frac{1}{2}. \tag{75}$$

The jump of ϕ_g at the phase-transition temperatures is of order of the square of order parameters. From Eq. (45) truncated the term of λ_{zz}^2, we obtain

$$\lambda_{zz}^3\approx\frac{1}{c_1\sqrt{A}(Y+\chi-1/2)(1+2B_1)} \tag{76}$$

or

$$\kappa_z^3\approx\frac{(1+2S_b)}{c_1(1-S_b)(Y+\chi-1/2)(1+2B_1)}, \tag{77}$$

where B_1 is given by Eq. (26). The temperature dependence of κ_z in the nematic and smectic phases is strongly related to S_b and B_1. For the N_1 and S_1 phases, the value of $S_b(<0)$ decreases with decreasing temperature and then the value of κ_z decreases with decreasing temperature as shown in Fig. 4. For the N_3 and S_3 phases, the value of $S_b(>0)$ increases with decreasing temperature and the value of κ_z has the same temperature dependence with S_b as shown in Fig. 6. In the smectic phases, the temperature dependence of B_1 strongly affects that of κ_z.

Finally we show the results for $c_{bb}=1$, which means that the nematic ordering can take place in the constituent pure semiflexible backbone chain. Figure 7 shows the phase diagram (swelling curve) on the reduced-temperature (τ)-volume fraction (ϕ_g) plane of the side-chain LC gel with $n_m=4$, $t=10$, $c=0.7$, $c_{mb}=-1$, and $c_{bb}=1$. The value of n_b is changed from 4 to 8. The solid lines correspond to the stable swelling curve and the dotted lines show the unstable regions. The dash-dotted lines indicate the first-order phase transition between two phases. When $c_{mb}=-1$, the mesogens tend to be perpendicular to the backbone chain. For a short backbone chain $n_b=4$, we find the two phase transitions. One is the isotropic-nematic $N_1(IN_1)$ phase transition at a higher temperature, where the gel is discontinuously collapsed with decreasing temperature. The other is the nematic N_1–smectic $S_1(N_1S_1)$ phase transition at a lower temperature, where the

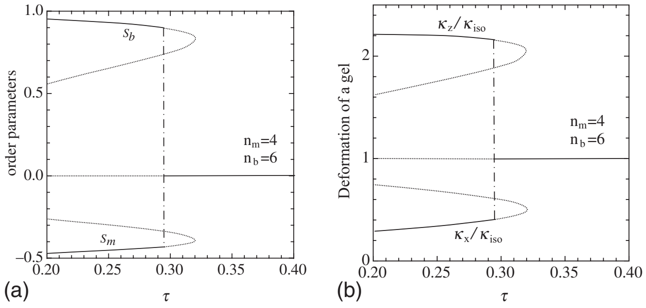

FIG. 8. (a) Order parameters S_m, S_b, and σ and (b) the deformations κ_z/κ_{iso} and κ_x/κ_{iso} of the gel, corresponding to $n_b=6$ in Fig. 7, plotted against the reduced temperature (τ).

volume of the gel discontinuously changes. For longer backbone chains (n_b=6 and 8), we have the first-order phase transition between the isotropic and N_2 phase. The first-order N_2S_2 phase transition appears at lower temperature, although it is not shown in this figure. Percec *et al.* [25] experimentally suggested that the formation of the mesophases, N_1 and N_2, for side-chain LC polymers is determined by the degree of polymerization of rigid-backbone chain. For short backbone chains, the nematic director is determined by the mesogens on the side groups and, for long backbone chains, the director is determined by the mesogenic backbone chain. Then, for long semiflexible backbone chains, the N_2 phase becomes more stable than the N_1 phase. On increasing n_b, the isotropic-nematic phase-transition temperature shifts to higher temperature because the attractive interaction between backbone chains becomes dominant for $c_{bb}=1$. Figure 8(a) shows the order parameters plotted against the reduced temperature for n_b=6 in Fig. 7. The dotted lines show the unstable regions. On decreasing temperature, the IN_2 phase transition takes place at τ=0.295, where we have $S_b>0$ and $S_m<0$. As shown in Fig. 7, the volume of the gel discontinuously changes at the IN_2 phase transition. Figure 8(b) shows the deformation (κ_z/κ_{iso}) of the gel plotted against the reduced temperature for n_b=6 in Fig. 7. In the N_2 phase, we have $\kappa_z/\kappa_{iso}>1$ and $\kappa_x/\kappa_{iso}<1$, where the gel is condensed along the parallel to the nematic director and the backbone chain has a prolate shape as shown in Fig. 1. The appearance of the S_2 phase depends on the value of the smectic interaction parameter c. For larger values of c, for example, when c=1, we have the isotropic-smectic $S_2(IS_2)$ phase transitions without the nematic N_2 phase. The LC gels lead to rich varieties of the structural changes in a mesoscopic scale. The conformations of backbone chains and mesogens are important to understand the volume phase transitions of LC gels.

V. SUMMARY

We have presented a theory to describe isotropic-nematic-smectic-*A* phase transition of side-chain liquid crystalline gels and considered three different nematic (N_1, N_2, and N_3) and smectic (S_1, S_2, and S_3) phases. We calculate the swelling curves of the gel, the orientational order parameters, and the deformation of the gel as a function of temperature and the length of a backbone chain. We find the discontinuous volume phase transitions of the LC gels at an isotropic-nematic, an isotropic-smectic-*A*, and a nematic-smectic-*A* phase transition. In the smectic-*A* phase, the gel is strongly deformed by the order parameter σ.

We also examined the swelling behavior of the LC gels depending on the anisotropic attractive interaction c_{bb} between backbone chains and the c_{mb} between backbone chain and mesogens. When c_{bb}=0, which corresponds to flexible backbone chains, the LC gel of short backbone chains changes from an isotropic to a smectic-*A* (S_1 or S_3) phase with decreasing temperature (Figs. 3 and 5). For long backbone chains, a nematic (N_1 or N_3) phase appears at a temperature range between an isotropic and a smectic-*A* phases. In the presence of the anisotropic interaction $c_{bb}(=1)$ between backbone chains, we have isotropic-nematic-smectic-*A* (IN_1S_1 or IN_2S_2) phase transitions. On increasing n_b, the IN_1 transition changes to IN_2 phase transition. The conformation of backbone chains and mesogenic side groups are important to understand the swelling behaviors of the LC gels. We hope that these results encourage further experimental studies of the volume phase transitions of liquid crystalline gels.

ACKNOWLEDGMENTS

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APPENDIX: FUNCTIONAL DERIVATIVES

In this appendix, we give the functional derivatives Eqs. (48) and (49). From Eq. (48), we have

$$\left(\frac{\delta F}{\delta f_b(\theta)}\right)_{\{\cdots\}} = \left(\frac{\delta F_{el}}{\delta f_b(\theta)}\right)_{\{\cdots\}} + \left(\frac{\delta F_{nem}}{\delta f_b(\theta)}\right)_{\{\cdots\}}, \tag{A1}$$

where the functional derivatives of the free energies F_{mix} and F_{sm} with respect to the distribution function become zero since the free energies F_{mix} and F_{sm} do not include the orientational order parameter S_b. The required derivatives of F are given by

$$\beta\left(\frac{\delta F_{el}}{\delta f_b(\theta)}\right)_{\{\cdots\}} = D_1(\phi_g, S_b, \sigma, \kappa_z) P_2(\cos\,\theta), \tag{A2}$$

$$D_1 \equiv \frac{\phi_g}{n}\left[\frac{1}{c_1\phi_g(1-S_b)^2\kappa_z} - \frac{\kappa_z^2}{(1+2S_b)^2} - \frac{3S_b}{(1+2S_b)(1-S_b)} - \frac{2b\sigma^2}{n_b t(1+2S_b)^2}\left(\frac{\kappa_z}{\sqrt{1+2S_b}} - 1\right)\left(\frac{2\kappa_z}{\sqrt{1+2S_b}} - 1\right)\right], \tag{A3}$$

and

$$\beta\left(\frac{\delta F_{nem}}{\delta f_b(\theta)}\right)_{\{\cdots\}} = \frac{\phi_b}{n_b}[\ln 4\pi f_b(\theta) + 1/(4\pi)] - (\nu_{bb}\phi_b^2 S_b + \nu_{mb}\phi_m\phi_b S_m) P_2(\cos\,\theta). \tag{A4}$$

We then obtain the distribution function Eq. (51).

Similarly, from Eq. (49), we have

$$\left(\frac{\delta F}{\delta f_m(\theta)}\right)_{\{\cdots\}} = \left(\frac{\delta F_{nem}}{\delta f_m(\theta)}\right)_{\{\cdots\}} + \left(\frac{\delta F_{sm}}{\delta f_m(\theta)}\right)_{\{\cdots\}}, \tag{A5}$$

where we note that the free energies F_{el} and F_{mix} do not include the orientational order parameter S_m. The required derivatives of F are given by

$$\beta\left(\frac{\delta F_{nem}}{\delta f_m(\theta)}\right)_{\{\cdots\}} = \frac{\phi_m}{n_m}[\ln 4\pi f_m(\theta) + 1/(4\pi)] - (\nu_{mm}\phi_m^2 S_m + \nu_{mb}\phi_m\phi_b S_b)P_2(\cos\theta), \tag{A6}$$

$$\beta\left(\frac{\delta F_{sm}}{\delta f_m(\theta)}\right)_{\{\cdots\}} = -\gamma\phi_m^2\sigma^2 P_2(\cos\theta). \tag{A7}$$

We then obtain the distribution function Eq. (53).

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