Statistics of wormlike chains. II. Phase transition of polymer liquid crystals and its mixture with low molecular weight liquid crystals

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A general self-consistent field (SCF) for the mixture of polymer and low molecular weight (LMW) molecules has been derived by variation principle. Considering a Maier–Saupe type of interaction, the analytical expressions of the SCF for polymer liquid crystals (PLCs) and the mixture of PLCs and LMW liquid crystals are obtained, from which the phase behaviors of PLCs as well as the mixture are studied. The theoretical results are in agreement with experimental results by adjusting a parameter. © *1997 American Institute of Physics.* [S0021-9606(97)51005-1]

I. INTRODUCTION

In a previous article,[1] an analytical solution of the wormlike chain (WLC) model[2] has been derived for a single chain or dilute solution by functional integrals in momentum space which is equivalent to the normal mode analysis. In this paper, we consider a many-WLC system to investigate phase behaviors of polymer liquid crystals (PLCs) as well as its mixture with low molecular weight (LMW) liquid crystals (LC) with Maier–Saupe (MS) type interaction by self-consistent fields (SCF) theory.

The statistics for a many-chain system, even for a single polymer chain with interactions, is not an easy task. When the interaction, $v(\mathbf{r}(s)-\mathbf{r}(s'))$, exists the problem becomes a complex many-body problem which is generally dealt with by various approximations, for example, the self-consistent field (SCF) approach, the perturbation theory, the differential equation methods, and so on. The perturbation theory is the most basic method by which a perturbational expansion for the end to end distribution (EED) function, $G(\mathbf{R}0L0)$, is easily obtained and by a renormalization method many properties of the polymer chains, for example, scaling properties, are derived.[3] However, in order to study the phase transition of liquid crystals, the most powerful method is perhaps the SCF method. The SCF theory was used in quantum theory long ago which is called Hartree–Fock theory[4] and since the mean-field theory was extended to the continuum model in polymer physics by Edwards in 1960's,[5] Reiss and Freed have discussed this approach in details.[6,7] Although the SCF for polymer statistics was derived almost 30 years ago, only in recent years has it been used to study the phase transition of PLCs.[8] The SCF derived by Freed depends on the ends of the polymer chain through the three point Green's function so that the symmetry of translation and rotation is lost and therefore, the SCF becomes very complicated in its applications. In order to make the SCF theory suitable for PLCs, the infinite long chain limit is used to recover the translation invariance.[8]

To describe the phase transition from isotropic to nematic phases by SCF, two theories are often used. The famous Onsager's theory is based on the excluded volume of nonspherical molecules which leads to an anisotropic interaction and has a clear physical meaning and concrete forms for cylinder and elliptical molecules. This theory has been applied to the rodlike polymer[9] and WLC.[8] The SCF in this form cannot be exactly solved and by assuming a concrete form for distribution function or numerically, SCF can be obtained.[9] The other one is the Maier–Saupe (MS) theory[10] in which, based on the second order perturbation of quantum theory, a concrete interaction called dispersion energy is derived. The virtue of the MS theory is that this model can be solved exactly and is successful in predicting a number properties of the nematic phase as well as of nematic–isotropic phase transition.[11] Therefore, in this paper the MS type interaction is used.

Polymer liquid crystals have been given more and more attention in past two decades and much progress has been made.[12] It is believed many PLCs are composed by the wormlike chains and therefore the wormlike chain model has been used extensively to describe polymer liquid crystals.[8,9,11–13] Another interesting field concerning PLCs is the mixture of PLCs and LMW LCs which has been paid much attention in recent years[14,15] since the some PLCs are known to be soluble in appropriately chosen nematic solvents.[15] In contrast to LMW LC, the theory for PLCs is incomplete and the primary reasons are that most PLCs are composed of stiff (wormlike) main chain and side chain polymers which is mathematically difficult to deal with. Since for LMW LC the famous MS theory is confirmed to be successful in describing the phase transition from isotropic to nematic states, the aim of this paper is to extend the MS theory to PLCs as well as the mixture of PLCs and LMW LCs to study the behaviors and properties for phase transition of PLCs and the mixture.

In Sec. II by the variational principle the SCF is derived for a general interaction for PLCs and the mixture. Considering a concrete MS type interaction, the SCF is used to study the properties of PLCs in Sec. III and of the mixture in Sec. IV. Finally, the theoretical results are compared with experiments in Sec. V and a summary is given in Sec. VI.

II. THE SCF THEORY

A. The model

In this section we will derive the SCF for a general interaction, i.e., we consider an interaction depending on the position, $\mathbf{r}_i(s_i)$, and the tangent (orientation), $\mathbf{u}_i(s_i)$, of the monomer denoted by s_i of ith WLC and the position, $\mathbf{r}_j$, and the orientation, $\mathbf{a}_j$, of the jth LMW molecule for a mixed system composed of N_1 polymer chains and N_2 low molecular weight molecules, which can be written as

$$H=H_0+H_I. \tag{2.1}$$

with

$$\begin{aligned}H_I[\mathbf{r}_i(s),\mathbf{r}_j,\mathbf{a}_j]={}&\frac{1}{2}\sum_{i,j}^{N_1}\int ds_i\int ds_j\; V_1(\mathbf{r}_i(s_i),\mathbf{u}_i(s_i);\\&\mathbf{r}_j(s_j),\mathbf{u}_j(s_j))+\frac{1}{2}\sum_{\imath\neq j}^{N_2} V_2(\mathbf{r}_i,\mathbf{a}_i;\mathbf{r}_j,\mathbf{a}_j)\\&+\frac{1}{2}\sum_{i}^{N_1}\sum_{j}^{N_2}\int ds_i\; V_{12}(\mathbf{r}_\imath(s_i),\mathbf{u}_i(s_i);\\&\mathbf{r}_j,\mathbf{a}_j),\end{aligned} \tag{2.2}$$

where the first term is the interaction energy for inter- and intrapolymer chains, the second term is for the LMW molecules, and the third term is the interaction between the polymer chains and LMW molecules. The free Hamiltonian, H_0, should be selected as an exactly soluble model and here the limit of very long chain is also taken. Then the statistical weight factor can be written as

$$\begin{aligned}p[\mathbf{r}_i(s),\mathbf{r}_j,\mathbf{a}_J]&=A\;\exp(-H_0)\exp(-H_I)\\&=p_0[\mathbf{r}_i(s)]\exp(-H_I[\mathbf{r}_i(s),\mathbf{r}_j,\mathbf{a}_j]).\end{aligned} \tag{2.3}$$

Two simple models for H_0 may be considered, i.e., the ideal Gaussian chains (IGC) and the wormlike chains, then $p_0[\mathbf{r}_i(s)]$ is

$$p_{\mathrm{IGC}}[\mathbf{r}_i(s)]=A\;\exp\left[\sum_{i=1}^{N_1}\left(-\frac{3}{2l}\int\mathbf{u}_i^2(s_i)ds_i\right)\right] \tag{2.4}$$

for the IGC model or

$$\begin{aligned}p_{\mathrm{WLC}}[\mathbf{r}_i(s)]=A\;\exp\Bigg[\sum_{i=1}^{N_1}\Bigg(&-\frac{3}{2l}\int\mathbf{u}_i^2(s_i)ds_i\\&-\frac{\epsilon}{2}\int\dot{\mathbf{u}}_i^2(s_i)ds_i\Bigg)\Bigg]\end{aligned} \tag{2.5}$$

for WLC, where A is a normalized constant which is equal to the inverse of the partition function or can be determined by normalization. Since for $\epsilon\rightarrow 0$, $p_{\mathrm{WLC}}=p_{\mathrm{IGC}}$, we only need to consider the case of $p_0=p_{\mathrm{WLC}}$ in the following.

B. Derivation of the SCF from variational principle

Since for the WLC the probability (statistical weight factor) of a configuration is given by Eq. (2.3), the free energy of the mixture can be written as

$$\begin{aligned}F&=E-TS\\&=\int\prod_{i=1}^{N_1}\mathscr{D}[\mathbf{r}_i(s)]\prod_{j=1}^{N_2}d\mathbf{r}_j\;d\mathbf{a}_j\;p[\mathbf{r}_\imath(s),\mathbf{r}_j,\mathbf{a}_j](H_0+H_I)\\&\quad+\int\prod_{i=1}^{N_1}\mathscr{D}[\mathbf{r}_i(s)]\prod_{j=1}^{N_2}d\mathbf{r}_j\;d\mathbf{a}_j\;p[\mathbf{r}_i(s),\mathbf{r}_j,\mathbf{a}_j]\\&\quad\times\ln p[\mathbf{r}_i(s),\mathbf{r}_j,\mathbf{a}_j],\end{aligned} \tag{2.6}$$

where $\mathscr{D}[\mathbf{r}_\imath(s)]$ denotes the functional integration and for convenience $\beta=1/k_BT$ is set to be one which will be recovered when needed. Following Reiss' idea,[6] we introduce the mean-field approximation, which will be determined by the self-consistent method,

$$\begin{aligned}&p_{\mathrm{mean}}[\mathbf{r}_i(s),\mathbf{r}_j,\mathbf{a}_J]\\&\quad=p_{\mathrm{WLC}}[\mathbf{r}_i(s)]\exp\Bigg[-\sum_{i=1}^{N_1}\int ds_i\;v_1(\mathbf{r}_i(s_i),\mathbf{u}_i(s_i))\\&\qquad-\sum_{i=1}^{N_2}v_2(\mathbf{r}_i,\mathbf{a}_i)\Bigg]\\&\quad=\prod_i p[\mathbf{r}_i(s)]\prod_J p(\mathbf{r}_j,\mathbf{a}_j).\end{aligned} \tag{2.7}$$

In the following, the subscript mean in $p_{\mathrm{mean}}[\mathbf{r}_i(s_i),\mathbf{r}_j,\mathbf{a}_J]$ will be omitted and the same notation $p[\mathbf{r}_i(s),\mathbf{r}_j,\mathbf{a}_j]$ is used for simplicity which should not be confused with the one in Eq. (2.3). Substituting it into the free energy and considering the identities of the molecules, we have

$$
\begin{aligned}
F={}&\frac{N_1}{2}\int \mathscr{D}[\mathbf{r}(s)]\int ds_1\, ds_2\, V_1(\mathbf{r}(s_1),\mathbf{u}(s_1);\mathbf{r}(s_2),\mathbf{u}(s_2))p[\mathbf{r}(s)]+\frac{N_1(N_1-1)}{2}\int\prod_{i=1}^{2}(\mathscr{D}[\mathbf{r}_i(s)]p[\mathbf{r}_i(s)]ds_i)\\
&\times V_1(\mathbf{r}_1(s_1),\mathbf{u}_1(s_1);\mathbf{r}_2(s_2),\mathbf{u}_2(s_2))+\frac{N_2(N_2-1)}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{a}_1\, d\mathbf{a}_2\, V_2(\mathbf{r}_1,\mathbf{a}_1;\mathbf{r}_2,\mathbf{a}_2)p(\mathbf{r}_1,\mathbf{a}_1)p(\mathbf{r}_2,\mathbf{a}_2)\\
&+\frac{N_1N_2}{2}\int ds_1\, \mathscr{D}[\mathbf{r}(s)]d\mathbf{r}_1\, d\mathbf{a}_1\, p(\mathbf{r}_1,\mathbf{a}_1)p[\mathbf{r}(s)]V_{12}(\mathbf{r}_1,\mathbf{a}_1;\mathbf{r}(s_1),\mathbf{u}(s_1))+N_1\int \mathscr{D}[\mathbf{r}(s)]p[\mathbf{r}(s)]\Bigg(\ln p[\mathbf{r}(s)]+\lambda_1\\
&+\frac{3}{2l}\int \mathbf{u}^2(s_1)ds_1+\frac{\epsilon}{2}\int \dot{\mathbf{u}}^2(s_1)ds_1\Bigg)+N_2\int d\mathbf{r}_1\, d\mathbf{a}_1\, p(\mathbf{r}_1,\mathbf{a}_1)(\ln p(\mathbf{r}_1,\mathbf{a}_1)+\lambda_2),
\end{aligned}
\tag{2.8}
$$

where Lagrange multipliers, λ_1 and λ_2, are introduced for the normalizations of $p[\mathbf{r}(s)]$ and $p(\mathbf{r}_1,\mathbf{a}_1)$. By variation about v_1 we obtain

$$
\begin{aligned}
\delta F={}&N_1\int \mathscr{D}[\mathbf{r}(s)]\delta p[\mathbf{r}(s)]\Bigg\{\frac{1}{2}\int ds_1\, ds_2\, V_1(\mathbf{r}(s_1),\mathbf{u}(s_1);\mathbf{r}(s_2),\mathbf{u}(s_2))+(N_1-1)\\
&\times\int \mathscr{D}[\mathbf{r}_2(s)]p[\mathbf{r}_2(s)]ds_1\, ds_2\, V_1(\mathbf{r}(s_1),\mathbf{u}(s_1);\mathbf{r}_2(s_2),\mathbf{u}_2(s_2))\\
&+\frac{N_2}{2}\int ds_1\, d\mathbf{r}_1\, d\mathbf{a}_1\, p(\mathbf{r}_1,\mathbf{a}_1)V_{12}(\mathbf{r}_1,\mathbf{a}_1;\mathbf{r}(s_1),\mathbf{u}(s_1))-\int ds_1\, v_1(\mathbf{r}(s_1),\mathbf{u}(s_1))+\lambda_1'\Bigg\}.
\end{aligned}
\tag{2.9}
$$

Substituting

$$
\delta p[\mathbf{r}(s)]=-p[\mathbf{r}(s)]\int ds_1\, \delta v_1(\mathbf{r}(s_1),\mathbf{u}(s_1))=-p[\mathbf{r}(t)]\int ds\, d\mathbf{r}\, d\mathbf{u}\, \delta v_1(\mathbf{r},\mathbf{u})\delta(\mathbf{r}-\mathbf{r}(s))\delta(\mathbf{u}-\mathbf{u}(s))
\tag{2.10}
$$

into the above equation we obtain

$$
\begin{aligned}
\delta F={}&-N_1\int d\mathbf{r}\, d\mathbf{u}\, ds\, \delta v_1(\mathbf{r},\mathbf{u})\int d\mathbf{r}_1\, d\mathbf{u}_1\, ds_1\, \mathscr{D}[\mathbf{r}(t)]p[\mathbf{r}(t)]\delta(\mathbf{r}-\mathbf{r}(s))\delta(\mathbf{u}-\mathbf{u}(s))\delta(\mathbf{r}_1-\mathbf{r}(s_1))\delta(\mathbf{u}_1-\mathbf{u}(s_1))\\
&\times\Bigg\{\frac{1}{2}\int d\mathbf{r}_2\, d\mathbf{u}_2\, ds_2\, V_1(\mathbf{r}_1,\mathbf{u}_1;\mathbf{r}_2,\mathbf{u}_2)\delta(\mathbf{r}_2-\mathbf{r}(s_2))\delta(\mathbf{u}_2-\mathbf{u}(s_2))+(N_1-1)\\
&\times\int d\mathbf{r}_2\, d\mathbf{u}_2\, ds_2\, \mathscr{D}[\mathbf{r}_2(t)]p[\mathbf{r}_2(t)]V_1(\mathbf{r}_1,\mathbf{u}_1;\mathbf{r}_2,\mathbf{u}_2)\delta(\mathbf{r}_2-\mathbf{r}_2(s_2))\delta(\mathbf{u}_2-\mathbf{u}_2(s_2))\\
&+\frac{N_2}{2}\int d\mathbf{r}_1'\, d\mathbf{a}_1'\, p(\mathbf{r}_1',\mathbf{a}_1')V_{12}(\mathbf{r}_1',\mathbf{a}_1';\mathbf{r}_1,\mathbf{u}_1)-v_1(\mathbf{r}_1,\mathbf{u}_1)+\lambda_1'\Bigg\}.
\end{aligned}
\tag{2.11}
$$

From the definitions of the correlation function

$$
\begin{aligned}
&\int \mathscr{D}[\mathbf{r}(t)]\delta(\mathbf{r}-\mathbf{r}(s))\delta(\mathbf{u}-\mathbf{u}(s))\delta(\mathbf{r}_1-\mathbf{r}(s_1))\delta(\mathbf{u}_1-\mathbf{u}(s_1))\delta(\mathbf{r}_2-\mathbf{r}(s_2))\delta(\mathbf{u}_2-\mathbf{u}(s_2))p[\mathbf{r}_2(t)]\\
&\quad=C(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2;\mathbf{u},\mathbf{u}_1,\mathbf{u}_2;s,s_1,s_2),
\end{aligned}
\tag{2.12}
$$

$$
\int \mathscr{D}[\mathbf{r}(t)]\delta(\mathbf{r}-\mathbf{r}(s))\delta(\mathbf{u}-\mathbf{u}(s))\delta(\mathbf{r}_1-\mathbf{r}(s_1))\delta(\mathbf{u}_1-\mathbf{u}(s_1))p[\mathbf{r}(t)]=C(\mathbf{r},\mathbf{r}_1;\mathbf{u},\mathbf{u}_1;s,s_1),
\tag{2.13}
$$

$$
\int \mathscr{D}[\mathbf{r}(t)]\delta(\mathbf{r}-\mathbf{r}(s))\delta(\mathbf{u}-\mathbf{u}(s_1))p[\mathbf{r}(t)]=C(\mathbf{r};\mathbf{u};s),
\tag{2.14}
$$

we have

$$\delta F=-N_1\int d\mathbf{r}\,d\mathbf{u}\,ds\,d\mathbf{r}_1\,d\mathbf{u}_1\,ds_1\,\delta v_1(\mathbf{r},\mathbf{u})\left\{\int d\mathbf{r}_2\,d\mathbf{u}_2\,ds_2\,V_1(\mathbf{r}_1,\mathbf{u}_1;\mathbf{r}_2,\mathbf{u}_2)C(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2;\mathbf{u},\mathbf{u}_1,\mathbf{u}_2;s,s_1,s_2)\right.$$
$$+(N_1-1)\int d\mathbf{r}_2\,d\mathbf{u}_2\,ds_2\,V_1(\mathbf{r}_1,\mathbf{u}_1;\mathbf{r}_2,\mathbf{u}_2)C(\mathbf{r},\mathbf{r}_1;\mathbf{u},\mathbf{u}_1;s,s_1)C(\mathbf{r}_2;\mathbf{u}_2;s_2)-(v_1(\mathbf{r}_1,\mathbf{u}_1)+\lambda_1')C(\mathbf{r},\mathbf{r}_1;\mathbf{u},\mathbf{u}_1;s,s_1)$$
$$\left.+\frac{N_2}{2}\int d\mathbf{r}_1'\,d\mathbf{a}_1'\,p(\mathbf{r}_1',\mathbf{a}_1')V_{12}(\mathbf{r}_1',\mathbf{a}_1';\mathbf{r}_1,\mathbf{u}_1)C(\mathbf{r},\mathbf{r}_1;\mathbf{u},\mathbf{u}_1;s,s_1)\right\}. \tag{2.15}$$

Finally, we obtain the SCF for polymer chains

$$v_1(\mathbf{r}_1,\mathbf{u}_1)=\lambda'+N_1\int d\mathbf{r}_2\,d\mathbf{u}_2\,ds_2\,V_1(\mathbf{r}_1,\mathbf{u}_1;\mathbf{r}_2,\mathbf{u}_2)C(\mathbf{r}_2;\mathbf{u}_2;s_2)+\frac{N_2}{2}\int d\mathbf{r}_1'\,d\mathbf{a}_1'\,p(\mathbf{r}_1',\mathbf{a}_1')V_{12}(\mathbf{r}_1',\mathbf{a}_1';\mathbf{r}_1,\mathbf{u}_1)$$
$$+\int d\mathbf{r}_2\,d\mathbf{u}_2\,ds_2\,V_1(\mathbf{r}_1,\mathbf{u}_1;\mathbf{r}_2,\mathbf{u}_2)\left[\frac{C(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2;\mathbf{u},\mathbf{u}_1,\mathbf{u}_2;s,s_1,s_2)}{C(\mathbf{r},\mathbf{r}_1;\mathbf{u},\mathbf{u}_1;s,s_1)}-C(\mathbf{r}_2;\mathbf{u}_2;s_2)\right]. \tag{2.16}$$

The last term can be omitted because (1) it is very small as compared with the second term in the first line if $N_1 \gg 1$ and (2) the terms in square is partly cancelled each other, for example, if an approximation $C(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2;\mathbf{u},\mathbf{u}_1,\mathbf{u}_2;s,s_1,s_2)=C(\mathbf{r},\mathbf{r}_1;\mathbf{u},\mathbf{u}_1;s,s_2)C(\mathbf{r}_2;\mathbf{u}_2;s_2)$ is taken the last term will vanish. Similarly considering a variation on v_2 it is easy to obtain the SCF for LMW molecules

$$v_2(\mathbf{r},\mathbf{a})=\lambda''+(N_2-1)\int d\mathbf{r}'\,d\mathbf{a}'\,p(\mathbf{r}',\mathbf{a}')V_2(\mathbf{r},\mathbf{a};\mathbf{r}',\mathbf{a}')$$
$$+\frac{N_2}{2}\int d\mathbf{r}'\,d\mathbf{u}'\,ds\,C(\mathbf{r}';\mathbf{u}',s)V_{12}(\mathbf{r},\mathbf{a};\mathbf{r}',\mathbf{u}'). \tag{2.17}$$

C. The SCF for a uniform system

Generally, the interaction should depend on the position and the orientation of the monomers of PLCs which can be separated into two parts: one depends only on the position and the other depends on both position and orientation

$$V_1(\mathbf{r}_1(s_1),\mathbf{u}_1(s_1);\mathbf{r}_2(s_2),\mathbf{u}_2(s_2))$$
$$=V_a(\mathbf{r}_1(s_1);\mathbf{r}_2(s_2))+V_b(\mathbf{r}_1(s_1),\mathbf{u}_1(s_1);\mathbf{r}_2(s_2),\mathbf{u}_2(s_2)). \tag{2.18}$$

For systems possessing translational invariance we have the following points: (1) the interaction will depend on the difference of the position, $\mathbf{r}_1(s_1)-\mathbf{r}_2(s_2)$; (2) the distribution $C(\mathbf{r};\mathbf{u};s)$ will be independent of position

$$C(\mathbf{r};\mathbf{u};s)=\frac{1}{\Omega}\,C(\mathbf{u};s), \tag{2.19}$$

where Ω is the volume of the system. Therefore, V_a will contribute a constant term to the potential which can be absorbed into the normalization constant and only V_b will contribute to the mean field. A special case is that if V_a is taken as the excluded volume, $V_a=w_0\delta(\mathbf{r}_1(s_1)-\mathbf{r}_2(s_2))$; it is proved in Ref. 8(b) V_a has no contribution to the SCF. Similar consideration for interactions V_2 and V_{12}, the SCF becomes

$$v_1(\mathbf{u})=N_1\int d\mathbf{u}'\,ds'\,V_1(\mathbf{u},\mathbf{u}')C(u';s')$$
$$+\frac{N_2}{2}\int d\mathbf{a}\,p(\mathbf{a})V_{12}(\mathbf{a},\mathbf{u}), \tag{2.20}$$

$$v_2(\mathbf{a})=(N_2-1)\int d\mathbf{a}'\,p(\mathbf{a}')V_2(\mathbf{a},\mathbf{a}')$$
$$+\frac{N_1}{2}\int d\mathbf{u}\,ds\,C(\mathbf{u};s)V_{12}(\mathbf{a},\mathbf{u}), \tag{2.21}$$

where λ' and λ'' which will be determined by normalization are omitted here and $V_i(\mathbf{u},\mathbf{u}')$ are given by

$$V_1(\mathbf{u},\mathbf{u}')=\frac{1}{\Omega}\int V_1(\mathbf{r}_1-\mathbf{r}_2,\mathbf{u}_1,\mathbf{u}_2)d\mathbf{r}_2$$
$$=\frac{1}{\Omega}\int V_1(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)d\mathbf{r}, \tag{2.22}$$

$$V_2(\mathbf{a},\mathbf{a}')=\frac{1}{\Omega}\int V_2(\mathbf{r},\mathbf{a},\mathbf{a}')d\mathbf{r},$$
$$V_{12}(\mathbf{a},\mathbf{u})=\frac{1}{\Omega}\int V_{12}(\mathbf{r},\mathbf{a},\mathbf{u}_2)d\mathbf{r}. \tag{2.23}$$

D. Derivation of free energy with the SCF approximation

Substituting the SCF into Eq. (2.8), the free energy of the mixture with SCF approximation can be written as

$$F=F_0-\frac{N_1}{2}\int d\mathbf{r}_1\,d\mathbf{u}_1\,ds_1\,v_1(\mathbf{r}_1,\mathbf{u}_1)C(\mathbf{r}_1;\mathbf{u}_1;s_1)$$
$$-\frac{N_2}{2}\int d\mathbf{r}_1\,d\mathbf{a}_1\,v_2(\mathbf{r}_1,\mathbf{a}_1)p(\mathbf{r}_1,\mathbf{a}_1), \tag{2.24}$$

where

$$F_0=-N_2\int \exp(-v_2(\mathbf{r}_1,\mathbf{a}_1))d\mathbf{r}_1\, d\mathbf{a}_1 -N_1\int \mathscr{D}[\mathbf{r}(s)]\exp\left[-\int\left(v_1(\mathbf{r}(s_1),\mathbf{u}(s_1)) +\frac{3}{2l}\,\mathbf{u}^2(s_1)+\frac{\epsilon}{2}\,\dot{\mathbf{u}}^2(s_1)\right)ds_1\right]. \tag{2.25}$$

In the derivation the approximation discussed below Eq. (2.16) is used. For a uniform system or an interaction only depending of the orientations of the monomers and LMW molecules the free energy becomes

$$\dot{F}=F_0-\frac{N_1}{2}\int d\mathbf{u}\, ds\, v_1(\mathbf{u})C(\mathbf{u};s) -\frac{N_2}{2}\int d\mathbf{a}\, v_2(\mathbf{a})p(\mathbf{a}), \tag{2.26}$$

where

$$F_0=-N_2\int \exp(-v_2(\mathbf{u}))d\mathbf{u}-N_1\int \mathscr{D}[\mathbf{r}(s)] \times\exp\left[-\int\left(v_1(\mathbf{u}(s_1))+\frac{3}{2l}\,\mathbf{u}^2(s_1)+\frac{\epsilon}{2}\,\dot{\mathbf{u}}^2(s_1)\right)ds_1\right]. \tag{2.27}$$

III. MAIER–SAUPE THEORY FOR POLYMER LIQUID CRYSTALS

A. SCF for PLCs

In this section we will apply the results in the above section and the previous article[1] to the PLCs and show how the Maier–Saupe theory could be extended to PLCs. Generally, two interactions are often used: one is Onsager type[8,9]

$$V_1(\mathbf{u},\mathbf{u}')=2L^2D|\sin\,\theta| \tag{3.1}$$

and the second one is Maier–Saupe type[10]

$$V_1(\mathbf{u},\mathbf{u}')=V_0P_2(\cos\,\theta), \tag{3.2}$$

where P_2 is the Legendre function. The virtue of the first type is that the interaction can directly be related with the shape of the molecules from which nonspherical molecules can lead to the nematic phase, but it seems that it is difficult to solve the SCF exactly by an analytical expression, therefore a form of the distribution of the orientation must be assumed. The second type can be derived from perturbation theory of quantum theory and can be solved exactly with an analytical expression. Actually, any anisotropic interaction can be expanded in terms of Legendre functions and if the system is invariant under space reflection the interaction will have the form given by Eq. (3.2) by neglecting higher order Legendre functions.

Since MS type interaction can be solve exactly, in following the MS type interaction is used, i.e., the interaction between two monomers at s and s' should be written as

$$V_1(\mathbf{u}_i(s_i),\mathbf{u}_j(s_j))=(v_1/\Omega)[(3/2)(\mathbf{u}_i(s_i)\cdot\mathbf{u}_j(s_j))^2-1/2], \tag{3.3}$$

where v_1 is the strength of the interaction and Ω the volume of the system. Now we prove that the SCF for this interaction is

$$v_1(\mathbf{u})=v_1\rho_1\overline{S}[(3/2)(\mathbf{u}_0\cdot\mathbf{u})^2-1/2], \tag{3.4}$$

where ρ_1 is the monomer density of polymer solution N_1L/Ω, L is the length of the chain, $\mathbf{u}_0$ is the preferred direction, and S is the order parameter which is defined below [Eq. (3.9)]. Substituting the above interaction (3.3) into SCF (2.20) and setting $V_{12}=0$, then from the result in the previous paper[1] we have

$$v_1(\mathbf{u})=N_1\int d^3u'\; ds'(v_1/\Omega)((3/2)(\mathbf{u}(s)\cdot\mathbf{u}(s'))^2-1/2) \times A\,\sin\left(-\frac{(u_z')^2}{4a_{2z}}-\frac{(u_{xy}')^2}{4a_{2xy}}\right) \tag{3.5}$$

and if we consider the approximation, $|\mathbf{u}|=|\mathbf{u}'|=1$, as discussed in the previous paper,[1] we obtain

$$\begin{aligned}v_1(\mathbf{u})&=\int d\theta_2\, d\phi_2\, v_1\rho_1\,\sin\,\theta_2((3/2)\cos^2\,\theta_{12}-1/2)\\&\quad\times A\,\exp\left(-\frac{\cos^2\,\theta_2}{4a_{2z}}-\frac{\sin^2\,\theta_2}{4a_{2xy}}\right)\\&=v_1\rho_1((3/2)\cos^2\,\theta_1-1/2)\\&\quad\times\int \sin(\theta_2)d\theta_2\, d\phi_2((3/2)\cos^2\,\theta_2-1/2)\\&\quad\times A\,\exp\left(-\frac{\cos^2\,\theta_2}{4a_{2z}}-\frac{\sin^2\,\theta_2}{4a_{2xy}}\right)\\&=v_1\rho_1\overline{S}((3/2)\cos^2\,\theta_1-1/2)\end{aligned} \tag{3.6}$$

with a_{2z} and a_{2xy} given in the previous paper[1]

$$a_{2z}=\frac{1}{4}\sqrt{\frac{l_z}{3\epsilon}},\quad a_{2xy}=\frac{1}{4}\sqrt{\frac{l}{3\epsilon}}, \tag{3.7}$$

$$\frac{1}{l_z}=\frac{1}{l}\,(1+v_1\rho_1\overline{Sl}), \tag{3.8}$$

where $\overline{S}$ is the orientation order parameter

$$\overline{S}=2\pi A\int d\theta_2\,\sin\,\theta_2((3/2)\cos^2\,\theta_2-1/2) \times\exp\left(-\frac{\cos^2\,\theta_2}{4a_{2z}}-\frac{\sin^2\,\theta_2}{4a_{2xy}}\right) \tag{3.9}$$

and A is determined by the following equation:

$$A^{-1}=2\pi\int d\theta_2\,\sin\,\theta_2\,\exp\left(-\frac{\cos^2\,\theta_2}{4a_{2z}}-\frac{\sin^2\,\theta_2}{4a_{2xy}}\right). \tag{3.10}$$

This is a self-consistent equation for order parameter, $\overline{S}$ and the above equations are just the generalization of MS SCF for PLCs.

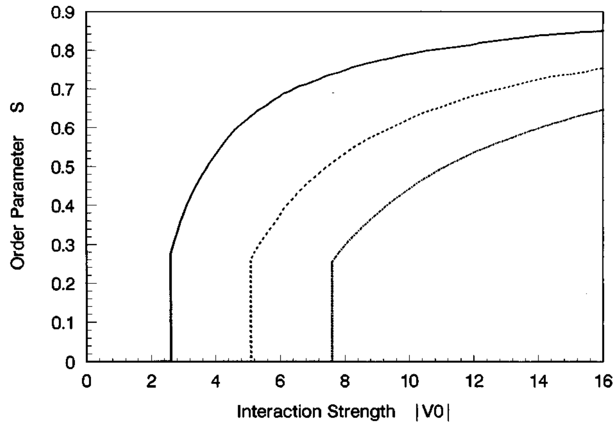

FIG. 1. The order parameter $\bar{S}$ of PLCs versus the strength of the interaction (by cooling), $V_0=\rho_1|v_1|$, for different ϵ: solid line for $\epsilon=3$, dashed line for $\epsilon=3/2$ and dot-dashed line for $\epsilon=1$ and arbitrary unit is used here and the other figures.

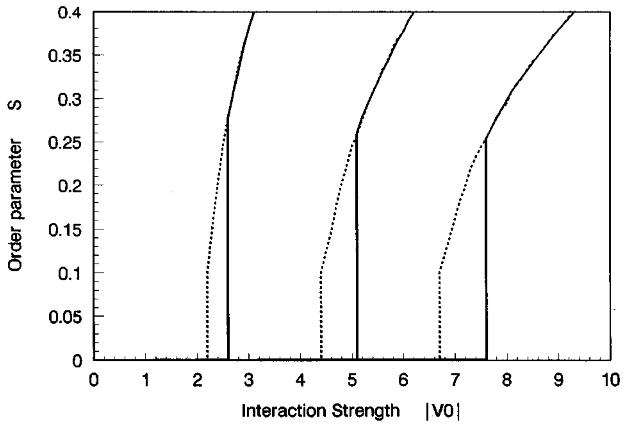

FIG. 2. The order parameter $\bar{S}$ of PLCs versus the strength of the interaction V_0 by dropping (solid line) and rising (dashed line) temperature for different ϵ as in the Fig. 1.

B. Solution of the SCF equation for PLCs

1. Numerical calculation

Although we have obtained the concrete expression of SCF, the order parameter must be obtained by solving numerically a system of transcendental equations (3.7) to (3.10). After solving these equations the WLCs exhibit a phase transition from isotropic phase to nematic phase. Figure 1 shows the numeral solutions of Eqs. (3.7)–(3.10) for the negative interaction and different bending elastic coefficients from which we obtain the following conclusions: (1) The figure shows clearly a first order phase transitions from isotropic phase to nematic phase; (2) the phase transitions always take place at the condition

$$\epsilon v_1\rho_1=-\frac{15}{2} \tag{3.11}$$

which is explained in the following [see Eq. (3.13)]; (3) at the phase transition points the order parameters S are the same (about 0.26) for the different bending elastic coefficients and (4) Fig. 2 shows supercooled and superheated phenomena by rising and dropping temperature, respectively.

2. The condition of phase transition

If we assume near the critical temperature (concentration) of phase transition the order parameter takes an infinitesimal value, the following equation is easily derived:

$$\begin{aligned} C(\mathbf{U};s)&=C(\theta)\\ &=A\exp[-(\alpha_z-\alpha_{xy})\epsilon\cos^2\theta]\\ &=A\exp(-\epsilon v_1\rho_1\bar{S}\cos^2\theta)\\ &\simeq A(1-\epsilon v_1\rho_1\bar{S}\cos^2\theta), \end{aligned} \tag{3.12}$$

where the condition $|\mathbf{u}|=1$ is also used. The above equation shows why the phase transitions are only dependent on the variable, $\epsilon v_1\rho_1$ and now we will prove Eq. (3.11). For an infinitesimal order parameter, S, and from Eq. (3.9) the following result is easily obtained:

$$\bar{S}=\frac{\int(\frac{3}{2}\cos^2\theta-\frac{1}{2})C(\theta)\sin\theta\,d\theta}{\int C(\theta)\sin\theta\,d\theta}\simeq-\frac{2}{15}\epsilon v_1\rho_1\bar{S}. \tag{3.13}$$

In order that $\bar{S}$ has a nonzero solution, Eq. (3.11) must be fulfilled. From the above equation the phase diagram is easily drawn and here it is not discussed further. It should be noticed that: (1) When $\epsilon\to 0$, the phase transition could take place only with a very large v_1 which means for IGC the phase transition cannot take place and this conclusion is different from the results in Ref. 8(a) in which the phase transition can occur for IGCs. A similar relation is also obtained by Gupta and Edwards[8(b)] whose results is $\epsilon v_1\rho_1\approx 5.92$. (2) Although the WLCs can exhibit a discotic-like phase ($S<0$) in an external field (see the previous paper[1] when $v_0>0$), from Eq. (3.11) the discotic-like phase cannot occur since Eq. (3.11) cannot have a solution for a positive interaction $v_1>0$. The reason can also be seen from Eq. (3.6), i.e., for positive interaction, $v_1>0$, we may find that the SCF will be negative if $S<0$, then the negative SCF leads to $S>0$ and the SCF will be positive if $S>0$ then the positive SCF leads to $S<0$. If the numerical calculation is carried out one will find the order parameter will alternate between positive and negative values. Therefore, a positive interaction cannot result in a discotic-like phase. In Ref. 8(b) it is shown that the discotic-like phase possesses a higher free energy than that of the isotropic and nematic phases, which means the discotic-like phase is unstable and is in agreement with our results.

3. Expression of the free energy for PLCs

Substituting the SCF (3.6) into Eq. (2.26) the free energy is easily derived

$$F=F_0-\frac{N_1L}{2}v_1\rho_1\overline{S}\int d\mathbf{u}((3/2)\cos^2(\theta_1)-1/2)C(\mathbf{u};s)$$
$$=F_0-\tfrac{1}{2}\Omega v_1\rho_1^2\overline{S^2}, \qquad (3.14)$$

where F_0 is given by Eq. (2.27) in the above section.

IV. MS THEORY FOR THE MIXTURE OF PLCs AND LMW LCs

A. SCF for the mixture of PLCs and LMW LCs

In this section we consider the mixture composed of PLCs and LMW LCs and study the properties and behaviors of the WLCs in nematic solvents. Since interaction (3.2) is a very general form as discussed below Eq. (3.2) and in Sec. II C, the interactions of LMW molecules and between LMW and PLC molecules are also taken as MS type

$$V_2(\mathbf{a}_i,\mathbf{a}_j)=\frac{v_2}{\Omega}\left[\frac{3}{2}(\mathbf{a}_i\cdot\mathbf{a}_j)^2-\frac{1}{2}\right]=\frac{v_2}{\Omega}\left[\frac{3}{2}\cos^2\theta_{ij}-\frac{1}{2}\right], \qquad (4.1)$$

$$V_{12}(\mathbf{a}_i,\mathbf{u}_j(s_j))=\frac{v_{12}}{\Omega}\left[\frac{3}{2}(\mathbf{a}_i\cdot\mathbf{u}_j(s_j))^2-\frac{1}{2}\right]$$
$$=\frac{v_{12}}{\Omega}\left[\frac{3}{2}\cos^2\theta_{ij}(s_j)-\frac{1}{2}\right] \qquad (4.2)$$

and the interaction for PLCs, V_1, is given in the previous section. Substituting these interactions into the SCF

$$v_1(\mathbf{u})=N_1\int d\mathbf{u}'\ ds'\ V_1(\mathbf{u},\mathbf{u}')C(\mathbf{u}';s')$$
$$+\frac{N_2}{2}\int d\mathbf{a}\ p(\mathbf{a})V_{12}(\mathbf{a},\mathbf{u}), \qquad (4.3)$$

$$v_2(\mathbf{a})=(N_2-1)\int d\mathbf{a}'\ p(\mathbf{a}')V_2(\mathbf{a},\mathbf{a}')$$
$$+\frac{N_1}{2}\int d\mathbf{u}\ ds\ C(\mathbf{u};s)V_{12}(\mathbf{a},\mathbf{u}), \qquad (4.4)$$

we obtain the final forms of SCF of the mixture

$$v_1(\mathbf{u})=v_1(\theta)=(v_1\rho_1\overline{S_1}+\tfrac{1}{2}v_{12}\rho_2\overline{S_2})((3/2)\cos^2\theta-1/2), \qquad (4.5)$$

$$v_2(\mathbf{a})=v_2(\theta')=(v_2\rho_2\overline{S_2}+\tfrac{1}{2}v_{12}\rho_1\overline{S_1})((3/2)\cos^2\theta'-1/2), \qquad (4.6)$$

where $\overline{S_1}$ and $\overline{S_2}$ are the orientation order parameters of PLC and LMW LC

$$\overline{S_1}=2\pi A_1\int d\theta_2\ \sin\ \theta_2((3/2)\cos^2\ \theta_2-1/2)$$
$$\times\exp\left(-\frac{\cos^2\theta_2}{4a_{2z}}-\frac{\sin^2\theta_2}{4a_{2xy}}\right), \qquad (4.7)$$

$$\overline{S_2}=2\pi A_2\int d\theta_2\ \sin\ \theta_2((3/2)\cos^2\ \theta_2-1/2)$$
$$\times\exp[-(v_2\rho_2\overline{S_2}+\tfrac{1}{2}v_{12}\rho_1\overline{S_1})((3/2)\cos^2\ \theta_2-1/2)], \qquad (4.8)$$

a_{2z} and a_{2xy} are the same as Eq. (3.7), and l_z, the constrained condition and the normalization constants A_1 and A_2 are given by

$$\frac{l}{l_z}=1+(v_1\rho_1\overline{S_1}+(1/2)v_{12}\rho_2\overline{S_2})l, \qquad (4.9)$$

$$1+0.5/\sqrt{1+(v_1\rho_1S_1+(1/2)v_{12}\rho_2S_2)l}=\sqrt{3\epsilon/l}, \qquad (4.10)$$

$$A_1^{-1}=2\pi\int d\theta_2\ \sin\ \theta_2\ \exp\left(-\frac{\cos^2\theta_2}{4a_{2z}}-\frac{\sin^2\theta_2}{4a_{2xy}}\right), \qquad (4.11)$$

$$A_2^{-1}=2\pi\int d\theta_2\ \sin\ \theta_2\ \exp(-v_2(\theta_2)). \qquad (4.12)$$

This is a set of self-consistent equations for order parameters, S_i, and the above equations are just the generalization of MS SCF to mixture of PLCs and LMW LCs.

B. The conditions of phase transition of the mixture

The SCFs of the mixture are complicated and in order to inspect some properties we first derive the conditions of the phase transition. For small order parameters we can expand the SCF in terms of the parameters. For distribution functions we have

$$C(\mathbf{u},s)=C(\theta)$$
$$\approx A[1-\tfrac{3}{4}(v_1\rho_1\overline{S_1}+(1/2)v_{12}\rho_2\overline{S_2})l\ \cos^2\ \theta]$$
$$\approx A[1-(v_1\rho_1\overline{S_1}+(1/2)v_{12}\rho_2\overline{S_2})\epsilon\ \cos^2\ \theta], \qquad (4.13)$$

$$p(\mathbf{a})=p(\theta)\approx A[1-(v_2\rho_2\overline{S_2}+(1/2)v_{12}\rho_1\overline{S_1})$$
$$\times(3/2)\cos^2\ \theta], \qquad (4.14)$$

and substituting them into Eqs. (4.7) and (4.8) we obtain the conditions of the phase transition

$$\overline{S_1}=-\frac{2}{15}(v_1\rho_1\overline{S_1}+(1/2)v_{12}\rho_2\overline{S_2})\epsilon, \qquad (4.15)$$

$$\overline{S_2}=-\frac{3}{15}(v_2\rho_2\overline{S_2}+(1/2)v_{12}\rho_1\overline{S_2}). \qquad (4.16)$$

From these equation we obtain the following conclusions:

(1) For the case of the WLCs in nematic solvents, i.e., the temperature of the phase transition (TPT) of LMW LCs is far below that of PLCs, when the temperature near TPT of LMW LCs, we may set $S_1=0$ then the condition of the phase transition for LMW LCs is

$$v_2\rho_2=-\frac{15}{3} \qquad (4.17)$$

which is different from that of PLCs (3.11).

(2) If TPT of LMW LCs is far above that of PLCs, the condition is just Eq. (3.11).

(3) If $v_1\rho_1$ and $v_2\rho_2$ satisfy

$$\frac{v_1\rho_1}{v_2\rho_2} = \frac{3}{2}, \tag{4.18}$$

the WLCs and LMW molecules will have the same TPT. Actually, this relation does not need to be satisfied exactly because the interaction between WLCs and LMW molecules, V_{12}, will make the TPTs of PLCs and LMW LCs coincident.

(4) In condition (1) the order parameter of WLCs is given by Eq. (4.15)

$$\overline{S_1} = \frac{-v_{12}\rho_2\epsilon\overline{S_2}}{15+2v_1\rho_1\epsilon} \tag{4.19}$$

from which we find a negative interaction between the WLCs and LMW molecules will induce WLCs oriented in the direction of LMW molecules. When $15 \gg 2v_1\rho_1\epsilon$ (i.e., TPT of PLC is far above that of LMW LC), S_1 will linearly depend on the density of the LMW molecules, the interaction strength, v_{12} (i.e., inverse proportion to temperature), and S_2. But for a positive interaction, $v_{12}>0$, the situation is very complicated as discussed in the above section [see the discussion below Eq. (3.13)].

C. The solution of the SCF for the mixture

Now let us consider the phase behaviors of the mixture by solving the SCFs given above. Here, we also consider the case of the WLCs in nematic solvents, i.e., the TPT of LMW LCs is below that of PLCs. Therefore, we only study how the LMW LCs influence the phase behaviors of WLCs and for the case of the TPT of PLCs is below that of LMW LCs a similar conclusion is easily obtained.

In order to investigate the properties of the mixture, the density fraction of the mixture is introduced

$$\rho = \rho_1 + \rho_2, \quad \rho_1 = c\rho, \quad \rho_2 = (1-c)\rho \tag{4.20}$$

and the temperature dependence is recovered by introducing the effective temperature, i.e., by replacements

$$v_1 \to v_1\tilde{T}, \quad v_2 \to v_2\tilde{T}, \quad v_{12} \to v_{12}\tilde{T}, \tag{4.21}$$

where the effective temperature is given by $\tilde{T} = 1/k_BT$ and in the following we will drop the tilde on the $\tilde{T}$. It is also assumed that the effective monomer length l and bending elastic coefficient ϵ do not depend on the temperature.

Figure 3 shows the final numerical solution of Eqs. (4.7)–(4.12) for the fraction $c=0.5$. If there is no interaction between the polymer chains and the LMW molecules, i.e., $V_{12}=0$, the above equations become two independent equations which is just the case discussed in the above section. With increasing interaction between the WLCs and LMW molecules, V_{12}, the TPT and the order parameter, $\overline{S_2}$ of LMW LC are almost not changed and the TPT of PLC is changed obviously. The most significant change for PLCs is that the phase transition of PLC becomes second or higher order from the first order phase transition. For the strong interaction, V_{12}, the orientation of WLCs is like the case of the chain in an external field as discussed in the previous paper.[1] Figure 3 shows the case that the TPTs of PLC and LMW LC are far from each other when $V_{12}=0$ and if the TPTs of PLC and LMW LC are near each other the result is quite different. For the later case, even a weak interaction will make TPTs of PLC and LMW LC coincident with each other and a strong interaction will lower their TPT evidently.

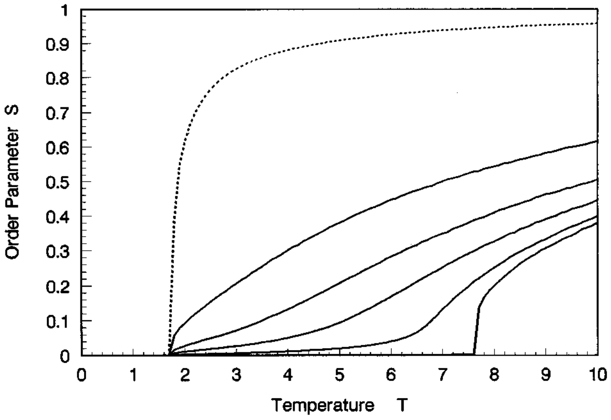

FIG. 3. The order parameters $\overline{S}$ of the mixture, the dashed line for LMW LC and solid line for PLC, versus temperature for different interactions, $|v_{12}|$: from the top solid line down, $v_{12}=-1.5$, -0.5, -0.2, -0.05, and 0 and the order parameter of LMW LC is changed little for different v_{12}. The other parameters are $\epsilon=1$, $v_1=-1.8$, $v_2=-5$ and $c=0.5$.

Figure 4 shows the phase behaviors of the mixture for the different density fraction c and interaction, V_{12}, between the chains and the LMW molecules. Figure 4(a) shows the phase behaviors of the mixture for a weak interaction $V_{12}=0.5$ from which we find that for low density of LMW molecules, $c>0.87$, the phase transition of PLC will first take place then it induces orientation for LMW molecules, while for high density of LMW molecules, $c<0.87$, the phase transition of LMW LC will first take place, then orientation of PLC is induced by the LMW molecules. Figures 4(a)–4(d) show the dependence of phase behaviors of the mixture on the different interaction V_{12}. From these figures we can find that for weak interactions, $V_{12}<0.5$, the order parameter of PLC induced by LMW LC is linearly dependent on temperature as shown by Eq. (4.19) and the phase transition of PLC becomes second or higher order. While for the strong interaction, $V_{12}>1$, the LMW LC will approximately induce a first order phase transition and for stronger interaction, $V_{12}>2.5$, the PLC behaves like the behaviors in the external field [see Fig. 4(d) and the previous paper[1]].

V. COMPARISON WITH EXPERIMENTS AND DISCUSSION

Preliminary results of comparison with experimental data and some conclusive remarks are given in this section and further detailed results will be given elsewhere. As we know, Onsager and Maier–Saupe theories are successful in explaining experimental results of the LMW LC. Based on this fact Khokhlov and Semenov first extended Onsager

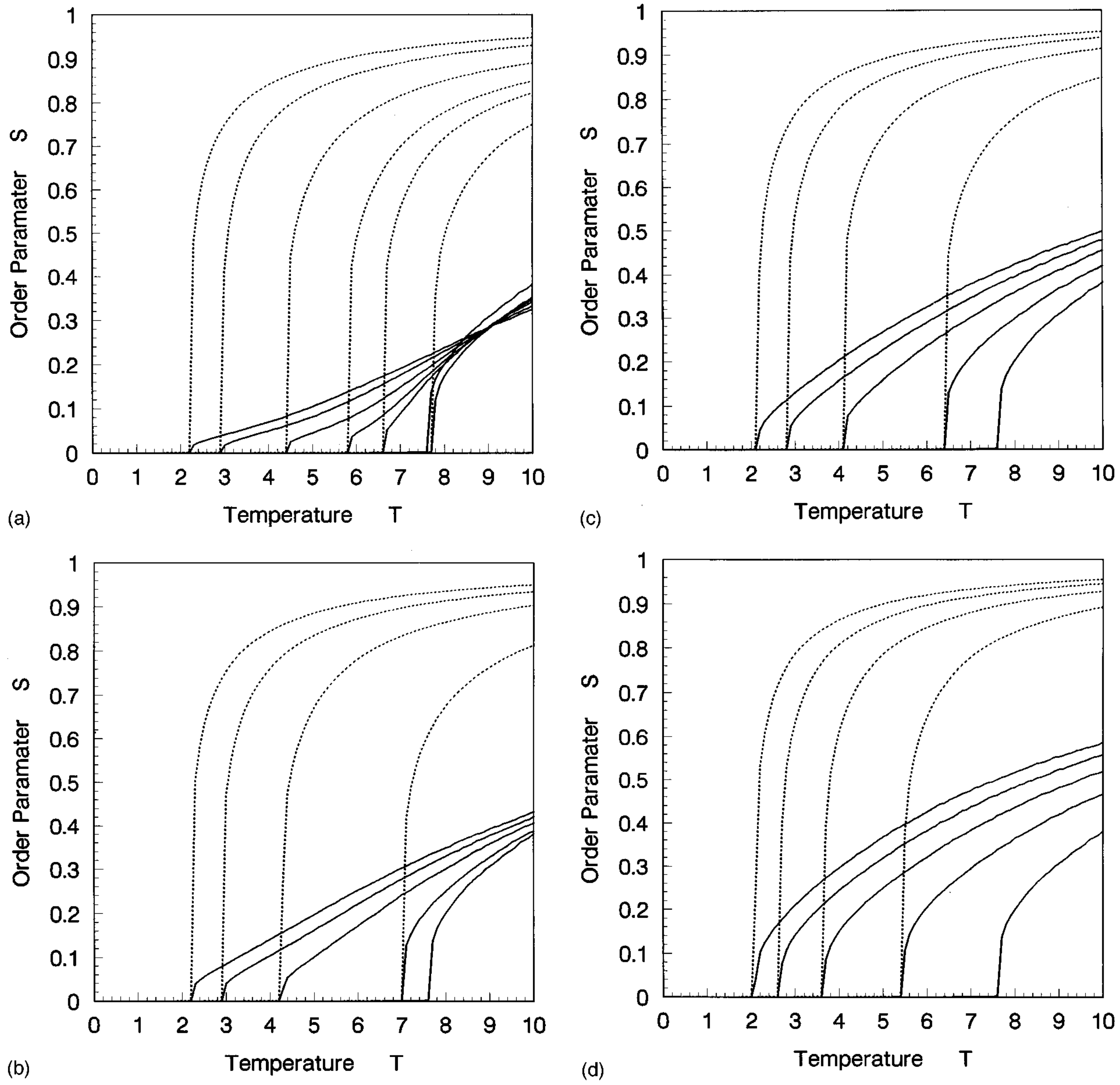

FIG. 4. The order parameter $\overline{S}$ of the mixture, the dashed line for LMW LC and solid line for PLC, versus temperature for different density fractions c. (a) From right to left, $c=0.9$, 1., 0.87, 0.85, 0.8, 0.7 and 0.6. (b)–(d) From right to left, $c=1.$, 0.9, 0.8, 0.7, and 0.6. The other parameters are $\epsilon=1$, $v_1=-0.9$, $v_2=-5$, and $v_{12}=0.5$, 1.0, 1.5, and 2.5 for (a) to (d).

theory to PLC[13] and exactly self-consistent solving Onsager equation is given by Chen.[8(a)] In principle, no adjusted parameter is needed in the original Onsager theory, however, the persistence length is difficult to determine experimentally and, therefore, is often used as an adjusted parameter[13,16] since the persistence length also depends on temperature.[17] However, usual Onsager theory from virial expansion is not enough to explain experiments and therefore the extension to higher solute densities based on the second order virial expansion is established.[13,16] The same situation is also encountered here (see the following). In contrast to Onsager theory, in MS theory there are two parameters to be determined: the elastic coefficient ϵ and the interaction strength $v_1\rho_1$. Since ϵ can be determined by the relation $\overline{l}=(2/3)\epsilon$ (see the previous paper[1]), i.e., $\epsilon=1.5$, if the persistence length, $\overline{l}$, is used as the unit, the only parameter, interaction strength, can be used as an adjusted parameter.

Although MS theory are available for both thermotropic and lyotropic PLCs, here, as an application, we only compare it with the experimental results of lyotropic PLC which can also be compared with Onsager theory.[13,16] Although increasing concentration is equivalent to increasing temperature in effect, the interaction strength is quite different for thermotropic and lyotropic LCs, i.e., it may be considered as a constant for thermotropic LC since the concentration will change little but it is not the case for lyotropic LC. A straightforward comparison with Onsager theory we will find the dependence of the interaction strength on the concentra-

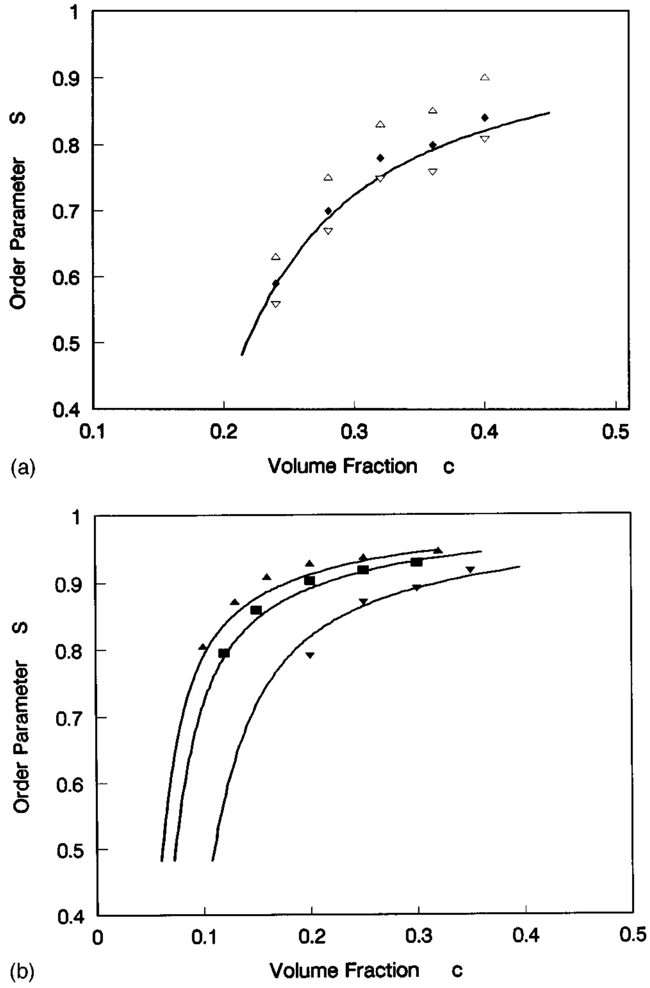

FIG. 5. Comparison with experimental data from Ref. 16(a) (a) and Ref. 16(b) (b) for order parameters versus concentration c. The experimental data are fitted by theoretical results with different v_0 [$v_0=560$ solid line in (a) and $v_0=2000$, 1666, and 1111 from top solid line down in (b)].

tion, c, is very complicated.[18] $v_1 \propto a+bc+\cdots$ and if we simply let $v_1 \propto c$ the results are agreement with the experiments. Figure 5 shows the comparison between the theoretical and experimental results with the interaction strength as the adjusted parameter for different experiments,[16] in which $v_1\rho_1$ is set to be $v_1\rho_1=v_0c^2$ with the concentration c. From the figures we find the theoretical results are quite in agreement with the experiments.

In order to obtain the critical temperature (concentration) and order parameter, free energy should be calculated since the state of the system is determined by minimizing free energy. In more exact meaning, the condition determined by Eq. (3.11) is an approximation of the critical temperature (concentration) since it is generally a local minimum of free energy [denoted often by T^* (c^*) and S^* in the literature] and, however, from Landau–Gennes theory the critical temperature is very close to it. Gupta and Edwards obtained the ratio of the critical concentration to the local minimum as $c/c^*=1.014\,34$ and $S=0.25$ ($S^*=0.186$) with Onsager type interaction. From these results, it is estimated the critical order parameter should be about $S=0.3$–0.4 since $S^*=0.26$. It seems all these theories (Onsager and MS theory) predict lower critical order parameter than that of experiments. Therefore, the free energy should be calculated for a complete theory and comparison with experiments and, especially, for the mixture of PLCs with LMW LCs, and this work will be finished in the next step.

Finally, from the point of view of the molecular interaction, which is generally described by a type of short range repulsive and long range attractive interaction, since Onsager and MS theories represent two special cases for repulsive and attractive interaction, respectively, it seems that a better theory should be a combination of these two theories.

VI. SUMMARY

In this paper a very general SCF was derived by variation principle. By considering the MS type interactions we extend MS theory to the polymer liquid crystals as well as the mixture of PLCs and LMW LCs. By virtue of MS type interaction an analytical expressions of the SCF are obtained, from which the properties and phase behaviors of PLC and the mixture have been studied. Finally, the theoretical results are compared with the experiments.

Moreover, the following conclusions are obtained for PLC: (1) Interactions depending only on the position of the monomers have no contribution to the phase transition and a special case is also obtained for the excluded volume interaction in Refs. 8(b) and 8(c). (2) A first order phase transitions from isotropic phase to nematic phase is shown clearly which is consistent with the results obtained by the other authors[8] and the experiments.[16] (3) The phase transitions always take place approximately at the condition $\epsilon v_1\rho_1=-15/2$. (4) At the critical points of the phase transition of the order parameters S (in more exact meaning S^*) is the same (about 0.26) and independent of the bending elastic coefficients and concentration. (5) Supercooled and superheated phenomena can be found at TPT. (6) For the IGC the phase transition will not occur which is consistent with Ref. 8(b). (7) Discotic-like phase cannot take place.

Furthermore, for the mixture of PLCs and LMW LCs we have: (1) similar to PLCs, the condition of phase transition for LMW LCs is $v_2\rho_2=-15/3$ which is different from that of PLCs (3.11), (2) if $v_1\rho_1$ and $v_2\rho_2$ satisfy $v_1\rho_1/v_2\rho_2=3/2$, the WLCs and LMW molecules will have the same TPT, (3) when TPT of LMW LCs is far below that of PLCs, the LMW LCs will induce orientation for WLCs and the orientation order parameter of WLCs will be linearly dependent on the density of the LMW molecules and the interaction strength, v_{12} and inversely proportional to temperature and (4) after solving the SCF equations, the dependence of phase behaviors of the mixture on the density fraction and the interaction, v_{12}, is clearly shown in the Figs. 3 and 4.

As we know, the phase transition should take place at the minimum of the free energy, therefore as a complete theory the free energy should be discussed and since the calculation is complicated it is left to the future. However, from the discussions and results in the Refs. 8 and 10 the orientation can really make the free energy minimum and solving the SCF and minimizing the free energy are coincident with each other except at the critical point. Finally, from the point of view of experiment, the orientation order parameter and the phase transition can be measured by many methods, such as neutron scattering and NMR, therefore we expect the theoretical results of the mixture could be compared with experiments in the future. Especially, the parameters, such as the interaction strength and elastic coefficient, ϵ, as well as its relation with temperature are urgently needed to be determined by experiments.

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[18] This means that the Onsager and MS theories must be modified for higher solute density. As we know, the Onsager theory is also a mean-field approximation in which for higher density solutions it is modified by $A(c)=4c(1-3c/4)/(1-c)^2\simeq 4c(1+5c/4+\cdots)$ and $B(c,x)=[c(1-3v/4)/(1-c^2)][3x^2/2(1+3x/2)]$ (see Refs. 13, 16). Here, $v_1\rho_1$ corresponds to $B(c,x)$, therefore $v_1\rho_1\propto ac+bc^2+\cdots$.