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Study of phase transition in homogeneous, rigid extended nematics and magnetic suspensions using an order-reduction method

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We study the phase transition in rigid extended nematics and magnetic suspensions by solving the Smoluchowski equation for magnetically polarized rigid nematic polymers and suspensions in equilibrium, in which the molecular interaction is modeled by a dipolar and excluded volume potential. The equilibrium solution (or the probability distribution of the molecular distribution) is given by a Boltzmann distribution parametrized by the (first-order) polarity vector and the (second-order) nematic order tensor along with material parameters. We show that the polarity vector coincides with one of the principal axes of the nematic order tensor so that the equilibrium distribution can be reduced to a Boltzmann distribution parametrized by three scalar order parameters, i.e., a polar order parameter and two nematic order parameters, governed by three nonlinear algebraic-integral equations. This reduction in the degree of freedom from 8 (3 in the polarity vector and 5 in the nematic order tensor) to 3 significantly simplifies the solution procedure and allows one to conduct a complete analysis on bifurcation diagrams of the order parameters with respect to the material parameters. The stability of the equilibria is inferred from the second variation of the free energy density.
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I. INTRODUCTION

The Doi-Hess kinetic theory is developed for flows of rigid nematic liquid crystals.[1,2] It is also applicable to rigid rodlike particle dispersions in viscous solvent. Lately, it has been extended to model magnetic dispersions in viscous solvent by Bhandar and Wiest.[3] Magnetic dispersions are interesting materials that have many applications in industries.[4] The interesting issues for magnetic dispersions are how the anisotropic particles orient and how the orientation evolves in time under various conditions.

In Ref. 3, Bhandar and Wiest studied the equilibrium orientation of magnetic dispersions and the orientational dynamics in imposed shear using a closure approximation. They noted a new transition from the isotropic to nematic phase using the approximation. We will revisit the issue by solving the Smoluchowski equation exactly in equilibrium, bypassing the closure approximation, which may introduce fictitious solutions, and direct numerical discretization of the Smoluchowski equation. Recently, a number of papers have emerged addressing the properties of the Smoluchowski equation and its solution properties for the Doi-Hess model,[2,5–26] in which the existence, multiplicity, and stability of equilibrium solutions are rigorously studied and justified.

In this paper, we extend the previous work on the Smoluchowski equation, especially the work of Wang *et al.*[25] on the exact solution of the Smoluchowski equation with an intermolecular potential consisted of either a dipolar interaction potential or an excluded volume potential to derive the exact solution for the Smoluchowski equation with an intermolecular potential consisted of both the dipolar and excluded volume potential. We will first show that the equilibrium solution, which is the probability distribution function (pdf) for the molecular orientation, is of a Boltzmann type and parametrized by a polarity vector (the first moment of the pdf) and a nematic order tensor (the second moment of the pdf). We then prove mathematically that the equilibrium polarity vector is coaxial with the nematic order tensor, i.e., the polarity vector must parallel to one of the principal axes of the nematic order tensor; thereby, we establish that the equilibrium solution can be parametrized by three scalar order parameters and the material constants, in which the three order parameters are governed by three nonlinear algebraic-integral equations. This approach allows one to single out the three essential modes responsible for the equilibrium solution of the Smoluchowski equation, eliminating the need of using spherical harmonic expansions or other elaborate numerical approximations to attain solutions of the Smoluchowski equation. With the reduced system of equations, we are able to derive the complete bifurcation phase diagram in the parameter space of the strength of the dipolar potential versus that of the excluded-volume one, and thereby to understand the phase transition in the material system governed by the Smoluchowski equation along with the intermolecular potentials completely.

In a very recent paper, Gopinath *et al.* studied the transition to nematic phase in the neighborhood of the isotropic state asymptotically using the spherical harmonic expansion of the pdf solution of the Smoluchowski equation.[26] Our results extend their work with the Maier-Saupe potential to the entire parameter space and all equilibrium solutions.[27–29]

In the past, a model known as p1-p2 model was used to study the phase behavior in crystals[30] and ferroelectric liquid crystals.[31–34] Using a mean field version of the p1-p2 model, Krieger and James was able to obtain the phase diagram in the parameter space encompassing two tricritical points and a triple point.[30] The p1-p2 model is the uniaxial limit of our model. In this regard, our work in this paper also extends the early work by providing all equilibria of the Smoluchowski equation, stable and unstable alike, as well as revealing the detailed phases including the metastable ones and the limits of metastability for various phases.[35]

II. EQUILIBRIUM SOLUTION FOR EXTENDED (POLAR) NEMATICS

We consider the rigid extended nematics in which the nematic molecules are magnetically polar. For these nematics, the molecular interaction includes not only the excluded volume effect, but also the magnetic dipole-dipole interaction.[3] Let $f(\mathbf{m},t)$ be the probability density function (pdf) for nematic molecules in direction $\mathbf{m}$ at time t. The total interaction potential for the solution of rigid extended nematic polymers is given by

$$V = -\alpha kT\langle \mathbf{m}\rangle \cdot \mathbf{m} - \frac{3NkT}{2}\langle \mathbf{mm}\rangle : \mathbf{mm}, \quad (1)$$

where $\mathbf{m}$ is a unit vector for the axes of symmetry of the molecule, α the strength of the dipole-dipole interaction, N a dimensionless parameter describing the strength of the excluded volume potential, and

$$\langle(\bullet)\rangle = \int_{\|\mathbf{m}\|=1} (\bullet) f d\mathbf{m} \quad (2)$$

is the ensemble average with respect to the probability density function f, which is a solution of the Smoluchowski equation.

The steady state solution of the Smoluchowski equation,

$$\frac{\partial}{\partial t} f = \mathcal{R} \cdot (D_r f \mathcal{R}\mu), \quad (3)$$

where $\mu = \ln f + (1/kT)V$ is the normalized chemical potential given by[25]

$$f = \frac{1}{Z} e^{-V/kT}, \quad (4)$$

where $Z = \int_{\|\mathbf{m}\|=1} e^{-V/kT}$ is the partition function. In the above expression, $\mathcal{R}$ the rotational gradient operator,[1] and D_r the rotary diffusivity, which is assumed a constant for simplicity in this study. (We note that the steady state solution is given by the same form should the rotary diffusivity is a positive function of $\mathbf{m}$.) Notice that the pdf solution is parametrized by the first and second moment tensors, $\langle \mathbf{m}\rangle$ and $\langle \mathbf{mm}\rangle$, respectively, along with the material parameters α and N. The first and second moment tensors have 8 degrees of freedom or 8 independent components collectively, which are defined implicitly through (4). We next introduce a reduction procedure to reduce the degree of freedom from 8 to 3.

First we show that the degree of freedom can be reduced from 8 to 5 in the coordinate system set by the principal axes of the second moment. Let $\mathbf{n}, \mathbf{n}_\perp, \mathbf{n}^*$ denote the three orthonormal eigenvectors of the second moment tensor $\langle \mathbf{mm}\rangle$. We parametrize the first moment vector $\langle \mathbf{m}\rangle$ and $\mathbf{m}$ with respect to the basis as follows:

$$\begin{aligned} \mathbf{m} &= \cos\theta \mathbf{n} + \sin\theta\cos\phi \mathbf{n}_\perp + \sin\theta\sin\phi \mathbf{n}^*, \\ \langle \mathbf{m}\rangle &= s_1[\cos\theta' \mathbf{n} + \sin\theta'\cos\phi' \mathbf{n}_\perp + \sin\theta'\sin\phi' \mathbf{n}^*], \end{aligned} \quad (5)$$

where s_1 is the polar order parameter, and θ', ϕ' are the Euler angles for the first moment vector or the polarity vector $\langle \mathbf{m}\rangle$. When $s_1=0$, the material is purely nematic, whereas it is extended nematic or polar nematic if $s_1 \neq 0$. We adopt the biaxial representation for the second moment tensor:[36,37]

$$\langle \mathbf{mm}\rangle = s\left(\mathbf{nn} - \frac{\mathbf{I}}{3}\right) + \beta(\mathbf{n}_\perp\mathbf{n}_\perp - \mathbf{I}/3) + \mathbf{I}/3, \quad (6)$$

where s and β are the pair of the nematic order parameters describing the birefringence about two principal axes.

With the above parametrization, the equilibrium probability density function can be rewritten as

$$\begin{aligned} f &= \frac{1}{Z} e^{h}, \\ h &= \alpha s_1[\cos\theta'\cos\theta + \sin\theta'\sin\theta\cos(\phi-\phi')] \\ &\quad + \frac{3N}{2}\left[\left(s - \frac{\beta}{2}\right)(\cos^2\theta - 1/3) + \frac{\beta}{2}\cos 2\phi \sin^2\theta\right]. \end{aligned} \quad (7)$$

The order parameters are given by

$$\begin{aligned} s_1 &= \langle \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi-\phi')\rangle, \\ \beta &= \langle \sin^2\theta\cos 2\phi\rangle, \quad s = \langle P_2(\cos\theta)\rangle + \beta/2, \end{aligned} \quad (8)$$

where $P_2(z) = (3z^2-1)/2$ is the second-order Legendre polynomial. In the coordinate system set by the principal axes of the nematic tensor, the pdf solution is parameterized by five scalar variables: three order parameters s_1, s, β, and two angle parameters θ', ϕ'. There are three constraints associated with the parametrization of $\mathbf{m}$ in the coordinate set by the second moment:

$$\langle\cos\theta\sin\theta\cos\phi\rangle=\langle\cos\theta\sin\theta\sin\phi\rangle=\langle\sin^2\theta\sin\phi\cos\phi\rangle=0. \quad (9)$$

Let $\mathbf{p}$ and $\mathbf{q}$ be two orthonormal vectors perpendicular to the first moment vector. Then

$$\langle\mathbf{m}\cdot\mathbf{p}\rangle=\langle\mathbf{m}\cdot\mathbf{q}\rangle=0. \quad (10)$$

This hints an additional reduction in the degree of freedom in the representation of the pdf solution.

Next, we prove a theorem to establish the relationship between the first moment vector and the second moment tensor and thereby to attain the explicit values of θ' and ϕ' and further reduction in the degree of freedom in the Boltzmann expression.

Theorem 1: *The polarity vector is either zero or coaxial with the second order nematic order tensor. That is, the first moment vector* $\langle\mathbf{m}\rangle$ *either vanishes or parallels to one of the eigenvectors of the second moment tensor* $\langle\mathbf{mm}\rangle$: $\theta'=0$ *or* $\theta'=\pi/2$ *and* $\phi'=0,\pi/2$.

Proof: First of all, if $s_1=0$, then the first moment vanishes. Therefore, we only need to show that the first moment must parallel to one of the eigenvectors of the second moment tensor whenever $s_1\neq 0$. We define

$$h=\alpha s_1[\lambda_1\cos\theta\cos\theta'+\lambda_2\sin\theta\sin\theta'\cos(\phi-\phi')]+\frac{3N}{2}[(s-\beta/2)(\cos^2\theta-1/3)+(\beta/2)\sin^2\theta\cos(2\phi)], \quad (11)$$

$$F(\lambda_1,\lambda_2)=\int_0^{2\pi}d\phi\int_0^{\pi}\sin^2\theta\cos\theta\cos(\phi-\phi')e^h d\theta.$$

It follows from $\langle\cos\theta\sin\theta\cos\phi\rangle=0$, $\langle\cos\theta\sin\theta\sin i\rangle=0$ that, for all ϕ',

$$\langle\cos\theta\sin\theta\cos(\phi-\phi')\rangle=0. \quad (12)$$

Equation (12) implies $F(1,1)=0$.

$$F(1,0)=\int_0^{2\pi}d\phi\int_0^{\pi}\sin^2\theta\cos\theta\cos(\phi-\phi')e^{\alpha s_1\cos\theta\cos\theta'+(3N/2)[(s-\beta/2)(\cos^2\theta-1/3)+(\beta/2)\sin^2\theta\cos 2\phi]}d\theta$$
$$=\int_0^{\pi}\sin^2\theta\cos\theta e^{\alpha s_1\cos\theta\cos\theta'+(3N/2)(s-\beta/2)(\cos^2\theta-1/3)}d\theta\times\int_0^{2\pi}(\cos\phi\cos\phi'+\sin\phi\sin\phi')e^{(3N/2)(\beta/2)\sin^2\theta\cos 2\phi}d\phi=0.$$

Thus, there is a $\lambda_2^*\in(0,1)$ such that $(\partial F/\partial\lambda_2)(1,\lambda_2^*)=0$:

$$\frac{\partial F}{\partial\lambda_2}(\lambda_1,\lambda_2)=\text{const}\int_0^{2\pi}d\phi\int_0^{\pi}\sin^2\theta\cos\theta\cos^2(\phi-\phi')\times e^{\alpha s_1(\lambda_1\cos\theta\cos\theta'+\lambda_2\sin\theta\sin\theta'\cos(\phi-\phi'))+\cdots}d\theta.$$

Because $\cos\theta$ is an odd function about $\theta=\pi/2$ while $\sin(\theta)$ and $\cos^2(\theta)$ are even,

$$\frac{\partial F}{\partial\lambda_2}(0,\lambda_2)=\text{const}\int_0^{2\pi}d\phi\int_0^{\pi}\sin^2\theta\cos\theta\cos^2(\phi-\phi')\times e^{\alpha s_1(\lambda_2\sin\theta\sin\theta'\cos(\phi-\phi'))+\cdots}d\theta=0$$

for any values of λ_2. Letting $\lambda_2=\lambda_2^*$, we have $(\partial F/\partial\lambda_2)(0,\lambda_2^*)=0$, $(\partial F/\partial\lambda_2)(1,\lambda_2^*)=0$; then there is a $\lambda_1^*\in(0,1)$, such that $(\partial^2F/\partial\lambda_1\partial\lambda_2)(\lambda_1^*,\lambda_2^*)=0$, where

$$\frac{\partial^2F}{\partial\lambda_1\partial\lambda_2}=\text{const}\sin 2\theta'\int_{\|\mathbf{m}\|=1}\sin^2 2\theta\cos^2(\phi-\phi')\times e^h/Zd\mathbf{m}.$$

This implies

$$\sin 2\theta'=0. \quad (13)$$

Thus, $\theta'=0,\pi/2$.

In the case of $\theta'=\pi/2$, we define

$$G(\lambda_1,\lambda_2)=\int_{\|\mathbf{m}\|=1}\sin^2\theta\cos\phi\sin\phi e^g d\mathbf{m},$$

$$g=\frac{3N}{2}[(s-\beta/2)(\cos^2\theta-1/3)+(\beta/2)\sin^2\theta\cos 2\phi]+\alpha s_1(\lambda_1\cos\phi\cos\phi'+\lambda_2\sin\phi\sin\phi').$$

From $\langle\sin^2\theta\sin\phi\cos\phi\rangle=0$, we have $G(1,1)=0$. Notice that

$$G(0,1)=\int_0^\pi \sin^3\theta e^{(3N/2)(s-\beta/2)(\cos^2\theta-1/3)}d\theta\left(\int_0^\pi+\int_\pi^{2\pi}\right)\sin 2\phi e^{\alpha s_1\sin\phi\sin\phi'+(\beta/2)\sin^2\theta\cos 2\phi}d\phi;$$

$\sin\phi$ and $\cos 2\phi$ are even functions about $\phi=\pi/2,3\pi/2$, and $\sin 2\phi$ is an odd function about $\phi=\pi/2,3\pi/2$. It can be easily shown that $G(0,1)=0$. Thus, there is a $\lambda_1^*\in(0,1)$ such that $(\partial G/\partial\lambda_1)(\lambda_1^*,1)=0$. On the other hand,

$$\frac{\partial G}{\partial\lambda_1}(\lambda_1,0)=\text{const}\cos\phi'\int_0^{2\pi}d\phi\int_0^\pi \sin^3\theta\cos^2\phi\sin\phi e^{\alpha s_1(\lambda_1\cos\phi\cos\phi')+\cdots}d\theta$$
$$=\text{const}\cos\phi'\int_0^\pi \sin^3\theta e^{3N/2(s-\beta/2)(\cos^2\theta-1/3)}d\theta\left(\int_0^{\pi/2}+\int_{\pi/2}^{3\pi/2}+\int_{3\pi/2}^{2\pi}\right)\cos^2\phi\sin\phi e^{\alpha s_1\lambda_1\cos\phi\cos\phi'+\cdots}d\phi,$$

$\cos\phi$ is an even function about 0, π, and $\sin\phi$ is an odd function about them. It can also be shown $(\partial G/\partial\lambda_1)(\lambda_1,0)=0$. Using the same method above for F, we conclude that there is a $\lambda_2^*\in(0,1)$ such that $(\partial^2 G/\partial\lambda_1\partial\lambda_2)(\lambda_1^*,\lambda_2^*)=0$, so $\sin 2\phi'=0$; i.e., $\phi'=0$ or $\pi/2$.

The same result can be proved using another approach in which the Euler angles are not required. We select x, y, and z axes such that the second moment is diagonal. That is, $\langle m_im_j\rangle=0$ for $i\neq j$. We want to prove $\langle\mathbf{m}\rangle$ is parallel to one of the principal axes of the second moment $\langle\mathbf{mm}\rangle$. We prove this by contradiction.

First we denote the principal axes of $\langle\mathbf{mm}\rangle$ as $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$. Let $\langle\mathbf{m}\rangle=r_1\mathbf{e}_1+r_2\mathbf{e}_2+r_3\mathbf{e}_3$. Suppose at least two of r_1, r_2, and r_3 are nonzero (otherwise, $\langle\mathbf{m}\rangle$ is already parallel to one of the principal axes of $\langle\mathbf{mm}\rangle$). Without loss of generality, we assume both $r_1>0$ and $r_2>0$ (we can always rename x, y, and z axes to achieve this). The total potential, then, is

$$\begin{aligned}\frac{V(m_1,m_2,m_3)}{kT}&=-(r_1m_1+r_2m_2+r_3m_3)\\&\quad-(c_1m_1^2+c_2m_2^2+c_3m_3^2)\\&\equiv-(r_1m_1+r_2m_2+r_3m_3)-V_2(m_1,m_2,m_3),\end{aligned}\tag{14}$$

where $c_j=(3N/2)\langle m_jm_j\rangle$. Notice that V_2 is an even function of m_1 and m_2, which is going to play a crucial role in the analysis below. We will show $\langle m_1m_2\rangle>0$, which contradicts the selection of the principal axes.

$$\begin{aligned}\langle m_1m_2\rangle&=\frac{1}{Z}\int_{\|\mathbf{m}\|=1}m_1m_2\exp[r_1m_1+r_2m_2+r_3m_3+V_2(m_1,m_2,m_3)]d\mathbf{m}\\&=\frac{1}{Z}\int_{\|\mathbf{m}\|=1\text{ with }m_1>0,m_2>0}m_1m_2\exp[r_3m_3+V_2(m_1,m_2,m_3)][\exp(r_1m_1+r_2m_2)\\&\quad-\exp(-r_1m_1+r_2m_2)-\exp(r_1m_1-r_2m_2)+\exp(-r_1m_1-r_2m_2)]d\mathbf{m}\\&=\frac{4}{Z}\int_{\|\mathbf{m}\|=1\text{ with }m_1>0,m_2>0}m_1m_2\exp[r_3m_3+V_2(m_1,m_2,m_3)]\sinh(r_1m_1)\sinh(r_2m_2)d\mathbf{m}>0.\end{aligned}\tag{15}$$

Now that the first moment must be parallel to one of the eigenvectors of the second moment, we can find all the equilibrium solutions of the Smoluchowski equation by solving the governing equations for the three order parameters; i.e., s, β, s_1, at $\theta'=0$. We remark that the other cases, i.e., $\theta'=\pi/2$ and $\phi'=0$ or $\phi'=\pi/2$, can be handled by a reparametrization of the Euler angles.[36,37] Now, the degree of freedom in the equilibrium solution is reduced to 3.

The stability of the steady states is inferred from the second variation of the free energy density of the material system. The free energy density of the nematic polymer system is given by

$$A[f]=\int_{\|\mathbf{m}\|=1}\left[kT\ln f+\frac{V}{2}\right]fd\mathbf{m}.\tag{16}$$

From (7), we arrive at the free energy density at equilibrium:

$$\begin{aligned}A[f]&=\int_{\|\mathbf{m}\|=1}\left[-kT\ln Z-\frac{V}{2}\right]fd\mathbf{m}\\&=-kT\left[\ln Z-\frac{N}{2}(s^2-s\beta+\beta^2)-\frac{\alpha}{2}s_1^2\right]+\text{const.}\end{aligned}\tag{17}$$

The global stable solution yields the smallest free energy density, while the local stable ones correspond to the local minimum of the free energy density.

Solution symmetry

So far, we have shown that the steady state solution in the coordinate system set by the eigenvectors of the second moment can be parametrized by three scalar order parameters. It has been known that the solution of the Smoluchowski equation corresponding to pure nematics is invariant with respect to the SO(3) group.[11,20,22] This property is held for the extended nematics as well since there is no external field to specify a distinguished or preferred direction in equilibrium. This SO(3) degeneracy is consistent with our reduction procedure alluded to earlier.

The steady state pdf solution is known should the system of three nonlinear algebraic-integral equations (8) be solved. It is impossible to derive analytic solutions for the system. Thus, we resort to numerical methods next.

III. PHASE DIAGRAMS FOR EXTENDED NEMATICS

We study how the equilibrium solutions vary with respect to material parameters, particularly α and N.

The following theorem establishes a lower bound on the material parameter α below which the material is purely nematic.

Theorem 2: *There exist only purely nematic equilibria* $(s_1=0)$ *when* $\alpha \leqslant 1$.

Proof: Let

$$\begin{aligned}
F_1(s_1) &= \int_0^{2\pi} d\phi \int_0^{\pi} \cos\theta e^{\alpha s_1 \cos\theta + (3N/2)((s-\beta/2)(\cos^2\theta - 1/3) + (\beta/2)\sin^2\theta\cos 2\phi)} d\theta/Z \\
&= \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos\theta e^{\alpha s_1 \cos\theta + (3N/2)((s-\beta/2)(\cos^2\theta - 1/3) + (\beta/2)\sin^2\theta\cos 2\phi)} d\theta/Z \\
&\quad + \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos(\pi-\theta) e^{\alpha s_1 \cos(\pi-\theta) + (3N/2)[(s-\beta/2)(\cos^2(\pi-\theta) - 1/3) + (\beta/2)\sin^2\theta\cos 2\phi]} d\theta/Z \\
&= \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos\theta e^{(3N/2)((s-\beta/2)(\cos^2\theta - 1/3) + (\beta/2)\sin^2\theta\cos 2\phi)} (e^{\alpha s_1\cos\theta} - e^{-\alpha s_1 \cos\theta}) d\theta/Z.
\end{aligned}$$

If $\alpha<0$, $F_1(s_1)>0$ when $s_1<0$, and $F(s_1)<0$ when $s_1>0$. Thus, for any s,β, only $s_1=0$ satisfies the equation $s_1=F_1(s_1)$. We introduce

$$G_1(s_1) = s_1 - F(s_1).$$

We note that

$$\frac{dG_1}{ds_1} = 1 - \alpha\langle\cos^2\theta\rangle + \alpha\langle\cos\theta\rangle^2.$$

If $0 \leqslant \alpha \leqslant 1$, $dG_1/ds_1>0$, indicating that $G(s_1)$ is an increasing function of s_1. Since $G_1(0)=0$, $G_1(s_1)\neq 0$ for $s_1\neq 0$. Hence, $s_1=0$ is the only solution.

Again, the same result can be established using a counterproof. From the result of Theorem 1, we assume $\langle \mathbf{m}\rangle = r_1\mathbf{e}_1$. We will show that when $\alpha\leqslant 1$ (i.e., the strength of the dipole-dipole interaction is weak), r_1 must be zero so the only equilibrium is nonpolar. We prove it by contradiction. Suppose $r_1>0$ (otherwise we can change the coordinate system to achieve this):

$$\begin{aligned}
r_1 = \langle m_1\rangle &= \frac{\int_S m_1 \exp[\alpha r_1 m_1 + V_2(m_1,m_2,m_3)]dS}{\int_S \exp[\alpha r_1 m_1 + V_2(m_1,m_2,m_3)]dS} \\
&= \frac{\int_{S \text{ with } m_1>0} m_1 \exp[V_2(m_1,m_2,m_3)]\sinh(\alpha r_1 m_1)dS}{\int_{S \text{ with } m_1>0} \exp[V_2(m_1,m_2,m_3)]\cosh(\alpha r_1 m_1)dS}.
\end{aligned} \tag{18}$$

Using the fact that $\tanh(x)<x$ for $x>0$, we have

$$\begin{aligned}
& m_1 \exp[V_2(m_1,m_2,m_3)]\sinh(\alpha r_1 m_1) \\
&\quad \leqslant \exp[V_2(m_1,m_2,m_3)]\cosh(\alpha r_1 m_1)\tanh(\alpha r_1 m_1) \\
&\quad < \alpha r_1 \exp[V_2(m_1,m_2,m_3)]\cosh(\alpha r_1 m_1).
\end{aligned} \tag{19}$$

Substituting this inequality into the expression for r_1 above, we obtain

$$r_1 < \alpha r_1, \tag{20}$$

which is a contradiction when $\alpha \leqslant 1$ and $r_1>0$. □

Remark: At the presence of an imposed magnetic field $\mathbf{H}$, the total potential is given by

$$V = -(\alpha kT\langle \mathbf{m}\rangle)\cdot \mathbf{m} - \frac{3NkT}{2}\langle \mathbf{mm}\rangle:\mathbf{mm} - \frac{\chi_a}{2}\mathbf{HH}:\mathbf{mm}, \tag{21}$$

where χ_a is the difference of susceptibility parallel and perpendicular to the molecular direction $\mathbf{m}$, known as the material anisotropy. It can be shown that Theorem 2 applies as well; i.e., the extended nematics are purely nematic when $\alpha \leqslant 1$ regardless of the orientation of the external field $\mathbf{H}$. In fact, it is established in Ref. 25 that $\mathbf{H}$ must parallel to one of the principal axis directions.

For pure nematics, the equilibrium phase diagram is well known.[27–29] For $\alpha > 1$, however, polar nematic equilibria may exist. We examine the equilibria diagram numerically next. First, we note that, for any values of α and N, $s_1=0$ is a solution. Thus, all the purely nematic equilibria well-studied before[27,28,37] are also equilibria of the extended nematics. However, their stability can be altered because there can exist a nonzero stable polar order parameter such that the purely nematic equilibria are unstable in certain parameter regimes.

We examine the second variation of the free energy density along stable uniaxial equilibrium branches to figure out the stability criteria (see Appendix A). For the isotropic equilibrium given by $s_1 = s = \beta = 0$, the second variation of the free energy density can be calculated explicitly:

$$\delta^2 A|_{s_1=0,s=0,\beta=0} = kT[(\alpha - \alpha^2/3)\delta^2 s_1 + N(1-N/5)\delta^2 s - N(1-N/5)\delta s\,\delta\beta + N(1-N/5)\delta^2\beta]. \tag{22}$$

This shows explicitly that $\alpha=3$ and $N=5$ are two critical values for the strength of the dipolar potential and the excluded volume potential, respectively. For the isotropic nematic branch ($s=0$, $\beta=0$),

$$\alpha_c^{(0)} = 3 \tag{23}$$

is the critical dipolar strength beyond which the isotropic polar order parameter becomes unstable, whereas

$$N_c^{(1)} = 5 \tag{24}$$

is the critical concentration beyond which the isotropic equilibrium is unstable. Thus, for $\alpha < 3$, $N < 5$, the isotropic equilibrium is stable.

For uniaxial nematics $s \neq 0$, $\beta = 0$ on the other hand (see, for example, Fig. 3), the second variation is given by

$$\delta^2 A = kT\alpha\left(1 - \frac{\alpha(1+2s)}{3}\right)\delta s_1^2 + kTN(\delta s, \delta\beta)\cdot C\cdot(\delta s,\delta\beta)^T, \tag{25}$$

where

$$C = \begin{pmatrix} \frac{5}{2} - \frac{3}{4s}\left(\frac{e^{3Ns/2}}{\psi(s)} - 1\right) + \frac{N}{4}(1+2s)^2 & -\frac{5}{4} + \frac{3}{8s}\left(\frac{e^{3Ns/2}}{\psi(s)} - 1\right) - \frac{N}{8}(1+2s)^2 \\ -\frac{5}{4} + \frac{3}{8s}\left(\frac{e^{3Ns/2}}{\psi(s)} - 1\right) - \frac{N}{8}(1+2s)^2 & \frac{25}{16} - \frac{N}{32}(1-20s-8s^2) - \frac{9}{32s}\left(\frac{e^{3Ns/2}}{\psi(s)} - 1\right) \end{pmatrix}, \tag{26}$$

$$\psi(s) = \int_0^1 e^{3Nsz^2/2}dz. \tag{27}$$

The critical value for α is

$$\alpha_c^{(1)} = \frac{3}{1+2s}, \tag{28}$$

beyond which the uniaxial nematic equilibrium is unstable due to the instability in the polar order parameter s_1. From Theorem 2, it follows that

$$\alpha_c^{(1)} > 1 \tag{29}$$

in order for the nonzero polar order parameter to emerge via a bifurcation from the purely nematic branch. This implies $s>0$. Our numerical experiments show that the bifurcation leading to stable solutions can only takes place along the highly aligned uniaxial branch $s \geqslant 0$, implying $\alpha_c^{(1)} \leqslant 3 = \lim_{s\to 0}\alpha_c^{(1)} = \alpha_c^{(0)}$. The Hessians in (22) and (25) also reveal the classical phase transition concentration $N_c^{(1)}=5$ along the isotropic branch and $N_c^{(2)} \approx 4.49$ along the prolate nematic branch.[25]

Recall that the nonzero order parameter s in uniaxial nematics ($\beta=0$) is given by a single integral equation[37,38]

$$\frac{1+2s}{3}\int_0^1 e^{3Nsz^2/2}dz = \int_0^1 z^2 e^{3Nsz^2/2}dz. \tag{30}$$

Combining (28) and (30), we arrive at the function relation between $\alpha_c^{(1)}$ and the critical value of N denoted as $N_c^{(3)}$, at which the polar nematic phase forms due to a bifurcation out of the uniaxial nematic branch $s>0$, $\beta=0$ or out of $s_1=0$ in the polar order parameter space. We note that, since the governing equation for the equilibrium order parameters (s_1, s, β) is symmetric about s_1, the nonzero equilibrium solutions of s_1 always come in pairs. The function relation between $\alpha_c^{(1)}$ and $N_c^{(3)}$ is plotted in Fig. 1, consisting of the solid curve down to the point ($\alpha_c^{(1)}=1.82127937$, $N_c^{(2)}=4.49$) and the dotted one which ends at ($\alpha_c^{(1)}=3$, $N_c^{(1)}=5$). We notice that the curve is not monotonic. At $N<N_c^{(1)}=5$, there are

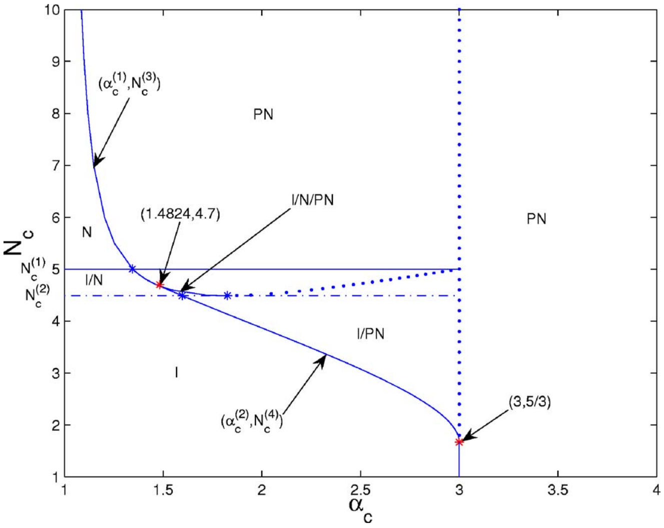

FIG. 1. (Color online) The phase diagram in parameter space (α,N). The solid and dashed curves are limits of metastability. Tricritical points are labeled by stars. The $(\alpha_c^{(1)},N_c^{(3)})$ curve terminates at $(1.82127937,N_c^{(2)})$, while curve $(\alpha_c^{(2)},N_c^{(4)})$ begins at the first tricritical point $(1.4824,4.7)$ and ends at the second tricritical point $(3,5/3)$. I: isotropic phase, N: nematic phase, PN: polar nematic phase.

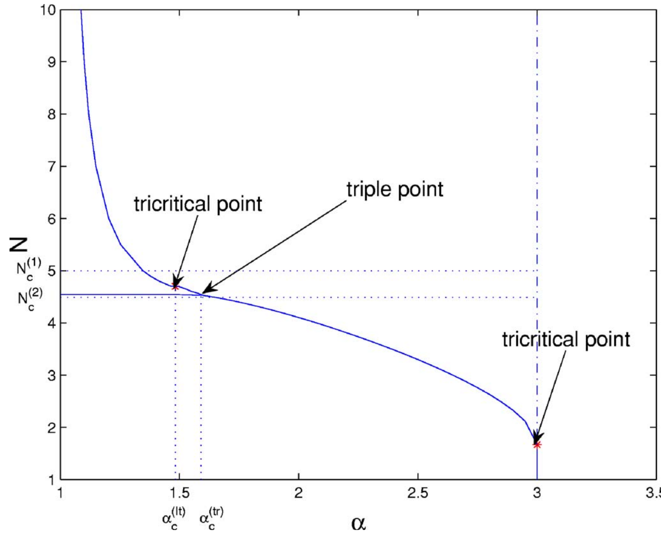

FIG. 2. (Color online) The phase transition curves and globally stable phase diagram in parameter space (α,N). Tricritical points are labeled by stars. The solid curves are phase transition curves. The solid curves between the two tricritical points are the second order phase transition curves. The others are the first-order phase transition curves. The solid (nearly) straight line is another second-order phase transition curve. The first tricritical point is located at $(1.4824,4.7)$ and the second tricritical point is at $(3,5/3)$.

two α corresponding to a single value of N; one is bigger than 1.82127937, while the other is smaller than it. Along this critical curve, there exists a tricritical point at $(\alpha_c^{1t}=1.4824,\ N_c^{(3t)}=4.7)$, where the phase transition changes from the second order to the first one. The governing equation for the tricritical point is given in Appendix B. The formation of the polar nematic phase below and above the tricritical point $\alpha_c^{(1t)}$ at α is quite distinctive.

When $\alpha_c^{(1)}<\alpha_c^{(1t)}$, the polar nematic is created via a one-dimensional transcritical pitchfork bifurcation out of the zero polar order parameter branch at $N_c^{(3t)}$ (see Fig. 3). There are coexistent regions for $N\in[N_c^{(2)},N_c^{(1)}]$, where either the isotropic/nematic phase (labeled as I/N in Fig. 1) coexists or the isotropic/polar-nematic phase (labeled as I/PN in Fig. 1) coexists. When $\alpha_c^{(1t)}<\alpha_c^{(1)}<1.82127937$, the polar nematic phase is born out of a hysteresis bifurcation consisting of a subcritical pitchfork bifurcation out of the zero polar order parameter branch (or the uniaxial prolate nematic branch) along with a pair of turning point bifurcations at $(\alpha_c^{(2)},N_c^{(4)})$. The curve $(\alpha_c^{(2)},N_c^{(4)})$ originates from the tricritical point $(1.4824,4.7)$, as shown in Fig. 1. Between $\alpha_c^{(1t)}<\alpha_c^{(1)}<1.82127937$, there exist possibly three coexistent regions: one is a triphasic region where isotropic/nematic/polar-nematic (labeled as I/N/PN in Fig. 1) coexist, the others are biphasic regions where isotropic/nematic or isotropic/polar-nematic phase coexist, as shown in Fig. 1. The curve terminates at the second tricritical point $(\alpha_c^{(3)}=3,\ N_c^{(4)}=5/3)$. When $1.82127937<\alpha<3$ and $N_c^{(4)}<N<5$, isotropic/polar-nematic phase coexists. The curves $(0\leqslant\alpha\leqslant1.82127937,\ N=N_c^{(2)})$, $(0\leqslant\alpha\leqslant3,\ N=N_c^{(1)})$, $(\alpha_c^{(1)},N_c^{(3)})$, and $(\alpha_c^{(2)},N_c^{(4)})$ define the limits of the metastability.[35]

Figure 1 depicts the limit curves of the metastability, the uniphasic, biphasic, and triphasic regions in the parameter space (α,N). Below the second tricritical point $(3,5/3)$, the phase transition from the isotropic to polar-nematic phase becomes second order. Figure 2 shows the globally stable phase transition curves in solid, in which the triple point is shown explicitly. We next detail on the bifurcations of the equilibrium solutions at representative values of α and N, respectively. We solve the governing integral equation systems numerically using Gauss quadratures. We first fix α and look into the bifurcation of the solutions via N.

Figure 3 depicts the bifurcation diagram for all equilibria at $\alpha=1.3<\alpha_c^{(1t)}$. There exist two well-known critical concentrations for purely nematic order parameters $N_c^{(2)}=4.49$ and $N_c^{(1)}=5$ such that a turning point bifurcation takes place at $N_c^{(2)}$ yielding a pair of prolate nematic order parameters and a double saddle node bifurcation occurs at $N_c^{(1)}$, leading to unstable isotropic and nematic phases beyond $N_c^{(1)}$.[36,37] Given the coupling of the polarity to the nematic order, a transcritical pitchfork bifurcation takes place at a concentration $N_c^{(3)}$: $N_c^{(2)}<N_c^{(3)}$ along the stable branch of the prolate nematic order parameter, which can be read off from the solid curve in Fig. 1 at $\alpha=1.3$. The polarity enhanced nematic order parameter s is of higher numerical value than the one corresponding to the purely nematic. The phase transition between the isotropic and nematic one is the first order, while the transition from nematic to polar nematic at higher concentration is apparently the second order. This is a generic diagram for all $1<\alpha<\alpha_c^{(1)}$.

Figure 4 depicts the bifurcation diagram for all equilibria at $\alpha=1.5$. Different from the case pictured in Fig. 3, the polar order parameter bifurcates out of the zero value branch via a pair of hysteresis bifurcations consisting of a subcritical pitchfork bifurcation at $N_c^{(3)}$ and connected at a pair of turning point bifurcations at smaller concentration $N_c^{(4)}$. Between $N_c^{(2)}$ and $N_c^{(3)}$, there exist three phases: isotropic, nematic, and

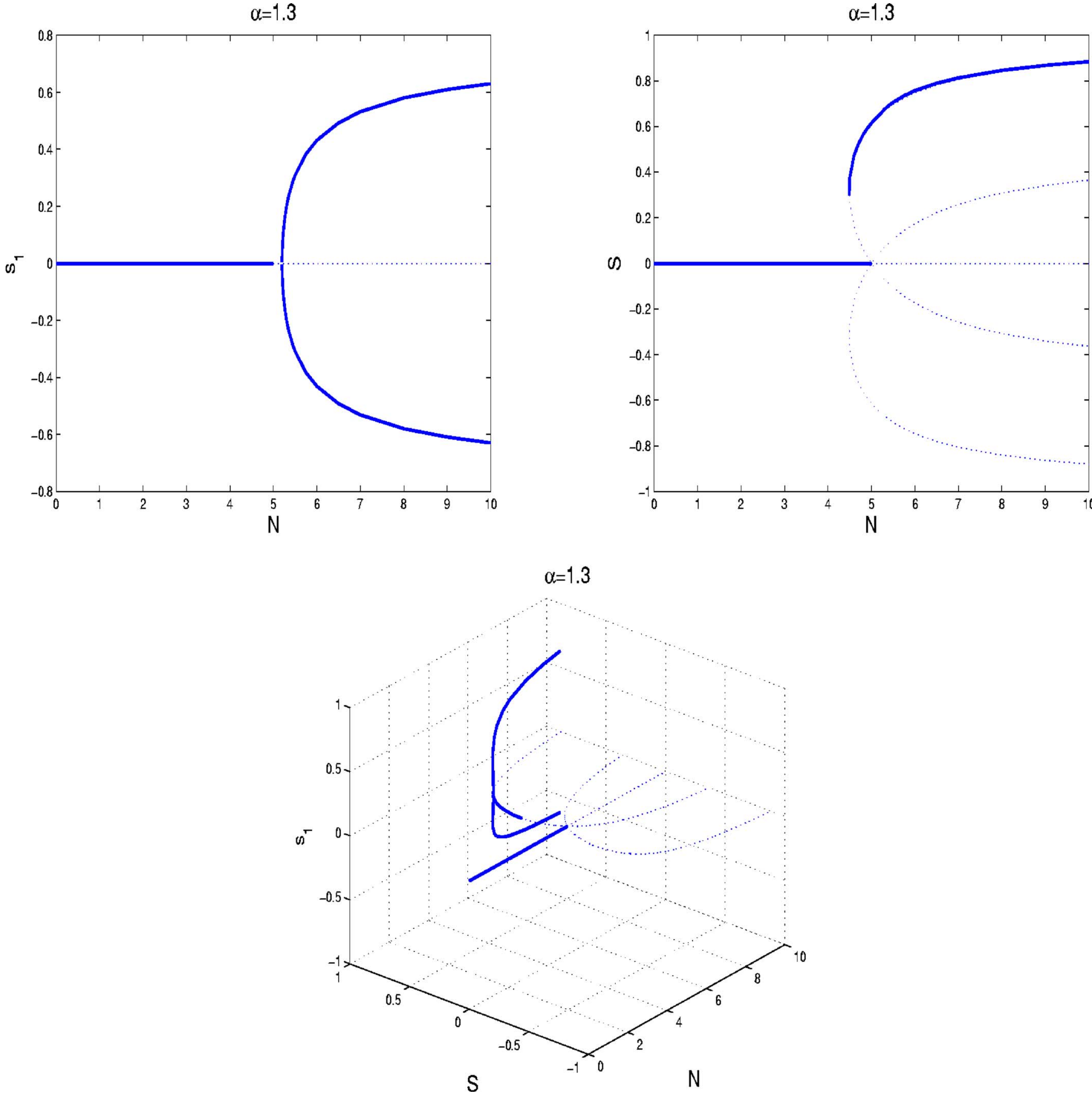

FIG. 3. (Color online) The bifurcation diagram of equilibria as functions of concentration N in terms of order parameters s_1, s, β at $\alpha=1.3$. There exist three critical values of N: $N_c^{(2)}=4.49$, $N_c^{(1)}=5$, $N_c^{(3)}$. For $0<N<N_c^{(1)}$, the isotropic phase $s_1=s=\beta=0$ is the unique stable equilibrium. At $N_c^{(2)}$, a stable, prolate purely nematic phase forms through a saddle node (turning point) bifurcation. For $N_c^{(2)}<N<N_c^{(1)}$, the stable isotropic phase, and a stable prolate pure nematic phase coexist along with an unstable prolate phase, identical to the pure nematic case. At $N_c^{(3)}$, a pitchfork bifurcation takes place along the highly aligned prolate nematic branch, giving rise to a pair of stable nonzero polar order parameters in s_1. The new stable branch of equilibrium projected onto the space of s gives rise to a new branch of prolate nematic phase with enhanced alignment. This is the generic scenario as we vary α between 1 and $\alpha_c^{(1t)}$.

polar nematic. Two phase transitions are possible. Between $N_c^{(4)}$ and $N_c^{(2)}$ or $N_c^{(3)}$ and $N_c^{(1)}$, there exist two phases: isotropic and polar nematic.. This is the generic scenario for $\alpha<\alpha_c^{(3)}$, which is the intersection of the lower solid curve with the line $N=N_c^{(2)}$ in Fig. 1.

Figure 5 portraits another scenario of phase bifurcation diagram at $\alpha_c^{(1t)}<\alpha=1.75<1.82127937$, where $N_c^{(4)}<N_c^{(2)}$. The scenario of coexisting phases go through single isotropic phase at $0<N<N_c^{(4)}$; isotropic/polar-nematic biphases at $N_c^{(4)}<N<N_c^{(2)}$; isotropic, nematic, and polar-nematic triphases at $N_c^{(2)}<N<N_c^{(3)}$; isotropic/polar-nematic biphases at $N_c^{(3)}<N<N_c^{(1)}$; and single polar nematic phase at $N>N_c^{(1)}$. This is a representative diagram for $\alpha_c^{(3)}<\alpha<1.82127937$.

Figure 6 depicts the bifurcation diagram for all equilibria

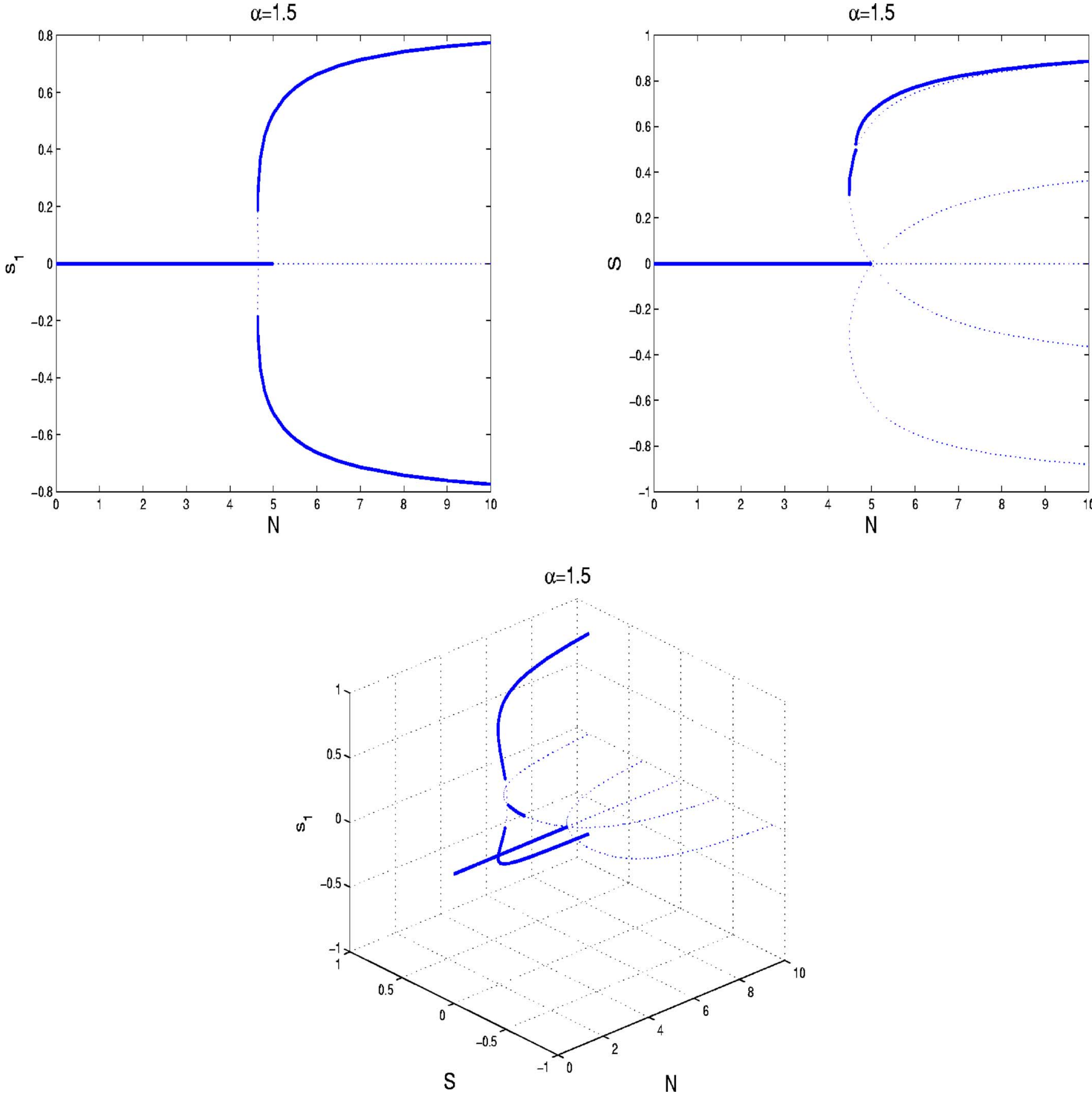

FIG. 4. (Color online) The bifurcation diagram of equilibria as functions of concentration N in terms of order parameters s_1, s, β at $\alpha=1.5$. There exist four critical values of N: $N_c^{(1)}=4.49$, $N_c^{(2)}=5$, $N_c^{(3)}$, $N_c^{(4)}$. For $0<N<N_c^{(4)}$, the isotropic phase $s_1=s=\beta=0$ is the unique stable equilibrium. At $N_c^{(2)}$, a stable, prolate purely nematic phase forms through a saddle node (turning point) bifurcation. A subcritical pitchfork bifurcation takes place at $N_c^{(3)}$ yielding a pair of unstable polar nematics. The unstable polar nematics go through a turning point bifurcation at $N_c^{(4)}$ to regain stability. For $N_c^{(2)}<N<N_c^{(4)}$, the stable isotropic phase, and a stable prolate pure nematic phase coexist; while $N_c^{(4)}<N<N_c^{(3)}$, isotropic, pure nematic, and polar nematic phases coexist. When $\min(N_c^{(3)},N_c^{(1)})<N<N_c^{(1)}$, the isotropic and polar nematic phases coexist. Beyond $N_c^{(1)}$, the only stable phase is the polar nematic one. This is the generic scenario as we vary α between $\alpha_c^{(1t)}$ and $\alpha_c^{(3)}$, which is given by the intersection of the lower solid curve with $N_c^{(2)}$ in Fig. 1.

at $\alpha=2.8$. As the value of α increases from 1.82127937 to 3, the critical concentration $N_c^{(3)}$ (corresponding to the pitchfork bifurcation along the polar order parameter branch) increases from $N_c^{(3)}=4.49$ toward $N_c^{(1)}=5$. The corresponding bifurcation also changes to a pair of hysteresis bifurcations consisting of a subcritical pitchfork at $N_c^{(3)}$ and a pair of turning point bifurcations at $N_c^{(4)}$. The bifurcation point along the less aligned, purely nematic prolate branch $(N_c^{(3)},s)$ also slides toward $(N_c^{(1)},0^+)$, whereas the critical concentration $N_c^{(4)}$ corresponding to the new turning point bifurcation along the polar order parameter branch decreases monotonically. In this case, a pair of unstable polar, biaxial equilibria also come into existence at higher concentration.

We have noted that $\alpha=3$ is special, yielding a tricritical

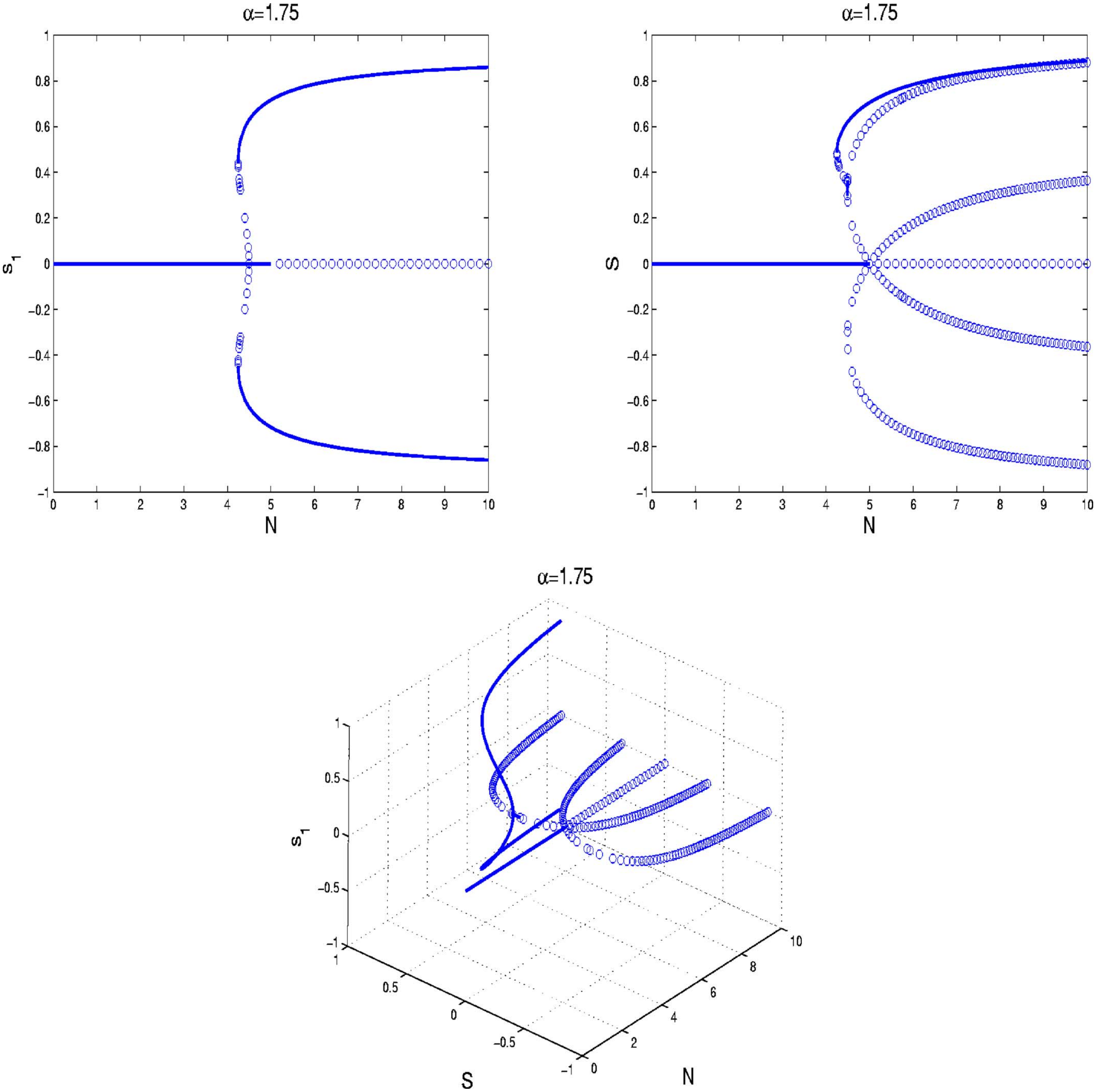

FIG. 5. (Color online) The bifurcation diagram of equilibria as functions of concentration N in terms of order parameters s_1, s, β at $\alpha=1.75$. There exist four critical values of N: $N_c^{(1)}=4.49$, $N_c^{(2)}=5$, $N_c^{(3)}>N_c^{(4)}$. For $0<N<N_c^{(4)}$, the isotropic phase $s_1=s=\beta=0$ is the unique stable equilibrium. At $N_c^{(4)}$, a stable, prolate polar nematic phase forms through a saddle node (turning point) bifurcation. A stable pure nematic phase forms at $N_c^{(2)}$ via a turning point bifurcation. It soon goes through a subcritical pitchfork bifurcation at $N_c^{(3)}$ yielding a pair of unstable polar nematics. For $N_c^{(4)}<N<N_c^{(2)}$, the stable isotropic phase and a stable polar nematic phase coexist; while $N_c^{(2)}<N<N_c^{(3)}$, isotropic, pure nematic, and polar nematic phases coexist. When $\min(N_c^{(3)},N_c^{(1)})<N<N_c^{(1)}$, the isotropic and polar nematic phases coexist. Beyond $N_c^{(1)}$, the only stable phase is the polar nematic one. This is behavior together with that alluded to in the previous figure constitutes the generic phase scenario as we vary α between $\alpha_c^{(3)}$ and 1.82127937.

point at $N=5/3$. We detail the bifurcations of solutions as function of N in Fig. 7. The hysteresis bifurcation combination degenerates into a single transcritical pitchfork bifurcation making the polar nematic phase stable and the isotropic phase unstable beyond $N=5/3$. All other pure nematic phases are unstable now.

Figure 8 depicts a bifurcation diagram of all equilibria at $\alpha=3.05$ while N varies. In the range of $\alpha>3$, the isotropic state becomes completely unstable. There exists only a stable polar nematic phase with a prolate, uniaxial, nematic order parameter for all values of $N>0$. Unstable polar, biaxial nematic states may also exist at higher values of N.

We next present the bifurcation diagrams with respect to α at two representative values of concentration. Figure 9

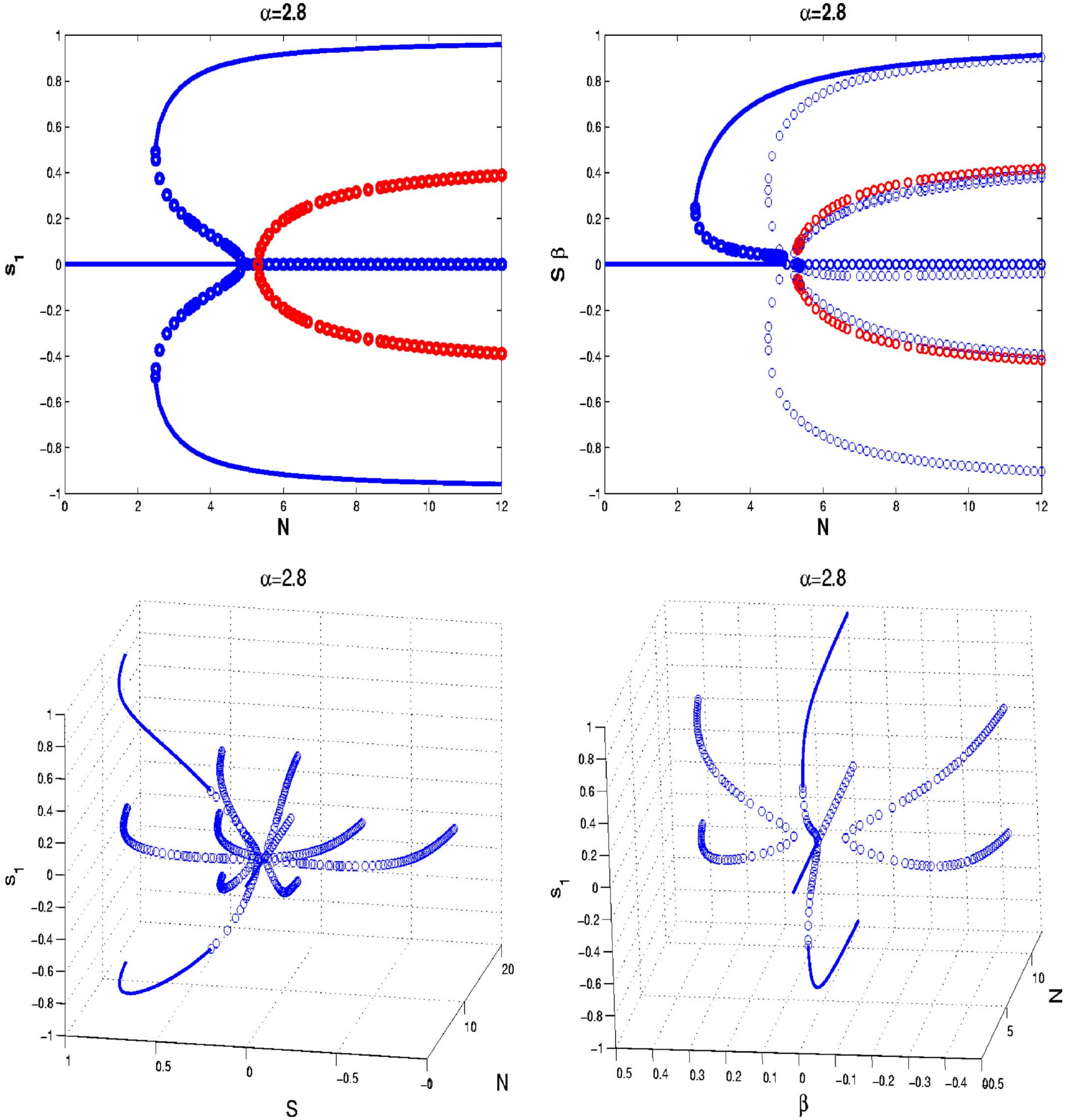

FIG. 6. (Color online) The bifurcation diagram of the order parameters s_1, s, β as functions of N at $\alpha=2.8$. The polar order parameter undergoes two bifurcations. First, it undergoes a hysteresis bifurcation consisting of a subcritical pitchfork bifurcation at $N_c^{(3)}$ and a secondary turning point bifurcation at $N_c^{(4)}$, yielding two pairs of nonzero polar order parameter branches, among which one with the larger numerical value is stable while the other is unstable. Second, it undergoes a transcritical pitchfork bifurcation at $N_c^{(5)}$ leading to two unstable branches of the polar order parameters corresponding to two unstable biaxial nematic branches. The turning point bifurcation at $N_c^{(4)}$ yields a highly aligned prolate, stable, nematic phase, and an unstable, less aligned nematic phase. The isotropic state is stable up to $N_c^{(2)}=5$. The biaxial nematic order parameters are plotted in red circled curves.

depicts a bifurcation diagram of all equilibria at a fixed value of $N=4.75$. At this value of N, an isotropic and a stable uniaxial prolate order parameter s coexist at $\alpha=0$. The isotropic one is stable up to $\alpha=3$ and then becomes unstable through a subcritical pitchfork bifurcation. The prolate nematic order corresponds to zero polar order (pure nematics) up to $\alpha_c^{(1)}=1.437$ and then switches to a more aligned prolate polar nematic branch through a transcritical pitchfork bifur-

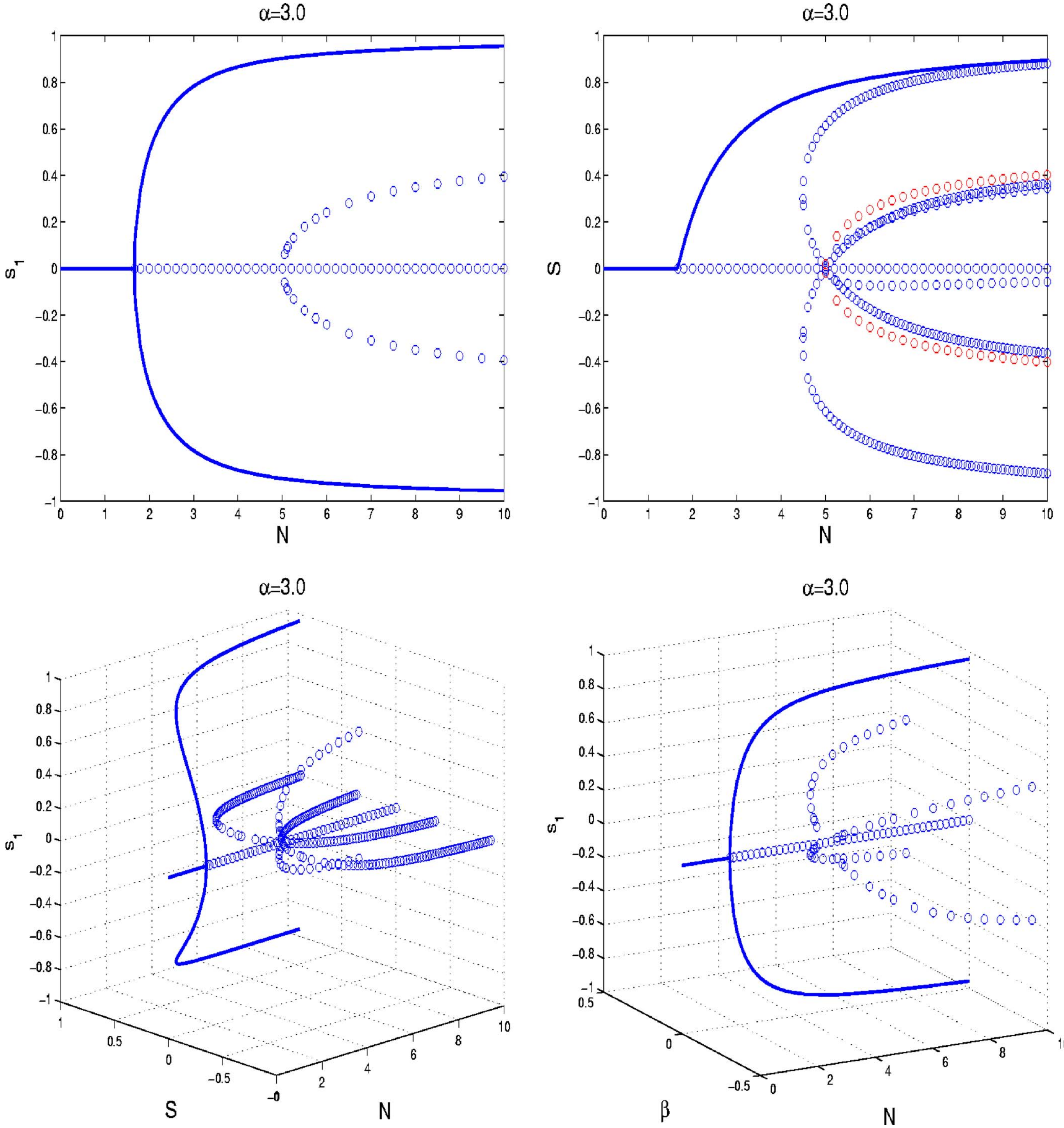

FIG. 7. (Color online) The bifurcation diagram of the order parameters s_1, s, β as functions of N at $\alpha=3$. The polar order parameter undergoes a transcritical pitchfork bifurcation at $N=5/3$ yielding two pairs of stable, nonzero polar order parameter branches; second, it undergoes a secondary transcritical pitchfork bifurcation at $N_c^{(5)}$ leading to two unstable branches of the polar order parameters corresponding to two unstable biaxial nematic branches. The isotropic state is stable up to $N=5/3$. This is a degenerate case encompassing the tricritical point $(3,5/3)$.

cation. Biaxial states exist at higher values of α, but are all unstable.

Figure 10 depicts the bifurcation diagram at an elevated value of $N=5.5$. At this concentration, the only stable steady state at $\alpha=0$ is the highly aligned, uniaxial, prolate nematic phase. It corresponds to the zero polar order parameter branch and is stable up to $\alpha_c^{(1)}=1.25$. It then bifurcates into a more aligned prolate polar nematic phase while the polar order parameter goes through a transcritical pitchfork bifurcation. Again, biaxial states are born and annihilated through some fancy pitchfork and turning point bifurcations.

In summary, Fig. 1 provides an atlas for the equilibrium solutions of the Smoluchowski equation for extended nematics. uniphasic, biphasic, and even triphasic regions can exist

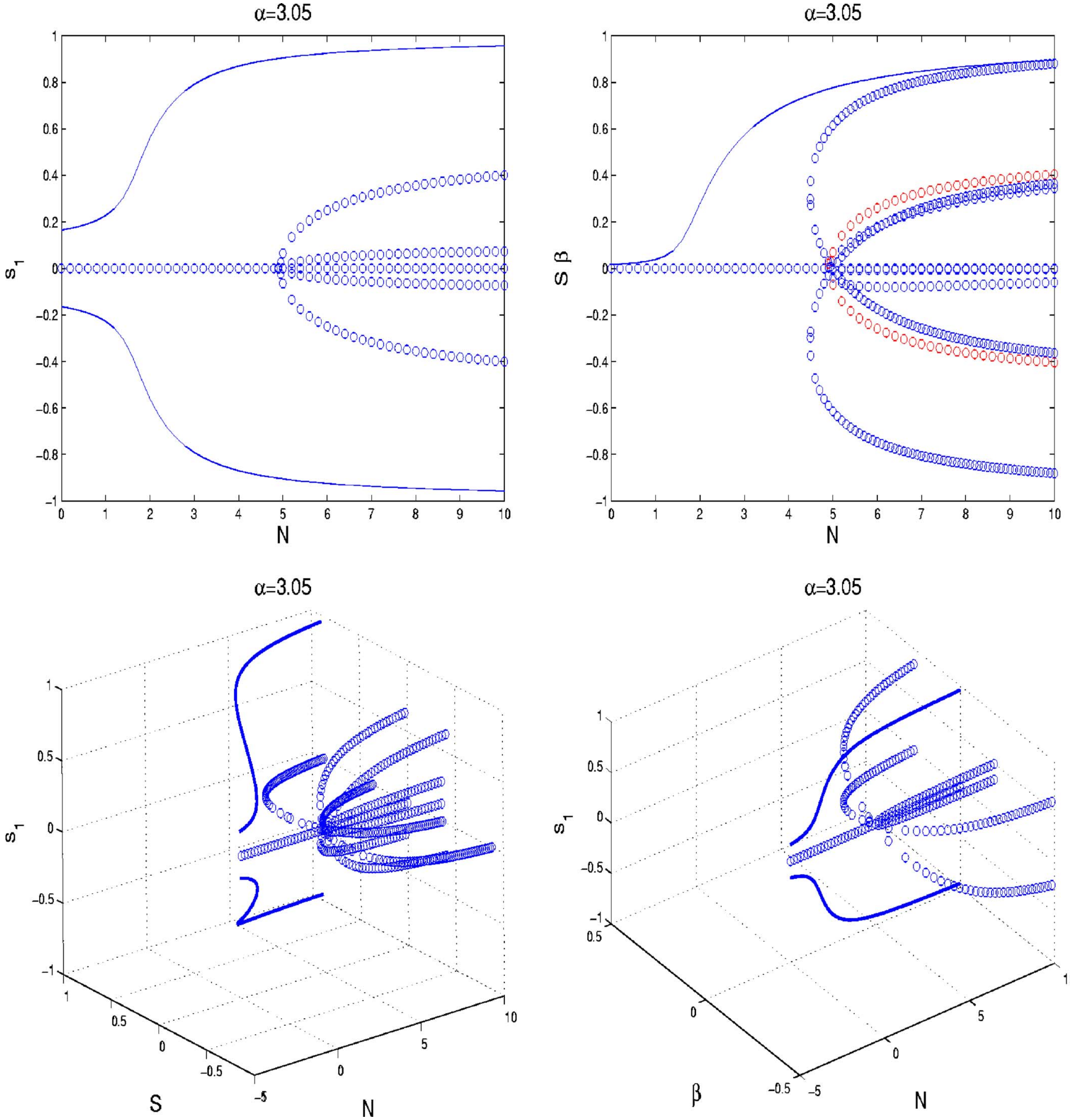

FIG. 8. (Color online) The bifurcation diagram of order parameters s_1, s, β as functions of N at $\alpha=3.05$. When $\alpha \geqslant 3$, a pair of polar nematics exist and is stable for all values of N; two pairs of unstable nonzero polar order parameters emerge as results of transcritical bifurcations along the zero polar order parameter branch, one of which yields the unstable biaxial nematic order parameter branches, plotted in red circles. The purely nematic equilibria are all unstable.

in parameter space (α, N). Two tricritical points are identified to indicate change of phase transition behavior. Biaxial equilibria are observed, but are unstable.

IV. CONCLUSION

We have studied the equilibrium solutions of the Smoluchowski equation for flows of extended (polar) nematic liquid crystal polymers where the molecular interaction is modeled by a dipole-dipole interaction together with the Maier-Saupe excluded volume potential. We show that the first moment or the polarity vector must parallel to one of the principal axes of the second moment so that the equilibrium solution of the Smoluchowski equation is reduced to a Boltzmann function parametrized by only three scalar order parameters along with the material parameters. The equilibrium

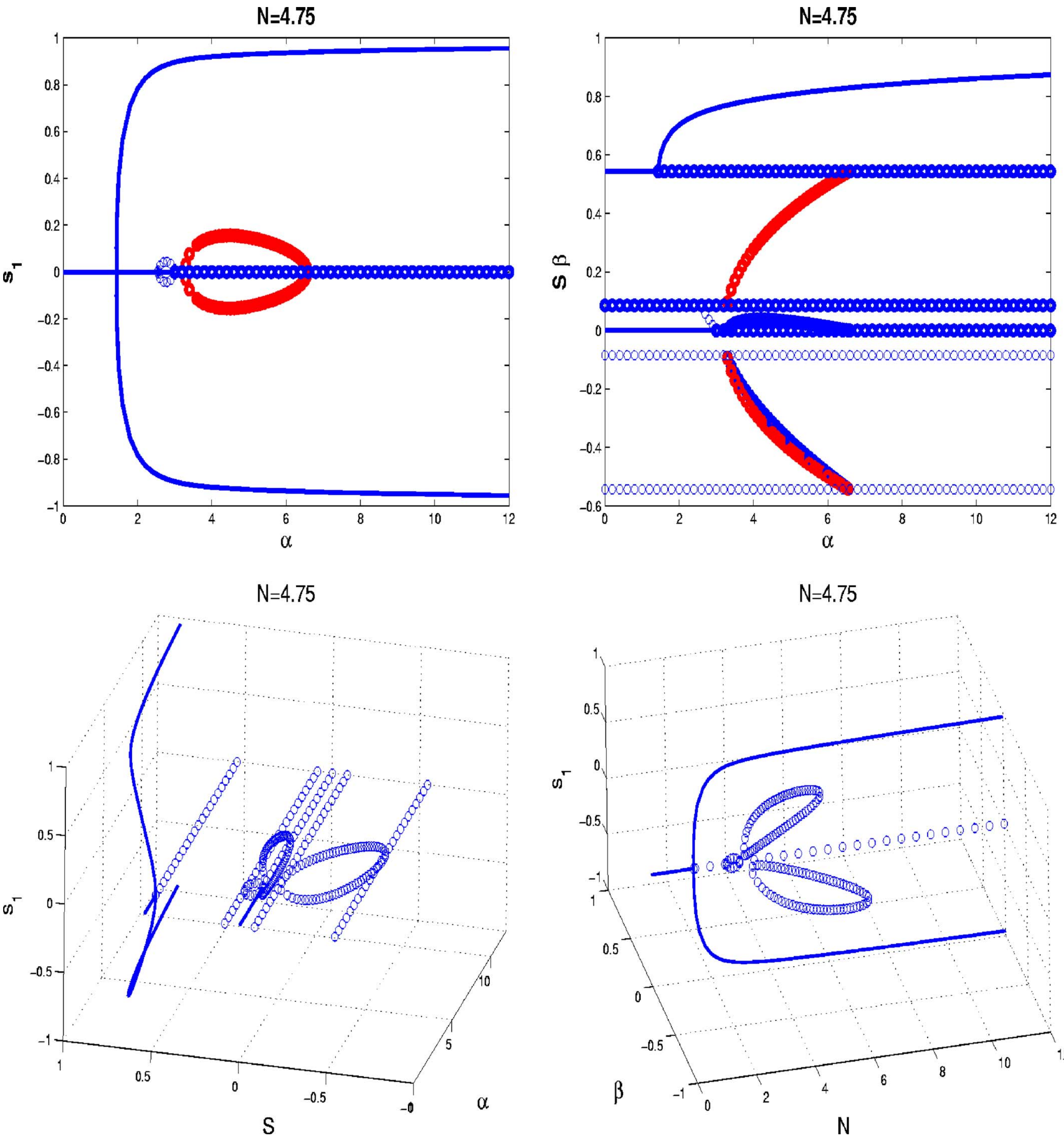

FIG. 9. (Color online) The bifurcation diagram of order parameters s_1, s, β as functions of α at $N=4.75$. The isotropic state is stable up to $\alpha=3$. It loses stability due to a subcritical pitchfork bifurcation along the zero polar order parameter branch. At the critical value $\alpha_c=1.437$, a transcritical pitchfork bifurcation takes place yielding a pair of stable polar order nematic branches corresponding to the stable highly aligned prolate nematic order parameter branch in s. The purely nematic prolate order parameter loses stability at α_c. Biaxial phases can form at high values of α, depicted in red circles.

solutions are sought by solving three coupled nonlinear algebraic-integral equations avoiding a complicated spherical harmonic expansion procedure used in the past.[6,15,26] Due to the coupling of the polar order parameter s_1 and the nematic order parameters (s,β), new polar nematic and biaxial phases are formed and phase transitions are observed. A phase diagram for stable phases are obtained and two tricritical points are identified in parameter space (α,N). All stable solutions are shown to be uniaxial. A comprehensive analysis on bifurcation diagrams for all equilibria are presented at selected values of α and N, respectively. The results also apply to the magnetic suspensions in viscous solvent since the Doi-Hess theory equipped with the same potential applies to these fluids as well.[3] The reduction procedure developed in this paper can be extended to the case when external magnetic or flow field is imposed or inhomogeneous system

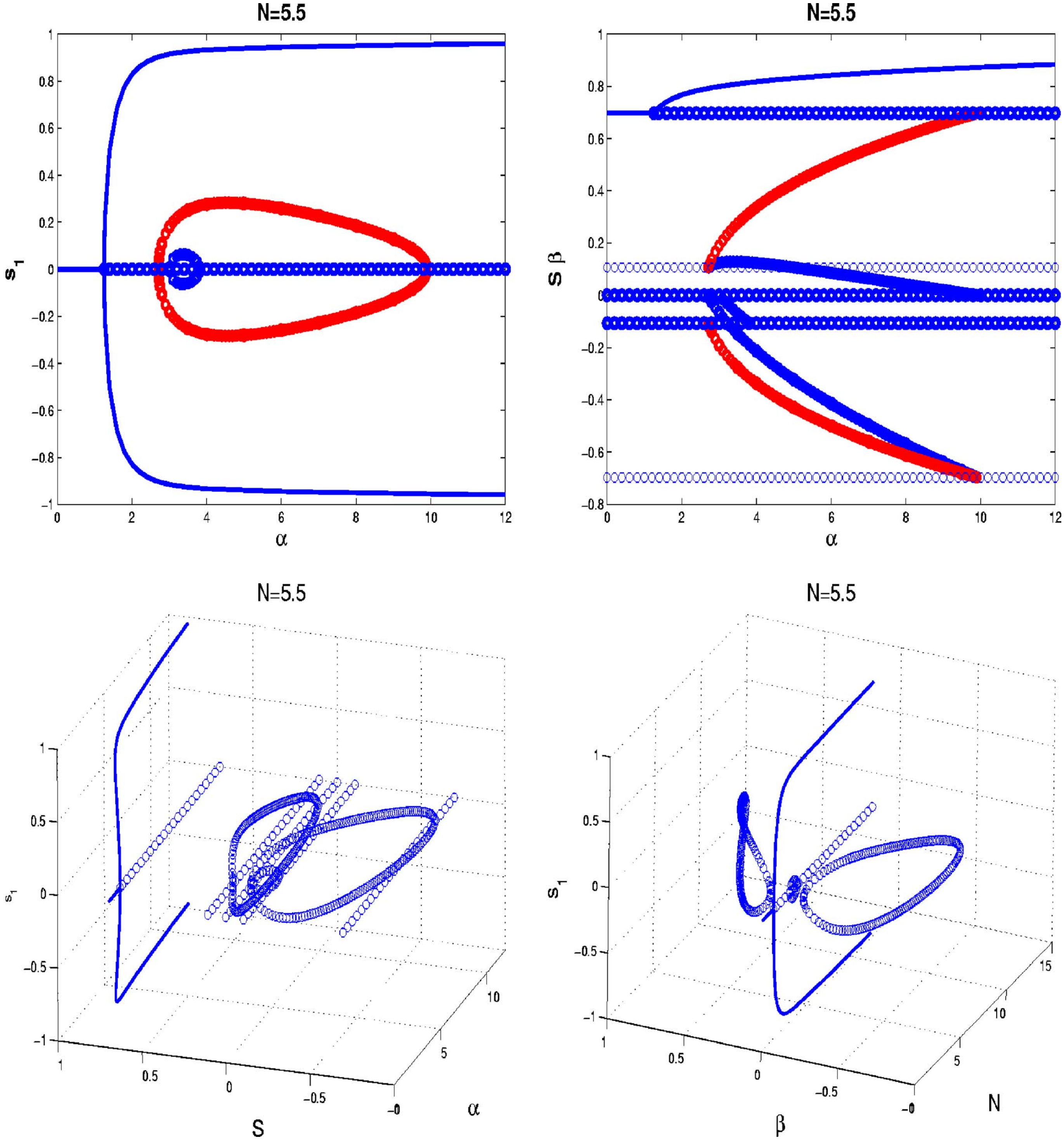

FIG. 10. (Color online) The bifurcation diagram of order parameters s_1, s, β as functions of α at $N=5.5$. The isotropic state is unstable for all $\alpha>0$. The stable prolate nematic order parameter s is stable up to a critical value of $\alpha_c=1.25$ and then bifurcates into a highly aligned prolate uniaxial order as the polar order bifurcates into a pair of nonzero order branches through a transcritical pitchfork bifurcation. Biaxial phases exist at high values of α, depicted in red circles.

bypassing the spherical harmonic expansion approach if only the stable solutions are desired.

ACKNOWLEDGMENTS

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APPENDIX A: FREE ENERGY DENSITY AND ITS SECOND VARIATION

The free energy density at equilibrium is given by

$$A[f] = -kT\ln Z + \frac{kT}{2}[\alpha s_1^2 + N(s^2 - s\beta + \beta^2)],$$

$$Z = \int_{\|m\|=1} e^{\alpha s_1 \cos\theta + (3N/2)[(s-\beta/2)(\cos^2\theta - 1/3) + (\beta/2)\sin^2\theta\cos 2\phi]} \times d\mathbf{m}. \tag{A1}$$

Its first and second derivatives are given by

$$\frac{\partial A}{\partial s_1} = \alpha kT(s_1 - \langle\cos\theta\rangle),$$

$$\frac{\partial A}{\partial s} = kTN\left(s + \frac{1-\beta}{2} - \frac{3}{2}\langle\cos^2\theta\rangle\right),$$

$$\frac{\partial A}{\partial \beta} = kTN\left(\beta + \frac{1-s}{2} - \frac{3}{2}\langle\sin^2\theta\cos^2\phi\rangle\right),$$

$$\frac{\partial^2 A}{\partial s_1^2} = \alpha kT - \alpha^2 kT(\langle\cos^2\theta\rangle - \langle\cos\theta\rangle^2) = \alpha kT - \alpha^2 kT\left(\frac{1+2s-\beta}{3} - s_1^2\right),$$

$$\frac{\partial^2 A}{\partial s_1\partial s} = -\frac{3N\alpha kT}{2}(\langle\cos^3\theta\rangle - \langle\cos\theta\rangle\langle\cos^2\theta\rangle) = -\frac{3N\alpha kT}{2}\left(\langle\cos^3\theta\rangle - s_1\frac{1+2s-\beta}{3}\right), \tag{A2}$$

$$\frac{\partial^2 A}{\partial s_1\partial \beta} = -\frac{3N\alpha kT}{2}(\langle\cos\theta\sin^2\theta\cos^2\phi\rangle - \langle\cos\theta\rangle\langle\sin^2\theta\cos^2\phi\rangle) = -\frac{3N\alpha kT}{2}\left(\langle\cos\theta\sin^2\theta\cos^2\phi\rangle - s_1\frac{1-s+2\beta}{3}\right),$$

$$\frac{\partial^2 A}{\partial s^2} = kTN - \frac{9N^2kT}{4}(\langle\cos^4\theta\rangle - \langle\cos^2\theta\rangle^2) = kTN - \frac{9N^2kT}{4}\left(\langle\cos^4\theta\rangle - \frac{(1+2s-\beta)^2}{9}\right),$$

$$\frac{\partial^2 A}{\partial s\partial\beta} = -\frac{kTN}{2} - \frac{9N^2kT}{4}(\langle\cos^2\theta\sin^2\theta\cos^2\phi\rangle - \langle\cos^2\theta\rangle \times \langle\sin^2\theta\cos^2\phi\rangle) = -\frac{kTN}{2} - \frac{9N^2kT}{4}\left(\langle\cos^2\theta\sin^2\theta\cos^2\phi\rangle - \frac{(1+2s-\beta)(1-s+2\beta)}{9}\right),$$

$$\frac{\partial^2 A}{\partial\beta^2} = kTN - \frac{9N^2kT}{4}(\langle\sin^4\theta\cos^4\phi\rangle - \langle\sin^2\theta\cos^2\phi\rangle^2) = kTN - \frac{9N^2kT}{4}\left(\langle\sin^4\theta\cos^4\phi\rangle - \frac{(1-s+2\beta)^2}{9}\right).$$

At the isotropic branch ($s_1=0, s=0, \beta=0$), the second variation of the free energy density is

$$\delta^2 A|_{s_1=0,s=0,\beta=0} = kT[(\alpha - \alpha^2/3)\delta^2 s_1 + N(1-N/5)\delta^2 s - N(1-N/5)\delta s\,\delta\beta + N(1-N/5)\delta^2\beta].$$

Thus, the isotropic equilibrium is unstable whenever $\alpha > 3$ or $N > 5$.

For the nonzero purely uniaxial nematic equilibria: $s \neq 0\beta=0$,

$$\delta^2 A = kT\alpha\left(1 - \frac{\alpha(1+2s)}{3}\right)\delta s_1^2 + kTN(\delta s, \delta\beta)\cdot C\cdot(\delta s, \delta\beta)^T, \tag{A3}$$

where

$$C = \begin{pmatrix} \frac{5}{2} - \frac{3}{4s}\left(\frac{e^{3Ns/2}}{\psi(s)} - 1\right) + \frac{N}{4}(1+2s)^2 & -\frac{5}{4} + \frac{3}{8s}\left(\frac{e^{3Ns/2}}{\psi(s)} - 1\right) - \frac{N}{8}(1+2s)^2 \\ -\frac{5}{4} + \frac{3}{8s}\left(\frac{e^{3Ns/2}}{\psi(s)} - 1\right) - \frac{N}{8}(1+2s)^2 & \frac{25}{16} - \frac{N}{32}(1-20s-8s^2) - \frac{9}{32s}\left(\frac{e^{3Ns/2}}{\psi(s)} - 1\right) \end{pmatrix}, \tag{A4}$$

$$\psi(s) = \int_0^1 e^{3Nsz^2/2}dz. \tag{A5}$$

APPENDIX B: CONDITIONS FOR TRICRITICAL POINTS

Since the tricritical points appears along the uniaxial branches, we focus on the free energy density in the limit of uniaxial phase:

$$A[f] = -kT\left[\ln Z - \frac{N}{2}s^2 - \frac{\alpha}{2}s_1^2\right],$$

$$Z = \int_0^{2\pi}\int_0^{\pi} e^{(3N/2)s(\cos^2\theta - 1/3) + \alpha s_1\cos\theta}\sin\theta\, d\theta\, d\phi. \tag{B1}$$

The first variation of the free energy density about s_1, s yields the equation for s_1 and s. Since A is symmetric in s_1, $(\partial^2 A/\partial s\partial s_1)|_{s_1=0}=0$. Along the zero polar order parameter branch ($s_1=0$), the Hessian of the second variation is diagonal:

$$\delta^2 A = \delta s_1^2 \frac{\partial^2 A}{\partial s_1^2} + \delta s^2 \frac{\partial^2 A}{\partial s^2}. \tag{B2}$$

The condition for tricritical points follows from[39]

$$\frac{\partial^2 A}{\partial s_1^2} = 0, \frac{\partial^4 A}{\partial s_1^4}\frac{\partial^2 A}{\partial s^2} - 3\left(\frac{\partial^3 A}{\partial s_1^2 \partial s}\right)^2 = 0. \tag{B3}$$

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