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## ONE ORDER PARAMETER TENSOR MEAN FIELD THEORY FOR BIAxIAL LIQUID CRYSTALS

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**ABSTRACT.** In this paper, we present a simple one tensor mean field model of biaxial nematic liquid crystals. The salient feature of our approach is that material parameters appear explicitly in the order parameter tensor. We construct the free energy from a mean field potential based on anisotropic dispersion interactions, identify the order parameter tensor and its elements, and obtain self-consistent equations, which are then solved numerically. The results are illustrated in a 3D ternary phase diagram. The phase behavior can be simply related to molecular parameters. The results may be useful for designing molecules that show a thermotropic biaxial phase.

**1. Introduction.** Nematic liquid crystals exhibiting biaxial phases have attracted a great deal of attention in the last three decades both theoretically [2, 3, 4, 6, 7, 8, 10, 11, 13, 14, 16, 17, 19, 20, 23, 24, 25, 29, 30], [33]–[37], [39, 40] and experimentally [1, 26, 28, 41]. Their constituent elements typically lack cylindrical symmetry, and can be modeled as ellipsoids or rectangular slabs with different lengths along the principal axes, or as particles having anisotropic dielectric susceptibilities with distinct eigenvalues. In the literature, Maier-Saupe theory [19, 20, 37, 39], Landau theory [2, 3, 4, 17, 29, 40], Onsager theory [30], and Monte Carlo simulations/molecular dynamics [6, 7, 10, 13, 25, 33] have been used to describe their thermotropic phase behavior. Mean field theories using both scalar [39] and tensor order parameters have been introduced. In the tensor models, both one tensor [2, 4, 19] and two tensor [17, 37, 40] descriptions have been used. Hydrodynamic kinetic theory of biaxial liquid crystal polymers has also been recently studied [35, 36].

In 1970, Freiser [19] published the first mean field theory of biaxial liquid crystals using an approach similar to that of Maier and Saupe [27]. This was subsequently elaborated [20], but the definition of the order parameter tensor  $Q$  was only implicit, and no phase diagram was presented. In 1972, Shih and Alben [34] studied a lattice model of hard core biaxial particles. In 1973, Alben [2] used Landau theory to predict biaxial nematics phases, expanding the free energy to sixth order in terms of the order parameter tensor  $Q$ , and predicted two second-order transitions

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which meet at a first order phase boundary in a sharp cusp. In 1974, Straley [39] introduced four scalar order parameters in a Maier-Saupe type mean field theory. These were defined as orientational averages of functions of the three Euler angles, their connection with molecular orientation was not made explicit. In 1985, Allender and Lee [3] used Landau theory to describe biaxial and uniaxial nematics based on six fundamental invariants. In 1997, Vissenberg *et. al.* [40] considered the generalized Landau-de Gennes theory with two order parameter tensors  $\mathbf{Q}^u$  and  $\mathbf{Q}^b$  together with spatial gradient and surface terms. In 2003, Sonnet *et. al.* [37] proposed a quadrupolar biaxial interaction potential between long and shorter axes of biaxial mesogens; a series of papers followed, exploring Maier-Saupe type and Landau theories and Monte Carlo simulations based on this interaction potential [11, 16, 17]. A first order transition between isotropic and biaxial nematic phases and tricritical points which separate first-order and second order transition from isotropic and biaxial nematic phases were predicted through mean field theory, Landau theory and computer simulations. In 2005, Longa and Pajak [23] studied the generalized Lebwohl-Lasher biaxial model, and predicted the direct isotropic-biaxial nematic phase transition in particular, and in 2008, Allender and Longa [4] reexamined the sixth-order Landau-de Gennes free energy in terms of a single order tensor parameter and provided phase diagrams under various choices of the Landau coefficients.

We point out here that when Landau theory is used to study the phase behavior of liquid crystals, there may be ambiguities which can make precise interpretation of the results difficult. In Landau theory, the free energy density is expressed as a series expansion in terms of the order parameter(s). In nematic liquid crystals, orientational order is frequently described in terms of second rank symmetric traceless tensors. Regardless of the definition of these tensors, the form of the Landau free energy, dictated by symmetry, is the same, predicting the same temperature/field dependence of the order parameter(s). For example, it makes no difference whether the order parameter tensor  $\mathbf{Q}$  is defined as [9]

$$\mathbf{Q} = \frac{1}{2} \langle 3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I} \rangle, \quad (1)$$

or as [2]

$$\mathbf{Q} = \langle \hat{\mathbf{l}}\hat{\mathbf{l}} - \hat{\mathbf{m}}\hat{\mathbf{m}} \rangle, \quad (2)$$

where  $\hat{\mathbf{l}}$ ,  $\hat{\mathbf{m}}$  and  $\hat{\mathbf{n}}$  are molecule-fixed orthogonal unit vectors and the brackets  $\langle \cdot \rangle$  denote the ensemble average; the form of the free energy and the predictions regarding  $\mathbf{Q}$  in Landau theory are identical. Since the coefficients in the free energy expansion are general, the definition of  $\mathbf{Q}$ , other than being second rank positive symmetric traceless tensor, does not enter Landau theory. The physical interpretation of  $\mathbf{Q}$ , however, in the biaxial case at least, is different in the above two cases. Any attempt to identify  $\mathbf{Q}$  with molecular tensors is thus meaningless if not associated with a molecular interpretation of the Landau coefficients. The same argument holds if two order parameter tensors are used. The form of the free energy and the predictions of Landau theory do not depend on the order parameter tensor definitions. Although Landau theory predicts the correct phase behavior, the results cannot be uniquely related to molecular orientation order or linked unambiguously to experimental measurements. In order to link the predictions from theory to experimental results, fitting scheme are often used to obtain the Landau coefficients. We are not

aware of similar ambiguities in systems with lower symmetry, that is, with vector or scalar order parameters.

An alternate approach to describe the phase behavior is via Maier-Saupe type mean field theories, which allow the construction of the free energy in terms of the order parameter(s). The single particle effective potential is constructed from explicitly defined intermolecular interactions, and this pseudopotential depends on the orientation of particles. The order parameter is clearly defined, and the form of the free energy and the predictions of the model, depend on this definition. Although neither necessary nor always well justified, the free energy may be expanded in a power series in terms of the order parameter, leading to results similar to Landau theory. The difference is that the coefficients in the expansion are no longer general, they are defined in terms of the interparticle interaction potential. Formally, therefore, the ambiguity in the Landau theory of nematics can be lifted by restricting the values of the expansion coefficients. Work with constrained Landau theories is being carried out [5].

In this paper, we revisit Freiser's mean field model, but with explicitly defined molecular parameters. We derive the free energy of a fluid of biaxial particles interacting via London dispersion forces. We identify a single tensor order parameter  $\mathbf{\Gamma}$  which contains material parameters (electric polarizabilities), minimize the free energy, and solve the resulting self-consistent equations numerically. We illustrate our results with a 3D ternary phase diagram in terms of relevant physical parameters and temperature. We show the subsequent first order and second order transitions from isotropic to uniaxial nematic, and to biaxial nematic phases as temperature decreases. Our explicit model describes the orientational order of each principal axis of the constituents particles, and can be related to both one- and two-tensor Landau theory descriptions. Our results can serve as a guide to the molecular design of materials with thermotropic biaxial phases.

**2. Molecular theory for biaxial molecules.** We consider biaxial nematic interactions in  $3D$ . The London-Van der Waals interaction energy between polarizable molecules, considered previously [8, 10, 14, 23, 24] has the form

$$\mathcal{E}_{12}(\vec{\mathbf{r}}, \Omega_1, \Omega_2) = -\frac{u}{(4\pi\epsilon_0)^2 r^6} (\boldsymbol{\alpha}^{(1)} \cdot (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I})) : ((3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \boldsymbol{\alpha}^{(2)}), \quad (3)$$

where  $u$  is an oscillator strength with units of energy,  $\epsilon_0$  is the permeability of free space,  $\Omega_i$  denotes the orientation of the  $i$ th molecule,  $\boldsymbol{\alpha}^i$  is the d.c. polarizability tensor [18, 22] of the  $i$ th molecule,  $\vec{\mathbf{r}}$  is the intermolecular vector,  $\hat{\mathbf{r}}$  is the unit vector along  $\vec{\mathbf{r}}$ ,  $\mathbf{I}$  is the identity matrix, the  $(\cdot)$  operator denotes the inner product (contraction on one index) and the  $(:)$  operator the scalar product of two tensors. The polarizability tensor for a biaxial molecule is

$$\boldsymbol{\alpha} = \alpha_l \hat{\mathbf{l}}\hat{\mathbf{l}} + \alpha_m \hat{\mathbf{m}}\hat{\mathbf{m}} + \alpha_n \hat{\mathbf{n}}\hat{\mathbf{n}}, \quad (4)$$

and the orientation of the molecule is defined by its orthogonal eigenvectors  $\hat{\mathbf{l}}$ ,  $\hat{\mathbf{m}}$  and  $\hat{\mathbf{n}}$ . The potential energy of molecule 1 due to its interactions with its neighbors is

$$\mathcal{E}_1(\Omega_1) = \int \int \mathcal{E}_{12}(\vec{\mathbf{r}}, \Omega_1, \Omega_2) P(\Omega_2) \rho(\vec{\mathbf{r}}) d\vec{\mathbf{r}} d\Omega_2$$

$$\begin{aligned}
& -\frac{1}{2} \int \int \int \mathcal{E}_{12}(\vec{\mathbf{r}}, \Omega_1, \Omega_2) P(\Omega_2) \rho(\vec{\mathbf{r}}) d\vec{\mathbf{r}} d\Omega_2 P(\Omega_1) d\Omega_1 \\
& = I_1 - \frac{1}{2} \langle I_1 \rangle, \tag{5}
\end{aligned}$$

where  $P(\Omega)$  is the single particle orientational distribution function. The first term, the average pair energy, gives the correct torque on molecule 1, while the second, independent of the orientation of molecule 1, ensures the correct average energy [31]. We assume that the number density  $\rho$  is uniform, then

$$\begin{aligned}
I_1 &= -\frac{\rho u}{(4\pi\epsilon_0)^2} \int \int \frac{1}{r^6} (\boldsymbol{\alpha}^{(1)} \cdot (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I})) : ((3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \boldsymbol{\alpha}^{(2)}) P(\Omega_2) d\vec{\mathbf{r}} d\Omega_2 \\
&= -\frac{\rho u}{3(4\pi\epsilon_0)^2} \int \int \frac{1}{r_0^3} (\boldsymbol{\alpha}^{(1)} \cdot (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I})) : (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \boldsymbol{\alpha}^{(2)} P(\Omega_2) d\vec{\mathbf{r}} d\Omega_2, \tag{6}
\end{aligned}$$

where the integration is over the three Euler angles, and  $r_0 = r_0(\hat{\mathbf{r}}, \Omega_1, \Omega_2)$  is the distance of closest approach of two molecules when the centers are along the direction  $\hat{\mathbf{r}}$ . We note that usually this term is treated as a constant, independent of molecular orientation and the direction of the intermolecular vector. In fact,  $r_0$  can vary by up to a factor of the aspect ratio of molecules for different orientations of the molecules  $\Omega_1, \Omega_2$  and of the intermolecular vector  $\hat{\mathbf{r}}$ . This  $r_0$  term enters the orientational distribution function, and can be expected to affect the phase behavior significantly. Efforts have been made to incorporate hard-core interactions between particles together with the long range attractive potential [21, 38]. For simplicity, in this paper, we also treat  $r_0$  as a constant, but plan to explore and expand on this issue elsewhere. We write the single particle energy as

$$\begin{aligned}
\mathcal{E}_1 &= -\frac{\rho u}{3(4\pi\epsilon_0)^2 r_0^3} (\alpha_l \hat{\mathbf{l}}\hat{\mathbf{l}} + \alpha_m \hat{\mathbf{m}}\hat{\mathbf{m}} + \alpha_n \hat{\mathbf{n}}\hat{\mathbf{n}}) : \langle \alpha_l \hat{\mathbf{l}}\hat{\mathbf{l}} + \alpha_m \hat{\mathbf{m}}\hat{\mathbf{m}} + \alpha_n \hat{\mathbf{n}}\hat{\mathbf{n}} \rangle \\
&+ \frac{1}{2} \frac{\rho u}{3(4\pi\epsilon_0)^2 r_0^3} \langle \alpha_l \hat{\mathbf{l}}\hat{\mathbf{l}} + \alpha_m \hat{\mathbf{m}}\hat{\mathbf{m}} + \alpha_n \hat{\mathbf{n}}\hat{\mathbf{n}} \rangle^2. \tag{7}
\end{aligned}$$

In our notation, the square of a tensor denotes the scalar inner product, i.e.,  $Q^2 = Q : Q$ . We note that

$$\hat{\mathbf{l}}\hat{\mathbf{l}} + \hat{\mathbf{m}}\hat{\mathbf{m}} + \hat{\mathbf{n}}\hat{\mathbf{n}} = \mathbf{I}. \tag{8}$$

It is convenient to introduce the traceless tensors

$$\begin{aligned}
\mathbf{q}^l &= \frac{1}{2} (3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I}), \\
\mathbf{q}^m &= \frac{1}{2} (3\hat{\mathbf{m}}\hat{\mathbf{m}} - \mathbf{I}), \\
\mathbf{q}^n &= \frac{1}{2} (3\hat{\mathbf{n}}\hat{\mathbf{n}} - \mathbf{I}),
\end{aligned} \tag{9}$$

and their averages

$$\begin{aligned}
Q^l &= \langle \mathbf{q}^l \rangle, \\
Q^m &= \langle \mathbf{q}^m \rangle, \\
Q^n &= \langle \mathbf{q}^n \rangle.
\end{aligned} \tag{10}$$

The single particle potential Eq. (7) can be written in terms of these as

$$\begin{aligned} \mathcal{E}_1 = & -\frac{\rho u}{3(6\pi\varepsilon_0)^2 r_0^3} (\alpha_l \mathbf{q}^l + \alpha_m \mathbf{q}^m + \alpha_n \mathbf{q}^n) : (\alpha_l \mathbf{Q}^l + \alpha_m \mathbf{Q}^m + \alpha_n \mathbf{Q}^n) \\ & + \frac{1}{2} \frac{\rho u}{3(6\pi\varepsilon_0)^2 r_0^3} (\alpha_l \mathbf{Q}^l + \alpha_m \mathbf{Q}^m + \alpha_n \mathbf{Q}^n)^2. \end{aligned} \quad (11)$$

We note that

$$\mathbf{q}^l + \mathbf{q}^m + \mathbf{q}^n = \mathbf{Q}^l + \mathbf{Q}^m + \mathbf{Q}^n = \mathbf{0}. \quad (12)$$

We next define the average polarizability

$$\bar{\alpha} = \frac{\alpha_l + \alpha_m + \alpha_n}{3}, \quad (13)$$

and the dimensionless polarizabilities

$$a_i = \frac{\alpha_i}{3\bar{\alpha}}, \quad i = l, m, n, \quad (14)$$

and note that

$$\sum_i a_i = 1. \quad (15)$$

We next define the dimensionless tensors

$$\boldsymbol{\gamma} = a_l \mathbf{q}^l + a_m \mathbf{q}^m + a_n \mathbf{q}^n \quad (16)$$

and

$$\boldsymbol{\Gamma} = a_l \mathbf{Q}^l + a_m \mathbf{Q}^m + a_n \mathbf{Q}^n. \quad (17)$$

The single particle potential in terms of these is just

$$\mathcal{E}_1 = -\rho U [\boldsymbol{\gamma} : \boldsymbol{\Gamma} - \frac{1}{2} \Gamma^2], \quad (18)$$

where

$$U = \frac{u\bar{\alpha}^2}{3(2\pi\varepsilon_0)^2 r_0^3}. \quad (19)$$

The Helmholtz free energy density is given by

$$\mathcal{F} = -\rho kT \ln \int e^{-\frac{\mathcal{E}_1}{kT}} d\Omega, \quad (20)$$

and substitutions gives

$$\mathcal{F} = \frac{1}{2} \rho^2 U \Gamma^2 - \rho kT \ln \int e^{\frac{\rho U}{kT} \boldsymbol{\gamma} : \boldsymbol{\Gamma}} d\Omega. \quad (21)$$

Our free energy density  $\mathcal{F}$  is a function of a single tensor order parameter  $\boldsymbol{\Gamma}$ , the system order parameter, which contains explicit information about the orientation of molecules ( $\mathbf{Q}^i$ ) and about material parameters ( $a_i$ ). If the free energy is minimized with respect to  $\boldsymbol{\Gamma}$ , we obtain the self-consistent equation

$$\boldsymbol{\Gamma} = \frac{\int \boldsymbol{\gamma} e^{\frac{\rho U}{kT} \boldsymbol{\gamma} : \boldsymbol{\Gamma}} d\Omega}{\int e^{\frac{\rho U}{kT} \boldsymbol{\gamma} : \boldsymbol{\Gamma}} d\Omega}. \quad (22)$$

Eq. (22) looks similar to the self-consistent equation for uniaxial nematics [32], however, here there are additional free parameters, the  $a_i$ s, and the integration is over three Euler angles. Unlike the model with two tensor parameters or four scalar parameters, we only need to solve two scalar equations. That is because  $\boldsymbol{\Gamma}$  is symmetric and traceless, and in its eigenframe, there are only two independent eigenvalues. The order parameter tensor  $\boldsymbol{\Gamma}$  differs from the traditional uniaxial order

parameter tensor  $\mathbf{Q}$  in that it includes information about molecular polarizabilities, while  $\mathbf{Q}$  does not.

Once  $\mathbf{\Gamma}$  is determined, one can obtain the individual order parameters for the molecular eigenvectors  $\hat{\mathbf{l}}$ ,  $\hat{\mathbf{m}}$  and  $\hat{\mathbf{n}}$ , since

$$\mathbf{Q}^i = \langle \mathbf{q}^i \rangle = \frac{\int \mathbf{q}^i e^{\frac{\rho U}{kT} \boldsymbol{\gamma} : \mathbf{\Gamma}} d\Omega}{\int e^{\frac{\rho U}{kT} \boldsymbol{\gamma} : \mathbf{\Gamma}} d\Omega}. \quad (23)$$

If the free energy density in Eq. (21) is expanded in terms of the order parameter  $\mathbf{\Gamma}$ , an expression similar to the Landau free energy is obtained; however, the coefficients are not general, but are given in terms of  $\frac{\rho U}{kT}$ . If the temperature dependence of the expansion coefficients is ignored for all but the quadratic terms, and the coefficients are regarded as arbitrary, a Landau free energy is obtained in terms of the single order parameter tensor  $\mathbf{\Gamma}$ , which contains both orientational information and material parameters. If  $\mathbf{\Gamma}$  is written as the sum in Eq. (17), a two order parameter version (or even three order parameter version, with the constraint of Eq. (12)) is obtained. We note that the usual temperature dependence of the quadratic term originates in the competition between the first, temperature independent energy term on the right side of Eq. (21) and the second, temperature dependent entropic term, coming from the integral. This implies that all quadratic terms, including cross-terms in the two order parameter version, will have the same, usual temperature dependence. This expansion allows a connection between our Maier-Saupe type mean field theory and existing Landau theories of biaxial nematics.

**3. Reparametrization.** We consider the coordinate transformation

$$\begin{aligned} a_l - \frac{1}{3} &= r \cos(\theta + 2\pi/3), \\ a_m - \frac{1}{3} &= r \cos(\theta - 2\pi/3), \\ a_n - \frac{1}{3} &= r \cos \theta. \end{aligned} \quad (24)$$

We then have

$$r = \sqrt{\frac{2}{3}} \sqrt{(a_l - \frac{1}{3})^2 + (a_m - \frac{1}{3})^2 + (a_n - \frac{1}{3})^2}, \quad (25)$$

and

$$\tan \theta = \frac{1}{\sqrt{3}} \frac{(a_l - a_m)}{(\frac{1}{3} - a_n)}, \quad (26)$$

or

$$\tan 3\theta = \frac{1}{3\sqrt{3}} \frac{(a_l - a_m)(a_m - a_n)(a_n - a_l)}{(a_l - \frac{1}{3})(a_m - \frac{1}{3})(a_n - \frac{1}{3})}. \quad (27)$$

Now, we reparametrize the particle by a new set of parameters  $r$  and  $\theta$ , where  $r$  is a measure of the extent to which the particle deviates from an isotropic sphere, while  $\theta$  provides information on the shape anisotropy. We note that

$$\begin{aligned} \frac{\boldsymbol{\gamma}}{r} : \frac{\mathbf{\Gamma}}{r} &= (\cos(\theta + 2\pi/3) \mathbf{q}^l + \cos(\theta - 2\pi/3) \mathbf{q}^m + \cos \theta \mathbf{q}^n) : \\ &(\cos(\theta + 2\pi/3) \mathbf{Q}^l + \cos(\theta - 2\pi/3) \mathbf{Q}^m + \cos \theta \mathbf{Q}^n), \end{aligned} \quad (28)$$

where the right hand side is only a function of  $\theta$ . The free energy density, measured in units of  $\rho kT$ , can be written as

$$\mathcal{F} = \frac{1}{2} \frac{\rho U r^2}{kT} \frac{\Gamma^2}{r^2} - \ln \int e^{\frac{\rho U r^2}{kT} \frac{\gamma}{r} \cdot \frac{\Gamma}{r}} d\Omega, \quad (29)$$

and we note that the effect of  $r$  is simply to rescale the temperature. The self-consistent equation is

$$\frac{\Gamma}{r} = \frac{\int \frac{\gamma}{r} e^{\frac{\rho U r^2}{kT} \frac{\gamma}{r} \cdot \frac{\Gamma}{r}} d\Omega}{\int e^{\frac{\rho U r^2}{kT} \frac{\gamma}{r} \cdot \frac{\Gamma}{r}} d\Omega}, \quad (30)$$

and so for our calculations, the only relevant anisotropy parameter is  $\theta$ . That is all that determines the structure of the phase diagram,  $r$  just scales the temperature. We recall that

$$U = \frac{u\bar{\alpha}^2}{(2\pi\epsilon_0)^2 r_0^3} = U'\bar{\alpha}^2, \quad (31)$$

then

$$\frac{\rho U r^2}{kT} = \frac{\rho U'}{kT} r^2 \bar{\alpha}^2. \quad (32)$$

Thus if

$$\tan \theta = \frac{1}{\sqrt{3}} \frac{(\alpha_l - \alpha_m)}{(\bar{\alpha} - \alpha_n)}, \quad (33)$$

and

$$r^2 \bar{\alpha}^2 = \frac{2}{27} ((\alpha_l - \bar{\alpha})^2 + (\alpha_m - \bar{\alpha})^2 + (\alpha_n - \bar{\alpha})^2) \quad (34)$$

are kept constant, then the phase behavior remains unchanged. This means that there are classes of molecules, with different shapes and polarizabilities, corresponding to the intersection of the above two surfaces, which possess identical phase behavior.

The corresponding Landau expansion of the free energy density near the isotropic-nematic transition can be written as (see Appendix)

$$\begin{aligned} \mathcal{F} \approx & \rho kT \left[ \frac{27}{80} \left( \frac{T}{T_c} - 1 \right) \left( \frac{\rho U r^2}{kT} \right)^2 \frac{\Gamma^2}{r^2} - \frac{81}{560} \cos 3\theta \left( \frac{\rho U r^2}{kT} \right)^3 \frac{\Gamma^3}{r^3} \right. \\ & + \frac{729}{44800} \left( \frac{\rho U r^2}{kT} \right)^4 \frac{(\Gamma^2)^2}{r^4} + \frac{6561}{246400} \cos 3\theta \left( \frac{\rho U r^2}{kT} \right)^5 \frac{\Gamma^2 \Gamma^3}{r^5} \\ & + \frac{81}{5120} \left( \frac{121743}{385385} \cos 6\theta + \frac{115911}{770770} \right) \left( \frac{\rho U r^2}{kT} \right)^6 \frac{(\Gamma^3)^2}{r^6} \\ & \left. - \frac{81}{5120} \left( \frac{243}{22022} \cos 6\theta + \frac{85131}{1101100} \right) \left( \frac{\rho U r^2}{kT} \right)^6 \frac{(\Gamma^2)^3}{r^6} \right], \quad (35) \end{aligned}$$

where  $T_c = \frac{\rho U}{k} \frac{27r^2}{40}$ , and  $\Gamma^3 = Tr(\mathbf{\Gamma} \cdot \mathbf{\Gamma} \cdot \mathbf{\Gamma})$ . Usually, the weak temperature dependence of  $\frac{\rho U r^2}{kT}$  is ignored in the vicinity of  $T_c$  and only the temperature dependence of the quadratic term is retained. Interestingly, of the two sixth order terms, the coefficient of the dominant one (involving  $(\Gamma^2)^3$ ) is negative. Nonetheless, the expansion gives a good approximation to the exact free energy in the neighborhood of small  $\mathbf{\Gamma}$ . Our expansion, however, is formally outside of the regimes considered in [4]. In order to get a positive expansion coefficient of the next highest even order term, we have to go to the 10th order. Since  $\frac{\Gamma}{r}$  is independent of  $r$ , this expansion clearly shows that the material parameter  $r$  only scales the temperature, and  $\theta$  is the parameter determining phase behavior.



The key result here is that even though we have three different polarizabilities, there is only one anisotropy parameter. If we parametrize our  $\mathbf{\Gamma}$  in terms of  $R$  and  $\Theta$  as Freiser [19], our Landau expansion is the same as his. However, since our  $\mathbf{\Gamma}$  can be expressed in terms of the  $Q^i$ 's, our results extend further, relating the phase behavior to polarizability in providing explicit information about molecular order. Our Landau expansion can also be reparameterized and restricted to third order to duplicate the Landau expansion in [23].

**4. Results and discussion.** We have three free parameters in the self-consistent equations (22): the dimensionless polarizabilities,  $a_l, a_m, a_n$  (subject to the constraint that  $\sum a_i = 1$ ) and the temperature  $T$ . To represent the 3D phase diagram while treating all three  $a_i$ 's equivalently, in Fig. 1, we use a property of an equilateral triangle. If a point inside an equilateral triangle with sides of unit length is projected onto the sides along the directions of the sides, the lengths of the line segments created by the projections along any side add to unity. If the lengths of these line segments correspond to the  $a_i$ 's, then each point in the triangle corresponds to a different molecular polarizability (similarly to ternary phase diagrams). The vertical axis in the diagram represents the dimensionless temperature, and the equilateral triangle in the horizontal plane represents material parameters. Without loss of generality, we only consider the shaded area in the triangle due to the three-fold and mirror symmetries of the equilateral triangle, Fig. 1(a). The self-consistent equation (22) is then solved numerically at discrete points in the three-parameter space. A three-point Gaussian quadrature rule is used to perform the 3D numerical integration, and Broyden method [12] is applied to solve the nonlinear equations. The equilibrium state corresponds to the lowest energy solution among the multiple solutions. The points where phase transitions take place are fitted by a smooth surface to obtain the 3D phase diagram.

The isotropic phase occurs when all the eigenvalues of  $\mathbf{\Gamma}$  are zero. The uniaxial nematic phase occurs when two eigenvalues of  $\mathbf{\Gamma}$  are the same and nonzero. Further, prolate and oblate uniaxial phases differ in that the distinct eigenvalue is the largest in the former case, and smallest in the latter. If all three eigenvalues are different, the phase is biaxial. The transition is first order if the derivative of the free energy with respect to temperature and the order parameter change discontinuously at the transition. If the derivative and the order parameter changes continuously, the transition is taken to be second order.

Three surfaces divide the whole space into four disjoint regions. The top red surface separates the isotropic phase and nematic phases. Two blue surfaces intersect with the red surface at one space curve, dividing the nematic region into two uniaxial regions, and one biaxial region.

Systems of isotropic particles with  $a_l = a_m = a_n$ , corresponding to the center of the large triangle, the system is in the isotropic phase for all temperatures. Systems of prolate uniaxial particles, with  $a_l > a_m = a_n$ , corresponding to the hypotenuse of the shaded right triangle, show no biaxial phase. Systems of oblate uniaxial particles with  $a_l = a_m > a_n$ , corresponding to the shortest side of the right triangle, show no biaxial phase. If  $a_l > a_m > \frac{1}{3} > a_n$ , then the system goes through a first order transition from the isotropic  $I$  to an oblate uniaxial nematic  $N_U^-$  phase, followed by a second order transition to the biaxial nematic  $N_B$  phase as the temperature is decreases. If  $a_l > \frac{1}{3} > a_m > a_n$ , the the system goes through a first order transition

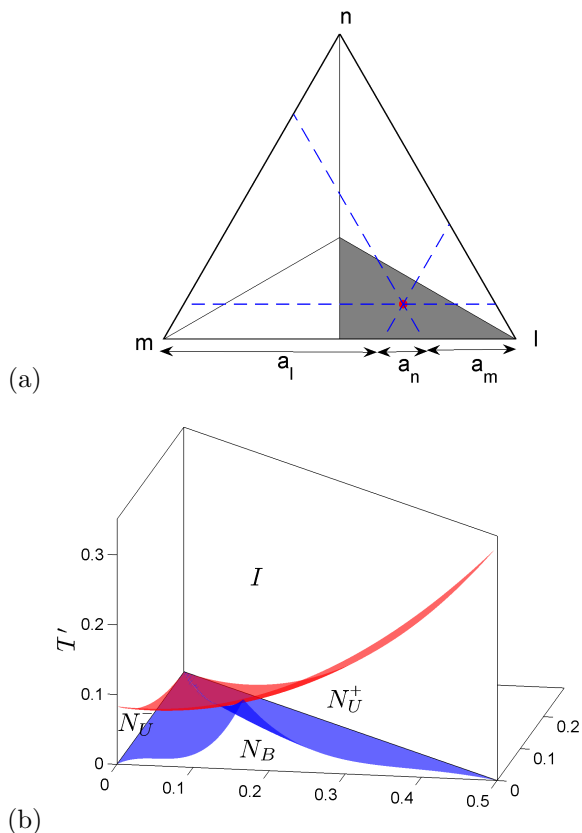


FIGURE 1. a. Triangle in the  $x - y$  plane with sides of unit length. Each point inside corresponds to a set of dimensionless polarizabilities  $(a_l, a_m, a_n)$  with  $\sum a_i = 1$ . The shaded area indicates the region where the phase diagram is calculated. The unshaded regions map onto this by permutation of subscripts. b. 3D ternary phase diagram; the vertical axis is the dimensionless temperature  $T' = \frac{kT}{\rho U}$ , the horizontal plane represents polarizabilities corresponding to the shaded triangle. The red surface represents the first order isotropic  $I -$  uniaxial nematic  $N_U$  phase transition, and the blue surfaces represent the uniaxial nematic  $N_U -$  biaxial nematic  $N_B$  phase transition. Along the intersection of the three surfaces, there is a second order phase transition from the isotropic  $I$  to the biaxial nematic  $N_B$  phase.

from the isotropic  $I$  to a prolate uniaxial nematic  $N_U^+$  phase, followed by a second order transition to the biaxial nematic  $N_B$  phase. If  $a_m = 1/3$ , then the system goes via a second order transition directly from the isotropic to the biaxial phase.

We next construct the individual axis order parameters  $Q^i$ 's from the order parameter  $\Gamma$ . Fig. 2a shows the eigenvalues of  $\Gamma$  for the biaxial molecules with arbitrarily chosen polarizabilities  $a_l = 0.6, a_m = 0.3, a_n = 0.1$  along the three principal

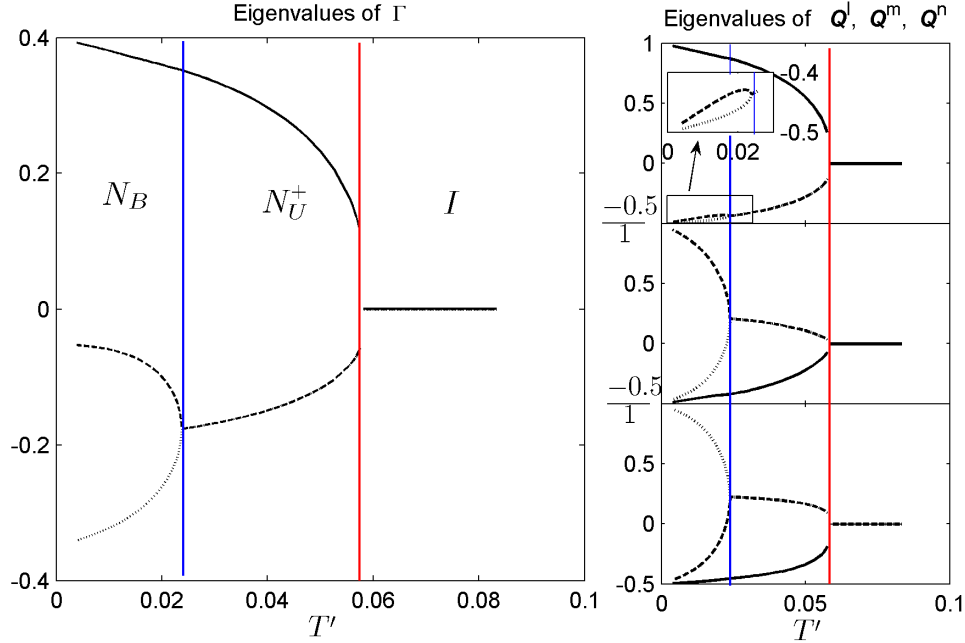


FIGURE 2. Eigenvalues of the order parameter tensor  $\Gamma$  (left) and the  $Q^i$ 's (right) vs. temperature for the case when the dimensionless polarizabilities  $a_l, a_m, a_n$  are 0.6, 0.3, 0.1. Different line styles denote the eigenvalues along the three principal axes. Solid lines represent the eigenvalues corresponding to the eigenvector with the largest eigenvalue of  $\Gamma$ , dashed lines represent the eigenvalues corresponding to the eigenvector with the intermediate eigenvalue of  $\Gamma$ , and dotted lines represent the eigenvalues corresponding to the eigenvector with the smallest eigenvalue of  $\Gamma$ .

axes. In general,  $\Gamma$  has three eigenvalues. All three are distinct in the biaxial  $N_B$  phase, two become identical in the uniaxial nematic  $N_U$  phases, and all three are identical and zero in the isotropic  $I$  phase. The first order nature of the  $I - N_U$  transition is evidenced by the jump in the eigenvalues of  $\Gamma$ . As the temperature decreases further, the lower eigenvalue branch with multiplicity 2 splits into two continuously at the transition to the biaxial  $N_B$  phase.

It is straightforward to show that the tensors  $\Gamma$  and  $Q^i$  are codiagonal. Fig. 2b, c, d shows the eigenvalues of  $Q^l, Q^m,$  and  $Q^n$  in the same eigenframe as  $\Gamma$ . The  $Q^i$ 's possess the same first order, and second order transitions as  $\Gamma$  at the same transition temperatures. In the isotropic  $I$  phase, all the  $Q^i$ 's have zero eigenvalues. In the prolate uniaxial nematic  $N_U^+$  phase, the distinct eigenvalue of  $Q^l$  is positive, which means that the axis  $\mathbf{l}$  associated with the largest polarizability  $a_l = 0.6$  tends to align in a preferred direction. The distinct eigenvalues of  $Q^m$  and  $Q^n$  are negative, which means that the minor axes  $\hat{\mathbf{m}}, \hat{\mathbf{n}}$  associated with the smaller polarizabilities  $a_m = 0.3$  and  $a_n = 0.1$  are randomly distributed in a plane which is orthogonal

to the preferred direction of  $\hat{\mathbf{I}}$ . In the biaxial  $N_B$  phase, the lower branch of the eigenvalues of  $Q^l$  splits into two with very weak biaxiality. In contrast, the higher branches of the eigenvalues of  $Q^m$  and  $Q^n$  split into two with strong biaxiality. The largest eigenvalues for all  $Q^i$ 's go to 1 and the smallest to  $-0.5$  as the temperature goes to zero, indicating that all the particles are identically oriented.

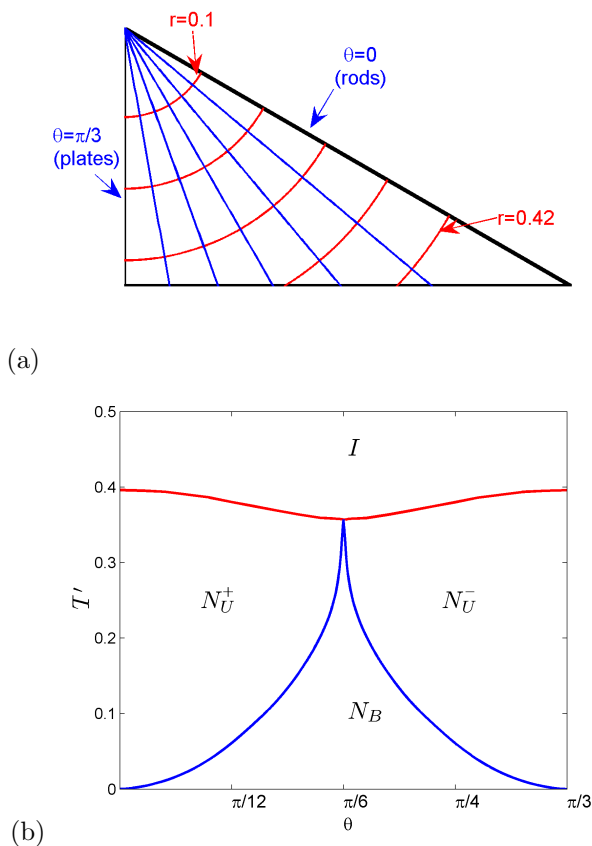


FIGURE 3. a. Contours of material parameters  $r$  (red) and  $\theta$  (blue) in the shaded area of the triangle. b. Phase diagram of biaxial particles for  $r = 0.23$ .  $\theta = 0$  corresponds to rod-like, while  $\theta = \pi/3$  corresponds to disc-like particles. The transition from the isotropic  $I$  to the uniaxial nematic  $N_U$  phase is first order, while to the biaxial nematic  $N_B$  phase is second order.

Fig. 3a shows the corresponding reparametrization from  $a_i$  to  $r$  and  $\theta$ . Note that Fig. 3b is similar to the typical phase diagrams in the literature, e.g. [2, 39]. Similar to polar coordinates, along each ray originating from the upper vertex of the triangle, the values of  $\theta$  are constant, and along each circular arc, the value of  $r$  is fixed.  $\theta$  is measured from the hypotenuse, corresponding to rod-like molecules, in a clockwise direction, reaching its maximum value of  $\frac{\pi}{3}$  at the shortest side, corresponding to disk-like molecules.  $r$  is 0 at the upper vertex of the triangle, increasing towards

the bottom side where it reaches its maximum value of  $2/3$ . Fig. 3b corresponds to the intersection of the 3D phase diagram surfaces and a surface with  $r = \text{const.}$  It is interesting to note the symmetry of the phase diagram with respect to  $\theta = \frac{\pi}{6}$ . The biaxial phase appears most likely for molecules for which  $\theta = \frac{\pi}{6}$ , corresponding to molecular polarizability  $a_m = 1/3$ . The  $I - N_U$  transition temperature is only weakly dependent on  $\theta$ , while the  $N_U - N_B$  transition temperature shows a strong dependence on  $\theta$ . The phase diagram for different values of  $r$  looks identical, except the vertical axis is rescaled by  $r$ .

**5. Conclusion.** A simple molecular theory, with one tensor order parameter is presented, where the single particle potential is derived from the Van der Waals interaction between polarizable biaxial molecules. The orientation of the molecules is given in terms of the orthogonal unit eigenvectors of the molecular polarizability tensor. The order parameter tensor for the system,  $\mathbf{\Gamma}$ , is a linear combination of the order parameter tensors of these eigenvectors, with the dimensionless polarizabilities as coefficients. A key feature of the system order parameter  $\mathbf{\Gamma}$  is that it contains material coefficients; this is reminiscent of de Gennes' proposal to define the order parameter through the dielectric tensor [15]. The self-consistent equation is obtained by minimizing the free energy with respect to the order parameter tensor  $\mathbf{\Gamma}$ , and is solved numerically at discrete points in the parameter space. The results are fitted by a smooth surface to obtain the 3D phase diagram. The main features are consistent with existing results in the literature. Expanding our free energy in terms of  $\mathbf{\Gamma}$  produces a Landau expansion with restricted order parameters, allowing unambiguous interpretation. Writing  $\mathbf{\Gamma}$  in terms of the  $\mathbf{Q}^i$ 's illustrates the connection between one- and two-order parameter tensor Landau descriptions. Our way of constructing the order parameter tensor allows us to obtain the individual order parameter tensor  $\mathbf{Q}^i$ 's, as has been shown. For positive polarizabilities  $\alpha_i$ , we find no first order uniaxial to biaxial nematic phase transitions or tricritical points. Our model indicates the existence of families of particles with different shapes and polarizabilities, but with identical phase behavior. Since the model parameters are molecular polarizabilities, these results are expected to be useful for the design of molecules capable of exhibiting a biaxial phase. Specifically, the thermotropic biaxial phase is most likely for molecules whose intermediate principal polarizability is equal to the average polarizability. Finally, we point out that the orientation dependence of the distance of closest approach of two particles has been ignored; including this dependence indicates a direction for improving this model.

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**Appendix A. Landau expansion.** We let  $f = \ln \int e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega = \ln g$ , with  $g(\eta) = \int e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega$ , and  $\eta = \frac{\rho U r^2}{kT}$ , and denote

$$\begin{aligned}
 g(\eta) &= \int e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega, & g(0) &= \int d\Omega = 1, \\
 g'(\eta) &= \int \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r} e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega, & g'(0) &= \int \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r} d\Omega = 0, \\
 g''(\eta) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^2 e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega, & g''(0) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^2 d\Omega = K_2 \frac{\Gamma^2}{r^4}, \\
 g'''(\eta) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^3 e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega, & g'''(0) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^3 d\Omega = K_3 \frac{\Gamma^3}{r^6}, \\
 g^{(4)}(\eta) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^4 e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega, & g^{(4)}(0) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^4 d\Omega = K_4 \frac{\Gamma^4}{r^8}, \\
 g^{(5)}(\eta) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^5 e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega, & g^{(5)}(0) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^5 d\Omega = K_5 \frac{\Gamma^5}{r^{10}}, \\
 g^{(6)}(\eta) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^6 e^{\eta \frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}} d\Omega, & g^{(6)}(0) &= \int \left(\frac{\gamma}{r} : \frac{\mathbf{\Gamma}}{r}\right)^6 d\Omega = K_6 \frac{\Gamma^6}{r^{12}}.
 \end{aligned} \tag{36}$$

If  $\mathbf{\Gamma}$  is symmetric and traceless, then we have the following relations between the powers of  $\mathbf{\Gamma}$ :

$$\Gamma^4 = \frac{1}{2}(\Gamma^2)^2, \Gamma^5 = \frac{5}{6}\Gamma^2\Gamma^3, \Gamma^6 = \frac{1}{4}(\Gamma^2)^3 + \frac{1}{3}(\Gamma^3)^2. \tag{37}$$

If  $\eta$  is small, we can expand  $f$  in  $\eta$  as:

$$f(\eta) = f(0) + f'(0)\eta + \frac{1}{2}f''(0)\eta^2 + \frac{1}{6}f'''(0)\eta^3 + \frac{1}{24}f^{(4)}(0)\eta^4 \tag{38}$$

$$+ \frac{1}{120}f^{(5)}(0)\eta^5 + \frac{1}{720}f^{(6)}(0)\eta^6 + O(\eta^7). \tag{39}$$

We also have

$$\begin{aligned}
 f'(0) &= \frac{g'(0)}{g(0)} = 0, \\
 f''(0) &= g''(0) = K_2 \frac{\Gamma^2}{r^4}, \\
 f'''(0) &= g'''(0) = K_3 \frac{\Gamma^3}{r^6}, \\
 f^{(4)}(0) &= g^{(4)}(0) - 3g''(0)^2 = \left(\frac{K_4}{2} - 3K_2^2\right) \frac{(\Gamma^2)^2}{r^8}, \\
 f^{(5)}(0) &= g^{(5)}(0) - 10g'''(0)g''(0) = \left(\frac{5}{6}K_5 - 10K_2K_3\right) \frac{\Gamma^2\Gamma^3}{r^{10}}, \\
 f^{(6)}(0) &= g^{(6)}(0) - 10g'''(0)^2 - 15g^{(4)}(0)g''(0) + 30g''^3(0) \\
 &= \left(\frac{K_6}{3} - 10K_3^2\right) \frac{(\Gamma^3)^2}{r^{12}} + \left(\frac{K_6}{4} - \frac{15K_4K_2}{2} + 30K_2^3\right) \frac{(\Gamma^2)^3}{r^{12}}.
 \end{aligned}
 \tag{40}$$

Since the values of  $K_2, \dots, K_6$  are independent of the tensor  $\Gamma$ , we choose the special form of  $\Gamma$  :

$$\Gamma = \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \frac{1}{2}I + \frac{3}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix},
 \tag{41}$$

and we have

$$\Gamma^2 = \frac{3}{2}, \Gamma^3 = \frac{3}{4}, \Gamma^4 = \frac{9}{8}, \Gamma^5 = \frac{15}{16}, \Gamma^6 = \frac{33}{32},
 \tag{42}$$

and

$$\gamma : \Gamma = \frac{3}{2}\gamma_{zz}.
 \tag{43}$$

We then evaluate the integrals

$$\begin{aligned}
 \frac{\int \gamma_{zz}^2 d\Omega}{8\pi^2} &= \frac{9}{20}r^2, \frac{\int \gamma_{zz}^3 d\Omega}{8\pi^2} = \frac{27}{140}r^3 \cos(3\theta), \frac{\int \gamma_{zz}^4 d\Omega}{8\pi^2} = \frac{243}{560}r^4, \\
 \frac{\int \gamma_{zz}^5 d\Omega}{8\pi^2} &= \frac{243}{616}r^5 \cos(3\theta), \frac{\int \gamma_{zz}^6 d\Omega}{8\pi^2} = \frac{729}{64064}r^6(49 + 4 \cos(6\theta)),
 \end{aligned}
 \tag{44}$$

and we have

$$\begin{aligned}
 K_2 &= \frac{1}{\Gamma^2} \frac{\int (\frac{3}{2}\gamma_{zz})^2 d\Omega}{8\pi^2} = \frac{3}{10} \left(\frac{3}{2}r\right)^2, \\
 K_3 &= \frac{1}{\Gamma^3} \frac{\int (\frac{3}{2}\gamma_{zz})^3 d\Omega}{8\pi^2} = \frac{9}{35} \left(\frac{3}{2}r\right)^3 \cos(3\theta), \\
 K_4 &= \frac{1}{\Gamma^4} \frac{\int (\frac{3}{2}\gamma_{zz})^4 d\Omega}{8\pi^2} = \frac{27}{70} \left(\frac{3}{2}r\right)^4, \\
 K_5 &= \frac{1}{\Gamma^5} \frac{\int (\frac{3}{2}\gamma_{zz})^5 d\Omega}{8\pi^2} = \frac{162}{385} \left(\frac{3}{2}r\right)^5 \cos(3\theta), \\
 K_6 &= \frac{1}{\Gamma^6} \frac{\int (\frac{3}{2}\gamma_{zz})^6 d\Omega}{8\pi^2} = \frac{243}{22022} \left(\frac{3}{2}r\right)^6 (49 + 4 \cos(6\theta)).
 \end{aligned}
 \tag{45}$$



So

$$\begin{aligned}
f'(0) &= 0, \\
f''(0) &= \frac{3}{10} \left(\frac{3}{2}\right)^2 \frac{\Gamma^2}{r^2}, \\
f'''(0) &= \frac{9}{35} \left(\frac{3}{2}\right)^3 \cos(3\theta) \frac{\Gamma^3}{r^3}, \\
f^{(4)}(0) &= -\frac{27}{350} \left(\frac{3}{2}\right)^4 \frac{(\Gamma^2)^2}{r^4}, \tag{46}
\end{aligned}$$

$$\begin{aligned}
f^{(5)}(0) &= -\frac{162}{385} \left(\frac{3}{2}\right)^5 \cos(3\theta) \frac{\Gamma^2 \Gamma^3}{r^5}, \\
f^{(6)}(0) &= \left(-\frac{121\,743}{385\,385} \cos 6\theta - \frac{115\,911}{770\,770}\right) \left(\frac{3}{2}\right)^6 \frac{(\Gamma^3)^2}{r^6} \\
&\quad + \left(\frac{243}{22\,022} \cos 6\theta + \frac{85131}{1101\,100}\right) \left(\frac{3}{2}\right)^6 \frac{(\Gamma^2)^3}{r^6}. \tag{47}
\end{aligned}$$

Thus, the free energy density can be expanded as

$$\begin{aligned}
\mathcal{F} &\approx \frac{1}{2} \rho^2 U \Gamma^2 - \frac{1}{2} \rho k T f''(0) \eta^2 - \frac{1}{6} \rho k T f'''(0) \eta^3 \\
&\quad - \frac{1}{24} \rho k T f^{(4)}(0) \eta^4 - \frac{1}{120} \rho k T f^{(5)}(0) \eta^5 - \frac{1}{720} \rho k T f^{(6)}(0) \eta^6 \\
&= \rho k T \left[ \frac{27}{80} \left(\frac{T}{T_c} - 1\right) \left(\frac{\rho U r^2}{k T}\right)^2 \frac{\Gamma^2}{r^2} - \frac{81}{560} \cos 3\theta \left(\frac{\rho U r^2}{k T}\right)^3 \frac{\Gamma^3}{r^3} \right. \\
&\quad + \frac{729}{44800} \left(\frac{\rho U r^2}{k T}\right)^4 \frac{(\Gamma^2)^2}{r^4} + \frac{6561}{246400} \cos 3\theta \left(\frac{\rho U r^2}{k T}\right)^5 \frac{\Gamma^2 \Gamma^3}{r^5} \\
&\quad + \frac{81}{5120} \left(\frac{121\,743}{385\,385} \cos 6\theta + \frac{115911}{770770}\right) \left(\frac{\rho U r^2}{k T}\right)^6 \frac{(\Gamma^3)^2}{r^6} \\
&\quad \left. - \frac{81}{5120} \left(\frac{243}{22022} \cos 6\theta + \frac{85131}{1101100}\right) \left(\frac{\rho U r^2}{k T}\right)^6 \frac{(\Gamma^2)^3}{r^6} \right], \tag{48}
\end{aligned}$$

where  $T_c = \frac{\rho U}{k} \frac{27 r^2}{40}$ .