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Maier-Saupe theory is the canonical mean field description of thermotropic nematic liquid crystals. In this paper, we examine the predictions of the theory in four spatial dimensions. Representations of the order parameter tensor and the existence of new phases are discussed. The phase diagram, based on numerical solution of the self-consistent equations and Landau theory is presented. Orientational order decreases as the number of spatial dimensions is increased.

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I. INTRODUCTION

Nematic liquid crystals are the simplest fluids with long range orientational order. They are also the working materials of the new ubiquitous liquid crystal displays. They are fascinating from both fundamental scientific as well as technological perspectives. Maier-Saupe theory [1], the first successful theoretical model of thermotropic nematic liquid crystals, is a mean field description of a system of cylindrically symmetric particles interacting via London dispersion forces. The theory provides an expression for the free energy in terms of an orientational order parameter. Minimizing the free energy with respect to the order parameter gives a self-consistent equation, whose solution yields the temperature dependence of the order parameter in equilibrium. The theory predicts a uniaxial nematic phase at low temperatures, and a first order phase transition to an isotropic liquid phase as the temperature is increased. Although originally derived in terms of a simple scalar order parameter, the theory is easily extended to provide a covariant description in terms of a second rank order parameter tensor. It has now been shown that in the absence of external fields and specialized boundary conditions, there is only a uniaxial solution [2] at low temperatures, however, fields and boundary conditions can give rise to biaxial solutions [3],[4] A Landau expression for the free energy can be obtained by expanding the Maier-Saupe free energy in a Taylor series in terms of the order parameter about $\boldsymbol{Q} = 0$, and replacing the expansion coefficients obtained by more general coefficients. Minimization of the Landau free energy, with terms up to sixth order or higher, can give rise to biaxial solutions [5].

Liquid crystals have been studied extensively in two- [6],[7],[8],[9] and three-dimensions ($3D$) (c.f. [1]). In order to gain additional insights into the dependence of liquid crystalline behavior on dimensionality, we have implemented Maier-Saupe theory in $4D$. Our work is a straightforward extension of the tensor version of Maier-Saupe theory to four spatial dimensions.

II. MAIER-SAUPE FORMALISM IN 3D

It is useful to review the salient features of Maier-Saupe (M-S) theory in $3D$. Although the original derivation has been carried out in coordinate dependent scalar form [1], it is straightforward to use a covariant Cartesian tensor representation. We consider a system of identical cylindrically symmetric particles with inversion symmetry. The orientation of one such particle is conveniently described by the quantity

$$\boldsymbol{q} = \frac{1}{2}(3\hat{\boldsymbol{l}}\hat{\boldsymbol{l}} - \boldsymbol{I}), \tag{1}$$

where $\hat{\boldsymbol{l}}$ a unit vector along the symmetry axis of the particle and $\boldsymbol{I}$ is the identity matrix. Since there is no way to uniquely define the direction of $\hat{\boldsymbol{l}}$, the appropriate descriptor of the orientation of particles with $D_{\infty h}$ symmetry is the dyad $\hat{\boldsymbol{l}}\hat{\boldsymbol{l}}$. For convenience, $\boldsymbol{q}$ is made traceless by subtracting $\boldsymbol{I}/3$ from $\hat{\boldsymbol{l}}\hat{\boldsymbol{l}}$, and normalized so that the largest

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possible eigenvalue is unity. The key property of the orientation descriptor $\boldsymbol{q}$ is that it is invariant under the allowed symmetry operations on the particle. A convenient representation for $\hat{\boldsymbol{l}}$ is

$$\hat{\boldsymbol{l}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta), \tag{2}$$

where θ and ϕ are the usual polar and azimuthal angles.

The order parameter tensor $\boldsymbol{Q}$ is just the ensemble average of the orientation descriptor $\boldsymbol{q}$, that is,

$$\boldsymbol{Q} = \langle \boldsymbol{q} \rangle = \int \frac{1}{2}(3\hat{\boldsymbol{l}}\hat{\boldsymbol{l}} - \boldsymbol{I}) f(\hat{\boldsymbol{l}}) \mathrm{d}\hat{\boldsymbol{l}}, \tag{3}$$

where $f(\hat{\boldsymbol{l}})$ is the single particle orientational probability distribution function; $\boldsymbol{Q}$ is a symmetric traceless 3×3 matrix. It can be diagonalized, and in its eigenframe it can be written as

$$\boldsymbol{Q} = \begin{pmatrix} -\frac{1}{2}(S-P) & 0 & 0 \\ 0 & -\frac{1}{2}(S+P) & 0 \\ 0 & 0 & S \end{pmatrix}, \tag{4}$$

where

$$S = \left\langle \frac{1}{2}(3\cos^2\theta - 1) \right\rangle, \tag{5}$$

and

$$P = \left\langle \frac{3}{2}\sin^2\theta\cos 2\phi \right\rangle. \tag{6}$$

The isotropic phase is described by $S = P = 0$; and $S \neq 0$ while $P = 0$ defines a uniaxial nematic phase if the $z-$axis is the eigenvector associating with the distinct eigenvalue.

The single particle potential, due to the interaction of the particle under consideration with the other particles in the system, is [10]

$$\mathcal{E} = -\rho U \boldsymbol{q} : \boldsymbol{Q} + \frac{1}{2}\rho U \boldsymbol{Q} : \boldsymbol{Q}, \tag{7}$$

where ρ is the number density, U is an interaction strength, and the operator (:) denotes the scalar product of two tensors. The Helmholtz free energy density is

$$\mathcal{F} = -\rho k T \ln \int e^{-\frac{\mathcal{E}}{kT}} d\Omega, \tag{8}$$

where $d\Omega$ is the element of solid angle. Minimizing the free energy with respect to $\boldsymbol{Q}$ gives the self-consistent equation

$$\boldsymbol{Q} = \frac{\int \boldsymbol{q} e^{\frac{\rho U \boldsymbol{q}:\boldsymbol{Q}}{kT}} d\Omega}{\int e^{\frac{\rho U \boldsymbol{q}:\boldsymbol{Q}}{kT}} d\Omega}. \tag{9}$$

Solving the self-consistent equation gives the temperature dependence of the scalar order parameters S and P; and evaluation of the corresponding free energy gives the phase behavior. In the absence of fields, only a uniaxial solution is found [2]. In the low temperature limit, the solutions were investigated by asymptotic expansion of integrals in the self-consistent equation [11].

The free energy density $\mathcal{F}$ in Eq. (8) can be expanded in terms of the order parameter $\boldsymbol{Q}$ about $\boldsymbol{Q} = \boldsymbol{0}$ to give the Landau-de Gennes (LdG) expansion

$$\begin{aligned} \mathcal{F}_{LdG} &= \frac{1}{2}a\boldsymbol{Q}^2 - \frac{1}{3}b\boldsymbol{Q}^3 + \frac{1}{4}c\boldsymbol{Q}^4 + \cdots \\ &= \frac{1}{4}a(3S^2 + P^2) - \frac{1}{4}bS(S^2 - P^2) + \frac{1}{32}c(3S^2 + P^2)^2 + \cdots. \end{aligned} \tag{10}$$

The expansion is only valid for small values of S. A particularly useful representation was proposed by Freiser [12],

$$S = r\cos\psi \text{ and } P = \sqrt{3}r\sin\psi. \tag{11}$$

In terms of these, the order parameter tensor $\boldsymbol{Q}$ becomes

$$\boldsymbol{Q} = diag(r\cos(\psi - \frac{2\pi}{3}), r\cos(\psi + \frac{2\pi}{3}), r\cos\psi), \tag{12}$$

and the LdG free energy becomes

$$\mathcal{F}_{LdG} = \frac{3}{4}ar^2 - \frac{1}{4}br^3\cos 3\psi + \frac{9}{32}cr^4 + \cdots . \tag{13}$$

The advantage of this formalism is its simplicity and clarity in indicating the three fold symmetry associated with interchanging axes (there are three set of solutions which are invariant under the interchange of axes.). We note that this may be regarded as a representation of the three eigenvalues of $\boldsymbol{Q}$ in terms of the inner product of a $2D$ vector

$$\mathbf{r} = (r\cos\psi, r\sin\psi), \tag{14}$$

with the three unit vectors in $2D$

$$\hat{\mathbf{a}} = (-\frac{1}{2}, \frac{\sqrt{3}}{2}), \tag{15}$$

$$\hat{\mathbf{b}} = (-\frac{1}{2}, -\frac{\sqrt{3}}{2}), \tag{16}$$

$$\hat{\mathbf{c}} = (1, 0). \tag{17}$$

Explicitly,

$$\boldsymbol{Q} = diag(\mathbf{r}\cdot\hat{\mathbf{a}}, \mathbf{r}\cdot\hat{\mathbf{b}}, \mathbf{r}\cdot\hat{\mathbf{c}}).$$

We now carry out a similar procedure in $4D$.

III. MAIER-SAUPE FORMALISM IN $4D$

The primary motivation to construct Maier-Saupe theory in $4D$ and to study its predictions is to gain insights into the role of dimensionality in orientational order. $2D$ nematics have received considerable attention [6–9, 13], however, we are not aware of any results in $4D$.

A. The Order Parameter Tensor

In $4D$, we again describe the orientation of a cylindrically symmetric particle in terms of a unit vector $\hat{\boldsymbol{l}}_{4D}$ along its symmetry axis. A convenient representation for $\hat{\boldsymbol{l}}_{4D}$ is

$$\hat{\boldsymbol{l}}_{4D} = (\sin\psi\sin\theta\cos\phi, \sin\psi\sin\theta\sin\phi, \sin\psi\cos\theta, \cos\psi), \tag{18}$$

where the angles ψ, θ and ϕ can be regarded as generalized coordinates. The normalized traceless orientational descriptor is

$$\boldsymbol{q}_{4D} = \frac{1}{3}(4\hat{\boldsymbol{l}}_{4D}\hat{\boldsymbol{l}}_{4D} - \boldsymbol{I}). \tag{19}$$

and the order parameter tensor is

$$\boldsymbol{Q}_{4D} = \langle \boldsymbol{q}_{4D} \rangle = \left\langle \frac{1}{3}(4\hat{\boldsymbol{l}}_{4D}\hat{\boldsymbol{l}}_{4D} - \boldsymbol{I}) \right\rangle, \tag{20}$$

which is a symmetric traceless 4×4 matrix.

We assume that the single particle potential, due to the interaction of the particle under consideration with other particles in the system, is again of the form

$$\mathcal{E} = -\rho U \boldsymbol{q}_{4D} : \boldsymbol{Q}_{4D} + \frac{1}{2}\rho U \boldsymbol{Q}_{4D} : \boldsymbol{Q}_{4D}. \tag{21}$$

The free energy density is

$$\mathcal{F} = -\rho kT \ln \int e^{-\frac{\mathcal{E}}{kT}} d\Omega, \tag{22}$$

where $d\Omega$ is the generalized element of solid angle associated with the generalized coordinates. As shown in the Appendix A, integration over the conjugate momenta gives

$$d\Omega = \sin^2\psi \sin\theta d\psi d\theta d\phi. \tag{23}$$

Minimizing the free energy with respect to $\boldsymbol{Q}_{4D}$ gives the self-consistent equation

$$\boldsymbol{Q}_{4D} = \frac{\int \boldsymbol{q}_{4D} e^{\frac{\rho U \boldsymbol{q}_{4d}:\boldsymbol{Q}_{4D}}{kT}} d\Omega}{\int e^{\frac{\rho U \boldsymbol{q}_{4D}:\boldsymbol{Q}_{4D}}{kT}} d\Omega} = \int \boldsymbol{q}_{4D} f(\hat{\boldsymbol{l}}_{4D}) d\hat{\boldsymbol{l}}_{4D}, \tag{24}$$

where the single particle orientational probability distribution function $f(\hat{\boldsymbol{l}})$ is given by

$$f(\hat{\boldsymbol{l}}_{4D}) = \frac{e^{\frac{\rho U \boldsymbol{q}_{4D}:\boldsymbol{Q}_{4d}}{kT}}}{\int e^{\frac{\rho U \boldsymbol{q}_{4D}:\boldsymbol{Q}_{4d}}{kT}} d\Omega}. \tag{25}$$

Solving the self-consistent equation gives the temperature dependence of the order parameter tensor; and evaluation of the corresponding the free energy gives the phase behavior.

B. Orientational Order and Phase Behavior

It is convenient to write $\boldsymbol{Q}_{4D}$ in its eigenframe as

$$\boldsymbol{Q}_{4D} = \begin{pmatrix} -\frac{1}{3}(V_{4D} + \frac{1}{2}(S_{4D} - P_{4D}) & 0 & 0 & 0 \\ 0 & -\frac{1}{3}(V_{4D} + \frac{1}{2}(S_{4D} + P_{4D}) & 0 & 0 \\ 0 & 0 & -\frac{1}{3}(V_{4D} - S_{4D}) & 0 \\ 0 & 0 & 0 & V_{4D} \end{pmatrix}, \tag{26}$$

where

$$V_{4D} = \left\langle \frac{1}{3}(4\cos^2\psi - 1) \right\rangle, \tag{27}$$

$$S_{4D} = \left\langle \frac{4}{3}\sin^2\psi(3\cos^2\theta - 1) \right\rangle, \tag{28}$$

$$P_{4D} = \left\langle 4\sin^2\psi \sin^2\theta \cos 2\phi \right\rangle. \tag{29}$$

The isotropic phase is defined by $P_{4D} = S_{4D} = V_{4D} = 0$, and $P_{4D} = S_{4D} = 0$ and $V_{4D} \neq 0$ defines the uniaxial nematic phase if z_4-axis is the vector associating with the distinct eigenvalue. A variety of non-uniaxial cases are possible. Rather than categorizing and naming these, we refer to them collectively as non-uniaxial.

To determine the behavior of the system, three coupled self-consistent equations (27-29) need to be solved simultaneously. This is done numerically; the integrals are approximated using the trapezoidal rule, and a quasi-Newton's method [14] is used to solve the nonlinear equations, starting from random initial guesses. The temperature dependence of the scalar order parameters is shown in Fig. 1.

Three distinct solutions are found: the isotropic solution with $P_{4D} = S_{4D} = V_{4D} = 0$; the uniaxial solution with $P_{4D} = S_{4D} = 0$ and $V_{4D} \neq 0$; and the non-uniaxial solution with $P_{4D} = 0$ and $S_{4D} = 4V_{4D} \neq 0$, i.e., the first eigenvalue equals the second, and the third equals the fourth.

The phase behavior is determined by comparing the free energy densities of the different solutions; this is shown in Fig. 2. The free energy density is a function of the scalar order parameters P_{4D}, S_{4D} and V_{4D}. The stability of the phases can be determined from principal curvatures of the surface of the free energy density. Since in our solutions $P_{4D} = 0$, we plot the free energy density as function of S_{4D} and V_{4D} in Fig. 3. In Fig. 3, A_1 and A_2 indicate the global minimum at temperature T ($< T_{IN}$), corresponding to the prolate uniaxial solution ($V_{4D} > 0$) in Figs. 1 and 2. B_1 and B_2 correspond to the oblate uniaxial solution ($V_{4D} < 0$) in Figs. 1 and 2; these are unstable saddle points. The solution A_1 is identical to A_2, and B_1 to B_2; the different locations correspond to an interchange of coordinate axes.

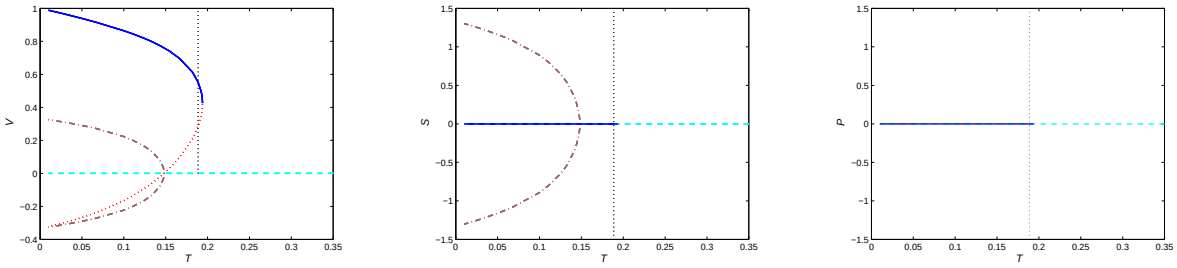

FIG. 1: Solutions of the self-consistent equations in $4D$ for the scalar order parameters. Temperature is in units of $k/\rho U$.

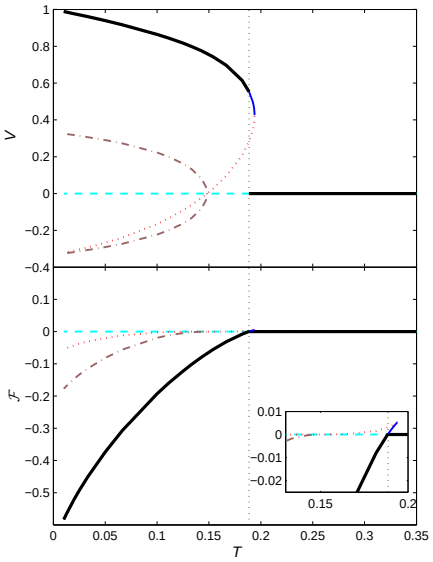

FIG. 2: Free energy density of the three sets of solutions vs. temperature in $4D$.

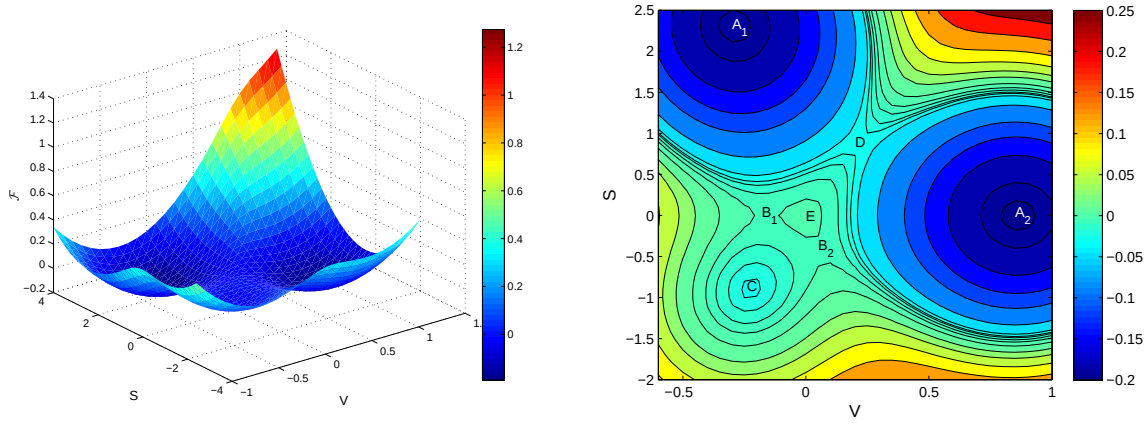

FIG. 3: Free energy density surface vs. V and P for a fixed temperature above the IN transition. a). side view; b). top view

C is a metastable local minimum while D is an unstable saddle point. They both correspond to the non-uniaxial solution in Figs. 1 and 2. E is a local maximum, corresponding to the isotropic solution.

At low temperatures, the lowest free energy solution is the uniaxial solution, as shown in Appendix C. There is a metastable non-uniaxial solution, but its free energy is never less than that of the uniaxial solution. At the dimensionless temperature, $T_{NI} = 0.189$, there is a first order phase transition between the uniaxial nematic and the isotropic phases, since the order parameter (Fig. 1) and the derivative of the free energy with respect to temperature (Fig. 2) change discontinuously at the transition.

It is interesting to note that the correspondence between the $4D$ nonuniaxial scalar order parameter (S_{4D} and P_{4D}) and $3D$ scalar order parameter (S and P)

$$S_{4D} = \frac{8}{3}\sin^2\psi S, \tag{30}$$

$$P_{4D} = \frac{8}{3}\sin^2\psi P. \tag{31}$$

We can project $4D$ into $3D$ by simply setting $\psi = \pi/2$ or equivalently $V_{4D} = 0$. In $4D$, $P_{4D} = 0$ and $S_{4D} \neq 0$ corresponds to unstable non-uniaxial nematic phase, while in $3D$, $P = 0$ and $S \neq 0$ is in the stable uniaxial nematic phase.

C. Landau Theory in $4D$

We note that the free energy density $\mathcal{F}$ in Eq. (8) can be expanded in terms of the order parameter $\boldsymbol{Q}_{4D}$ to give the LdG expansion

$$\mathcal{F}_{LdG} = \frac{1}{2}a\boldsymbol{Q}_{4D}^2 - \frac{1}{3}b\boldsymbol{Q}_{4D}^3 + \frac{1}{4}\left(c_1\left(\boldsymbol{Q}_{4D}^2\right)^2 + c_2\boldsymbol{Q}_{4D}^4\right) + \cdots, \tag{32}$$

here, different from the $3D$ case, there are two independent fourth-order terms. It becomes, in terms of S, P and V,

$$\mathcal{F}_{LdG} = \frac{1}{6}a(4V_{4D}^2 + \frac{1}{2}(S_{4D}^2 + \frac{1}{3}P_{4D}^2)) - \frac{1}{9}b(\frac{8}{3}V_{4D}^3 - \frac{1}{2}V(S_{4D}^2 + \frac{1}{3}P_{4D}^2) + \frac{1}{12}S_{4D}(S_{4D}^2 - P_{4D}^2)) + \frac{1}{36}\left(c_1(4V_{4D}^2 + \frac{1}{2}(S_{4D}^2 + \frac{1}{3}P_{4D}^2))^2 + c_2(\frac{28}{3}V_{4D}^4 + V_{4D}^2(S_{4D}^2 + \frac{1}{3}P_{4D}^2) - \frac{1}{3}V_{4D}S_{4D}(S_{4D}^2 - P_{4D}^2) + \frac{1}{8}(S_{4D}^2 + \frac{1}{3}P_{4D}^2)^2\right) + \ldots \tag{33}$$

We introduce a useful transformation, derived in the Appendix B, similar to that of Freiser in $3D$ [12],

$$V_{4D} = r\cos\theta, \tag{34}$$

$$S_{4D} = \sqrt{8}r\sin\theta\cos\phi, \tag{35}$$

$$P_{4D} = -2\sqrt{6}r\sin\theta\sin\phi. \tag{36}$$

In terms of this, the LdG free energy becomes

$$\mathcal{F}_{LdG} = \frac{2}{3}ar^2 - \frac{4}{27}br^3(5\cos^3\theta - 3\cos\theta + \sqrt{2}\cos 3\phi\sin^3\theta) + \frac{1}{108}(48c_1r^4 + c_2r^4(28\cos^4\theta - 24\cos^2\theta - 16\sqrt{2}\cos\theta\sin^3\theta\cos 3\phi + 24)), \tag{37}$$

Minimizing the $\mathcal{F}_{LdG}$ with respect to ϕ gives $\sin^3\theta\sin 3\phi = 0$, which gives $P_{4D} = 0$, in agreement with numerical results for Maier-Saupe theory. In this case, $\mathcal{F}_{LdG}$ can be written as

$$\mathcal{F}_{LdG} = \frac{2}{3}ar^2 - \frac{\sqrt{3}}{9}br^3(-\cos(3(\theta-\gamma)) + \cos(\theta-\gamma)) + \frac{1}{72}\left(32c_1r^4 + c_2r^4(-3\cos(4(\theta-\gamma)) - 4\cos(2(\theta-\gamma)) + 15)\right),$$

where $\cos\gamma = \frac{1}{\sqrt{3}}$. The uniaxial solution is obtained if $\theta = 0$ (i.e., $S_{4D} = 0$) or $\theta = \pi - 2\gamma$ (i.e., $S_{4D} = -8V_{4D}$). The non-uniaxial solution is obtained $\theta = \gamma$, which corresponds to $S_{4D} = 4V_{4D}$. A check of the Hessian of the free energy functional at these solutions indicates stability which is consistent with those of the numerical solutions from Maier-Saupe theory. There is also another set of solutions corresponding non-uniaxial solution in which there are three distinct eigenvalues if a is negative and relatively large. We found no solution corresponding to this in Maier-Saupe theory.

Dimension	Order parameters	T_{NI}	Order parameter at T_{NI}
$4D$	$V \neq 0$ $S = 0$ $P = 0$	0.189	$V = 0.553$
$3D$	$S \neq 0$ $P = 0$	0.220	$S = 0.429$
$2D$	$P \neq 0$	0.500	$P = 0$
$1D$	$O = 1$	∞	(No transition)

TABLE I: Order parameters and transition temperatures as functions of dimensionality.

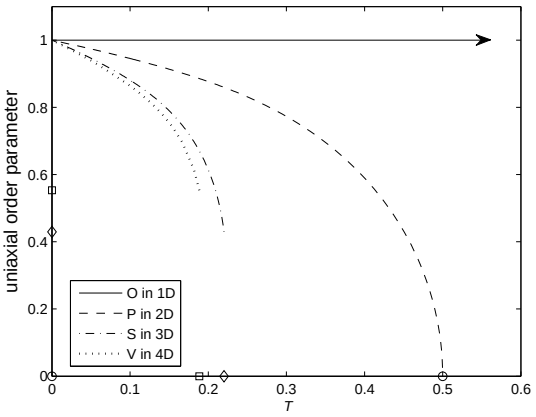

FIG. 4: Uniaxial order parameters as function of reduced temperature.

IV. DEPENDENCE OF ORIENTATIONAL ORDER ON DIMENSIONALITY

It is interesting to consider the dependence of orientational order on the spatial dimensionality of the system. In general, the orientational order parameter tensor of cylindrically symmetric rods nD is

$$\mathbf{Q}_{nD} = \frac{1}{n-1} < (n\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I}) > . \tag{38}$$

In $3D$ and $4D$, the eigenvalues can be decomposed into uniaxial and non-uniaxial contributions; the uniaxial solution always has the lowest free energy. If the dimensionality of the system is reduced by 1, (say going from $4D$ to $3D$), the uniaxial solution (V_{4D}) is disallowed in the reduced dimension, and the unfavorable non-uniaxial solution in the higher dimension (S_{4D}), projected onto the lower dimension, becomes the favored uniaxial solution (S) there. The cascading continues; the unfavored biaxial order parameter P in $3D$ becomes the uniaxial order parameter P_{2D} in $2D$. This scheme is shown in Table IV.

Here we have included the order parameter $P_{2D} = \langle \cos 2\phi \rangle$ in $2D$, and, for completeness, the order parameter $O = 1$ in $1D$. Fig. 4 below shows the uniaxial order parameters as function of dimensionless reduced temperature.

We note that with decreasing spatial dimension, the reduced nematic-isotropic transition temperature T_{NI} increases, and, at a given reduced temperature, the order parameter increases. We ascribe both of these effects to the decrease of entropy due to loss of orientational degrees of freedom, and expect these trends to continue through dimensions higher than 4.

V. SUMMARY

We have studied the phase behavior of a system of cylindrical symmetric particles in $4D$ via a Maier-Saupe type mean field theory in parallel with that of $3D$ uniaxial nematics. We have identified the appropriate orientation descriptor $\boldsymbol{q}_{4D}$ and orientational order parameter tensor $\boldsymbol{Q}_{4D}$, which was then used to characterize the phase behavior. We have constructed the single particle potential, and the corresponding Helmholtz free energy. Minimizing the free energy density with respect to the order parameter tensor $\boldsymbol{Q}_{4D}$, gave the a self-consistent equation, which was solved numerically. We have found that at high temperatures, only the isotropic phase exists; at low temperatures, the uniaxial nematic phase has lower free energy. The transition between the isotropic and the uniaxial nematic phase

is first order. At low temperatures, there also exist metastable/unstable non-uniaxial solutions. Landau theory is considered, and its solutions are compared with those of Maier-Saupe theory.

Interestingly, the scalar order parameters in $3D$ and $2D$ correspond to the non-uniaxial order parameters in $4D$ and $3D$ respectively. The value of the uniaxial order parameter at a given temperature, as well as the nematic-isotropic transition temperatures increase with decreasing spatial dimension due to loss of orientational degrees of freedom.

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Appendix A: Configuration Space

All discussion below refers to $4D$, so the subscript 4D is omitted for simplicity. Our intent here is to derive the configurational partition function in 4D consistently.

The orientation of a particle in $4D$ is represented in terms of three angles as

$$l_x = \sin\psi \sin\theta \cos\phi, \tag{A1}$$
$$l_y = \sin\psi \sin\theta \sin\phi, \tag{A2}$$
$$l_z = \sin\psi \cos\theta, \tag{A3}$$
$$l_w = \cos\psi. \tag{A4}$$

$\hat{\boldsymbol{l}}$ is a unit vector; the angles ψ, θ and ϕ are generalized coordinates. To ensure a consistent statistical mechanical description, *cf.* [15], we sum over states in configuration space to obtain the partition function. To do this, the momenta conjugate to the generalized coordinates ψ, θ and ϕ are needed. We first form the Lagrangian $\mathcal{L} = KE - PE$, and obtain the conjugate momenta. The kinetic energy KE associated with orientation is obtained by assuming that the molecule is a rod of length L and mass M in $4D$, and that each infinitesimal element dr of the rod has kinetic energy dKE given by

$$dKE = \frac{1}{2}(dm)v^2 = \frac{1}{2}(\frac{M}{L}dr)r^2(\frac{\partial \hat{\boldsymbol{l}}}{\partial t})^2, \tag{A5}$$

and

$$KE = \frac{1}{2}I(\frac{\partial \hat{\mathbf{l}}}{\partial t})^2. \tag{A6}$$

where $I = \frac{1}{12}ML^2$ is the moment of inertia. In our representation, the angular velocity is

$$\left(\frac{\partial \hat{\boldsymbol{l}}}{\partial t}\right)^2 = \dot{\psi}^2 + \sin^2\psi\dot{\theta}^2 + \sin^2\psi\sin^2\theta\dot{\phi}^2. \tag{A7}$$

We obtain the generalized momentum p_q corresponding to the variable q from

$$p_q = \frac{\partial \mathcal{L}}{\partial \dot{q}}. \tag{A8}$$

These are

$$p_\psi = I\dot{\psi}, \tag{A9}$$
$$p_\theta = I\sin^2\psi\dot{\theta}, \tag{A10}$$
$$p_\phi = I\sin^2\psi\sin^2\theta\dot{\phi}. \tag{A11}$$

The Hamiltonian is

$$\mathcal{H} = PE + \frac{p_\psi^2}{2I} + \frac{p_\theta^2}{2I\sin^2\psi} + \frac{p_\phi^2}{2I\sin^2\psi\sin^2\theta}. \tag{A12}$$

and we evaluate the partition function

$$q_{part} = \frac{1}{h^3}\int e^{-\frac{\mathcal{H}}{kT}} d\psi dp_\psi d\theta dp_\theta d\phi dp_\phi, \tag{A13}$$

and integrate over the momenta. This gives

$$q_{part} \sim \int e^{-\frac{PE}{kT}}\sin^2\psi\sin\theta d\psi d\theta d\phi. \tag{A14}$$

and we obtain:

$$d\Omega = \sin^2\psi\sin\theta d\psi d\theta d\phi. \tag{A15}$$

Appendix B: Parametrization of the scalar order parameters and the Landau Expansion in 4D.

We wish to write the eigenvalues of the $\boldsymbol{Q}$ tensor

$$\boldsymbol{Q} = \begin{pmatrix} -\frac{1}{3}(V + \frac{1}{2}(S-P)) & & & \\ & -\frac{1}{3}(V+\frac{1}{2}(S+P)) & & \\ & & -\frac{1}{3}(V-S) & \\ & & & V \end{pmatrix}, \tag{B1}$$

in a way which reflects the symmetry under the interchange of coordinate axes, similar to the scheme proposed by Freiser [12].

We construct four unit vectors in $3D$ such that the angle between any two of these is the same:

$$\hat{\mathbf{a}} = (-\frac{\sqrt{2}}{3}, -\frac{\sqrt{2}}{\sqrt{3}}, -\frac{1}{3}), \tag{B2}$$
$$\hat{\mathbf{b}} = (-\frac{\sqrt{2}}{3}, \frac{\sqrt{2}}{\sqrt{3}}, -\frac{1}{3}), \tag{B3}$$
$$\hat{\mathbf{c}} = (\frac{\sqrt{8}}{3}, 0, -\frac{1}{3}), \tag{B4}$$
$$\hat{\mathbf{d}} = (0, 0, 1). \tag{B5}$$

(These are vectors pointing to the vertices of a regular tetrahedron; the angle between any two of them is 70.53^o.) We then construct the vector $\mathbf{r}$ such that

$$\mathbf{r} = (r\sin\theta\cos\phi, r\sin\theta\sin\phi, r\cos\theta), \tag{B6}$$

and

$$\boldsymbol{Q} = diag(\hat{\mathbf{a}}\cdot\mathbf{r},\ \hat{\mathbf{b}}\cdot\mathbf{r},\ \hat{\mathbf{c}}\cdot\mathbf{r},\ \hat{\mathbf{d}}\cdot\mathbf{r}). \tag{B7}$$

This is always possible, since r has three degrees of freedom; the condition that $tr\mathbf{Q} = \mathbf{0}$ is satisfied since $\hat{\mathbf{a}} + \hat{\mathbf{b}} + \hat{\mathbf{c}} + \hat{\mathbf{d}} = 0$. Explicitly, we can write the scalar order parameters in terms of r, θ and ϕ as:

$$V = r\cos\theta, \tag{B8}$$

$$S = \sqrt{8}r\sin\theta\cos\phi, \tag{B9}$$

$$P = -2\sqrt{6}r\sin\theta\sin\phi. \tag{B10}$$

We note that this reduces the the usual $3D$ M-S theory when $\theta = \pi/2$.

The first four terms of the Landau expansion are

$$Tr\boldsymbol{Q} = 0, \tag{B11}$$

$$Tr\boldsymbol{Q}^2 = \frac{4}{3}r^2, \tag{B12}$$

$$Tr\boldsymbol{Q}^3 = \frac{4}{9}r^3(5\cos^3\theta - 3\cos\theta + \sqrt{2}\cos 3\phi\sin^3\theta), \tag{B13}$$

$$Tr\boldsymbol{Q}^4 = \frac{1}{27}r^4(28\cos^4\theta - 24\cos^2\theta - 16\sqrt{2}\cos\theta\sin^3\theta\cos 3\phi + 24). \tag{B14}$$

If we write the Landau free energy in terms of r, θ and ϕ, we obtain

$$\begin{aligned}\mathcal{F}_{LdG} = \frac{2}{3}ar^2 - \frac{4}{27}br^3(5\cos^3\theta - 3\cos\theta + \sqrt{2}\cos 3\phi\sin^3\theta) + \\ \frac{1}{108}(48c_1r^4 + c_2r^4(28\cos^4\theta - 24\cos^2\theta - 16\sqrt{2}\cos\theta\sin^3\theta\cos 3\phi + 24),\end{aligned} \tag{B15}$$

which is somewhat more tractable. Minimizing $\mathcal{F}_{LdG}$ with respect to ϕ gives

$$r^3\sin 3\phi\sin^3\theta(b + c_2r\cos\theta) = 0. \tag{B16}$$

Since in general we expect $cr\cos\theta$ to vary with temperature, whereas b does not, we conclude that

$$\sin 3\phi = 0. \tag{B17}$$

We choose the frame where $\phi = 0$, and we conclude that $P = 0$. That is, keeping terms in the Landau expansion to fourth order, we find that the free energy is minimized if $P = 0$, as in the case of 3D. We therefore expect solutions where at least two of the eigenvalues are the same; indeed, this was found in the numerical solutions of the self-consistent equation.

If $\cos 3\phi = 1$, $\mathcal{F}_{LdG}$ becomes

$$\begin{aligned}\mathcal{F}_{LdG} = \frac{2}{3}ar^2 - \frac{4}{27}br^3(5\cos^3\theta - 3\cos\theta + \sqrt{2}\sin^3\theta) + \\ \frac{1}{108}(48c_1r^4 + c_2r^4(28\cos^4\theta - 24\cos^2\theta - 16\sqrt{2}\cos\theta\sin^3\theta + 24),\end{aligned} \tag{B18}$$

which can be written as

$$\mathcal{F}_{LdG} = \frac{2}{3}ar^2 - \frac{\sqrt{3}}{9}br^3(-\cos(3(\theta-\gamma)) + \cos(\theta-\gamma)) + \frac{1}{72}(32c_1r^4 + c_2r^4(-3\cos(4(\theta-\gamma)) - 4\cos(2(\theta-\gamma)) + 15),$$

where $\cos\gamma = \frac{1}{\sqrt{3}}$. Minimizing $\mathcal{F}_{LdG}$ with respect to r and θ, we obtain

$$\frac{\partial\mathcal{F}_{LdG}}{\partial r} = \frac{4}{3}ar - \frac{\sqrt{3}}{3}br^2(-\cos(3(\theta-\gamma)) + \cos(\theta-\gamma)) + \frac{1}{18}(32c_1r^3 + c_2r^3(-3\cos(4(\theta-\gamma)) - 4\cos(2(\theta-\gamma)) + 15) = 0,$$

$$\frac{\partial\mathcal{F}_{LdG}}{\partial\theta} = -\frac{\sqrt{3}}{9}br^3(3\sin 3(\theta-\gamma) - \sin(\theta-\gamma)) + \frac{1}{18}c_2r^4(3\sin 4(\theta-\gamma) + 2\sin 2(\theta-\gamma)) = 0.$$

The values of r depend on the choice of parameters a, b, c_1,and c_2. The values of θ are more revealing of the phase behavior. Three of the non-isotropic solutions are

$$\theta = 0 \text{ or } \theta = \gamma \text{ or } \theta = \pi - 2\gamma.$$

The first solution corresponds to $S = 0$, i.e., the uniaxial solution. The second solution corresponds to $S = 4V$, the non-uniaxial solution when the eigenvalues are $\lambda_1 = \lambda_2 \neq \lambda_3 = \lambda_4$. The third solution $\theta = \pi - 2\gamma$ corresponds to $S = -8V$, which is same as the uniaxial solution corresponding to $\theta = 0$,except for the interchange of axes.

There is also another set of solutions for which the order parameter $\boldsymbol{Q}$ has four distinct eigenvalues. This occurs when the coefficient a is large and negative, there no corresponding solution in Maier-Saupe theory.

Appendix C: Solutions in Maier-Saupe theory at low temperature

Our intent here is to show that even in the limit of low temperatures, the solution space remains the same as at higher temperatures, that is, no new solutions appear as the sample is cooled.

It can be shown that when the temperature $T \to 0$, there can be only four solutions that satisfy the self-consistent equation

$$\boldsymbol{Q} = \frac{\int \boldsymbol{q} e^{\frac{\rho U \boldsymbol{q}:\boldsymbol{Q}}{kT}} d\Omega}{\int e^{\frac{\rho U \boldsymbol{q}:\boldsymbol{Q}}{kT}} d\Omega}.$$

The trivial solution is $\boldsymbol{Q} = 0$. The other solutions can be obtained by approximating the integrals by their asymptotes as $\frac{\rho U}{kT} \to \infty$, i.e.,

$$\int \boldsymbol{q} e^{\frac{\rho U \boldsymbol{q}:\boldsymbol{Q}}{kT}} d\Omega \approx C \sqrt{\frac{kT}{\rho U}} \boldsymbol{q}(\psi_0, \boldsymbol{\theta}_0, \phi_0)\, e^{\frac{\rho U \boldsymbol{q}(\psi_0,\theta_0,\phi_0):\boldsymbol{Q}}{kT}},$$

$$\int e^{\frac{\rho U \boldsymbol{q}:\boldsymbol{Q}}{kT}} d\Omega \approx C \sqrt{\frac{kT}{\rho U}}\, e^{\frac{\rho U \boldsymbol{q}(\psi_0,\theta_0,\phi_0):\boldsymbol{Q}}{kT}},$$

where $(\psi_0, \theta_0, \phi_0)$ is the maximizer of $\boldsymbol{q}(\psi, \theta, \phi) : \boldsymbol{Q}$, and C is a constant, which depends on $(\psi_0, \theta_0, \phi_0)$ only. Then we have

$$\boldsymbol{Q} = \boldsymbol{q}(\psi_0, \theta_0, \phi_0).$$

Care has to be taken in the degenerate cases, where one or two of the angles could be arbitrary. For example, if θ_0 and ϕ_0 are arbitrary, then

$$\boldsymbol{Q} = \frac{\int \boldsymbol{q} e^{\frac{\rho U \boldsymbol{q}:\boldsymbol{Q}}{kT}} d\Omega}{\int e^{\frac{\rho U \boldsymbol{q}:\boldsymbol{Q}}{kT}} d\Omega} \approx \frac{\int\int C\sqrt{\frac{kT}{\rho U}} \boldsymbol{q}(\psi_0, \theta, \phi) e^{\frac{\rho U \boldsymbol{q}(\psi_0,\theta,\phi):\boldsymbol{Q}}{kT}} d\cos\theta d\phi}{\int\int C\sqrt{\frac{kT}{\rho U}} e^{\frac{\rho U \boldsymbol{q}(\psi_0,\theta,\phi):\boldsymbol{Q}}{kT}} d\cos\theta d\phi} = \frac{\int\int \boldsymbol{q}(\psi_0, \boldsymbol{\theta}, \phi) d\cos\theta d\phi}{\int\int d\cos\theta d\phi}.$$

The maximizer $(\psi_0, \theta_0, \phi_0)$ of $\boldsymbol{q}(\psi, \theta, \phi) : \boldsymbol{Q}$ can be found by solving the following equations

$$\begin{aligned} (-3S + P\cos 2\phi)\sin 2\theta \sin^2\psi &= 0, \\ P\sin^2\theta \sin 2\phi \sin^2\psi &= 0, \\ (S - 16V + 3S\cos 2\theta + 2P\cos 2\phi \sin^2\theta)\sin 2\psi &= 0. \end{aligned}$$

We investigate all possible solutions for ψ, θ, ϕ, and conclude that there are three $\boldsymbol{Q}$s, which, in their eigenframes, have the forms

$$\begin{pmatrix} -1/3 & 0 & 0 & 0 \\ 0 & -1/3 & 0 & 0 \\ 0 & 0 & -1/3 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1/9 & 0 & 0 & 0 \\ 0 & 1/9 & 0 & 0 \\ 0 & 0 & 1/9 & 0 \\ 0 & 0 & 0 & -1/3 \end{pmatrix}, \begin{pmatrix} 1/3 & 0 & 0 & 0 \\ 0 & 1/3 & 0 & 0 \\ 0 & 0 & -1/3 & 0 \\ 0 & 0 & 0 & -1/3 \end{pmatrix}.$$

Substituting these solutions into the free energy density $\mathcal{F}$, it is readily seen that the first gives the lowest free energy. This is consistent with numerical results.