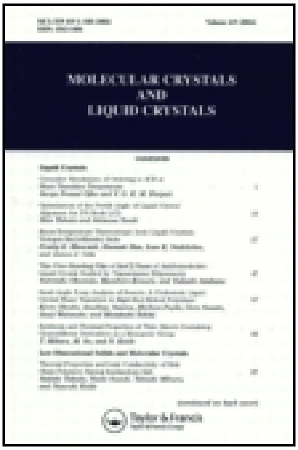

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FIELD EQUATION OF NEMATOSTATICS

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Abstract By generalizing the classical Maier-Saupe mean-field potential to distorted configurations, a general field equation of nematostatics is deduced, which can also be used within defect "cores". A detailed comparison with the deGennes phenomenological theory is presented, and the advantages of using a molecular-based approach are discussed.

INTRODUCTION

It is well known that liquid crystalline materials, both polymeric and of low molecular weigth, can present a polydomain texture, i.e., the orientation of the director, which defines the nematic order, can vary from point to point. For the case of smooth changes of the director in space ("smoothness" should of course be measured with respect to some characteristic molecular length), Frank elasticity theory holds, and the field equation for the director can be deduced at once[1]. On the other hand, discontinuities of the director field, usually termed "defects", very often occur, where the weak distortion assumption of Frank elasticity is perforce violated. In fact, the notion of director itself is lost when considering defect cores, and a new way of describing spatial orientational gradients is required. This was implicitly accounted for long ago by deGennes, who proposed an approach to nematostatics in which a tensorial order parameter is adopted as the local descriptor of both orientation and order in the material[2]. By using this theory, it has been possible to deal with defects[3, 4, 5], which are now understood in terms of local, partial isotropizations of the nematic phase, induced by distortions.

It should be mentioned, however, that the deGennes approach also has some definite drawbacks, due to its phenomenological nature. For example, the free energy density of the nematic phase is written down in terms of a series expansion of the order parameter tensor and of its gradients, but there is no clear indication on the radius of convergence of the expansion, and the coefficients of the series are in fact arbitrary quantities. The assumption of "smallness" of the order parameter tensor, whatever the smallness criterion might be, is then unwarranted, and the very use of an expansion procedure is questionable. (A complete and interesting discussion on this point can be found in Katriel et al.[6].) We will come back to this and other difficulties intrinsic to the phenomenological approach later in the paper.

In a completely different vein, the problem of determining the internal structure of defects has been tackled in recent years by use of Monte Carlo computer simulation techniques[7, 8, 9]. The simulation volume is filled with interacting "molecules" (e.g., spherocylindrical rods interacting by excluded volume forces only[8]), and the far-field director characteristic of any given defect is assigned once and for all in a boundary zone surrounding the volume itself. The system is then made to relax, and the equilibrium configuration is automatically attained. An indisputable merit of this approach is that stability of the calculated equilibrium configuration is certain; an obvious shortcoming is that, with present-day computers, it is only possible to simulate systems made up of a (relatively) small number of particles. Though this latter difficulty can be partially alleviated by using lattice models, i.e., "spin" systems where translational degrees of freedom are eliminated[7, 9], it is still true that a huge computational effort is needed.

In this work, we present an approach to nematostatics, inclusive of the nonlinear distortions within defect cores, which is also based on a molecular viewpoint. Contrary to the simulation approach, we do not deal with all the "molecules" in the system; a spatial-dependent distribution function of molecular orientations is introduced instead, so that the classical mean-field Maier-Saupe nematogenic potential[10] acting on a single molecule can be generalized to the case of distorted configurations. The general field equation of nematostatics (pertaining to this choice for the interaction potential) is then deduced by self-consistency, in close analogy to the standard Maier-Saupe procedure. This equation is valid for any distorted configuration of the nematics, and can be effectively used in calculations of defect core structures[11]. A simple example is also hinted to here, by considering the configuration of the nematics in a cylindrical geometry.

FIELD EQUATION OF NEMATOSTATICS

Let us consider a system of rigid rodlike molecules, each of them being identified by its position in space, **R**, and by its orientation **u**. As stated in the Introduction, we describe the system by means of a spatial-dependent distribution function: at a fixed location **R**, the distribution function f(**u**; **R**) gives the probability density that a molecule centered at **R** is oriented along **u**.

All macroscopic observables can be calculated as weighted averages over the distribution function. Of special relevance is the local second-order moment **S** of the distribution:

$$\mathbf{S} \equiv \langle \mathbf{uu} \rangle \equiv \int d\Omega\, f(\mathbf{u};\mathbf{R})\,\mathbf{uu} \tag{1}$$

where $d\Omega$ is the differential solid angle "centered" at **u**. Since the average in eq.(1) describes (partially at least) the molecular orientational situation at point **R**, it defines a tensorial order parameter. In the undistorted situation, by calling **n** the director of the nematic phase, it is $\langle \mathbf{uu} \rangle : \mathbf{nn} \propto S$, with S the usual scalar order parameter measuring the "molecular spread" around the director.

The extension of the classical Maier-Saupe mean-field potential to the distorted case is now worked out by considering the interactions between a test molecule at (**u**; **R**), and those falling within a suitable neighbourhood. The orientational distribution of the surrounding molecules changes from point to point within the neighbourhood, of course, because of the distortions. If the assumption is made that the distribution function varies slowly throughout the "active" neighbourhood, a series expansion of the distribution in the space variable **R** can be performed[11], and a drastic simplification follows. Indeed, a very simple expression for the mean-field potential is obtained in this case, which only involves the order parameter tensor **S**:

$$V(\mathbf{u};\mathbf{R}) = -kTU\left(\mathbf{S} + \ell^2\, \nabla^2 \mathbf{S}\right) : \mathbf{uu} \tag{2}$$

In eq.(2), kT is the Boltzmann factor, U the potential intensity, and ℓ a linear dimension characteristic of the chosen active neighbourhood, i.e., a characteristic interaction distance. (Different mean-field potentials can be obtained from other choices of the neighbourhood shape; see Marrucci and Greco[12].) Needless to say, eq.(2) properly reduces to the standard Maier-Saupe potential in the absence of spatial gradients.

Because we only deal with equilibrium situations, albeit distorted, f(**u**; **R**) must be a Boltzmann distribution. Equation (1) is then rewritten as:

$$\mathbf{S} = \frac{\int d\Omega\, \mathbf{uu} \exp[U\left(\mathbf{S} + \ell^2\, \nabla^2 \mathbf{S}\right) : \mathbf{uu}]}{\int d\Omega \exp[U\left(\mathbf{S} + \ell^2\, \nabla^2 \mathbf{S}\right) : \mathbf{uu}]} \tag{3}$$

(The denominator in eq.(3) is the normalization factor of the distribution.) The equilibrium problem is thus reduced to the problem of determining the tensor field **S**(**R**) which is the solution of eq.(3). It is worth remarking that eq.(3) is a self-consistency equation conceptually analogous to that used by Maier and Saupe for the undistorted case; the mathematics is much more complex when distortions are present, however, because of the *functional* character of the self-consistency in eq.(3).

A slight mathematical simplification is still possible by recognizing that the magnitude of the second term in eq.(2) must be small with respect to that of the first term. It is apparent that this order-of-magnitude estimate is linked to the already used assumption of expandibility of the distribution function, i.e., they are both valid (or both invalid) at the same time. As a matter of fact, for a given problem, validity of the expansion can only be justified afterwards, by looking at the actual solution. To proceed here, let us anyhow assume that the laplacian term in eq.(2) is small. We can then expand the term $\exp(U\ell^2\,\nabla^2\mathbf{S}:\mathbf{uu})$ in eq.(3) to obtain, after some calculations:

$$\mathbf{S} = \mathbf{P} + U\ell^2(\mathbf{Q} - \mathbf{PP}):\nabla^2\mathbf{S} \tag{4}$$

where:

$$\mathbf{P} = \frac{\int d\Omega\,\mathbf{uu}\exp(U\mathbf{S}:\mathbf{uu})}{\int d\Omega \exp(U\mathbf{S}:\mathbf{uu})} \tag{5}$$

$$\mathbf{Q} = \frac{\int d\Omega\,\mathbf{uuuu}\exp(U\mathbf{S}:\mathbf{uu})}{\int d\Omega \exp(U\mathbf{S}:\mathbf{uu})} \tag{6}$$

For any given U-value (i.e., for any given value of the scalar order parameter S at undistorted equilibrium), eq.(4) defines **S** implicitly, because **P** and **Q** are themselves **S**-dependent. Equation (4) is the general field equation of nematostatics, from which tensor field **S(R)** is obtained. Of course, specific boundary conditions must be assigned as well. Textured, defective situations can also be dealt with, because the tensor field **S(R)** is never discontinuous, contrary to what happens to the director field **n(R)**. Description of local anisotropy within defects is thus possible, and a "molecular" interpretation of defect cores can be given.

FREE ENERGY OF NEMATICS

Tensor field **S(R)** is the only unknown of the equilibrium problem, which must be determined by solving eq.(4). As already mentioned in the first Section, however, the deGennes approach to distorted equilibrium situations is also based on the introduction of a second-rank order parameter tensor as the descriptor of the local state of the nematics. The deGennes approach should then show many similarities to the one presented here. This Section and the next one are dedicated to illustrate these similarities and, more importantly, to stress the deep differences between these two formulations of nematostatics.

Let us consider the expression for the free-energy density A(**R**) in our "molecular-based" approach. Calling ν the number of molecules per unit volume, it is:

$$A(\mathbf{R}) \;=\; \nu\left[kT\left\langle \ln f(\mathbf{u};\mathbf{R})\right\rangle + \frac{1}{2}\left\langle V(\mathbf{u};\mathbf{R})\right\rangle\right] \tag{7}$$

Equation (7) is the standard form for free energy in a mean-field approximation[13]: the entropic contribution (the logarithmic term) is the one appropriate to a "free-particle" system, whereas the interaction term is simply one-half of the ensemble average of the single particle energy. The latter quantity being given by eq.(2), we have:

$$V(\mathbf{u};\mathbf{R}) \;=\; -kTU\left(\mathbf{S}:\mathbf{S} + \ell^2\,\mathbf{S}:\nabla^2\mathbf{S}\right) \tag{8}$$

The entropy density, $\left\langle \ln f(\mathbf{u};\mathbf{R})\right\rangle$, is also easily calculated, by recalling that f(**u**; **R**) is a Boltzmann distribution. The free energy density A(**R**) can thus be rewritten in terms of tensor **S**, as follows:

$$A(\mathbf{R}) = \nu kT\left[-\ln\left(\int d\Omega \exp(U\mathbf{S}:\mathbf{uu})\right) + \frac{U}{2}\mathbf{S}:\mathbf{S} + U\ell^2\left(\frac{1}{2}\mathbf{S} - \mathbf{P}\right):\nabla^2\mathbf{S}\right] \tag{9}$$

For future purposes of comparison with the phenomenological approach, let us rewrite the last term in eq.(9) in a different way. Since energy density expressions which give rise to volume integrals only differing by a surface contribution are in fact equivalent, we are allowed to integrate by parts the distortion free energy density in eq.(9), so as to obtain (indicial notation is needed here):

$$\left(\frac{1}{2}S_{ij} - P_{ij}\right)\partial_\alpha\partial_\alpha S_{ij} \;\approx\; -\frac{1}{2}\partial_\alpha S_{ij}\partial_\alpha S_{ij} + U\left(Q_{ijmn} - P_{ij}P_{mn}\right)\partial_\alpha S_{ij}\partial_\alpha S_{mn} \tag{10}$$

(Symbol ≈ means "equal to within surface terms", as explained above.) In eq.(10), the term containing **P** and **Q** (see eqs.(5) and (6), respectively) is nothing but a rewriting of $\nabla\mathbf{P}:\nabla\mathbf{S}$, which on its own comes from integration by parts of the very last term in eq.(9). We will presently show that the term $(Q_{ijmn}-P_{ij}P_{mn})\partial_\alpha S_{ij}\partial_\alpha S_{mn}$ is the true *mathematical source of distinction with respect to the phenomenological approach.*

COMMENTS ON THE CLASSICAL PHENOMENOLOGICAL APPROACH

Let us consider now the original free-energy density expression as it was given long ago by deGennes[2]:

$$\alpha(\mathbf{R}) = aS_{ij}S_{ji} + bS_{im}S_{mj}S_{ji} + c\left(S_{ij}S_{ji}\right)^2 + L\,\partial_\alpha S_{ij}\partial_\alpha S_{ij} \tag{11}$$

and let us first discuss the homogeneous case. The three initial terms in eq.(11) are meant to represent a "power series expansion" (near isotropy) of the order parameter tensor, but it has to be kept in mind that, ***unless some molecular theory is used as a basis to actually perform the expansion***, coefficients a, b, and c are in fact arbitrary quantities, to be fitted to data. On the other hand, if coefficients a, b, and c are calculated starting from a molecular theory, it often happens that the radius of convergence of the power series expansion is rather small when compared to the range of physically relevant values of the order parameter. Such is the case, e.g., for classical Maier-Saupe theory: the phenomenological approach already becomes invalid at "ordinary" values of the nematic order parameter[6].

More serious problems arise when considering distorted configurations *via* eq.(11). Indeed, since the coefficients of any phenomenological equation are material dependent, and the change in tensor **S** throughout a highly distorted nematics virtually corresponds to a "change of the material", coefficients a, b, c, and L in eq.(11) should themselves vary in space. In other words, coefficients a, b, c, and L in eq.(11) should be regarded as scalar functions of **S** (i.e., functions of the three scalar invariants of **S**). ***This is not usually the case***[3, 4, 5], however, which means that an inner contradiction undermines the theory, at least when it is applied to situations of nonlinear distortions.

In view of the conceptual importance of the considerations just made, let us discuss them further. In the original presentation of the phenomenological approach made by deGennes, it is clearly stated that eq.(11) only gives "the free energy density in the isotropic phase" (quoted from deGennes[2]). As a consequence, coefficients a, b, c, and L must be "evaluated" at isotropy, and are fixed once and for all. Use of eq.(11) is absolutely correct in this situation of "small deviations" from isotropy. When in a nematic state, eq.(11) is appropriate as well, *if* the assumption is made that only "weak distortions" are involved, which is the Frank elasticity asymptote of the theory. Indeed, in such a case it is:

$$\mathbf{S}(\mathbf{R}) = S_{eq}\left(\mathbf{n}(\mathbf{R})\mathbf{n}(\mathbf{R}) - \frac{1}{3}\mathbf{1}\right) + \frac{1}{3}\mathbf{1} \tag{12}$$

(**1** is the identity tensor), i.e., tensor **S** is uniaxial, and depends on position only through its principal eigenvector, the director **n**. From eq.(12) we have that scalar invariants of **S**, being expressible through the equilibrium order parameter S_{eq} only, are constant in space. Coefficients a, b, c, and L are thus constant in space, too, and use of eq.(11) is legitimate, with the already discussed *caveat* concerning the convergence of the power series.

It is now apparent why eq.(11) with constant coefficients cannot be used when large distortions occur, e.g., within defect cores. "Large" distortions imply a change in the "local material" with respect to the situation of the uniform state: the ellipsoid representing tensor **S** is then strongly deformed from its equilibrium shape, and *phenomenological coefficients are bound to vary*. Such a conclusion was already reached some years ago by Poniewierski and Sluckin[14], who also proposed that the constant coefficients in eq.(11) be replaced by invariant polynomial functions of the **S**-tensor. In this regard, however, it should be clearly understood that *from a phenomenological standpoint there is no hope of envisaging what the* **S***-dependence of the coefficients might be*. On the other hand, as eq.(10) shows, the functional form of these coefficients is easily worked out when starting from a molecular model. A molecular approach seems to the author the only effective way to tackle the difficult problem of nonlinear distortions without introducing new unknown parameters.

In concluding this Section, let us go back to the expression for free energy density in the context of a molecular approach, eq.(9), to stress again that: i) the only new parameter ℓ with respect to the undistorted case has the clear physical meaning of an interaction distance; ii) the **S**-dependence of the "coefficients" in eq.(9) (see eq.(10)) is dictated by the molecular model, with no further assumptions; iii) the self-consistency equilibrium equation, eq.(4), which of course can be derived from eq.(9), is in no way limited to small deviations from isotropy, or to small distortions of the nematic phase, and can thus be safely used to study defect cores.

A HINTED APPLICATION: NEMATIC IN A CYLINDRICAL GEOMETRY

Until today, the only explicit solution of eq.(4) which has been computed is the one for the simple case of the so-called ***hedgehog*** defect, i.e., the defect which is obtained if a spherical shell is filled with a nematic liquid crystal, and radial boundary anchoring for the director is assumed. In this case, a very symmetric configuration for the S-field is certainly possible, namely, the one corresponding to an r-dependent (r is the radial coordinate) uniaxial S everywhere:

$$\mathbf{S}(\mathbf{r}) = S(r)\left(\mathbf{rr}-\frac{1}{3}\mathbf{1}\right)+\frac{1}{3}\mathbf{1} \tag{13}$$

(**r** is the radial unit vector). The only unknown function in eq.(13) is the local order parameter S(r) around **r**. The calculated solution[11] shows that the ellipsoid of **S**, though remaining uniaxial, progressively deforms when entering the defect, to become spherical at the very center. The condition $S(r=0)=0$ means that the material becomes isotropic at the centerpoint, i.e., distortion is so large that the "natural" thermodynamic state of the material has been locally suppressed.

Interesting as these results may be, however, they are very specific to the hedgehog case. Indeed, for other types of defects, a complete isotropization is not plausible, though a marked decrease of the nematic order is surely expected; moreover, uniaxial symmetry is certainly lost while approaching a (non-hedgehog) defect core. The latter point is particularly relevant in what follows, since we are going to discuss a situation where ***biaxiality induced by the distortion*** is in fact the salient feature of the solution looked for.

Let us consider an (infinite) cylindrical shell filled with nematic. By indicating (with obvious notation) the unit vectors of the cylindrical geometry with **ρ**, **θ**, and **z**, tensor **S** will have the form:

$$\mathbf{S} = S_{\rho\rho}\boldsymbol{\rho\rho}+S_{\theta\theta}\boldsymbol{\theta\theta}+S_{zz}\mathbf{zz}+S_{\rho\theta}(\boldsymbol{\rho\theta}+\boldsymbol{\theta\rho})+S_{\rho z}(\boldsymbol{\rho}\mathbf{z}+\mathbf{z}\boldsymbol{\rho})+S_{\theta z}(\boldsymbol{\theta}\mathbf{z}+\mathbf{z}\boldsymbol{\theta}) \tag{14}$$

where, for the condition of unit trace to hold:

$$S_{\rho\rho}+S_{\theta\theta}+S_{zz} = 1 \tag{15}$$

In view of the symmetries, we impose that all the scalar functions S_{ij} do not depend on θ. We also assume that nothing depends on "altitude" z, and are thus left with five unknown functions of the radial variable ρ only. Since the problem still remains complex, however, and the purpose here is merely that of indicating how to proceed from the general equation towards the solution of a specific case, we make the additional assumption that the eigenvectors of tensor **S** everywhere coincide with the unit vectors of the cylindrical geometry. We can then write:

$$\mathbf{S} = S_{\rho\rho}(\rho)\rho\rho + S_{\theta\theta}(\rho)\theta\theta + S_{zz}(\rho)\mathbf{zz} \tag{16}$$

and, because of eq.(15), the problem is now reduced to the determination of two functions of the radial variable only.

It is worth remarking that the hypothesis made in writing down eq.(16) is a rather strong one. Suffice to say that no configuration of the nematics which is "escaped in the third direction" can be described by a tensor field **S** in the form of eq.(16). On the other hand, escaped configurations are believed to be favoured in a cylindrical capillary with either homeotropic or parallel boundary conditions[15], because they avoid the formation of an "energetically expensive" defect line along the capillary axis. Thus, by adopting eq.(16) we are solving a constrained equilibrium problem, and the solutions we are going to look for might not be the minimum energy solutions.

Differential equations for the functions $S_{\rho\rho}(\rho)$ and $S_{\theta\theta}(\rho)$ (for example) are readily derived from the general equation of nematostatics, eq.(4). First, tensor **S** from eq.(16) is substituted into eq.(4); the resulting equation is then scalarly multiplied by the dyads $\rho\rho$ and $\theta\theta$, respectively. A system of coupled equations is obtained, in the form:

$$\begin{cases} \dfrac{d^2S_{\rho\rho}}{d\rho^2} + \dfrac{1}{\rho}\dfrac{dS_{\rho\rho}}{d\rho} = F\left(S_{\rho\rho}, S_{\theta\theta}, \rho\right) \\[2ex] \dfrac{d^2S_{\theta\theta}}{d\rho^2} + \dfrac{1}{\rho}\dfrac{dS_{\theta\theta}}{d\rho} = G\left(S_{\rho\rho}, S_{\theta\theta}, \rho\right) \end{cases} \tag{17}$$

where the derivatives on the left-hand-side just give the laplacian operator in cylindrical coordinates, and F and G are very complex, yet known functions[16]. Actual solution of eq.(17) of course requires that tensor **S** be assigned on the cylinder surface.

Work is in progress to obtain solutions corresponding to various boundary conditions, and the results will be reported elsewhere[16]. We want only to describe here the very nice outcome of some preliminary calculations for the case of parallel boundary conditions, i.e., when the nematic field "at infinity" is tangential to the cylinder surface (and orthogonal to the cylinder axis). By going towards the cylinder axis, the computed solution becomes increasingly biaxial, up to a critical radius where *the principal eigenvector of tensor* **S** *switches from* **θ** *to* **z**; below this critical radius, tensor field progressively loses its biaxiality, to become uniaxial again (as it must be for symmetry reasons) on the cylinder axis, where $S_{zz} > S_{\rho\rho} = S_{\theta\theta}$. Thus, in a sense, a "molecular escape in the third direction" has occurred also in our constrained case, whereby the director close to the cylinder axis is vertical.

SUMMARY AND CONCLUSION

Classical continuum mechanical theory of nematics[1] cannot account for defects. In the current literature, there are two formulations of nematostatics inclusive of defects: the classical deGennes "analytic" approach[2], and the more recent numerical one, based on Monte Carlo simulations[7]. We have summarized here a third approach[11] which, though based on statistical mechanics, results in an analytic field equation. A detailed comparison with the classical phenomenological picture has been presented, to stress the merits (in our opinion) of the molecularly-based approach. Actual solutions of the field equation for specific cases have also been hinted to, which can be obtained with an enormously lower amount of numerical work than the simulation results. In conclusion, we believe that the proposed approach supplies us with new promising tools to face the very difficult problem of determining the internal structure of defect cores.

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