

Orientational Mechanisms in Liquid Crystalline Systems. 1. A Reaction Field Analytical Description of the Interaction between the Electric Quadrupole Moment of a Probe Solute and the Electric Field Gradient of a Nematic Solvent

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In the present paper, the fundamental problem of calculating the electric field gradient (EFG) experienced by a highly idealized solute, represented by a general point quadrupole immersed in an anisotropic uniaxial medium, has been tackled. Following a generalized reaction field approach (based upon the original ideas and the “mean-field philosophy” due to Kirkwood and Onsager) in the linear response approximation, a closed analytical expression of the EFG has been derived (to the best of our knowledge, for the first time). The obtained expression is particularly simple and elegant, also thanks to the oversimplifying approximation that the virtual cavity containing the solute is assumed to be perfectly spherical. This compact and manageable formula, obtained by a rigorous mathematical derivation (unlike other mean-field phenomenological models previously suggested in literature) can be useful to investigate and better understand a likely orientational mechanism, partly responsible for the ordering of small solutes dissolved in nematic mesophases, based on the interaction between the electric quadrupole of the solute and the electric field gradient of the anisotropic uniaxial medium (in the next paper of this issue, the formulation obtained in this work is widely tested on a variety of uniaxial and biaxial solutes dissolved in different nematic solvents).

1. Introduction

The property of orientational ordering represents the peculiar feature of liquid crystalline systems, and the full understanding of the underlying mechanisms is very important both for theoretical advancements and for technological applications in a host of fields. An effective way to study the ordering is the NMR spectroscopy of small probe molecules dissolved in liquid crystalline (typically, nematic) solvents¹ (henceforth, we will shortly denote this technique by the acronym LXNMR). Starting from a mean-field interpretation of the LXNMR-obtained order parameters of several small solutes in a certain number of different nematic solvents, it has been recently formulated the ansatz that just two independent mechanisms are sufficient to rationalize the ordering phenomena.² As a matter of fact, it is quite usual (and has been for a long time) to adopt the approximation of describing the anisotropic orientational potential $U(\Omega)$ (where $\Omega \equiv (\beta, \gamma)$ represents the set of Eulerian angles defining the orientation of the nematic director, fixing the Z axis of the laboratory, in the solute reference system; see Figure 1) as a sum of two contributions,³ a short-range term $U_{\text{sr}}(\Omega)$ (accounting for size and shape interactions and commonly recognized as dominant,^{4a} at least for solutes larger than H_2) and a second, longer-range potential $U_{\text{lr}}(\Omega)$, whose nature and role is not completely understood until now.

Several mechanisms (based on electrostatic, induction, and dispersion effects; see, for example, refs 3–8 and references therein) have been suggested (and often contradicted^{8,9}) as responsible for this second contribution to the orientational ordering. One of the most known hypotheses (based on the Buckingham multipole expansion approach⁴) involves the interaction between the electric quadrupole moment of the solute

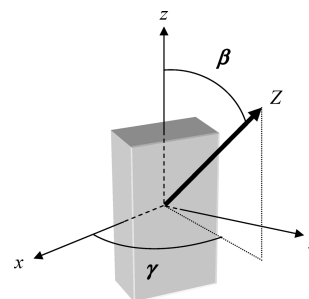


Figure 1. Orientation of the director in the frame of a biaxial solute, schematically represented as a gray parallelepiped.

(expressed by the tensor \mathbf{Q}) and the (only nominal?) electric field gradient (EFG) of the solvent.^{4,10} As a matter of fact, a molecule possessing a quadrupole moment interacts with a possibly present electric field gradient according to the following formal equation¹⁰

$$U_{\text{Q-EFG}} = -\frac{1}{3} \sum_{A,B=X,Y,Z} Q_{AB} F'_{AB} \quad (1)$$

where F'_{AB} are the components of the electric field gradient tensor. For a uniaxial medium (e.g., a nematic solvent) described in a LABoratory coordinate system (subscripts in capital letters) where the Z axis is along the mesophase director, $F'_{AB} = 0$ when $A \neq B$, and in order to satisfy simultaneously symmetry requirements and Laplace's equation, one must have

$$F'_{XX} = F'_{YY} = -\frac{1}{2} F'_{ZZ} \quad (2)$$

Then, under these conditions, the only independent element is F'_{ZZ} . Assuming F'_{ZZ} is an exclusive property of the solvent is a sufficient condition to maintain that this term does not depend

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on the pair of Eulerian angles (β, γ) , and it can be decoupled in eq 1. Moreover, by exploiting eq 2 and the traceless nature of \mathbf{Q} , eq 1 can be rewritten as

$$U_{\mathbf{Q}-\text{EFG}}(\beta, \gamma) = -\frac{1}{2}F'_{ZZ}\left[Q_{zz}P_2(\cos \beta) + \sqrt{\frac{2}{3}}\Delta Q\text{Re}[C_{22}(\beta, \gamma)]\right] \quad (3)$$

where the small subscripts indicate the coordinates in the MOlecular PAS (principal axis system) of the \mathbf{Q} tensor, $\Delta Q = Q_{xx} - Q_{yy}$, $P_2(\cos \beta)$ is the second-order Legendre polynomial, $C_{22}(\beta, \gamma)$ represents a modified spherical harmonic,¹¹ and $\text{Re}[C_{22}(\beta, \gamma)] = (3/8)^{1/2} \sin^2 \beta \cos(2\gamma)$ is its real part. The approach of assuming $U_{\text{ir}}(\Omega) \equiv U_{\mathbf{Q}-\text{EFG}}(\beta, \gamma)$ has been quite successful in the past, for its simplicity and practical implications (simply, the value of the parameter F'_{ZZ} can be optimized in order to reproduce as well as possible experimental data), but it was also debated and criticized for its naïveté and conceptual weakness.^{7c,8,9} Actually, the description is only phenomenological; there is no guarantee that F'_{ZZ} represents the real (if any) EFG present in the solvent and experienced by the solute. It could be also considered just as an ad hoc parameter (not necessarily related to some physical property of the solvent) needed to reproduce the data. Despite its clear limitations, the crude model of “ \mathbf{Q} –EFG” coupling is describing the main long-range orientational interaction allowed for the very useful creation of the so-called “zero-EFG” nematic mixtures (nicknamed magic mixtures^{4a}), where the practical experience shows that the ordering of the solutes (also larger than H_2) can be predicted (within a 10% of error) by taking into account only short-range orientational interactions^{4,12,13} (recently, new possible magic mixtures have been conjectured,¹⁴ and an effective relationship between the so-called EFG and the dielectric properties of the solvent has been obtained in an approximated way¹⁵). On the other hand, as said above, the very simple hypothesis that the \mathbf{Q} –EFG mechanism is mainly responsible for long-range orientational effects suffers from manifest flaws, and different criticisms have been raised in the past; (1) there is incontrovertible theoretical,¹⁶ experimental,^{6b,12,13} and computer simulation evidence^{17,18} that the so-called EFG is not an exclusive property of the solvent but that it depends also on the solute (in ref 15, this dependence has been obtained explicitly); (2) the value (and sometimes the sign) of the EFG obtained from LXNMR data of small solutes dissolved in a given nematic solvent often disagrees with results from NMR of noble gas isotopes dissolved in the same solvent;⁹ and (c) in dense systems, the convergence of the multipole expansion for the shortest solute–solvent distances represents a serious problem, and it should be taken into consideration^{4a,19a} (a study about polar and apolar solutes in nematic solvents indicates that electrostatic contributions are operative over very short intermolecular distances;^{7c} under this point of view, also, the “long-range” definition conventionally given to these orientational interactions could be questioned). In MC simulations, this fact suggested the idea of using distributed quadrupoles for the particles involved¹⁹ (the choice was taken also because the MC simulations by using particles with central-point quadrupoles were not able to predict the negative-order parameter experimentally found for acetylene dissolved in the EBBA nematic mesophase^{19a}). All of the points listed above are not necessarily independent; besides, some of them clearly depend on the strategic choice of adopting the simple and attractive (but sometimes, probably, too crude) “mean-field philosophy”, where the solvent is described as a continuum and any specification

concerning the molecular features of the single molecules of the solvent (shape and/or charge distribution) as well as orientational correlations between the probe and the solvent molecules is lacking.⁸ Intrigued by all of this contradictory evidence and looking for a reliable (at least, theoretically) point of reference to shed more light on the open questions, we decided to try to solve, in a general way (starting from the first principles of classical electrostatics²⁰), the fundamental problem of calculating the electric field gradient experienced by a highly idealized solute (represented by the equivalent series of point multipoles defined at a center²¹) immersed in an anisotropic uniaxial medium fully characterized by its dielectric tensor. In the case of a nonionic and apolar solute, we deal (in a first approximation) with a point quadrupole (fully characterized by its tensor \mathbf{Q}) positioned at the center of a spherical (for simplicity) cavity of radius R (strictly speaking, in this description, the quadrupolar solute is just a point singularity of the electric field²²). We tackle the problem by using the generalized reaction field (RF) model^{3,15,23} (based upon the original ideas of Kirkwood²⁴ and Onsager²²) in the linear response approximation²⁵ (LRA). There exist in literature studies about dipole-induced reaction fields in anisotropic media, also for nonspherical cavities (see, for example, refs 19–23 of ref 15); anyway, to the best of our knowledge, the general analytical problem of deriving the quadrupole-induced reaction field and its gradient in anisotropic media has never been solved before (in ref 15, just an approximated solution of the quadrupolar reaction tensor for the particular case of an axial quadrupole, representing the H_2 molecule, in a uniaxial environment is reported). By exploiting the theoretical apparatus developed in ref 25 to study the solvation in nematic phases comprised of polar mesogenic molecules and by resorting the mathematical technique of working in the reciprocal (Fourier-transformed) space, we have been successful in solving this fundamental problem in a close, quite elegant form. The obtained formulas will be used to calculate the $U_{\text{ir}}(\Omega)$ contribution for real cases (regarding both uniaxial and biaxial solutes in different nematic solvents; see ref 33), where long-range orientational effects appear to be particularly significant;^{10,12a,13,19} the theoretical predictions will be compared with experimental results to gather (if possible) useful hints about the general problem of orientational interactions.

2. Theoretical Results and Discussion

An effective, physical description of the concept of the reaction field is given in ref 26, where the reaction field of a molecule M is defined as the field produced at M by the surrounding medium which is polarized by M . In this definition, the solvent is implicitly considered as a polarizable continuum, and the electrostatic interaction between the medium and the solute charge distribution is expressed in terms of an electrostatic field having its origin in the polarization of the dielectric.²⁷ This concept was originally introduced by Onsager in his seminal paper²² concerning the case of a polar solute (ideally described as a point dipole in a spherical cavity) within a polarizable medium characterized by its dielectric constant ϵ . Actually, the RF model can be generalized to take into account interactions involving higher-order terms in the multipole expansion of the molecular charge distribution.²³ The RF model has been already used in describing the long-range orientational interactions experienced by small solutes dissolved in nematic solvents;^{3,5,15} the cited studies are basically phenomenological³ or limited to a particularly simple case (by adopting strong approximations)¹⁵ or carried out by effective but, unfortunately, complicated and computationally heavy numerical techniques. A rigorous, ana-

lytical approach to the generalized problem and, in particular, to the determination of the so-called EFG experienced by the solute in the nematic solvent is still lacking. In this paper, we tried to fill this gap by calculating (within a generalization of the Onsager's conceptual approach) the EFG experienced by a nonionic and apolar solute in a uniaxial medium fully characterized by its dielectric tensor. We considered a highly idealized solute represented by a point quadrupole at the center of a spherical cavity of radius R , and as said above, we tackled the problem by using the generalized RF model in the LRA.²⁵ The starting point of the mathematical derivation is represented by eq 19 of ref 25 (reported below as eq 4) giving the field $\mathbf{F}_o(\mathbf{r})$

$$\mathbf{F}_o(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{r}} \tilde{\mathbf{E}}_o(\mathbf{k}) \cdot \tilde{\chi}''(\mathbf{k}) \quad (4)$$

In this expression, \mathbf{r} represents the direct space; $\tilde{\mathbf{E}}_o(\mathbf{k})$ is the electric field (expressed in the reciprocal \mathbf{k} space) generated by the charge distribution representing the solute (henceforth, the tilde (\sim) symbol will distinguish the \mathbf{k} -depending physical quantities and the subscript σ will refer to the solute); the response function $\tilde{\chi}''(\mathbf{k})$ is given by²⁵

$$\tilde{\chi}''(\mathbf{k}) = \tilde{\chi}_\Sigma(\mathbf{k}) \cdot [\tilde{\chi}_\Sigma(\mathbf{k}) - \tilde{\chi}'(\mathbf{k})]^{-1} \quad (5)$$

where

$$\tilde{\chi}'(\mathbf{k}) = \int_\Omega d\mathbf{r} \chi_\Sigma(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (6)$$

The integration above is over the volume Ω formed by excluding from the liquid the volume hindered by the solute (which is twice the volume of the solute for spherical solutes but has a quite complex shape dependence for nonspherical solutes;²⁵ this is the reason why, in the following, we will assume for simplicity our solutes as spherical; moreover, the volume excluded in the integration will be pragmatically considered as the volume of the virtual cavity containing the solute); finally, the terms $\chi_\Sigma(\mathbf{r})$ and $\tilde{\chi}_\Sigma(\mathbf{k})$ in eq 5 represent the dipolar susceptibility of the pure solvent (symbolized by the subscript Σ) in the direct and reciprocal space, respectively. In their work cited in ref 25, the authors claim that “the field $\mathbf{F}_o(\mathbf{r})$ is a generalization of the reaction field, introduced by Onsager for a point dipole, to an arbitrary configuration of solute charges in a solute of arbitrary shape”.²⁵ In the same work, they showed that $\mathbf{F}_o(\mathbf{r})$ reduces to the expected limits in the case of spherical ionic and dipolar solutes;²⁵ however, the case of a solute described as a spherical point quadrupole is not treated. In the present paper, we decided to extend the treatment to this case and to exploit the mathematical apparatus given in ref 25 to obtain first $\mathbf{F}_o(\mathbf{r})$ and then the derivative with respect to Z of its Z component; this led to F'_{ZZ} , that is, the ZZ component of the electric field gradient tensor (also called EFG in this paper), in which we are interested. Since the complete derivation is very long (the interested reader is referred to the Appendix, where it is given in detail), in the following, we will give directly the final results; however, a few considerations are in order before. Although the mathematics is quite cumbersome and complicated, the result can be fortunately given in a closed, quite elegant form (see the following eq 7); however, we feel compelled to recall that the derivation has been carried out by adopting the very crude assumption that the virtual cavity containing the solute is perfectly spherical, hoping that the outcomes are sensible and the hints not completely compromised by this strong approximation. On the other hand, different, more realistic shapes of the cavity lead to about insuperable analytical complications. Of course, the problem could be tackled by a

numerical approach, but this is beyond the purpose of the present work, which is, on the contrary, aimed to produce a manageable formulation (able, if possible, to catch the essence of the phenomenon under consideration). Finally, the obtained expression for F'_{ZZ} is the following (see Appendix for details)

$$F'_{ZZ}(\beta, \gamma) = \pm \frac{6\pi}{R^5 \epsilon_0} \left(\frac{\Delta\epsilon}{\epsilon_{||}(1 - \epsilon_\perp + (\epsilon_{||} - 1)\Psi)} - \frac{3}{1 + 2\epsilon_s} \right) \times \left[Q_{zz} P_2(\cos \beta) + \sqrt{\frac{2}{3}} \Delta Q \text{Re}[C_{22}(\beta, \gamma)] \right] \quad (7)$$

where ϵ_0 is the vacuum permittivity, $\epsilon_{||}$ and ϵ_\perp are the parallel and perpendicular components (with respect to the nematic director) of the axially symmetric dielectric constant of the medium, $\Delta\epsilon = \epsilon_{||} - \epsilon_\perp$, $\epsilon_s = (\epsilon_{||} + 2\epsilon_\perp)/3$ (in the isotropic limit, $\epsilon_{||} = \epsilon_\perp = \epsilon_s \equiv \epsilon_{iso}$), R is the radius of the virtual spherical cavity containing the solute, and Ψ is given by²⁵

$$\Psi = \int_0^1 \frac{dz}{1 + (\epsilon_{||}/\epsilon_\perp - 1)z^2} = \begin{cases} \arctan \sqrt{\epsilon_{||}/\epsilon_\perp - 1} / \sqrt{\epsilon_{||}/\epsilon_\perp - 1} & \epsilon_{||} > \epsilon_\perp \\ 1 & \epsilon_{||} = \epsilon_\perp \\ \ln \left(\frac{1 + \sqrt{1 - \epsilon_{||}/\epsilon_\perp}}{1 - \sqrt{1 - \epsilon_{||}/\epsilon_\perp}} \right) / (2\sqrt{1 - \epsilon_{||}/\epsilon_\perp}) & \epsilon_{||} < \epsilon_\perp \end{cases} \quad (8)$$

(for the meaning of the symbols $P_2(\cos \beta)$ and $C_{22}(\beta, \gamma)$ in eq 7, see eq 3). The sign \pm in eq 7 means that it is impossible, in principle, to discriminate a priori between two possible mathematical solutions for $F'_{ZZ}(\beta, \gamma)$. This is because at the nematic–isotropic transition temperature $T = T_{NI}$ (where F'_{ZZ} has to vanish in order to satisfy simultaneously Laplace's equation and the isotropic symmetry requirement $F'_{XX} = F'_{YY} = F'_{ZZ}$), the following “isotropic” boundary condition holds (where the absolute value is involved)

$$\lim_{\epsilon_{||} \rightarrow \epsilon_\perp} \left| \left(\frac{\Delta\epsilon}{\epsilon_{||}(1 - \epsilon_\perp + (\epsilon_{||} - 1)\Psi)} - \frac{3}{1 + 2\epsilon_s} \right) \right| = 0 \quad (\text{in the isotropic limit, } \epsilon_{||} = \epsilon_\perp = \epsilon_s \equiv \epsilon_{iso}) \quad (9)$$

The “right” (i.e., physically sensible) solution will be therefore determined from time to time in order to make consistent the results (see ref 33, where the formula is tested on several cases). Looking at eq 7, it is worthwhile emphasizing that we obtained an expression of the EFG depending on the orientation (β, γ) of the solute. This is an expected (and reasonable) consequence of the fact that we adopted the RF approach to describe the phenomena; the reaction field (and its derivatives) induced along the director by the solute when it has a certain orientation (β_1, γ_1) can be, in principle, different from that originating from the same solute at a different orientation (β_2, γ_2). By introducing eq 7 into eq 3, we obtain the following expression for the mean-field anisotropic orientational potential U_{Q-EFG}

$$U_{Q-EFG}(\beta, \gamma) = \mp \frac{3\pi}{R^5 \epsilon_0} \left(\frac{\Delta\epsilon}{\epsilon_{||}(1 - \epsilon_\perp + (\epsilon_{||} - 1)\Psi)} - \frac{3}{1 + 2\epsilon_s} \right) \times \left[Q_{zz} P_2(\cos \beta) + \sqrt{\frac{2}{3}} \Delta Q \text{Re}[C_{22}(\beta, \gamma)] \right]^2 \quad (10)$$

Some more comments about the already discussed appearance of the sign \pm (which reflects itself in eq 10) are now required. We are unable to conclude, at the moment, if this sign

independence is a consequence of the “spherical cavity” assumption and/or if it is intrinsic to the used RF methodology. Anyway, this outcome can be exploited to overcome the following criticism (raised in ref 2 for the conceptual approach involving the interaction between the solute quadrupole and the “reaction EFG”); since the formulas obtained by this approach involve the square of the solute quadrupole, its sign is lost. Now, the found “physiological” sign independence leaves us free to determine the proper sign of eq 10, according to the physical consistency of the predicted results. The right sign could be (hopefully) rationalized a posteriori and, if possible, related to the original sign of the solute’s quadrupole (so that, in practice, a sort of “memory” of the sign is kept) and/or to some dielectric characteristic of the solvent. This peculiar aspect of the problem will be treated in detail in ref 33.

3. Conclusions

In the present paper, a compact analytical expression for the anisotropic orientational potential U_{Q-EFG} experienced by a general highly idealized quadrupolar solute in a uniaxial phase has been derived in a rigorous (although simplified) mathematical way by following the LRA-RF approach. In our opinion, this result is important for two main reasons; (1) from a purely theoretical point of view, the problem of determining the electric field gradient $F'_{ZZ}(\beta, \gamma)$ in a closed form had never been solved before (although, as said above, the spherical cavity approximation represents a considerable simplification of the analytical problem); (2) from a practical point of view, we think the expression that we found for U_{Q-EFG} is a simple and, at the same time, effective tool of investigation (of course, within the physiological limitations ingrained with the mean-field “way of thinking”). Unlike other phenomenological models previously suggested in the literature (where the physical interpretation of the interactions is only qualitative, sometimes not completely convincing, and, as a consequence, open to criticisms), our physically well-founded formulation, although oversimplified in the shape of the cavity, can be useful in interpreting and better understanding the real nature and the role of orientational mechanisms in liquid crystals. Of course, the approximations and the assumptions adopted in order to make analytically possible the mathematical derivation can restrict the breadth of applicability of the derived expressions. In the next paper,³³ we will show this formula “in action” in predicting the long-range contribution to the ordering of a variety of uniaxial and biaxial solutes dissolved in different nematic solvents whose experimental order parameters are available from the literature.

Appendix

Mathematical Derivation of Equation 7. As stated in the main body of the paper, we decided to exploit the mathematical apparatus given in ref 25 to obtain first the field $\mathbf{F}_o(\mathbf{r})$ given by eq 4 of the text (the equation is recalled below for convenience)

$$\mathbf{F}_o(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k} \cdot \mathbf{r}} \tilde{\mathbf{E}}_o(\mathbf{k}) \cdot \tilde{\chi}''(\mathbf{k}) \quad (4a)$$

Following V. Kapko and D. V. Matyushov, $\mathbf{F}_o(\mathbf{r})$ is “a generalization of the reaction field, introduced by Onsager for a point dipole, to an arbitrary configuration of solute charges”.²⁵ Once we have $\mathbf{F}_o(\mathbf{r})$, then the derivative with respect to Z of the Z component of the reaction field can be calculated; this

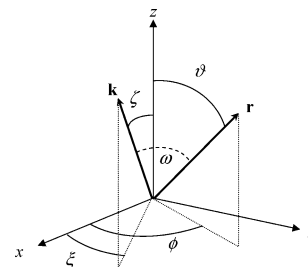


Figure A1. Absolute and relative orientation of the vectors \mathbf{r} and \mathbf{k} in the \mathbf{Q} PAS.

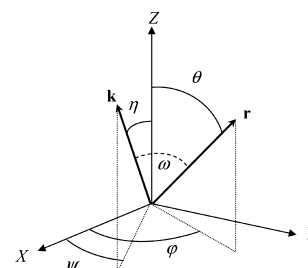


Figure A2. Absolute and relative orientation of the vectors \mathbf{k} and \mathbf{r} in the LAB frame.

leads to $F'_{ZZ}(\mathbf{r})$, that is, the ZZ component of the electric field gradient tensor, in which we are interested

$$F'_{ZZ}(\mathbf{r}) = \frac{\partial F_{\sigma_z}(\mathbf{r})}{\partial Z} \quad (A1)$$

In order to carry out what was planned above, we need the ingredients of eq 4. As a first step, we calculated $\tilde{\mathbf{E}}_o(\mathbf{k})$ starting from the potential in vacuo (subscript 0) V_0^Q generated by a quadrupolar distribution of point charges

$$V_0^Q = \frac{1}{8\pi\epsilon_0} \sum_{k,l} \frac{x_k x_l}{r^5} Q_{kl} \quad (A2)$$

where ϵ_0 is the vacuum permittivity, the x_i coordinates refer to the point r where the potential is calculated, and the electric quadrupole moment Q_{kl} of the system of N charges q_j is given by

$$Q_{kl} = \sum_{j=1}^N q_j (3\xi_k^j \xi_l^j - \delta_{kl} \rho_j^2) \quad (A3)$$

with the coordinates ξ_m^j giving the position ρ_j of the j th charge. Following the first principles of electrostatics, we can now write that the electric field $\mathbf{E}_o(\mathbf{r})$ produced by the solute (considered as a quadrupolar distribution of charges) as simply

$$\mathbf{E}_o(\mathbf{r}) = -\nabla V_0^Q \quad (A4)$$

and the searched $\tilde{\mathbf{E}}_o(\mathbf{k})$ is given by the relation²⁵

$$\tilde{\mathbf{E}}_o(\mathbf{k}) = \int_{\Omega} \mathbf{E}_o(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} \quad (A5)$$

where the integration is over the solvent volume Ω excluding the space occupied by the solute.

For the sake of convenience, we chose to work in the PAS of the \mathbf{Q} tensor and to give the components of the electric field $\mathbf{E}_o(\mathbf{r})$ in spherical polar coordinates (r, ϑ, ϕ) ; see Figure A1 also for the definition of the spherical variables of \mathbf{k} .

This leads to the following expressions

$$\begin{aligned}
E_{\sigma_x}(\mathbf{r}) &= \frac{\sin \vartheta \cos \phi}{8\pi\epsilon_0 r^4} [Q_{xx}(5 \sin^2 \vartheta \cos^2 \phi - 2) + 5Q_{yy} \sin^2 \vartheta \sin^2 \phi + 5Q_{zz} \cos^2 \vartheta] \\
E_{\sigma_y}(\mathbf{r}) &= \frac{\sin \vartheta \sin \phi}{8\pi\epsilon_0 r^4} [5Q_{xx} \sin^2 \vartheta \cos^2 \phi + Q_{yy}(5 \sin^2 \vartheta \sin^2 \phi - 2) + 5Q_{zz} \cos^2 \vartheta] \\
E_{\sigma_z}(\mathbf{r}) &= \frac{\cos \vartheta}{8\pi\epsilon_0 r^4} [5Q_{xx} \sin^2 \vartheta \cos^2 \phi + 5Q_{yy} \sin^2 \vartheta \sin^2 \phi + Q_{zz}(5 \cos^2 \vartheta - 2)]
\end{aligned} \tag{A6}$$

Moreover, by exploiting the so-called Rayleigh expansion²⁸ in the form given in ref 29, we can write

$$e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ia(\cos \omega)} = \sum_{L=0}^{\infty} (2L+1) i^L j_L(a) P_L(\cos \omega) \tag{A7}$$

where $a = |\mathbf{k}| |\mathbf{r}| = kr$, ω is the angle between the directions of \mathbf{k} and \mathbf{r} (see Figure A1), $j_L(a)$ is a spherical Bessel function of the first kind,³⁰ and $P_L(\cos \omega)$ the Legendre polynomials.³⁰ By introducing eqs A6 and A7 into eq A5, we obtain the following expressions

$$\left. \begin{aligned}
\tilde{E}_{\sigma_x}(\mathbf{k}) &= \frac{1}{8\pi\epsilon_0} \int_{\phi=0}^{2\pi} \int_{\vartheta=0}^{\pi} \int_{r=R}^{\infty} \left(\sum_{L=0}^{\infty} (2L+1) i^L j_L(a) P_L(\cos \omega) \right) \frac{\sin \vartheta \cos \phi}{r^2} \cdot [Q_{xx}(5 \sin^2 \vartheta \cos^2 \phi - 2) + 5Q_{yy} \sin^2 \vartheta \sin^2 \phi + 5Q_{zz} \cos^2 \vartheta] \sin \vartheta dr d\vartheta d\phi \\
\tilde{E}_{\sigma_y}(\mathbf{k}) &= \frac{1}{8\pi\epsilon_0} \int_{\phi=0}^{2\pi} \int_{\vartheta=0}^{\pi} \int_{r=R}^{\infty} \left(\sum_{L=0}^{\infty} (2L+1) i^L j_L(a) P_L(\cos \omega) \right) \frac{\sin \vartheta \sin \phi}{r^2} \cdot [5Q_{xx} \sin^2 \vartheta \cos^2 \phi + Q_{yy}(5 \sin^2 \vartheta \sin^2 \phi - 2) + 5Q_{zz} \cos^2 \vartheta] \sin \vartheta dr d\vartheta d\phi \\
\tilde{E}_{\sigma_z}(\mathbf{k}) &= \frac{1}{8\pi\epsilon_0} \int_{\phi=0}^{2\pi} \int_{\vartheta=0}^{\pi} \int_{r=R}^{\infty} \left(\sum_{L=0}^{\infty} (2L+1) i^L j_L(a) P_L(\cos \omega) \right) \frac{\cos \vartheta}{r^2} \cdot [5Q_{xx} \sin^2 \vartheta \cos^2 \phi + 5Q_{yy} \sin^2 \vartheta \sin^2 \phi + Q_{zz}(5 \cos^2 \vartheta - 2)] \sin \vartheta dr d\vartheta d\phi
\end{aligned} \right\} \tag{A8}$$

R being the radius of the virtual cavity containing the solute. The Rayleigh expansions in eq A8 should be, in principle, constituted by an infinite series of terms; however, the terms corresponding to $L = 0$ and 2 vanish due to their symmetry, and the term for $L = 1$ is null because it has as a factor the trace of \mathbf{Q} , which is a traceless tensor. Moreover, it is possible to verify that the terms for $L > 3$ are identically null; therefore, the only term which survives in the expansion is that corresponding to $L = 3$. The integrals of eq A8 can then be solved exactly (the calculations have been carried out by Mathematica 7 package³¹) to obtain finally the following compact result

$$\tilde{\mathbf{E}}_o(\mathbf{k}) = i\Lambda(kR)\mathbb{W}\mathbf{k} \tag{A9}$$

where the notation $\Lambda(kR)$ represents the following term (depending only on the magnitude of the \mathbf{k} vector and parametrized by R)

$$\Lambda(kR) = \frac{3kR \cos(kR) + ((kR)^2 - 3) \sin(kR)}{4\epsilon_0(kR)^5} = -\frac{j_2(kR)}{4\epsilon_0(kR)^2} \tag{A10}$$

with $j_2(kR)$ as the second-order spherical Bessel function of the first kind,³⁰ whereas the elements of the diagonal matrix $\mathbb{W}_{ab} = W_a \delta_{ab}$ of eq A9 are the following

$$\begin{aligned}
W_1 \equiv W_{k_x} &= 2 \left[5 \left(Q_{zz} P_2(\cos \xi) + \sqrt{\frac{2}{3}} \Delta Q \operatorname{Re}[C_{22}(\xi, \xi)] \right) + Q_{zz} - \Delta Q \right] \\
W_2 \equiv W_{k_y} &= 2 \left[5 \left(Q_{zz} P_2(\cos \xi) + \sqrt{\frac{2}{3}} \Delta Q \operatorname{Re}[C_{22}(\xi, \xi)] \right) + Q_{zz} + \Delta Q \right] \\
W_3 \equiv W_{k_z} &= 2 \left[5 \left(Q_{zz} P_2(\cos \xi) + \sqrt{\frac{2}{3}} \Delta Q \operatorname{Re}[C_{22}(\xi, \xi)] \right) - 2Q_{zz} \right]
\end{aligned} \tag{A11}$$

(the correspondences $W_1 \equiv W_{k_x}$, $W_2 \equiv W_{k_y}$, and $W_3 \equiv W_{k_z}$ have been added in eq A11 in order to better clarify which element of the \mathbb{W} matrix should be properly multiplied by the corresponding component of the \mathbf{k} vector in eq A9). The result of eq A9 has been obtained (as already specified above) by working in the PAS. Of course, in order to exploit eq 4 of the paper to find the desired $\mathbf{F}_o(\mathbf{r})$ reaction field experienced by the solute, we need the expression of the $\tilde{\mathbf{E}}_o(\mathbf{k})$ in the LAB frame. To do this, we have to proceed to the following transformation

$$[\tilde{\mathbf{E}}_o(\mathbf{k})]_{\text{LAB}} = \mathbf{R}[\tilde{\mathbf{E}}_o(\mathbf{k})]_{\text{PAS}} \tag{A12}$$

where \mathbf{R} is the rotation matrix relating the PAS to the LAB. Due to the uniaxiality of the nematic mesophase, the rotation matrix \mathbf{R} is effectively dependent only on the couple of the Eulerian angle (β, γ) (see Figure 1 of the paper), that is, $\mathbf{R} \equiv \mathbf{R}(\beta, \gamma)$. Moreover, since $\Lambda(kR)$ is an invariant, eq A12 can be usefully rewritten in the following form

$$[\tilde{\mathbf{E}}_o(\mathbf{k})]_{\text{LAB}} = i\Lambda(kR)\mathbb{W}_{\text{LAB}}\mathbf{k}_{\text{LAB}} \tag{A13}$$

where

$$\mathbb{W}_{\text{LAB}} = \mathbf{R}(\beta, \gamma)\mathbb{W}_{\text{PAS}}\mathbf{R}^{-1}(\beta, \gamma) \tag{A14}$$

and

$$\mathbf{k}_{\text{LAB}} = \mathbb{R}(\beta, \gamma) \mathbf{k}_{\text{PAS}} \quad (\text{A15})$$

By introducing eq A13 in the eq 4 of the paper, we obtain

$$\begin{aligned} \mathbf{F}_o(\mathbf{r}, \beta, \gamma) &= \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k} \cdot \mathbf{r}} [\tilde{\mathbf{E}}_o(\mathbf{k})]_{\text{LAB}} \cdot \tilde{\chi}''(\mathbf{k}) d\mathbf{k} \\ &= \frac{i}{(2\pi)^3} \int e^{-i\mathbf{k} \cdot \mathbf{r}} \Lambda(kR) \mathbb{W}_{\text{LAB}} \mathbf{k}_{\text{LAB}} \cdot \tilde{\chi}''(\mathbf{k}) d\mathbf{k} \quad (\text{A16}) \end{aligned}$$

Now, by developing the matrix product under the integral sign in eq A16, we are, in principle, in a position to formally write all three components of the reaction field $\mathbf{F}_o(\mathbf{r})$ in the LAB frame. In this work, as stated above, we are interested in the Z component $F_{oz}(\mathbf{r}, \beta, \gamma)$ that, from eq A16, can be written as

$$\begin{aligned} F_{oz}(\mathbf{r}, \beta, \gamma) &= \\ &= \frac{i}{(2\pi)^3} \int e^{-i\mathbf{k} \cdot \mathbf{r}} \Lambda(kR) \sum_{s,p=X,Y,Z} \tilde{\chi}''_{zs}(\mathbf{k}) W_{sp}^{\text{LAB}} k_p^{\text{LAB}} d\mathbf{k} \quad (\text{A17}) \end{aligned}$$

At this point, it is possible to calculate the derivative of eq A1 to write the formula of $F'_{zz}(\mathbf{r}, \beta, \gamma)$, that is, the ZZ component of the electric field gradient tensor in which we are interested in this work

$$\begin{aligned} F'_{zz}(\mathbf{r}, \beta, \gamma) &= \frac{\partial F_{oz}(\mathbf{r}, \beta, \gamma)}{\partial Z} \\ &= \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k} \cdot \mathbf{r}} \Lambda(kR) k_Z^{\text{LAB}} \sum_{s,p=X,Y,Z} \tilde{\chi}''_{zs}(\mathbf{k}) W_{sp}^{\text{LAB}} k_p^{\text{LAB}} d\mathbf{k} \quad (\text{A18}) \end{aligned}$$

Equation A18 can be conveniently rewritten by expressing the differential $d\mathbf{k}$ in its spherical form

$$d\mathbf{k} = k^2 dk \sin \eta d\eta d\psi \quad (\text{A19})$$

Henceforth, η and Ψ will be the polar and azimuthal angles defining the direction of \mathbf{k} in the LAB frame, whereas θ and φ will define the direction of \mathbf{r} in the LAB frame (see Figure A2).

Moreover, we will introduce the following symmetric matrix \mathbb{K} , obtained as a direct product of two unit vectors $\hat{\mathbf{k}} = \mathbf{k}/k$

$$\begin{aligned} \mathbb{K} &= \hat{\mathbf{k}} \otimes \hat{\mathbf{k}} = \begin{bmatrix} \hat{k}_x \\ \hat{k}_y \\ \hat{k}_z \end{bmatrix} \cdot \begin{bmatrix} \hat{k}_x & \hat{k}_y & \hat{k}_z \end{bmatrix} = \begin{bmatrix} \hat{k}_x^2 & \hat{k}_x \hat{k}_y & \hat{k}_x \hat{k}_z \\ \hat{k}_y \hat{k}_x & \hat{k}_y^2 & \hat{k}_y \hat{k}_z \\ \hat{k}_z \hat{k}_x & \hat{k}_z \hat{k}_y & \hat{k}_z^2 \end{bmatrix} \\ &= \begin{bmatrix} (\sin \eta \cos \psi)^2 & (\sin \eta)^2 \sin \psi \cos \psi & \sin \eta \cos \eta \cos \psi \\ (\sin \eta)^2 \sin \psi \cos \psi & (\sin \eta \sin \psi)^2 & \sin \eta \cos \eta \sin \psi \\ \sin \eta \cos \eta \cos \psi & \sin \eta \cos \eta \sin \psi & (\cos \eta)^2 \end{bmatrix} \quad (\text{A20}) \end{aligned}$$

By making use of the \mathbb{K} matrix (eq A20) of the differential $d\mathbf{k}$ in its spherical form (eq A19) and by considering that $\tilde{\chi}''(\mathbf{k})$ depends only on the direction of \mathbf{k} but not on its magnitude (in practice, $\tilde{\chi}''(\mathbf{k}) \equiv \tilde{\chi}''(\eta, \psi)$),²⁵ eq A18 can be rewritten as follows (in the following formulas, the single dependences are made explicit)

$$\begin{aligned} F'_{zz}(\mathbf{r}, \beta, \gamma) &= \\ &= \frac{1}{(2\pi)^3} \cdot \sum_{s,p=X,Y,Z} \int e^{-i\mathbf{k} \cdot \mathbf{r}} k^4 \Lambda(kR) \tilde{\chi}''_{zs}(\eta, \psi) W_{sp}^{\text{LAB}}(\beta, \gamma, \zeta, \xi) \times \\ &\quad K_{pz}^{\text{LAB}}(\eta, \psi) dk \sin \eta d\eta \sin \zeta d\zeta d\psi d\xi \quad (\text{A21}) \end{aligned}$$

where^{25,32}

$$\begin{aligned} \tilde{\chi}''_{zx}(\eta, \psi) &= -\frac{1}{4\pi} \left(\frac{\cos \eta \sin \eta \cos \psi (\varepsilon_{\parallel} - 1)(\varepsilon_{\perp} - 1)}{\varepsilon_{\perp} + \Delta \varepsilon \cos^2 \eta} \right) \left(\frac{(\varepsilon_{\perp} - 1)}{8\pi \Delta \varepsilon} (2\varepsilon_{\parallel} - \varepsilon_{\perp} - 1) - \frac{\varepsilon_{\parallel}}{\varepsilon_{\perp}} (\varepsilon_{\perp} - 1) \Psi \right) \quad (\text{A22}) \end{aligned}$$

(with $\tilde{\chi}''_{zx}(\eta, \psi) = \tilde{\chi}''_{zy}(\eta, \psi) \equiv \tilde{\chi}''_{\perp}(\eta, \psi)$ and $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) and

$$\begin{aligned} \tilde{\chi}''_{zz}(\eta, \psi) &\equiv \tilde{\chi}''_{\parallel}(\eta, \psi) = \frac{1}{4\pi} \left((\varepsilon_{\parallel} - 1) - \frac{\cos^2 \eta (\varepsilon_{\parallel} - 1)^2}{\varepsilon_{\perp} + \Delta \varepsilon \cos^2 \eta} \right) \left(-\frac{(\varepsilon_{\parallel} - 1)}{4\pi \Delta \varepsilon} (\varepsilon_{\perp} - 1 - (\varepsilon_{\perp} - 1) \Psi) \right) \quad (\text{A23}) \end{aligned}$$

with²⁵

$$\begin{aligned} \Psi &= \int_0^1 \frac{dz}{1 + (\varepsilon_{\parallel}/\varepsilon_{\perp} - 1)z^2} \\ &= \begin{cases} \arctan \sqrt{\varepsilon_{\parallel}/\varepsilon_{\perp} - 1} / \sqrt{\varepsilon_{\parallel}/\varepsilon_{\perp} - 1} & \varepsilon_{\parallel} > \varepsilon_{\perp} \\ 1 & \varepsilon_{\parallel} = \varepsilon_{\perp} \\ \ln \left(\frac{1 + \sqrt{1 - \varepsilon_{\parallel}/\varepsilon_{\perp}}}{1 - \sqrt{1 - \varepsilon_{\parallel}/\varepsilon_{\perp}}} \right) / (2\sqrt{1 - \varepsilon_{\parallel}/\varepsilon_{\perp}}) & \varepsilon_{\parallel} < \varepsilon_{\perp} \end{cases} \quad (\text{A24}) \end{aligned}$$

The integral of eq A21 can be conveniently rearranged in order to separate the terms depending on the magnitude of \mathbf{k} from those depending only on its direction, defined by (η, ψ)

$$\begin{aligned} F'_{zz}(\mathbf{r}, \beta, \gamma) &= \\ &= \sum_{s,p=X,Y,Z} \int \Gamma(\mathbf{r}, \eta, \psi) \tilde{\chi}''_{zs}(\eta, \psi) W_{sp}^{\text{LAB}}(\beta, \gamma, \zeta, \xi) \times \\ &\quad K_{pz}^{\text{LAB}}(\eta, \psi) \sin \eta d\eta \sin \zeta d\zeta d\psi d\xi \quad (\text{A25}) \end{aligned}$$

where

$$\Gamma(\mathbf{r}, \eta, \psi) = \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k} \cdot \mathbf{r}} k^4 \Lambda(kR) dk \quad (\text{A26})$$

The result of the integral in eq A26 for $k \rightarrow 0$ (i.e., in the continuum limit)²⁵ and $r = R$ (i.e., calculated at the surface of the virtual cavity containing the solute) is the following

$$\begin{aligned} \Gamma_{k \rightarrow 0}(\eta, \psi, \theta, \varphi) &= \frac{1}{32\pi^2 R^5 \varepsilon_0} \times \\ &\times \left[\frac{3}{2} + \frac{i}{\pi} \left(\frac{\cos \omega (3 \cos^2 \omega - 5)}{(\cos^2 \omega - 1)^2} - 3 \operatorname{arctgh}(\cos \omega) \right) \right] \quad (\text{A27}) \end{aligned}$$

where, by trivial algebra, it is possible to obtain the following basic relation involving the dependence of $\cos \omega$ on the sets of angles (η, Ψ) and (θ, Ψ) (see Figure A2)

$$\begin{aligned} \cos \omega &= \sin \theta \cos \varphi \sin \eta \cos \psi + \\ &\quad \sin \theta \sin \varphi \sin \eta \sin \psi + \cos \theta \cos \eta = \\ &\quad \cos(\varphi - \psi) \sin \eta \sin \theta + \cos \theta \cos \eta \quad (\text{A28}) \end{aligned}$$

In order to make the term $\Gamma_{k \rightarrow 0}(\eta, \psi, \theta, \varphi)$ of eq A27 purely real (as required by the fact that the electric field gradient has to be real to be physically sensible), we have to impose the condition that the imaginary part of eq A27 has to vanish

$$\frac{i}{\pi} \left(\frac{\cos \omega (3 \cos^2 \omega - 5)}{(\cos^2 \omega - 1)^2} - 3 \operatorname{arctanh}(\cos \omega) \right) = 0 \quad (\text{A29})$$

It can be shown that the condition of eq A29 is fulfilled when

$$\eta = -\arctan(\cot \theta \sec(\varphi - \psi)) \quad (\text{A30})$$

By introducing eq A27 into eq A25 (following the restriction fixed by eq A30), the integral of eq A25 can be solved analytically. The result of the integration of eq A25, under the “isotropic” boundary condition that the EFG has to vanish when $\varepsilon_{\parallel} = \varepsilon_{\perp} = \varepsilon_s \equiv \varepsilon_{\text{iso}}$ (in order to satisfy simultaneously Laplace’s equation and the isotropic symmetry requirement $F'_{XX} = F'_{YY} = F'_{ZZ}$), can be given in the following, quite elegant form

$$F'_{ZZ}(\beta, \gamma) = \pm \frac{6\pi}{R^5 \varepsilon_0} \left(\frac{\Delta\varepsilon}{\varepsilon_{\parallel}(1 - \varepsilon_{\perp} + (\varepsilon_{\parallel} - 1)\Psi)} - \frac{3}{1 + 2\varepsilon_s} \right) \times \\ \left[Q_{zz}P_2(\cos \beta) + \sqrt{\frac{2}{3}}\Delta Q \operatorname{Re}[C_{22}(\beta, \gamma)] \right] \quad (\text{A31})$$

which is exactly eq 7 of the text, quod erat demonstrandum. The sign \pm in eq A31 indicates that it is impossible to choose a priori between two possible mathematical solutions for $F'_{ZZ}(\beta, \gamma)$; this is because at $T = T_{\text{NI}}$ (NI: nematic–isotropic transition), the following “isotropic” boundary condition (where the absolute value is involved) holds

$$\lim_{\varepsilon_{\parallel} \rightarrow \varepsilon_{\perp}} \left(\frac{\Delta\varepsilon}{\varepsilon_{\parallel}(1 - \varepsilon_{\perp} + (\varepsilon_{\parallel} - 1)\Psi)} - \frac{3}{1 + 2\varepsilon_s} \right) = 0 \\ (\text{in the isotropic limit, } \varepsilon_{\parallel} = \varepsilon_{\perp} = \varepsilon_s \equiv \varepsilon_{\text{iso}}) \quad (\text{A32})$$

Therefore, both signs $+$ and $-$ preceding the term $[(\Delta\varepsilon/(\varepsilon_{\parallel}(1 - \varepsilon_{\perp} + (\varepsilon_{\parallel} - 1)\Psi))) - (3/(1 + 2\varepsilon_s))]$ in eq A31 are mathematically acceptable (see text for more explanations).

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References and Notes

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