

# An Explicit Relationship between the Dielectric Anisotropy and the Average Electric Field Gradient in Nematic Solvents

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Received: November 6, 2006; In Final Form: January 3, 2007

Nowadays, the interaction between the electric quadrupole moment of a probe-solute and the so-called average electric field gradient (EFG) of the nematic medium is commonly suggested as an important long-range mechanism contributing to the ordering of small molecules dissolved in nematic solvents. Anyway, an explicit relationship between the solvent's EFG and some macroscopic property of the medium has never been established explicitly. In this work, a derivation is carried out leading to a simple formula that shows that the EFG of a nematic solvent is directly related to the dielectric permittivity of the medium (in particular, to its dielectric anisotropy,  $\Delta\epsilon$ ) and to the quadrupole moment of the solute. The obtained expression (a) allows for immediate considerations about the sign and the value of EFG (and could be very useful in designing proper nematic mixtures with null EFG) and (b) reconciles two existing conceptual ways of describing long-range orientational interactions, revealing they are only seemingly different.

The ordering experienced by a small probe-molecule dissolved in a nematic solvent is usually thought as resulting from a combined action of short-range (SR) and long-range (LR) solute–solvent anisotropic interactions.<sup>1</sup> Nowadays, SR “size-shape” dependent ordering mechanisms are generally recognized as dominant;<sup>2</sup> anyway, LR effects are usually not negligible, and quite spectacular LR-dictated orientational phenomena (especially involving very small solutes) have been even recently observed.<sup>3</sup> A practical way to deal with LR orientational interactions can be represented by the so-called Buckingham multipole expansion (BME) approach.<sup>2</sup> In particular, the interaction described by the third term of the BME, i.e., that involving the solute's electric quadrupole moment and what can be formally defined (*vide infra*) as the solvent's average electric field gradient (EFG), has been recognized for a long time<sup>4,5</sup> to be considerably effective. An interesting application of this assessment has been the possibility to prepare (at a given temperature) “zero average EFG” (ZAEFG) nematic solvents by properly mixing liquid crystals with EFGs opposite in sign (see refs 1 and 2, where this topic is treated in detail, and a large number of publications from Burnell, de Lange, and co-workers, the inventors of these systems, over the last 20 years). The first (and most famous and used) of such mixtures is the 55 wt % ZLI1132+EBBA<sup>6</sup> (also called *Magic Mixture*), which is ZAEFG at 301.4 K, but also other ZAEFG mixtures (obtained, for example, by mixing the nematic mesophases EBBA and 5CB) have been reported.<sup>2,7</sup> This practice allowed for effective investigations and testing of solute–solvent SR orientating potentials only<sup>8–10</sup> (in principle, isolated from the LR part, because the bulk of the LR effects had been minimized by zeroing the EFG of the solvent).

From what was said above, it is obvious to conclude that it would be very useful to have a simple tool able to predict the sign of the average EFG of nematic solvents:<sup>11</sup> this could allow to select *a priori* possible good candidates (with EFGs opposite in sign)<sup>11b</sup> to devise new ZAEFG mixtures. The aforementioned

tool could be represented by a simple formula containing macroscopic, known (or easily measurable) properties of the mesophase. On the other hand, it is well-known from theory,<sup>12</sup> computer simulations,<sup>13</sup> and experiments<sup>3,5</sup> that the so-called EFG is not an exclusive property of the solvent; on the contrary, it is very sensitive to the nature of the solute. Thus, a right formula should also contain information about significant molecular properties of the solute. To our knowledge, such an expression has not yet been given explicitly. The aim of this work is exactly that of suggesting a way to estimate the nematic solvents' EFG (inclusive of the sign), accounting, at the same time, for its solute dependence. In few words, we will propose an explicit relationship (obtained under the “dilute-solution” implicit assumption and valid, as shown later in the paper, for real experimental conditions of solute's concentration) where the EFG, the dielectric permittivity of the medium (in particular, its dielectric anisotropy), and a molecular property of the solute (the electric quadrupole moment) are involved. To do this, we have to start from an alternative, interesting way to approach the LR interactions, namely, the application, in this context, of the generalized reaction field model,<sup>10,14a,14b</sup> a direct derivation of what was previously suggested by Dillet et al.<sup>15</sup> and by Lü et al.<sup>16</sup> as a generalization of the Kirkwood model of solvation for a molecule placed in a cavity surrounded by a dielectric continuum.<sup>17,18</sup> Following this approach, the solvation energy of the molecule can be written by making use of spherical tensor notation, such as

$$W_{\text{RF}}^{\text{Solv}} = -\frac{1}{2} \sum_l \sum_{m=-l}^l M_{lm} F_{lm} \quad (1)$$

with

$$F_{lm} = g_l M_{lm} \quad (2)$$

where  $M_{lm}$  represents the components of the multipole moment tensor of order  $l$ ,  $F_{lm}$  denotes the components of the correspond-

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ing reaction field tensor, and

$$g_l = \frac{(l+1)(\epsilon-1)}{(l+1)\epsilon+l} \frac{1}{R_0^{2l+1}} \quad (3)$$

where  $\epsilon$  is the dielectric permittivity of the medium and  $R_0$  is the radius of the cavity. If we assume, for more generality, the solute is polarizable (and passing, for a more transparent physical description, to the Cartesian tensor formalism, where the Einstein summation convention over the repeated indices is adopted), the eq 1 can be given as<sup>16</sup>

$$W_{\text{RF}}^{\text{Solv}} = -\frac{1}{2}[g_0 q^2 + g_1 \mu_\alpha^0 \mu_\alpha + \frac{1}{3}g_2 Q_{\alpha\beta}^0 Q_{\alpha\beta} + \dots] \quad (4)$$

where  $q$  is the charge;  $\mu^0$ ,  $Q^0$ , etc., are the permanent multipole moments of the solute; and  $\mu$ ,  $Q$ , etc., are the multipole moments of the perturbed solute molecule (their expressions, involving the polarizabilities, are given explicitly in eq 35 of ref 16). On the other hand, by following the above quoted BME approach, we can parallelly write the following expression for the energy of a solvated molecule<sup>2</sup>

$$W_{\text{BME}}^{\text{Solv}} = qV_0 - \mu_\alpha^0 F_\alpha - \frac{1}{3}Q_{\alpha\beta}^0 F'_{\alpha\beta} + \dots \quad (5)$$

where  $V_0$ ,  $F_\alpha$  and  $F'_{\alpha\beta}$  are, respectively, the potential, electric field, and electric field gradient experienced by the solute in the medium. The self-consistency of the problem requires now that  $W_{\text{RF}}^{\text{Solv}} = W_{\text{BME}}^{\text{Solv}}$ . From this condition, we obtain the following straightforward relations:

$$V_0 = -\frac{1}{2}g_0 q \quad (6a)$$

$$F_\alpha = \frac{1}{2}g_1 \mu_\alpha \quad (6b)$$

$$F'_{\alpha\beta} = \frac{1}{6}g_2 Q_{\alpha\beta} \quad (6c)$$

Of course, we are interested in eq 6c, giving an expression relating the EFG of the solvent with the  $g_2$  quantity (depending on the dielectric permittivity of the solvent) and the electric quadrupole moment of the solute molecule. This result is close to our final goal: the last step of this derivation is the generalization of eq 6c to take into account the anisotropy of the liquid crystalline environment. About this, it needs to emphasize that the  $g_1$  quantity (given as a constant in eq 3, for isotropic media) has an intrinsic tensorial nature; in particular, it is a fourth-rank tensor.<sup>10</sup> From this, eq 6c can be properly rewritten as

$$F'_{\alpha\beta} = \frac{1}{6}g_{\alpha\beta\gamma\delta} Q_{\gamma\delta} \quad (7)$$

For a nematic mesophase, it is convenient to express our quantities in a laboratory (Lab) reference system, where the  $Z$  axis is parallel to the mesophase director. In this system, due to the cylindrical symmetry of the phase,  $\langle F'_{\alpha\beta} \rangle = 0$  when  $\alpha \neq \beta$ ; moreover, in order to satisfy simultaneously symmetry requirements and Laplace's equation, we have that the relation  $\langle F'_{xx} \rangle = \langle F'_{yy} \rangle = -1/2 \langle F'_{zz} \rangle$  holds.<sup>4</sup> So  $\langle F'_{zz} \rangle$ , the only independent component of the average electric field gradient tensor, can be obtained from eq 7 in the form

$$\langle F'_{zz} \rangle = \frac{1}{6} \langle g_{zz\Gamma\Delta} Q_{\Gamma\Delta} \rangle \quad (8)$$

(note that the Greek subscripts of eq 7 now have been rewritten in capital characters to emphasize that the terms of eq 8 are given in the Lab frame; henceforth, small character subscripts will be adopted only for the molecular (Mol) frame). When the solute's quadrupolar tensor  $\mathbf{Q}$  is given in its molecular principal axis system (PAS), eq 8 becomes

$$\langle F'_{zz} \rangle = \frac{1}{6} \langle g_{zz\Gamma\Delta} \cos\theta_{a\Gamma} \cos\theta_{a\Delta} Q_{aa} \rangle \quad (9)$$

If an axial-quadrupole probe solute is chosen (with its cylindrical axis along the  $z$ -axis), we can exploit (a) the traceless nature of  $\mathbf{Q}$ , (b) the symmetry relation  $Q_{xx} = Q_{yy}$ , and (c) the properties of direction cosines, to rearrange, after trivial algebra, eq 9 in the following form

$$\langle F'_{zz} \rangle = \frac{Q_{zz}}{6} \left\{ g_{zzzz}(\theta) - \frac{1}{2} [g_{zzxx}(\theta) + g_{zzyy}(\theta)] \right\} P_2(\cos\theta) \quad (10)$$

where now  $\theta$  simply represents the angle between the solute's figure axis (coinciding with  $z$ ) and the mesophase director (fixing the  $Z$  direction) and  $P_2(\cos\theta)$  is the second Legendre polynomial (the dependence of the  $g_{ABCD}$  components on  $\theta$  has been explicitated in eq 10 in order to emphasize that the quadrupolar reaction tensor in the Lab frame depends on the orientation of the inducing-effect solute).

The problem now moves to the form of the  $g_{ABCD}(\theta)$  terms of eq 10. In the past, several authors studied the dipole-induced reaction fields in anisotropic media;<sup>19–23</sup> anyway, to the best of the author's knowledge, a derivation of the quadrupolar reaction tensor for an anisotropic uniaxial environment has never been done before. In this work, we carried out this derivation for an axial-quadrupole probe solute (e.g., dideuterium) by exploiting the fact that the charge distribution of the axial quadrupole can be described as a couple of equal, oppositely aligned (along the  $z$  symmetry axis) electric dipoles. Because the complete derivation is very long, here we will give the final results directly, referring the interested reader to the Appendix, where the complete derivation is given in detail. Then, the obtained expression for  $\langle F'_{zz} \rangle$  is

$$\langle F'_{zz} \rangle \approx \frac{Q_{zz}}{R_c^5} \left[ \frac{2\Delta\epsilon}{5(2\epsilon_s + 1)^2} (1-A) \right] [S_{zz}^2 + (S_{zz}/2) + \sigma^2] \quad (11)$$

where  $\Delta\epsilon = (\epsilon_{||} - \epsilon_{\perp})$ ,  $\epsilon_s = (\epsilon_{||} + 2\epsilon_{\perp})/3$ ,  $A = (36 + 79\epsilon_s)\Delta\epsilon/105\epsilon_s(2\epsilon_s + 1)$ , and  $R_c$  is the radius of a "virtual" cavity (assumed spherical for simplicity) where the solute is embedded;  $S_{zz} = \langle [P_2(\cos\theta)] \rangle$  is, of course, the order parameter of the cylindrical solute;  $\sigma^2 = \langle [P_2(\cos\theta)]^2 \rangle - \langle [P_2(\cos\theta)] \rangle^2$ ; and, finally, the symbol " $\approx$ " is used on purpose to emphasize the number of assumptions and approximations adopted in the derivation (see the Appendix for details). Because, as described in the Appendix and reported in Table 1,  $\sigma^2 \approx 1/5 \gg |S_{zz}|$  (and even more so  $\sigma^2 \gg S_{zz}^2$ ), eq 11 reduces to

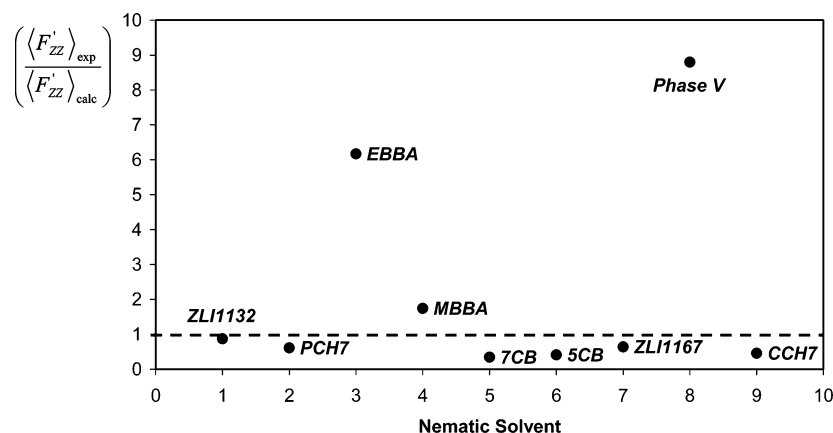
$$\langle F'_{zz} \rangle \approx \frac{Q_{zz}}{R_c^5} \frac{2\Delta\epsilon}{[5(2\epsilon_s + 1)]^2} (1-A) \quad (12)$$

where it clearly appears the EFG depends on the solvent's dielectric tensor and on the solute's electric quadrupole moment. This very compact formula is the expression we were looking for. In spite of its simplicity, eq 12 demonstrates efficacy in predicting all available "experimental" results<sup>4,11b,11c</sup> regarding  $\langle F'_{zz} \rangle$ .<sup>24</sup> This is shown well in Figure 1 and Table 1, where

**TABLE 1: Ingredients of Eq 12 (and of Eq 11, Which is the Less Approximated Form of Eq 12) for D<sub>2</sub> Dissolved in Different Nematic Solvents<sup>a</sup>**

nematic solvent	$\epsilon_{  }$	$\epsilon_{\perp}$	$\Delta\epsilon$	$\epsilon_s$	$S_{zz}$ (exp)	$S_{zz}^2$	$\sigma^2$	$B/kT$ (see appendix)	$\langle F'_{ZZ} \rangle/\text{esu}$ [exptl]	$\langle F'_{ZZ} \rangle/\text{esu}$ [calc from eq 12]	$\langle F'_{ZZ} \rangle/\text{esu}$ [calc from eq 11]
ZLI1132 ( $T = 298$ K)	<i>b</i> 17.69	<i>b</i> 4.56	<i>b</i> 13.13	<i>b</i> 8.94	<i>c</i> $1.10 \times 10^{-2}$	$1.21 \times 10^{-4}$	0.2030	<i>c</i> −0.048	<i>c</i> $6.07 \times 10^{11}$	$7.00 \times 10^{11}$	$7.31 \times 10^{11}$
PCH7 ( $T = 304$ K)	<i>d</i> 12.9	<i>d</i> 4.5	<i>d</i> 8.4	<i>d</i> 7.3	<i>e</i> $0.73 \times 10^{-2}$	$4.9 \times 10^{-5}$	0.2022	<i>e</i> −0.038	<i>e</i> $4.98 \times 10^{11}$	$8.14 \times 10^{11}$	$8.38 \times 10^{11}$
EBBA ( $T = 298$ K)	<i>f</i> 4.58	<i>f</i> 4.87	<i>f</i> −0.29	<i>f</i> 4.77	<i>c</i> $−1.40 \times 10^{-2}$	$1.96 \times 10^{-4}$	0.1973	<i>c</i> 0.049	<i>c</i> $−6.42 \times 10^{11}$	$−1.04 \times 10^{11}$	$−1.00 \times 10^{11}$
MBBA ( $T = 304$ K)	<i>g</i> 4.7	<i>g</i> 5.4	<i>g</i> −0.7	<i>g</i> 5.17	<i>e</i> $−0.74 \times 10^{-2}$	$5.5 \times 10^{-5}$	0.1983	<i>e</i> 0.030	<i>e</i> $−3.94 \times 10^{11}$	$−2.26 \times 10^{11}$	$−2.20 \times 10^{11}$
7CB ( $T = 308$ K)	<i>d</i> 15.7	<i>d</i> 6.0	<i>d</i> 9.7	<i>d</i> 9.23	<i>e</i> $0.3 \times 10^{-2}$	$0.9 \times 10^{-5}$	0.2010	<i>e</i> −0.018	<i>e</i> $2.30 \times 10^{11}$	$6.59 \times 10^{11}$	$6.67 \times 10^{11}$
5CB ( $T = 293$ K)	<i>d</i> 18.8	<i>d</i> 7.3	<i>d</i> 11.5	<i>d</i> 11.13	<i>h</i> $0.3 \times 10^{-2}$	$0.9 \times 10^{-5}$	0.2010	<i>h</i> −0.018	<i>h</i> $2.30 \times 10^{11}$	$5.61 \times 10^{11}$	$5.68 \times 10^{11}$
ZLI1167 ( $T = 308$ K)	<i>i</i> 7.5	<i>i</i> 3.6	<i>i</i> 3.9	<i>i</i> 4.9	<i>j</i> $1.24 \times 10^{-2}$	$1.53 \times 10^{-4}$	0.2026	<i>c</i> −0.045	<i>j</i> $5.92 \times 10^{11}$	$9.23 \times 10^{11}$	$9.64 \times 10^{11}$
phase V ( $T = 298$ K)	<i>k</i> 5.08	<i>k</i> 5.29	<i>k</i> −0.21	<i>k</i> 5.22	<i>c</i> $−1.23 \times 10^{-2}$	$1.51 \times 10^{-4}$	0.1975	<i>c</i> 0.044	<i>c</i> $−5.63 \times 10^{11}$	$−0.64 \times 10^{11}$	$−0.62 \times 10^{11}$
CCH7 ( $T = 351$ K)	<i>l</i> 7.6	<i>l</i> 4.2	<i>l</i> 3.4	<i>l</i> 5.3	<i>m</i> $0.47 \times 10^{-2}$	$2.20 \times 10^{-5}$	0.2028	<i>e</i> −0.047	<i>m</i> $3.48 \times 10^{11}$	$7.63 \times 10^{11}$	$7.83 \times 10^{11}$

<sup>a</sup> Moreover, the values  $Q_{zz} = 0.65 \times 10^{-26}$  esu<sup>4</sup> and  $R_c$  (assumed equal to D–D bond length; see Appendix) =  $0.74 \text{ \AA}$ <sup>26</sup> have been used for all the solvents. In the last three columns, “experimental”<sup>24</sup> and calculated (by eqs 11 and 12)  $\langle F'_{zz} \rangle$  values are reported for comparison. (1 esu = 1 statvolt cm<sup>-2</sup> =  $2.998 \times 106 \text{ V m}^{-2}$ ) <sup>b</sup> Technical data sheets by Merck. <sup>c</sup> From ref 4. <sup>d</sup> From the free version of LiqCryst Online 1999 Database (<http://liqcryst.chemie.uni-hamburg.de/en/lolas.php-V>). Vill and LCI Publisher: University of Hamburg, Germany) and references therein. <sup>e</sup> From ref 11b. <sup>f</sup> From ref 27a. <sup>g</sup> From ref 28a. <sup>h</sup> From ref 11c. <sup>i</sup> From ref 14c. <sup>j</sup> The present values, referred to the mesophase’s director, are negative twice those given in ref 4, where, on the contrary, data referred to the magnetic field (which is perpendicular to the director, the solvent’s diamagnetic anisotropy being  $\Delta\chi(\text{ZLI1167}) < 0$ ) are reported. <sup>k</sup> From ref 27b. <sup>l</sup> From ref 28b. <sup>m</sup> The present values, referred to the mesophase’s director, are negative twice those given in ref 11b, where data referred to the magnetic field (which is perpendicular to the director, the solvent’s diamagnetic anisotropy being  $\Delta\chi(\text{CCH7}) < 0$ ) are reported.

**Figure 1.** The ratio (given within a scale of an order of magnitude) between “experimental” and calculated  $\langle F'_{zz} \rangle$  values for the tested nematic solvents. The dashed line represents the perfect agreement.

“ingredients” of eqs 11 and 12 and their (in practice the same) predicted  $\langle F'_{zz} \rangle$  values for D<sub>2</sub> dissolved in several nematic solvents are reported and compared to the experimental ones.

Taking into account the strong approximations and assumptions to get a so “easy-to-handle” formula, the agreement between experimental and calculated  $\langle F'_{zz} \rangle$  values is really excellent (even surprisingly good), and this, in our opinion, makes the suggested formula safely acceptable as the searched “easy tool” for qualitative and semiquantitative EFG predictions.<sup>25</sup> The sign of experimental  $\langle F'_{zz} \rangle$  and its order of magnitude are indeed always well reproduced, and even the numerical values predicted by eqs 11–12 are quite similar to their experimental counterparts. Two interesting exceptions to this behavior are represented by “D<sub>2</sub>–EBBA” and “D<sub>2</sub>–Phase V” cases, where significant discrepancies are observed. Two possible (not mutually exclusive) reasons (we will call A and B) could in principle be invoked to explain the disagreement. The first (hypothesis A) is that large errors could affect

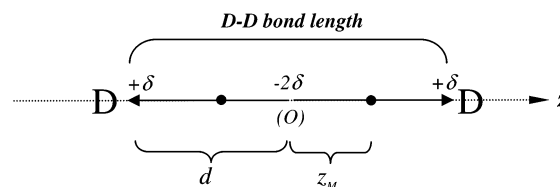
experimental  $\epsilon_{||}$  and  $\epsilon_{\perp}$  values. This possibility could be true for EBBA (where the values have been obtained by extrapolation<sup>27a</sup>), but it is hardly tenable for Phase V, whose dielectric permittivities have been measured with high precision<sup>27b</sup> (their values are reported as a function of temperature in Table 2 of the cited paper); so, this reason alone is not enough to explain the discrepancies. The other possible explanation (B) indirectly supports the effectiveness of eq 12. Hypothesis B lies in a certain degree of indeterminacy affecting the experimental  $\langle F'_{zz} \rangle$  values ascribed to EBBA and Phase V.<sup>4</sup> As a matter of fact, the two solvents are characterized by very small values of  $\Delta\epsilon$  (the lowest among those reported in Table 1); then, it is reasonable to expect that the EFG is very small (not exactly null, but quite near to zero), and consequently, its role in ordering phenomena involving D<sub>2</sub> in these two solvents is reduced. Under these conditions, the use of a method (that used in ref 4, to obtain the “experimental”  $\langle F'_{zz} \rangle$  from experimental order parameters  $S_{zz}$ ) where, on the contrary, the responsibility

of the solute's ordering is wholly attributed to the “Q–EFG” interaction (by “intentionally” neglecting the presence of other important orientational effects, as rightly recognized by the same authors in ref 11b) could produce quite artificial adjusted experimental  $\langle F'_{ZZ} \rangle$  parameters, affected by a significant indeterminacy. In light of this argument, we are led to conclude that the  $\langle F'_{ZZ} \rangle$  values of EBBA and Phase V given in ref 4 are probably overestimated *ab origine*, and this makes them not fully reliable to be taken as references of the “true” values. If this argument is correct, the large discrepancies of Figure 1 regarding EBBA and Phase V are not real but are rather deceptive and misleading about a bad performance of eq 12.

Even though, mathematically speaking, eq 12 has been obtained and tested (and it is therefore to be considered rigorously valid) only for small axial-quadrupole probe solutes such as dideuterium (quantitative estimates of  $\langle F'_{ZZ} \rangle$  for larger, general solutes need a generalization of eq 12, planned as a future work), some intriguing general concepts are nevertheless suggested by the obtained result, lending themselves to a whole string of further considerations we will develop in the following part of the paper. As a first step, it is worth emphasizing that, for realistic values of  $\Delta\epsilon$  and  $\epsilon_s$ , the  $(1 - A)$  term of eqs 11–12 obeys always the relation

$$(1 - A) > 0 \quad (13)$$

This implies the very important consequence that the sign of  $\langle F'_{ZZ} \rangle$  is the same as  $\Delta\epsilon$ . In other words, the sign of the EFG is strictly related to the dielectric anisotropy of the nematic medium, so that, in principle, ZAEFG magic mixtures could be obtained by properly mixing solvents with opposite dielectric anisotropies. The existing magic mixtures<sup>2</sup> confirm that, even without a theoretical background but rather following intuition and experience, this rule has been empirically observed: it can be easily verified that nematic solvents with opposite dielectric anisotropies have been always mixed to obtain ZAEFG mixtures. Besides this, another more general, interesting aspect can be treated, for which a short digression is useful. As implicitly stated above (when we introduced the reaction field approach to the description of LR orientational interactions), a responsibility of the dielectric permittivity of the solvent on the LR orientational mechanisms of the solute had already been found by Ferrarini et al. in refs 10, 14a, and 14b. In particular, in ref 14a (Section IV, p 7769), the authors say that “...The magnitude of electrostatic interactions for a given molecule depends upon the value of the average dielectric permittivity, while their orientational dependence is essentially determined by the dielectric anisotropy of the medium. ...”; moreover, in ref 14b (Section V, p 2845), the same authors say “...In the latter case ( $\Delta\epsilon = 0$ ) the orientational order is fully determined by the short-range interactions...”. As a kind of (quite obvious) byproduct of our present study, the two “conceptual” approaches of ascribing a role in LR orientational effects to the EFG of the solvent OR to its dielectric properties result to be only seemingly different. Actually, (a) to maintain that the LR orientational mechanisms reckon with EFG is basically equivalent to saying that they depend on the dielectric permittivity (and, in particular, on dielectric anisotropy) of the solvent, and (b) to assert that SR orientational mechanisms are totally (or considerably) responsible of the ordering of the solute when EFG is null (or very small) is equivalent to saying that the solute's order is essentially determined by SR interactions when  $\Delta\epsilon$  is 0 or very small (according to this statement, and also the hypothesis B given above, about a “not real” inadequacy of eq 12 in predicting  $\langle F'_{ZZ} \rangle$  values of EBBA and Phase V, becomes *a posteriori*



**Figure 2.** Schematization of dideuterium molecule as an axial quadrupole.

more plausible). So, sharing the same implications, the two existing conceptual approaches about LR ordering effects are fully reconciled.

**Acknowledgment.** This work has been supported by funds from Università della Calabria. The author is grateful to Prof. E. E. Burnell (University of British Columbia), Prof. C. A. de Lange (Vrije University, Amsterdam) and Prof. A. Ferrarini (Università di Padova) for their critical comments on the draft of the manuscript, and to Prof. D. V. Matyushov (Arizona State University) for helpful technical suggestions.

## Appendix

**Mathematical Derivation of Eqs 11–12.** The matrix formalism<sup>29</sup> in the column vector space and the Einstein summation convention over the repeated indices have been adopted to carry out this mathematical demonstration. For convenience, we decided to tackle the problem by working in the **Q** PAS Mol frame, whose origin is fixed exactly in the midpoint of the linear distribution of charges configuring the axial quadrupole. This charge distribution corresponds to a couple of equal, oppositely aligned (along the *z* symmetry axis) electric dipoles (see Figure 2).

It is well-known<sup>30,31</sup> that the quadrupole moment can be described as

$$\mathbf{Q} = 3 \sum_i \left[ \mathbf{x}_i \tilde{\mathbf{M}}_i - \frac{1}{3} (\tilde{\mathbf{X}}_i \mathbf{M}_i) \mathbf{E} \right] \quad (\text{A1})$$

where  $\tilde{\mathbf{M}}_i = [\mu_x^i, \mu_y^i, \mu_z^i]$  is the *i*-th electric dipole concurring to the formation of the quadrupole (the tilde symbol represents the operation of transposition of the matrix),  $\tilde{\mathbf{X}}_i = [x_{M_i}, y_{M_i}, z_{M_i}]$  is the vector giving the position of the *i*-th electric dipole in the molecular frame, and **E** is the unit matrix. For our axial quadrupole, constituted by **M**<sub>1</sub> and **M**<sub>2</sub> along *z*, the relations **M**<sub>1</sub> = −**M**<sub>2</sub> and **X**<sub>1</sub> = −**X**<sub>2</sub> hold, so that eq A1 becomes

$$\mathbf{Q} = 6 \left[ \mathbf{X} \tilde{\mathbf{M}} - \frac{1}{3} (\tilde{\mathbf{X}} \mathbf{M}) \mathbf{E} \right] \quad (\text{A2})$$

Eq A2 can be recast in the form

$$\mathbf{A} = \mathbf{X} \tilde{\mathbf{M}} \quad (\text{A3})$$

where **A** = [1/6 **Q** + **D**] and **D** = 1/3 (**X****M**)**E** (**D** is, of course, a diagonal matrix). We introduce now in the treatment another proper vector  $\tilde{\mathbf{K}} = [0 \ 0 \ 1/z_M]$  such that  $\tilde{\mathbf{K}} \mathbf{X} = 1$ . By left-multiplying both sides of eq A3 by  $\tilde{\mathbf{K}}$ , we can obtain the following expressions for  $\tilde{\mathbf{M}}$  and **M**:

$$\tilde{\mathbf{M}} = \tilde{\mathbf{K}} \mathbf{A}$$

and

$$\mathbf{M} = \tilde{\mathbf{A}} \mathbf{K} \quad (\text{A4})$$



Because the  $\mathbf{Q}$  tensor is symmetric and  $\mathbf{D}$ , as said above, is diagonal, the relation  $\mathbf{A} = \tilde{\mathbf{A}}$  results; i.e., the  $\mathbf{A}$  matrix is symmetric. This implies that eq A4 becomes

$$\tilde{\mathbf{M}} = \tilde{\mathbf{K}}\mathbf{A}$$

and

$$\mathbf{M} = \mathbf{A}\mathbf{K} \quad (\text{A5})$$

Now, the electrostatic interaction energy for an electric dipole can be written as<sup>10</sup>

$$W_M = -\frac{1}{2}\tilde{\mathbf{M}}\mathbf{g}_M\mathbf{M} \quad (\text{A6})$$

where  $\mathbf{g}_M$  is the second-order dipolar reaction tensor. For our system, composed of two electric dipoles arranged in order to configure the axial quadrupole, we assume that the electrostatic interaction energy can be approximated by

$$W_{(M_1+M_2)} \approx W_{M_1} + W_{M_2} = -\frac{1}{2}(\tilde{\mathbf{M}}_1\mathbf{g}_{M_1}\mathbf{M}_1 + \tilde{\mathbf{M}}_2\mathbf{g}_{M_2}\mathbf{M}_2) \quad (\text{A7})$$

which, in view of the above-mentioned relation  $\mathbf{M}_1 = -\mathbf{M}_2$ , becomes

$$W_{(M_1+M_2)} \approx -\frac{1}{2}\tilde{\mathbf{M}}(\mathbf{g}_{M_1} + \mathbf{g}_{M_2})\mathbf{M} \quad (\text{A8})$$

On the other hand, our system is still a quadrupole, so its electrostatic interaction energy can however be written in the form<sup>10</sup>

$$W_{(Q)} = -\frac{1}{6}\tilde{\mathbf{Q}}:\mathbf{g}_Q:\mathbf{Q} \quad (\text{A9})$$

where  $\mathbf{g}_Q$  is the fourth-order tensor whose form we are looking for.

The self-consistency of the problem requires that  $W_{(M_1+M_2)} = W_{(Q)}$ , so that, by exploiting eqs A8 and A9, we can write

$$-\frac{1}{2}\tilde{\mathbf{M}}(\mathbf{g}_{M_1} + \mathbf{g}_{M_2})\mathbf{M} = -\frac{1}{6}\tilde{\mathbf{Q}}:\mathbf{g}_Q:\mathbf{Q} \quad (\text{A10})$$

Now, we will focus our attention on the first member of eq A10. By using expressions A5 for  $\tilde{\mathbf{M}}$  and  $\mathbf{M}$ , we obtain

$$-\frac{1}{2}\tilde{\mathbf{M}}(\mathbf{g}_{M_1} + \mathbf{g}_{M_2})\mathbf{M} = -\frac{1}{2}\tilde{\mathbf{K}}\mathbf{A}\mathbf{T}\mathbf{A}\mathbf{K} \quad (\text{A11})$$

where the tensor  $\mathbf{T} = (\mathbf{g}_{M_1} + \mathbf{g}_{M_2})$  has been introduced for convenience. It is also possible to show, after trivial (but boring) algebra, that

$$\mathbf{A}\mathbf{T}\mathbf{A} = \mathbf{Q}\mathbf{B}\mathbf{Q} \quad (\text{A12})$$

where

$$\mathbf{B} = \left\{ \frac{(\mathbf{g}_{M_1} + \mathbf{g}_{M_2})}{36} + \frac{1}{6}[\mathbf{Q}^{-1}\mathbf{D}(\mathbf{g}_{M_1} + \mathbf{g}_{M_2}) + (\mathbf{g}_{M_1} + \mathbf{g}_{M_2})\mathbf{D}\mathbf{Q}^{-1}] + \mathbf{Q}^{-1}\mathbf{D}(\mathbf{g}_{M_1} + \mathbf{g}_{M_2})\mathbf{D}\mathbf{Q}^{-1} \right\} \quad (\text{A13})$$

In light of eqs A11 and A12, it is then possible to write

$$-\frac{1}{2}\tilde{\mathbf{K}}\mathbf{A}\mathbf{T}\mathbf{A}\mathbf{K} = -\frac{1}{2}\tilde{\mathbf{K}}\mathbf{C}\mathbf{K} \quad (\text{A14})$$

where  $\mathbf{C} = \mathbf{Q}\mathbf{B}\mathbf{Q}$ . At this point, also recalling we are working in the PAS for  $\mathbf{Q}$ , the following relation holds

$$\tilde{\mathbf{K}}\mathbf{C}\mathbf{K} = K_k C_{ki} K_i = K_k Q_{kk} B_{ki} Q_{ii} K_i = Q_{kk} H_{ki} B_{ki} Q_{ii} \quad (\text{A15})$$

where  $\mathbf{H} = \mathbf{K}\tilde{\mathbf{K}}$ . By exploiting the chain of eqs A11, A14, and A15, eq A10 can be written as

$$-\frac{1}{2}Q_{kk} H_{ki} B_{ki} Q_{ii} = -\frac{1}{6}Q_{kk} g_{kkii}^Q Q_{ii} \quad (\text{A16})$$

where the generic element  $g_{kkii}^Q$  of the fourth-rank quadrupolar reaction tensor  $g_Q$  is given by

$$g_{kkii}^Q = 3(H_{ki} B_{ki}) \quad (\text{A17})$$

Due to the form of  $\mathbf{K}$ , only the term  $H_{zz}$  survives; so, eq A16 reduces to

$$-\frac{1}{2}Q_{zz} H_{zz} B_{zz} Q_{zz} = -\frac{1}{6}Q_{zz} g_{zzzz}^Q Q_{zz} \quad (\text{A18})$$

From eq A18, the following relation results:

$$g_{zzzz}^Q = 3(H_{zz} B_{zz}) \quad (\text{A19})$$

where

$$H_{zz} = \frac{1}{z_M^2} \quad (\text{A20})$$

and

$$B_{zz} = (g_{zz}^{M_1} + g_{zz}^{M_2}) \left[ \frac{1}{36} + \frac{1}{9}(w + w^2) \right] \quad (\text{A21})$$

where  $g_{aa}^{M_1}$  and  $g_{aa}^{M_2}$  are elements, expressed in the PAS, of the  $\mathbf{g}_{M_1}$  and  $\mathbf{g}_{M_2}$  aforementioned second-order dipolar reaction tensors, and  $w = z_M \mu_z / Q_{zz}$ . As shown in Figure 2, the  $z_M$  coordinate (locating the electric dipole with respect to the origin of the system) is such that  $z_M = 1/2d$  (where  $d$  is the distance of separation of the  $+\delta$  and  $-\delta$  partial charges); this implies that  $\mu_z = \delta d = 2\delta z_M$ , from which the relation  $z_M \mu_z = 2\delta z_M^2$  follows. On the other hand, in the same system, we can also write<sup>32</sup>  $Q_{zz} = 2\delta d^2 = 8\delta z_M^2$ , so that, from the previous relations,  $w = 1/4$  results. This, from eq A21, entails that

$$B_{zz} = \frac{(g_{zz}^{M_1} + g_{zz}^{M_2})}{16} \quad (\text{A22})$$

Moreover, by introducing eqs A20 and A22 in eq A19 and assuming  $g_{zz}^{M_1} \approx g_{zz}^{M_2}$ , we obtain that the term  $g_{zzzz}^Q$  in the PAS is

$$g_{zzzz}^Q \approx 3 \left( \frac{1}{z_M^2} \frac{2g_{zz}^M}{16} \right) = \frac{3g_{zz}^M}{8z_M^2} \quad (\text{A23})$$

Now, it is possible to give the terms  $g_{zzxx}(\theta)$ ,  $g_{zzyy}(\theta)$ , and  $g_{zzzz}(\theta)$  of eq 10 of the text, as functions of  $g_{zzzz}^Q$  (taking also into account the other components  $g_{zzyy}^Q$  and  $g_{zzxx}^Q$  are

null), by passing from the PAS to the Lab system in the following way:<sup>33</sup>

$$g_{ZZXX}(\theta) = \cos\theta_{zZ} \cos\theta_{zZ} \cos\theta_{xX} \cos\theta_{xX} g_{ZZXX}^Q + \cos\theta_{zZ} \cos\theta_{zZ} \cos\theta_{yX} \cos\theta_{yX} g_{ZZYY}^Q + \cos\theta_{zZ} \cos\theta_{zZ} \cos\theta_{zX} \cos\theta_{zX} g_{ZZZZ}^Q = \cos^2\theta_{zZ} [\cos^2\theta_{xX} g_{ZZXX}^Q + \cos^2\theta_{yX} g_{ZZYY}^Q + \cos^2\theta_{zX} g_{ZZZZ}^Q] = \cos^2\theta [\cos^2\theta_{zX} g_{ZZZZ}^Q] \quad (\text{A24})$$

If  $g_{ZZZZ}^Q$ , as given by eq A23, is introduced in eq A24, we obtain

$$g_{ZZXX}(\theta) = \frac{3}{8z_M^2} \cos^2\theta [\cos^2\theta_{zX} g_{zz}^M] \quad (\text{A25})$$

The term in the square brackets of eq A25 corresponds to  $g_{XX}^M$ , i.e., the XX-th component of the dipolar reaction field in the Lab frame. Eq A25 can then be rewritten as

$$g_{ZZXX}(\theta) = \frac{3}{8z_M^2} \cos^2\theta [g_{XX}^M] \quad (\text{A26})$$

In a similar way, it is possible to show that

$$g_{ZZYY}(\theta) = \frac{3}{8z_M^2} \cos^2\theta [g_{YY}^M] \quad (\text{A27})$$

$$g_{ZZZZ}(\theta) = \frac{3}{8z_M^2} \cos^2\theta [g_{ZZ}^M] \quad (\text{A28})$$

The form of the tensor  $\mathbf{g}^M$  for a “spherical” dipole solute (i.e., for a dipolar solute placed in a “virtual” spherical cavity) in a nematic liquid crystal is known.<sup>34</sup> The tensor is diagonal in a Lab frame whose Z is along the director, so that we can express it in terms of parallel and perpendicular components with respect to the nematic director

$$g_{ZZ}^M = g_{||}^M \quad (\text{A29})$$

$$g_{XX}^M = g_{YY}^M = g_{\perp}^M \quad (\text{A30})$$

In light of eqs A29 and A30, we have

$$g_{ZZZZ}(\theta) = \frac{3}{8z_M^2} \cos^2\theta [g_{||}^M] \quad (\text{A31})$$

$$g_{ZZXX}(\theta) = g_{ZZYY}(\theta) = \frac{3}{8z_M^2} \cos^2\theta [g_{\perp}^M] \quad (\text{A32})$$

By introducing these expressions in eq 10 of the paper, we have

$$\langle F'_{ZZ} \rangle = \frac{Q_{zz}}{16z_M^2} (g_{||}^M - g_{\perp}^M) \langle \cos^2\theta P_2(\cos\theta) \rangle \quad (\text{A33})$$

or, equivalently (because the relation  $\cos^2\theta = 2/3 P_2(\cos\theta) + 1/3$  holds)

$$\langle F'_{ZZ} \rangle = \frac{Q_{zz}}{16z_M^2} (g_{||}^M - g_{\perp}^M) \left\{ \frac{2}{3} [P_2(\cos\theta)]^2 + \frac{1}{3} [P_2(\cos\theta)] \right\} \quad (\text{A34})$$

The terms  $g_{||}^M$  and  $g_{\perp}^M$  are given by<sup>34</sup>

$$g_{||}^M = \frac{1}{R_c^3} \frac{\epsilon_{||} - n_{||}(\epsilon_{||} + 2)}{\epsilon_{||} - n_{||}(\epsilon_{||} - 1)} \quad (\text{A35})$$

$$g_{\perp}^M = \frac{1}{R_c^3} \frac{\epsilon_{\perp} - n_{\perp}(\epsilon_{\perp} + 2)}{\epsilon_{\perp} - n_{\perp}(\epsilon_{\perp} - 1)} \quad (\text{A36})$$

where  $R_c$  is basically the radius of the “virtual” cavity (assumed spherical for simplicity) where the solute is embedded, and

$$n_{||} = \frac{\epsilon_{||}(\psi - 1)}{\epsilon_{\perp} - \epsilon_{||}} \quad (\text{A37})$$

$$n_{\perp} = \frac{1 - n_{||}}{2} \quad (\text{A38})$$

with

$$\psi = \int_0^1 \frac{dz}{1 + (\epsilon_{||}/\epsilon_{\perp} - 1)z^2} = \begin{cases} \arctan \sqrt{\epsilon_{||}/\epsilon_{\perp} - 1} / \sqrt{\epsilon_{||}/\epsilon_{\perp} - 1} & \epsilon_{||} > \epsilon_{\perp} \\ 1 & \epsilon_{||} = \epsilon_{\perp} \\ \ln \left( \frac{1 + \sqrt{1 - \epsilon_{||}/\epsilon_{\perp}}}{1 - \sqrt{1 - \epsilon_{||}/\epsilon_{\perp}}} \right) / (2\sqrt{1 - \epsilon_{||}/\epsilon_{\perp}}) & \epsilon_{||} < \epsilon_{\perp} \end{cases} \quad (\text{A39})$$

(in the isotropic limit, when  $\epsilon_{||} = \epsilon_{\perp}$ , then  $n_{||} = n_z = 1/3$  and  $n_{\perp} = n_x = n_y = 1/3$ ).

By considering dideuterium as our solute, it is reasonable to assume (as shown in Figure 2) that  $z_M$  is a quarter of the D—D bond length; i.e.,  $z_M = DD/4$ . If we crudely estimate  $R_c = DD$ , the term  $16z_M^2$  of eq A34 amounts exactly to  $R_c^2$ . With this assumption, and by introducing eqs A35 and A36 in eq A34, we obtain

$$\langle F'_{ZZ} \rangle = \frac{Q_{zz}}{3R_c^5} \left[ \frac{\epsilon_{||} - n_{||}(\epsilon_{||} + 2)}{\epsilon_{||} - n_{||}(\epsilon_{||} - 1)} - \frac{\epsilon_{\perp} - n_{\perp}(\epsilon_{\perp} + 2)}{\epsilon_{\perp} - n_{\perp}(\epsilon_{\perp} - 1)} \right] \{ 2\langle [P_2(\cos\theta)]^2 \rangle + \langle [P_2(\cos\theta)] \rangle \} \quad (\text{A40})$$

This quite complicated formula can be given in a simplified and quite elegant form by expanding the square-bracketed term in powers of the parameter  $\Delta\epsilon = (\epsilon_{||} - \epsilon_{\perp})$ .<sup>34</sup> The expansion, truncated after the quadratic term (rather than after the linear, as done in ref 34) in order to account for larger  $\Delta\epsilon$  values, gives

$$\langle F'_{ZZ} \rangle = \frac{Q_{zz}}{R_c^5} \left[ \frac{\Delta\epsilon}{5(2\epsilon_s + 1)^2} (1 - A) \right] \{ 2\langle [P_2(\cos\theta)]^2 \rangle + \langle [P_2(\cos\theta)] \rangle \} \quad (\text{A41})$$

where  $\epsilon_s = \{(\epsilon_{||} + 2\epsilon_{\perp})\}/3$  and  $A = \{(36 + 79\epsilon_s)\Delta\epsilon\}/\{105\epsilon_s(2\epsilon_s + 1)\}$  (it is worth emphasizing (see text) that, for realistic values of  $\Delta\epsilon$  and  $\epsilon_s$ , the relation  $(1 - A) > 0$  safely holds).

The terms  $\langle [P_2(\cos\theta)]^2 \rangle$  and  $\langle [P_2(\cos\theta)] \rangle$  are given by the following relations:

$$\langle [P_2(\cos\theta)]^2 \rangle = \frac{\int_0^\pi [P_2(\cos\theta)]^2 \exp\left(-\frac{U(\theta)}{kT}\right) \sin\theta d\theta}{\int_0^\pi \exp\left(-\frac{U(\theta)}{kT}\right) \sin\theta d\theta} \quad (\text{A42})$$

$$\langle [P_2(\cos \theta)] \rangle = \frac{\int_0^\pi [P_2(\cos \theta)] \exp\left(-\frac{U(\theta)}{kT}\right) \sin \theta d\theta}{\int_0^\pi \exp\left(-\frac{U(\theta)}{kT}\right) \sin \theta d\theta} = S_{zz} \quad (\text{A43})$$

(where  $S_{zz}$  is, of course, the order parameter of the cylindrical solute). By taking into account the statistics relation concerning the second moment

$$\langle [P_2(\cos \theta)]^2 \rangle - \langle [P_2(\cos \theta)] \rangle^2 = \sigma^2 \quad (\text{A44})$$

eq A41 can be finally written as

$$\langle F'_{zz} \rangle \approx \frac{Q_{zz}}{R_c^5} \left[ \frac{2\Delta\epsilon}{5(2\epsilon_s + 1)^2} (1 - A) \right] [S_{zz}^2 + (S_{zz}/2) + \sigma^2] \quad (\text{A45})$$

where the symbol “ $\approx$ ” is used on purpose, to emphasize the number of assumptions and approximations adopted in the derivation. The eq A45 corresponds to the eq 11 reported in the text, *quod erat demonstrandum*. Once the value of  $S_{zz}$  is known (e.g., from NMR experiments<sup>4,11b,11c</sup>), the value of  $\sigma^2$  can be obtained by evaluating the integral of eq A42, where the usual general formula<sup>35</sup> (consistent with any second-rank kind of anisotropic interaction)  $U(\theta)/kT = BP_2(\cos \theta)$  can be used, where  $B$  is a proper parameter to be adjusted in order to reproduce as well as possible the experimental order parameters  $S_{zz}$ . Usually, because  $\sigma^2 \gg |S_{zz}|$  (and even so more  $\sigma^2 \gg S_{zz}^2$ ), eq A45 can be given in a further simplified form:

$$\langle F'_{zz} \rangle \approx \frac{Q_{zz}}{R_c^5} \left[ \frac{2\Delta\epsilon}{5(2\epsilon_s + 1)^2} (1 - A) \right] \sigma^2 \quad (\text{A46})$$

where, from eq A44,

$$\sigma^2 \approx \langle [P_2(\cos \theta)]^2 \rangle \quad (\text{A47})$$

Moreover, the  $B$  values<sup>4,11b,11c</sup> are so small (Table 1) that the relation  $U(\theta)/kT \ll 1$  usually holds. This implies that

$$\exp\left(-\frac{U(\theta)}{kT}\right) \approx 1 - \frac{U(\theta)}{kT} = 1 - BP_2(\cos \theta) \quad (\text{A48})$$

If eq A48 is introduced in eq A42, we obtain

$$\begin{aligned} \langle [P_2(\cos \theta)]^2 \rangle &= \frac{\int_0^\pi [P_2(\cos \theta)]^2 [1 - BP_2(\cos \theta)] \sin \theta d\theta}{\int_0^\pi [1 - BP_2(\cos \theta)] \sin \theta d\theta} = \\ &= \frac{\int_0^\pi [P_2(\cos \theta)]^2 \sin \theta d\theta - B \int_0^\pi [P_2(\cos \theta)]^3 \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta - B \int_0^\pi P_2(\cos \theta) \sin \theta d\theta} \end{aligned} \quad (\text{A49})$$

The integrals of eq A49 have the following values:

$$\left. \begin{aligned} \int_0^\pi \sin \theta d\theta &= 2 \\ \int_0^\pi P_2(\cos \theta) \sin \theta d\theta &= 0 \\ \int_0^\pi [P_2(\cos \theta)]^2 \sin \theta d\theta &= 0.4 \\ \int_0^\pi [P_2(\cos \theta)]^3 \sin \theta d\theta &= 0.114 \end{aligned} \right\} \quad (\text{A50})$$

Moreover, (see Table 1 of text) because  $B$  (in  $kT$  units) =  $O(10^{-2})$ , where  $O(\cdot)$  denotes the Landau's order-of-magnitude symbol, the relation

$$\int_0^\pi [P_2(\cos \theta)]^2 \sin \theta d\theta \gg B \int_0^\pi [P_2(\cos \theta)]^3 \sin \theta d\theta \quad (\text{A51})$$

can be suggested. In light of eqs A47–A51, it follows that

$$\sigma^2 \approx \langle [P_2(\cos \theta)]^2 \rangle \approx \frac{\int_0^\pi [P_2(\cos \theta)]^2 \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta} = \frac{0.4}{2} = 0.2 \quad (\text{A52})$$

When the obtained value  $\sigma^2 = 1/5$  is put in eq A46, the following relation is obtained:

$$\langle F'_{zz} \rangle \approx \frac{Q_{zz}}{R_c^5} \frac{2\Delta\epsilon}{5(2\epsilon_s + 1)^2} (1 - A) \quad (\text{A53})$$

which is exactly the eq 12 of the text, *quod erat demonstrandum*.

## References and Notes

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(24) It is worth emphasizing that the adjective “experimental”, when referred to  $\langle F'_{ZZ} \rangle$ , should not be understood as a directly measured datum but rather as an outcome resulting from the adoption of a model interpreting experimental data, from which the value of  $\langle F'_{ZZ} \rangle$  is obtained: this clarification is useful to better understand what follows in the text.

(25) Besides the approximations described in the Appendix, it should be taken into account also the fact that, in the test of eqs 11–12, an unperturbed  $D_2$  quadrupole moment has been used (always the same for all the tested solvents, in place of the perturbed solvent-dependent  $Q$  required by the formulas; see Table 1). Anyway, according to the nature of the present work, this can be certainly considered a minor approximation.

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