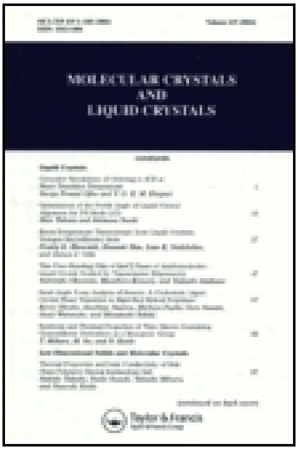

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Dipole-Dipole Correlation in Nematic Liquid Crystals

D. A. Dunmur [a] & W. H. Miller [a]
[a] Department of Chemistry, The University, Sheffield, S3 7HF, U.K.

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Dipole–Dipole Correlation in Nematic Liquid Crystals

D. A. DUNMUR and W. H. MILLER
Department of Chemistry, The University, Sheffield, S3 7HF, U.K.

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The theory of dipole–dipole correlation in nematic liquid crystals is presented and it is shown that different models for the internal field lead to different values for dipole correlation factors. Results of calculations are presented for three liquid crystals and commented upon. Using the calculated correlation factors and a simplified dielectric theory, predictions are made of the temperature derivatives of the mean permittivity and permittivity anisotropy and compared with experimental values.

INTRODUCTION

It is more than twenty years since Maier and Saupe presented[1] a molecular statistical theory of nematic liquid crystals, yet their theory still stands[2] as one of the most successful attempts to describe the properties of liquid crystals in molecular terms. Although the results of the Maier–Saupe theory have not been significantly improved upon, the basic hypotheses of the theory have been reappraised[3] in the light of more sophisticated theories.[4,5] For example Maier and Saupe attributed the stabilising nematic potential to anisotropic dispersion forces, but it now seems clear[6] that the stability of the liquid crystalline phase results from a coupling between anisotropic repulsive forces and isotropic attractive forces. Furthermore, by restricting attention to dispersion forces, the role of dipole–dipole interactions in determining the properties of liquid crystals has been largely neglected. While it is probably true that dipolar interactions are only of marginal importance in stabilising the nematic phase, it has been suggested[7,8] that they are of much more significance in determining the formation of smectic phases.

Of course the major effect of dipolar groups attached to mesogenic molecules is observed with the dielectric properties of mesophases.[9] Generally mesogens with large dipole moments along the long molecular axis have a large positive permittivity anisotropy while molecules with dipoles across the long molecular axis have small or negative anisotropies. The dependence of the permittivity components on temperature is determined partly by the order parameter and partly by the intermolecular interactions between molecular dipoles. There is a wide variety of behaviour observed for the temperature dependence of the permittivity components, and depending on the mesogen these components may increase or decrease with increasing temperature. Similarly the mean permittivity may increase or decrease with temperature for some materials and is essentially independent of temperature for others. It has also been observed[10] that there may be a discontinuity in the mean permittivity at nematic to isotropic phase transitions, and that changes in permittivity components[11] or their temperature derivatives[12] also occur at smectic to nematic transitions. Thus there is much to explain with respect to the low frequency dielectric properties of liquid crystals.

Attempts to produce a theory for the dielectric properties of nematic liquid crystals began with the work of Maier and Meier,[13] who combined the Onsager description of dielectric liquids with the Maier–Saupe mean field theory of the nematic phase. This theory neglects dipole–dipole interactions between molecules, and predicts that the temperature dependence of permittivity anisotropy follows that of the order parameter, while the mean permittivity decreases with increasing temperature and is continuous at the nematic to isotropic transition. One unsatisfactory aspect of the theory as originally formulated is that, in defining the reaction field and cavity field, it neglects the macroscopic anisotropy of the permittivity. Correcting this deficiency[12] makes a quantitative difference for the results of the Maier and Meier theory, but it does nothing to improve the agreement between the values of molecular parameters predicted by the theory and free molecule values obtained from dilute solution measurements.

Specific dipole–dipole interactions are included in the Kirkwood–Frölich theory of liquid dielectrics, and Bordewijk[14] has extended this theory to anisotropic dielectrics. This theory may be used in conjunction with known values of molecular properties to evaluate dipole–dipole correlation factors for liquid crystals. Results on the alkyl-cyano-biphenyl series of liquid crystals[12,23] indicate that there is significant anti-parallel ordering of the molecular dipoles, and suggest that any successful theory for the dielectric properties of liquid crystals must take account of short-range dipole–dipole interactions. There is some structural evidence[15,16] from X-ray diffraction that in the nematic phases of some strongly polar mesogens there is considerable anti-parallel ordering of the molecules to which dipole–dipole interactions must contribute. The part played by dipoles in determining the properties of liquid crystals has been considered by

Madhusudana and Chandrasekhar,[17] who found that inclusion of short-range dipole–dipole interactions raised the order parameter. They also adapted the Maier and Meier theory to take account of anti-ferroelectric ordering, and predicted a small incremental change in the mean permittivity at the nematic to isotropic transition.

In any theory of anisotropic dielectrics there are two problems: one is to take account of the long-range polarisation of the anisotropic medium, which determines the field experienced by a molecule, and the other is to account satisfactorily for the short-range interactions which modify the response of a molecule to an internal electric field. If attention is restricted to pairwise interactions, then the latter may be described in terms of a Kirkwood correlation factor g, defined as

$$g = 1 + \left\langle \sum_{i \neq j} \cos \theta_{ij} \right\rangle \tag{1}$$

where θ_{ij} is the angle between the dipolar axes on molecules i and j, and the angular brackets denote an ensemble average. The evaluation of g depends on the formulation of the internal field i.e. how the long-range polarisation of the medium is accounted for, and various approaches have been developed. In this paper we wish to compare the various methods that have been described for the determination of g-factors for nematic liquid crystals. We will attempt to assess the different formulations of the internal electric field on the basis of their relative success in describing the dielectric behaviour observed for different mesogens. Apart from the information such studies give on the theories of anisotropic dielectrics, there is considerable practical importance in the study of the temperature dependence of the permittivity of liquid crystals. The threshold voltage and other operational parameters of liquid crystal displays depend on the anisotropy of the permittivity,[18] and the multiplexability of matrix displays may be limited by the temperature dependence of the permittivity. Thus an understanding of the factors that determine the dielectric behaviour of liquid crystals will aid the development of new materials having better display properties.

THEORY

In this section we wish to outline briefly the various approaches that have been developed to take account of dipole–dipole correlation in the dielectric theories of nematic liquid crystals.

The definition (Eq. (1)) for the dipole correlation factor is independent of an external axis system, however for macroscopically aligned unaxial liquid crystals, the correlation factors extracted from measurements of the principal permittivities are the projections of the local dipole correlation on axes parallel and perpendicular to the director. It is convenient therefore to introduce two correlation factors $g_{\|}$ and $g_{\perp}$ which are defined with respect to these axes:

$$g_{\|} = 1 + \frac{\langle \sum_{j \neq i} u^i_{\|} \mu^j_{\|} \rangle}{\langle \mu^{i2}_{\|} \rangle}$$

and

$$g_{\perp} = 1 + \frac{\langle \sum_{j \neq i} \mu^i_{\perp} \mu^j_{\perp} \rangle}{\langle \mu^{i2}_{\perp} \rangle} \tag{2}$$

$\mu^i_{\|}$ and $\mu^i_{\perp}$ are the components of the molecular dipole $\boldsymbol{\mu}^i$ parallel and perpendicular to the director respectively, and their ensemble averages are:

$$\langle \mu^{i2}_{\|} \rangle = \frac{\mu_l^2(2S+1)}{3} + \frac{\mu_t^2(1-S)}{3}$$

and

$$\langle \mu^{i2}_{\perp} \rangle = \frac{\mu_l^2(1-S)}{3} + \frac{\mu_t^2(S+2)}{6} \tag{3}$$

We assume that it is possible to define a molecular axis (e.g. the principal axis of the maximum polarizability component) such that the microscopic order parameter is defined as:

$$S = \tfrac{1}{2}\langle 3\cos^2\theta_i - 1 \rangle \tag{4}$$

θ_i is the angle between the unique molecular axis of molecule i and the director, and μ_l and μ_t are the components of the molecular dipole moment parallel and perpendicular to the unique molecular axis. The factors $g_{\|}$ and $g_{\perp}$ can be related to the total dipole correlation factor in the nematic phase g_N, which is independent of the macroscopic orientation of the director.

$$\begin{aligned} g_N = {} & g_{\|}[\mu_l^2(2S+1) + \mu_t^2(1-S)]/3\mu^2 \\ & + 2g_{\perp}[2\mu_l^2(1-S) + \mu_t^2(S+2)]/6\mu^2 \end{aligned} \tag{5}$$

$$\mu^2 = \mu_l^2 + \mu_t^2$$

Bordewijk[14] has extended the Kirkwood–Fröhlich theory of isotropic dielectric fluids to anisotropic systems. In applying this theory to nematic liquid crystals he considered two limiting cases for which the internal field could be evaluated. For ideal order ($S = 1$) the relationships between the molecular dipole and the measured permittivity components (ε_λ) become:

$$\frac{(\varepsilon_\lambda - n_\lambda^2)[\varepsilon_\lambda + (n_\lambda^2 - \varepsilon_\lambda)\Omega_\lambda^\varepsilon]}{\varepsilon_\lambda[1 + (n_\lambda^2 - 1)\Omega_\lambda^s]^2} = \frac{N}{\varepsilon_0 kT} g_\lambda \langle \mu_\lambda^2 \rangle \tag{6}$$

where:

$$\Omega_\lambda^\varepsilon = a^3(2\varepsilon_\parallel^{1/2}\varepsilon_\perp)^{-1} \int_0^\infty \left[\left(\frac{S + a^2}{\varepsilon_\lambda}\right)R\right]^{-1} \mathrm{d}S; \quad R^2 = \left(\frac{S + a^2}{\varepsilon_\parallel}\right)\left(\frac{S + a^2}{\varepsilon_\perp}\right)^2$$

$$\lambda = \parallel, \perp$$

$$\Omega_\lambda^s = \left(\frac{abc}{2}\right) \int_0^\infty [(s + \lambda^2)R]^{-1}\, \mathrm{d}S; \quad R^2 = (S + a^2)(S + b^2)(S + c^2)$$

$$\lambda = a, b, c$$

The subscript λ refers to directions parallel or perpendicular to the director, $\Omega_\lambda^\varepsilon$ and Ω_λ^s are depolarisation factors for anisotropy in the permittivity and cavity shape respectively, and n_λ^2 is the high frequency permittivity (refractive index). Since the temperature dependence of the permittivity components is due primarily to the change of order parameter with temperature, the result for ideal order is not particularly useful. The other limiting case considered by Bordewijk was for isotropic polarizability, and the result obtained is:

$$\frac{(\varepsilon_\lambda - n_\lambda^2)[\varepsilon_\lambda + (n_\lambda^2 - \varepsilon_\lambda)\Omega_\lambda^\varepsilon]}{\varepsilon_\lambda(n_\lambda^2 - 1)^2} = \frac{\varepsilon_0 g_\lambda \langle \mu_\lambda^2 \rangle}{N\alpha^2 kT} \tag{7}$$

α is the isotropic molecular polarizability. Again this result describes an unphysical situation, since if the polarizability anisotropy is zero, one expects on symmetry grounds that the order parameter would also equal zero.

The anisotropic Kirkwood–Fröhlich theory can only be applied to partially ordered systems if some model is adopted for the internal field. One approach is to replace the isotropic polarizability in Eq. (7) by the average of the molecular polarizability components in the macroscopic axis system, giving:[12, 19]

$$\frac{(\varepsilon_\lambda^2 - n_\lambda^2)[\varepsilon_\lambda + (n_\lambda^2 - \varepsilon_\lambda)\Omega_\lambda^\varepsilon]}{\varepsilon_\lambda(n_\lambda^2 - 1)^2} = \frac{\varepsilon_0 g_\lambda \langle \mu_\lambda^2 \rangle}{N\alpha_\lambda^2 kT} \tag{8}$$

with $\alpha_\parallel = \alpha + 2\Delta\alpha S/3$ and $\alpha_\perp = \alpha - \Delta\alpha S/3$ ($\Delta\alpha$ is the anisotropy of the molecular polarizability). This is equivalent to replacing the internal field tensor by its average value, and assuming that the induced polarisation can be determined by averaging separately over the internal field tensor and the molecular polarizability. A rather different model has been proposed by

Bordewijk and de Jeu[20] based on the experimentally observed proportionality between the birefringence ($\Delta n^2 = n_\parallel^2 - n_\perp^2$) and the product of the number density and order parameter. The model has a rather surprising consequence that the principal axes of the internal field tensor coincide with the principal axes of the molecular polarizability tensor i.e. as a molecule rotates the internal field tensor rotates with it. In a sense this model introduces an effective polarizability which itself must depend on the local structure of the fluid. The resultant relationships between the pemittivity components and molecular parameters are:[21]

$$\frac{(\varepsilon_\lambda - n_\lambda^2)[\varepsilon_\lambda + (n_\lambda^2 - \varepsilon_\lambda)\Omega_\lambda^\varepsilon]}{\varepsilon_\lambda} = \frac{Ng_\lambda\langle\mu_{d\lambda}^2\rangle}{\varepsilon_0 kT} \tag{9}$$

$$\langle\mu_{d\parallel}^2\rangle = \frac{\mu_l^2(1+2S)}{3(1-\varepsilon_0^{-1}N\alpha_l\Omega_l^s)^2} + \frac{\mu_t^2(1-S)}{3(1-\varepsilon_0^{-1}N\alpha_t\Omega_t^s)^2}$$

and

$$\langle\mu_{d\perp}^2\rangle = \frac{\mu_l^2(1-S)}{3(1-\varepsilon_0^{-1}N\alpha_l\Omega_l^s)^2} + \frac{\mu_t^2(S+2)}{6(1-\varepsilon_0^{-1}N\alpha_t\Omega_t^s)^2}$$

α_l and α_t are principal components of the molecular polarizability. For a molecule with $\mu_t = 0$ Eqs. (9) reduce to Eqs. (6) for $S = 1$.

Madhusudana and Chandrasekhar extended the Maier and Meier theory of the dielectric properties of nematogens to include dipole–dipole correlation. For the general case of an off-axis dipole their equations become:

$$(\varepsilon_\parallel - 1) = \varepsilon_0^{-1}NLF\left\{\alpha + \frac{2\Delta\alpha S}{3} + \frac{Fg_\parallel}{3kT}[\mu_l^2(2S+1) + \mu_t^2(1-S)]\right\}$$

$$(\varepsilon_\perp - 1) = \varepsilon_0^{-1}NLF\left\{\alpha - \frac{\Delta\alpha S}{3} + \frac{Fg_\perp}{6kT}[2\mu_l^2(1-S) + \mu_t^2(S+2)]\right\} \tag{10}$$

L and F are isotropic cavity field and reaction field factors. Although Eqs. (10) contain only an approximate description of the internal field, they are useful because unlike the Kirkwood–Fröhlich equations they provide a simple relationship between molecular parameters and the components of the permittivity tensor. From Eq. (10) the mean permittivity ($\bar{\varepsilon}$) is given by:

$$\bar{\varepsilon} = 1 + \varepsilon_0^{-1}NLF\left(\alpha + \frac{Fg_N\mu^2}{3kT}\right) \tag{11}$$

and in the isotropic liquid phase the permittivity is:

$$\varepsilon_i = 1 + \varepsilon_0^{-1}NLF\left(\alpha + \frac{Fg_i\mu^2}{3kT}\right) \tag{12}$$

which reduces to the Kirkwood–Fröhlich result for isotropic fluids if the Lorenz–Lorentz relationship is used for α. Putting $S = 0$ in the expression (5) for g_N gives:

$$3(g_N)_{S=0} = g_{\parallel} + 2g_{\perp} \tag{13}$$

and the extent to which $(g_N)_{S=0}$ differs from g_i is a measure of the change in short-range dipole–dipole correlation at the nematic to isotropic transition. The change in the mean permittivity at this transition is given by the difference between Eqs. (11) and (12):

$$\delta\bar{\varepsilon}_{NI} = \frac{\mu^2}{3\varepsilon_0 k}\left\{\frac{N_i L_i F_i^2 g_i}{T_i} - \frac{N_N L_N F_N^2 g_N}{T_N}\right\} \tag{14}$$

If it is further assumed that the number densities and internal field factors L and F are equal at the transition, then Eq. (14) reduces to:

$$\delta\bar{\varepsilon}_{NI} = -\frac{NLF^2 S_{NI}}{9\varepsilon_0 k T_{NI}}(2\mu_l^2 - \mu_t^2)(g_{\parallel} - g_{\perp}) \tag{15}$$

S_{NI} and T_{NI} are the transitional order parameter and temperature. Both positive and negative dielectric increments are predicted by Eq. (15) depending on the molecular dipole moment and correlation factors. While most single component polar liquid crystals have a positive $\delta\bar{\varepsilon}_{NI}$, recent work[22] has shown that their mixtures may have zero or even slightly negative dielectric increments.

CALCULATIONS AND DISCUSSION

To assess the different models for the internal electric field in nematic liquid crystals, we have calculated the correlation factors for three liquid crystals, two of positive dielectric anisotropy and one with a negative anisotropy. The choice of nematogens for study is rather restricted since it is necessary to know the free molecule values for the dipole moments and polarizability components.

Our results are presented in Table II for calculations based on three different formulations of the Bordewijk–Kirkwood–Fröhlich theory. Also listed in Table I are the appropriate molecular parameters and values for the permittivities and refractive indices used in the calculations. The g-factors are sensitive to the parameters used in the calculations, and for this reason results for $g_{\parallel}(b)$ and $g_{\perp}(b)$ for 5CB and 7CB differ slightly from earlier published values.[12] For consistency we have assumed that the shape factor in Eqs. (6) and (9) is equal to one third (corresponding to a spherical cavity).

TABLE I

Parameters used in calculations

Liquid crystal	Permittivities and refractive indices				Molecular properties			
	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$n_{\parallel}$	$n_{\perp}$	$\mu_l/10^{-30}$ Cm	$\mu_t/10^{-30}$ Cm	$\alpha/10^{-40}$ J^{-1} C^{2}m^2	$\Delta\alpha/10^{-40}$ J^{-1} C^{2}m^2
44′ *n*-pentyl-cyano-biphenyl (5CB)	17.3	7.3	1.708	1.537	15.9	—	37.5	19.6
44′ *n*-heptyl-cyano-biphenyl (7CB)	15.8	6.0	1.681	1.521	16.4	—	42.4	17.6
4-methoxy-benzylidene 4′-*n*-butyl aniline (MBBA)	4.68	5.13	1.734	1.551	1.22	7.24	34.8	7.0

TABLE II

Dipole correlation factors in nematic liquid crystals

Liquid crystal (temperature†)	$g_{\parallel}$			$g_{\perp}$			Eq. (5) g_N			Eq. (13) $(g_N)_{S=0}$			
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	g_i
5CB (29°C)	0.23	0.33	0.19	0.39	0.69	1.00	0.28	0.45	0.73	0.34	0.57	0.73	0.53
7CB (36°C)	0.24	0.33	0.19	0.36	0.65	1.00	0.28	0.43	0.73	0.32	0.54	0.73	0.51
MBBA (40°C)	1.05	0.73	0.53	0.75	0.82	0.59	0.80	0.80	0.58	0.85	0.79	0.57	0.82

† Temperatures are chosen to give equal reduced temperatures of 0.98 ($S = 0.497$).

[a] Bordewijk–de Jeu empirical internal field (Ref. 20). Eq. (9).

[b] A Kirkwood–Frohlich internal field for partial order (Refs. 12 and 19). Eq. (8).

[c] Kirkwood–Fröhlich–Bordewijk internal field for ideal order (Ref. 14). Eq. (6).

All three models suggest relatively high correlation in 5CB and 7CB, while MBBA with an off-axis dipole has g-factors closer to unity. In the absence of any other evidence it is difficult to comment objectively on the results. The calculations based on model (b) give that g_i is approximately equal to $(g_N)_{S=0}$, which would be consistent with the view that there is no dramatic change in short range order at the nematic to isotropic transition.

One consistency test that can be applied to the results is to compare the calculated and experimental discontinuities in the mean permittivity at the nematic to isotropic transition. The results of this calculation using Eq. (14) are given in Table III and again the model (b) appears to give best agreement with experiment.

TABLE III

Calculated and experimental dielectric increments [Eq. (15)]

		$\delta\bar{\varepsilon}_{NI}$(calc)		
	$\delta\bar{\varepsilon}_{NI}$(expt)	(a)	(b)	(c)
5CB	0.67	3.79	1.00	−3.54
7CB	0.68	3.01	0.91	−3.28
MBBA	0.02	−0.02	−0.02	+0.57

The permittivity of dielectric liquids decreases with increasing temperature in accord with the simple Debye theory. However with nematic liquid crystals the mean permittivity may increase or decrease with temperature depending on the particular mesogen. Some understanding of this can be achieved from the Maier–Meier–Madhusudana–Chandrasekhar formulation of the dielectric theory of nematogens. If it is assumed that the dipole terms in Eqs. (10) and (11) predominate then one obtains a simple expression for the temperature variation of the mean permittivity:

$$\frac{1}{\bar{\varepsilon}}\frac{\mathrm{d}\bar{\varepsilon}}{\mathrm{d}T} = \frac{1}{g_N}\left\{\frac{\mathrm{d}g_N}{\mathrm{d}T} - \frac{g_N}{T}\right\} \tag{16}$$

In the absence of correlation ($g_N = 1$) Eq. (16) predicts a temperature dependence for $\bar{\varepsilon}$ in accordance with the simple Debye theory. A further simplification of Eq. (16) may be made if it is assumed that the temperature dependence of g_N is due primarily to the order parameter. There is some evidence for this since values calculated[19] for $g_{\|}$ and $g_{\perp}$ are approximately constant over the nematic temperature range. From Eqs. (5) and (16) we obtain:

$$\frac{1}{\bar{\varepsilon}}\frac{\mathrm{d}\bar{\varepsilon}}{\mathrm{d}T} = \frac{1}{g_N}\left\{\frac{(2\mu_l^2 - \mu_t^2)(g_\parallel - g_\perp)}{3\mu^2}\frac{\mathrm{d}S}{\mathrm{d}T} - \frac{g_N}{T}\right\} \tag{17}$$

A similar straightforward procedure yields an expression for the temperature derivative of the permittivity anisotropy. The expression is not particularly compact and is not given here, although it can easily be obtained from Eq. (10). Values for the temperature derivatives of the mean permittivity and permittivity anisotropy calculated using this simple theory are given in Table IV and compared with experimental results. In all these calculations we have assumed that the order parameter and its variation with temperature are given by the Maier–Saupe mean field theory, and only results for the internal field model (b) are reported. Agreement between calculated and experimental values is reasonable in some cases and poor in others. It must be emphasized however that the calculated permittivity derivatives are very sensitive to the order parameter, and better agreement between theory and experiment can be achieved if experimental order parameters are substituted for the mean field values used in these calculations.

TABLE IV

Calculated and experimental temperature derivatives of the permittivity using different models for the internal field

		$\frac{1}{\varepsilon}\frac{\mathrm{d}\bar{\varepsilon}}{\mathrm{d}T}\times 10^3$		$\frac{1}{\Delta\varepsilon}\frac{\mathrm{d}\Delta\bar{\varepsilon}}{\mathrm{d}T}\times 10^2$	
		calc.	expt.	calc.	expt.
5CB	(a)	−0.3		−2.9	
	(b)	0.8	3.8	−3.7	−3.5
	(c)	2.5		8.3	
7CB	(a)	−1.1		−2.5	
	(b)	0.5	7.8	−3.3	−2.8
	(c)	2.4		8.1	
MBBA	(a)	−2.3		−3.1	
	(b)	−3.4	−1.0	−1.6	−4.6
	(c)	−3.4		−1.6	

CONCLUSIONS

In this paper we have attempted to examine in some detail the correlation of molecular dipoles in three nematic liquid crystals. Although different models for the internal electric field lead to different correlation factors, all our results suggest that the dipole–dipole correlation in 5CB and 7CB is much greater than in the Schiff's base MBBA. The existence of antiparallel dipole correlation in the alkyl-cyano-biphenyls suggests relatively strong molecular interactions perpendicular to the director, and can be associated with the tendency of these compounds to form smectic phases. Of particular interest is the extent to which the dipole–dipole correlation projects onto axes parallel and perpendicular to the director. If molecules in the nematic phase rotate independently about their long molecular axes, then one would expect the perpendicular correlation factor to equal unity. The fact that $g_\perp$ is not equal to one indicates that components of the molecular dipole perpendicular to the director are also correlated. One might expect this effect to be largest in molecules having off-axis dipoles, but such molecules are often bent, and steric considerations may prevent the correlation of dipoles on neighbouring molecules. Dipole–dipole interactions are weak compared with the forces responsible for the stabilisation of the nematic phase, thus the existence of dipole–dipole correlation in nematogens is determined primarily by steric considerations, and the strength and orientation of the molecular dipole is only of secondary importance. However a generalisation based on this work is that strongly polar linear molecules will have a low $g_\parallel$ while *linear* molecules with large off axis dipoles will have a low $g_\perp$.

By making some rather severe approximations it is possible to relate the temperature derivatives of the mean permittivity and permittivity anisotropy to the correlation factors. Our result (Eqs. (16) and (17)) for the temperature derivative of $\bar{\varepsilon}$ qualitatively explains the variety of behaviour observed for the variation of the mean permittivity with temperature in terms of the magnitude and sign of $\mathrm{d}g_N/\mathrm{d}T$. Quantitative agreement between the simple theory and experiment cannot really be expected, but it is hoped that the results of the simple approach developed in this paper will provide a basis for the interpretation of the wide range of dielectric behaviour exhibited by nematic liquid crystals.

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