CHAPTER II

THEORIES OF THE DIELECTRIC PROPERTIES OF NEMATICS

The dielectric anisotropy of a nematic is determined by two factors: (i) the polarizability anisotropy ($\triangle\alpha$) which, for elongated molecules always makes a positive contribution and (ii) the permanent dipole moment (μ). The sign and value of $\triangle\varepsilon$ is determined by the relative strengths of these two factors. The aim of the theory is to relate tho dielectric constants of the medium to the polarizability anisotropy and the permanent dipole moment of the molecule.

Maier and Meier's theory of dielectric anisotropy

Maier and Meier[1] extended the Onsager's theory[2] of dielectric permittivity to nematics using the molecular field approximation.[3] Onsager derived the theory for isotropic polar liquids by assuming a molecule, represented by a polarisable point dipole of moment μ, in a spherical cavity of molecular dimensions surrounded by a continuous dielectric medium of dielectric constant ϵ.

We choose XYZ as the space-fixed coordinate system, Z being parallel to the unique axis of the medium and $\xi \eta \zeta$ as the molecule-fixed coordinate system, the ζ axis coinciding with the long axis of the molecule, the angle between Z and ζ being θ. Let ν be the Eulerian angle between the ξ axis and the line of intersection of the XY and $\xi \eta$ planes and ν' the angle between this line and X. Further we assume that the dipole moment μ is making an angle β with the long molecular axis.

If α_l and α_t are the molecular polarizabilities along and perpendicular to the long molecular axis, then the mean polarizability

$$\bar{\alpha} = \frac{1}{3}(\alpha_l + 2\alpha_t) \quad . \qquad (2.1)$$

The effective induced dipole moment per molecule along the unique axis is given by

$$\bar{m}_{\parallel} = [\alpha_l \cos^2\theta + \alpha_t \sin^2\theta)FhE_{\parallel}\ , \qquad (2.2)$$

where $h = \dfrac{3\bar{\varepsilon}}{2\bar{\varepsilon} + 1}$ is the cavity field factor, $\bar{\varepsilon}[= \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})]$ the mean dielectric constant, $F = \dfrac{1}{1 - \bar{\alpha}f}$, $f = \dfrac{4\pi N_A \rho(2\bar{\varepsilon} - 2)}{3M(2\bar{\varepsilon} + 1)}$ the reaction field factor, ρ the density, M the molecular weight, N_A the Avagadro number and $E_{\parallel}$ the applied field parallel to the unique axis.

Making use of the definition of the order parameter s given by (1.1) and (2.1) we can rewrite

$$\bar{m}_{\parallel} = [\bar{\alpha} + \tfrac{2}{3}\Delta\alpha s]hFE_{\parallel}\ , \qquad (2.3)$$

where $\Delta\alpha = \alpha_l - \alpha_t$. For nematics $\Delta\alpha$ is always positive. Similarly the effective induced dipole moment per molecule perpendicular to the unique axis is given by

$$\bar{m}_{\perp} = [\bar{\alpha} - \tfrac{1}{3}\Delta\alpha s]hFE_{\perp}\ . \qquad (2.4)$$

According to Onsager's theory the potential energy of the dipoles due to the external field

$$U = -h(\mu \cdot E)$$

is quite small since only low fields are involved. To this we have to add the orientational energy (U_1) of the nematic[3]

$$U_1 = -\frac{A}{V^2}(3\cos^2\theta_1 - 1)s\,. \qquad \text{(a. 5)}$$

Making use of the approximation that

$$\exp[-(U + U_1)/kT] = (1 - U/kT)\exp(-U_1/kT)$$

we can write the effective dipole moments along the field directions as

$$\bar{\mu}_{\parallel} = \frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}[1 + (\mu_z h E_{\parallel}/kT)]\mu_z\, W(\theta)\sin\theta\, d\theta\, d\nu\, d\nu'}{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}[1 + (\mu_z h E_{\parallel}/kT)]W(\theta)\sin\theta\, d\theta\, d\nu\, d\nu'} \qquad (2.6)$$

and

$$\bar{\mu}_{\perp} = \frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} [1 + (\mu_x h E_{\perp} /kT)]\mu_x \; W(\theta)\sin\theta \, d\theta \, d\nu \, d\nu'}{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} [1 + (\mu_x h E_{\perp} /kT)] W(\theta)\sin\theta \, d\theta \, d\nu \, d\nu'} , \qquad (2.7)$$

where

$\mu_z = F\mu[\cos\beta \cos\theta + \sin\beta \sin\nu \sin\theta]$,

$\mu_x = F\mu[\cos\beta \sin\nu' \sin\theta + \sin\beta(\cos\nu' \cos\nu - \sin\nu \sin\nu' \cos\theta)]$

and $W(\theta) = \exp(-U_1/kT)$ is the probability of a molecule having an orientation between θ and $\theta + d\theta$.

The integration of (2.6) and (2.7) leads to

$$\bar{\mu}_{\parallel} = \frac{\mu^2}{2kT}[2\cos^2\beta(1 - \langle\sin^2\theta\rangle) + \sin^2\beta \langle\sin^2\theta\rangle]hF^2E_{\parallel} \qquad (2.8)$$

and

$$\bar{\mu}_{\perp} = \frac{\mu^2}{2kT}[\cos^2\beta \langle\sin^2\theta\rangle + \sin^2\beta(1 - \tfrac{1}{2}\langle\sin^2\theta\rangle)]hF^2E_{\perp} . \qquad (2.9)$$

Using the dafinition of the order parameter we can reduce (2.8) and (2.9) to

$$\bar{\mu}_{\parallel} = \frac{\mu^2}{3kT}[1 - (1 - 3\cos^2\beta)s]hF^2E_{\parallel} \qquad (2.10)$$

and

$$\bar{\mu}_\perp = \frac{\mu^2}{3kT}\left[1 + \frac{1}{2}(1 - 3\cos^2\beta)s\right]hF^2E_\perp . \qquad (2.11)$$

Now the principal dielectric constant along the unique axis can be determined from

$$\frac{\epsilon_\parallel - 1}{4\pi} E_\parallel = \frac{N_A\rho}{M}(\bar{m}_\parallel + \bar{\mu}_\parallel) . \qquad (2.12)$$

Substituting for $\bar{m}_\parallel$ and $\bar{\mu}_\parallel$ from (2.3) and (2.10) we get

$$\epsilon_\parallel = 1 + 4\pi\frac{N_A\rho\, hF}{M}\left\{\bar{\alpha} + \frac{2}{3}\Delta\alpha s + \frac{F\mu^2}{3kT}\left[1-(1-3\cos^2\beta)s\right]\right\} . \qquad (2.13)$$

Similarly

$$\frac{\epsilon_\perp - 1}{4\pi} E_\perp = \frac{N_A\rho}{M}(\bar{m}_\perp + \bar{\mu}_\perp) . \qquad (2.14)$$

Substituting for $\bar{m}_\perp$ and $\bar{\mu}_\perp$ from (2.4) and (2.11) we get

$$\epsilon_\perp = 1+4\pi\frac{N_A\rho\, hF}{M}\left\{\bar{\alpha} - \frac{1}{3}\Delta\alpha s + \frac{F\mu^2}{3kT}\left[1 + \frac{1}{2}(1 - 3\cos^2\beta)s\right]\right\} . \qquad (2.15)$$

Therefore the dielectric anisotropy

$$\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp = \frac{4\pi N_A\rho\, hF}{M}\left[\Delta\alpha - \frac{F\mu^2}{2kT}(1 - 3\cos^2\beta)\right]s . \qquad (2.16)$$

The widely varying dielectric properties of nematic liquid crystals can be explained qualitatively on the basis of this equation. The value of $\Delta\varepsilon$ can be negative or positive depending on the relative strengths of the two terms in the square brackets. If β is zero or very small the two terms add up to give a strong positive dielectric anisotropy. When $\beta \simeq 55°$, the second term vanishes and the contribution to $\Delta\varepsilon$ is only from $\Delta\alpha$. For higher values of β, $\Delta\varepsilon$ will be negative or positive depending on whether the dipolar contribution is greater or less than the polarizability anisotropy contribution.

Maier and Meier[1] measured the principal dielectric constants of p-azoxyanisole (PAA) and found the dielectric anisotropy to be negative. We have reproduced their measurements in figure 2.1. They also calculated $\Delta\varepsilon$ from (2.16). The molecular polarizabilities of PAA were estimated from the refractive index measurements

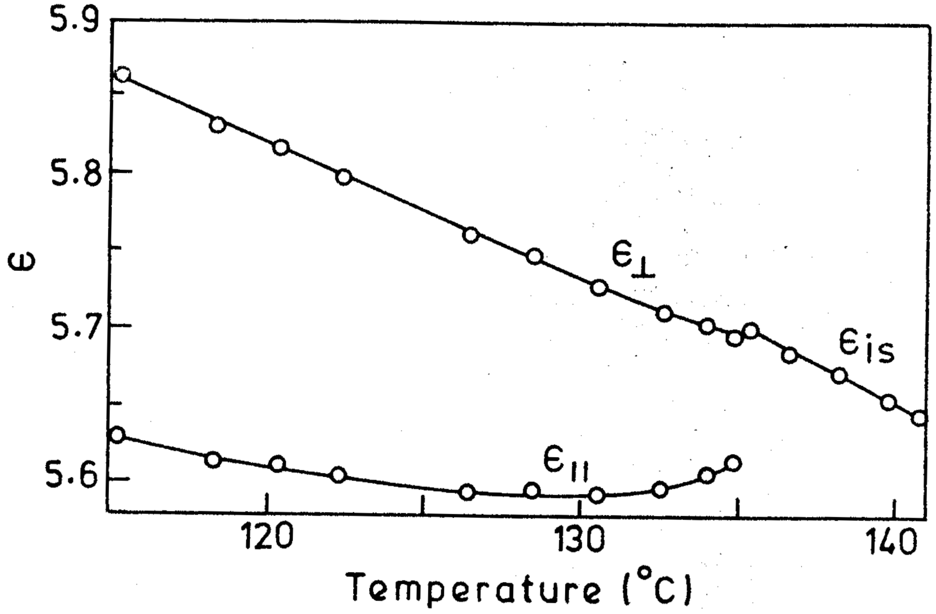

Figure 2.1

Principal dielectric constants of p-azoxyanisole. $\epsilon_{\|}$ and $\epsilon_\perp$ are the values for measuring fields parallel and perpendicular to the optic axis and ϵ_{is} the isotropic value. (After Maier and Meier[1]) in the solid phase. The values of μ and β were estimated to be 2.2 Debye and 62.5° respectively from Kerr constant measurements in dilute solutions and dielectric measurements in the isotropic phase. The value of $\Delta\varepsilon$, calculated using these values and the theoretical value of s, turned out to be negative in fair agreement with the experimental data.

From (2.13) and (2.15) we can also calculate the mean dielectric constant in the nematic phase.

$$\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp}) = 1 + 4\pi \frac{N_A \rho h F}{M} \left(\bar{\alpha} + \frac{F\mu^2}{3kT}\right) \qquad (2.17)$$

The isotropic value of the dielectric constant can be obtained by putting $s = 0$ in either (2.13) or (2.15).

$$\varepsilon_{is} = 1 + 4\pi \frac{N_A \rho h F}{M} \left(\bar{\alpha} + \frac{F\mu^2}{3kT}\right) \qquad (2.18)$$

(2.17) and (2.18) imply that $\bar{\varepsilon}$ and ε_{is} should coincide T_{NI} for all nematics. but $\bar{\varepsilon}$ is found to coincide with ε_{is} only for the nonpolar p,p'-di-n-alkylazobenzenes.4 However in compounds in which the molecule has a component of the dipole moment along the long molecular axis, $\bar{\varepsilon}$ is experimentally found to be less than ε_{is}. In the case of PAA[4] the difference between $\bar{\varepsilon}$ and ε_{is} was found to be $\sim 1\%$. For strongly polar molecules[5] the difference can be as much as 4-5% as we shall see in chapters III and IV. The Maier and Meier equation is not able to account for this difference between $\bar{\varepsilon}$ and ε_{is} because it completely neglects the near neighbour correlations.

Madhusudana and Chandrasekhar[6] have proposed a theory of antiparallel near neighbour correlations in nematics composed of strongly polar molecules. They have included an antiparallel short range order term in the interaction potential. Using this modified form of the potential in the Maier-Meier theory of dielectric anisotropy, they showed theoretically that $\bar{\varepsilon}$ should be less than the extrapolated isotropic value. Let us briefly discuss their theory.

Theory of antiferroelectric short range order

theory is based an a method developed originally by Bethe[7] for treating order-disorder effects in binary alloys. We choose a space fixed coordinate system XYZ, with the Z axis parallel to the unique axis of the medium. It is assumed that each molecule is surrounded by s nearest neighbours ($s \geqslant 3$) and that no two of them are nearest neighbours of each other. This implies that in writing down the interaction between the central molecule and its s nearest neighbours, we neglect the interaction between any two of the s neighbours. Let $E(\theta_{0j})$ be the orientational energy of interaction between the central molecule 0 and one of its nearest neighbours j. θ_{0j} is a function of the spherical coordinates θ_0, φ_0, θ_j and φ_j. Similarly let $V(\theta_j)$ be the interaction energy between j and the remaining molecules of the uniaxial medium. The relative weight for a given configuration of a cluster of $(s + 1)$ molecules is given by

$$\prod_{j=1}^{z} f(\theta_{0j})\, g(\theta_j)\ , \qquad (2.19)$$

where $f(\theta_{0j}) = \exp[-E(\theta_{0j})/kT]$,

$g(\theta_j) = \exp[-V(\theta_j)/kT]$.

The relative probability that the central molecule 0 and one of its nearest neighbours, say 1, are oriented along θ_0, φ_0 and θ_1, φ_1 respectively is

$$\psi(\theta_0,\varphi_0;\theta_1,\varphi_1) = f(\theta_{01})g(\theta_1)\prod_{j=2}^{z}\iint f(\theta_{0j})g(\theta_j)d(\cos\theta_j)d\varphi_j\ . \qquad (2.20)$$

Since this probability should be the same irrespective of which molecule is regarded as the central one

$$\psi(\theta_0,\varphi_0;\ \theta_1,\varphi_1) = \psi(\theta_1,\varphi_1;\ \theta_0,\varphi_0)\ , \qquad (2.21)$$

which is the consistency relation due to Krieger and James.[8] (2.21) can be reexpressed in the form

$$\frac{g(\theta_0)}{\left[\iint f(\theta_{0j})g(\theta_j)d(\cos\ \theta_j)d\varphi_j\right]^{z-1}} = \text{constant}\ , \qquad (2.22)$$

which has to be satisfied for all values of θ and φ.

Now we have to consider the form of the orientation potentials $E(\theta_{0j})$ and $V(\theta_j)$. For simplicity let us assume that the molecules are cylindrically symmetric and that the dipole moment is along the long molecular axis. Evidently by virtue of the anisotropic shape of the molecule the nearest neighbours will have a tendency to assume an antiparallel orientation. However, the absence of long range translational order in the nematic phase precludes the possibility of antiferroelectric long range order. Under these conditions we can assume the pair potentials to be of the form

$$E(\theta_{0j}) = A^{*}P_1(\cos\theta_{0j}) - B^{*}P_2(\cos\theta_{0j}) \qquad (2.23)$$

and

$$V(\theta_j) = -BP_2(\cos\theta_j) \, . \qquad (2.24)$$

The first term in (2.23) signifies antiparallel ordering. P_1 and P_2 are Legendre polynomials of the first and second order, A^*, B^* and B are the interaction parameters. Using (2.23) and (2.24) in (2.22) we get the consistency relation

$$\frac{\exp[BP_2(\cos\theta_0)/kT]}{\left[\int\!\!\int \exp\left\{-(A^*/kT)P_1(\cos\theta_{0j}) + (B^*/kT)P_2(\cos\theta_{0j}) + (B/kT)P_2(\cos\theta_j)\right\} d(\cos\theta_j)d\varphi_j\right]^{z-1}} = \text{constant}\,. \tag{2.25}$$

This relation has to be satisfied for all values of $P_2(\cos\theta_0)$. If A^*/B^* is known, the parameter influencing the long range order can be determined in terms of B^* at all temperatures.

The short range order parameters are given by

$$\left\langle P_1(\cos\theta_{0j})\right\rangle = \frac{\int\cdot\cdot\int P_1(\cos\theta_{0j})\psi(\theta_0,\varphi_0;\theta_j,\varphi_j)d(\cos\theta_0)d\varphi_0\; d(\cos\theta_j)d\varphi_j}{\int\cdot\cdot\int\psi(\theta_0,\varphi_0;\theta_j,\varphi_j)d(\cos\theta_0)d\varphi_0\; d(\cos\theta_j)d\varphi_j} \tag{2.26}$$

and

$$\left\langle P_2(\cos\theta_{0j})\right\rangle = \frac{\int\cdot\cdot\int P_2(\cos\theta_{0j})\psi(\theta_0,\varphi_0;\theta_j,\varphi_j)d(\cos\theta_0)d\varphi_0\; d(\cos\theta_j)d\varphi_j}{\int\cdot\cdot\int\psi(\theta_0,\varphi_0;\theta_j,\varphi_j)d(\cos\theta_0)d\varphi_0\; d(\cos\theta_j)d\varphi_j} \tag{2.27}$$

The long range order parameter

$$s = \frac{\int \cdot \cdot \int P_2(\cos\theta_0)\psi(\theta_0,\varphi_0;\theta_j,\varphi_j)d(\cos\theta_0)d\varphi_0 \; d(\cos\theta_j)d\varphi_j}{\int \cdot \cdot \int \psi(\theta_0,\varphi_0;\theta_j,\varphi_j)d(\cos\theta_0)d\varphi_0 \; d(\cos\theta_j)d\varphi_j} \; . \tag{2.28}$$

The curves for the short range order parameters $\langle P_1(\cos\theta_{0j})\rangle$ and $\langle P_2(\cos\theta_{0j})\rangle$ and long range order parameter s as functions of temperature are given in figure 2.2 for a representative value of $A^*/B^* = 0.5$. All the curves show discontinuity at T_{NI}; s drops to zero at the transition, but the short range order persists even in the isotropic phase. The negative value of $\langle P_1(\cos\theta_{0j})\rangle$ signifies antiparallel ordering.

Let us now apply this model to investigate the dielectric properties of the ordered phase. We follow closely the treatment of Maier and Meier discussed earlier. Here the Maier-Saupe distribution function $W(\theta)$ is replaced by $\psi(\theta_0,\varphi_0;\theta_j,\varphi_j)$ to get the modified

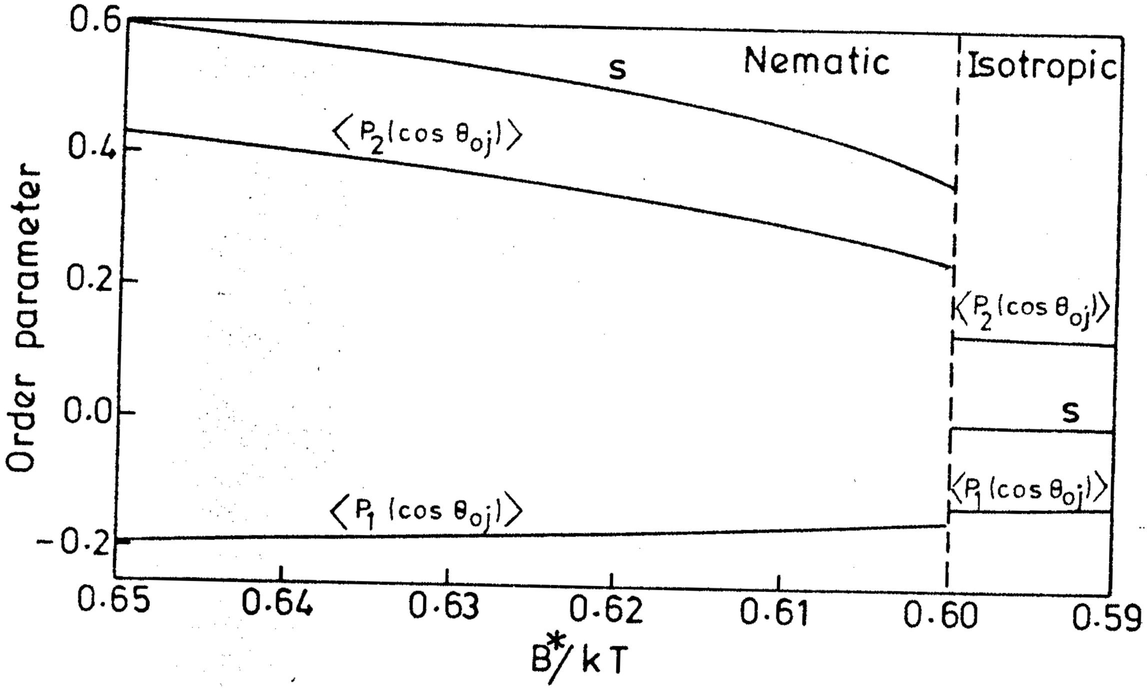

Figure 2.2

Short range order parameters $\langle P_1(\cos\theta_{0j})\rangle$ and $\langle P_2(\cos\theta_{0j})\rangle$ and the long range order parameter a versus B^*/kT. The curves are for $A^*/B^* = 0.5$. (After Madhusudana and Chandrasekhar[6]).

fawn of (2.6) and (2.7).

$$\bar{\mu}_{\parallel} = \frac{\int\cdots\int[1+(\mu_{z0}+\mu_{zj})hE_{\parallel}/kT]\mu_{z0}\psi(\theta_0,\varphi_0;\theta_j,\varphi_j) \times \sin\theta_0\,d\theta_0\,d\varphi_0\,\sin\theta_j\,d\varphi_j\,d\theta_j\,d\nu'_3\,d\nu'_0}{\int\cdots\int[1+(\mu_{z0}+\mu_{zj})hE_{\parallel}/kT]\psi(\theta_0,\varphi_0;\theta_j,\varphi_j) \times \sin\theta_0\,d\theta_0\,d\varphi_0\,\sin\theta_j\,d\varphi_j\,d\theta_j\,d\nu'_j\,d\nu'_0} \qquad (2.29)$$

and

$$\bar{\mu}_{\perp} = \frac{\int\cdots\int[1+(\mu_{x0}+\mu_{xj})hE_{\perp}/kT]\mu_{x0}\psi(\theta_0,\varphi_0;\theta_j,\varphi_j) \times \sin\theta_0\,d\theta_0\,d\varphi_0\,\sin\theta_j\,d\theta_j\,d\varphi_j\,d\nu'_j\,d\nu'_0}{\int\cdots\int[1+(\mu_{x0}+\mu_{xj})hE_{\perp}/kT]\psi(\theta_0,\varphi_0;\theta_j,\varphi_j) \times \sin\theta_0\,d\theta_0\,d\varphi_0\,\sin\theta_j\,d\theta_j\,d\varphi_j\,d\nu'_j\,d\nu'_0}, \qquad (2.30)$$

where $\mu_{z0} = \mu F \cos\theta_0$

and $\mu_{x0} = \mu F \sin\theta_0 \sin\nu'_0$.

After integration the above integrals reduce to

$$\bar{\mu}_{\parallel} = \frac{hF^2\mu^2}{kT}[\left\langle\cos^2\theta_0\right\rangle + \left\langle\cos\theta_0\cos\theta_j\right\rangle]E_{\parallel} \qquad (2.31)$$

and

$$\bar{\mu}_{\perp} = \frac{hF^2\mu^2}{kT}[\frac{1}{2}\left\langle\sin^2\theta_0\right\rangle + \left\langle\sin\nu'_0\sin\nu'_j\sin\theta_0\sin\theta_j\right\rangle]E_{\perp}. \qquad (2.32)$$

Substituting in (2.12) for $\bar{m}_{\parallel}$ and $\bar{\mu}_{\parallel}$ from (2.3) and (2.31) we get

$$\varepsilon_{\parallel} = 1 + 4\pi \frac{N_A \rho h F}{M}\left[\bar{\alpha} + \tfrac{2}{3}\Delta\alpha s + \frac{F\mu^2}{3kT}(2s+1) + \frac{F\mu^2}{kT}\left\langle \cos\theta_0 \cos\theta_j \right\rangle\right] \tag{2.33}$$

Similarly from (2.4), (2.14) and (2.32) we get

$$\varepsilon_{\perp} = 1 + 4\pi \frac{N_A \rho h F}{M}\left[\bar{\alpha} - \tfrac{1}{3}\Delta\alpha s + \frac{F\mu^2}{3kT}(1-s) + \frac{F\mu^2}{3kT}\left\langle \sin\nu'_0 \sin\nu'_j \sin\theta_0 \sin\theta_j \right\rangle\right]. \tag{2.34}$$

The temperature variation of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and $\bar{\varepsilon}$ calculated from (2.33) and (2.34) is shown in figure 2.3. The parameters used in the calculations are $\rho = 1.2$, $\alpha = 28 \times 10^{-24}$ cm^3, $\Delta\alpha = 15 \times 10^{-24}$ cm^3, $\mu = 5.0$ Debye and the theoretically derived value of s from figure 2.2. We notice that $\bar{\varepsilon}$ increases by a few per cent on going from the nematic to the isotropic phase because of the diminution in $\left\langle P_1(\cos\theta_{0j})\right\rangle$ Also the magnitude of the dielectric anisotropy agrees well with the values of $\Delta\varepsilon$ measured for strongly polar

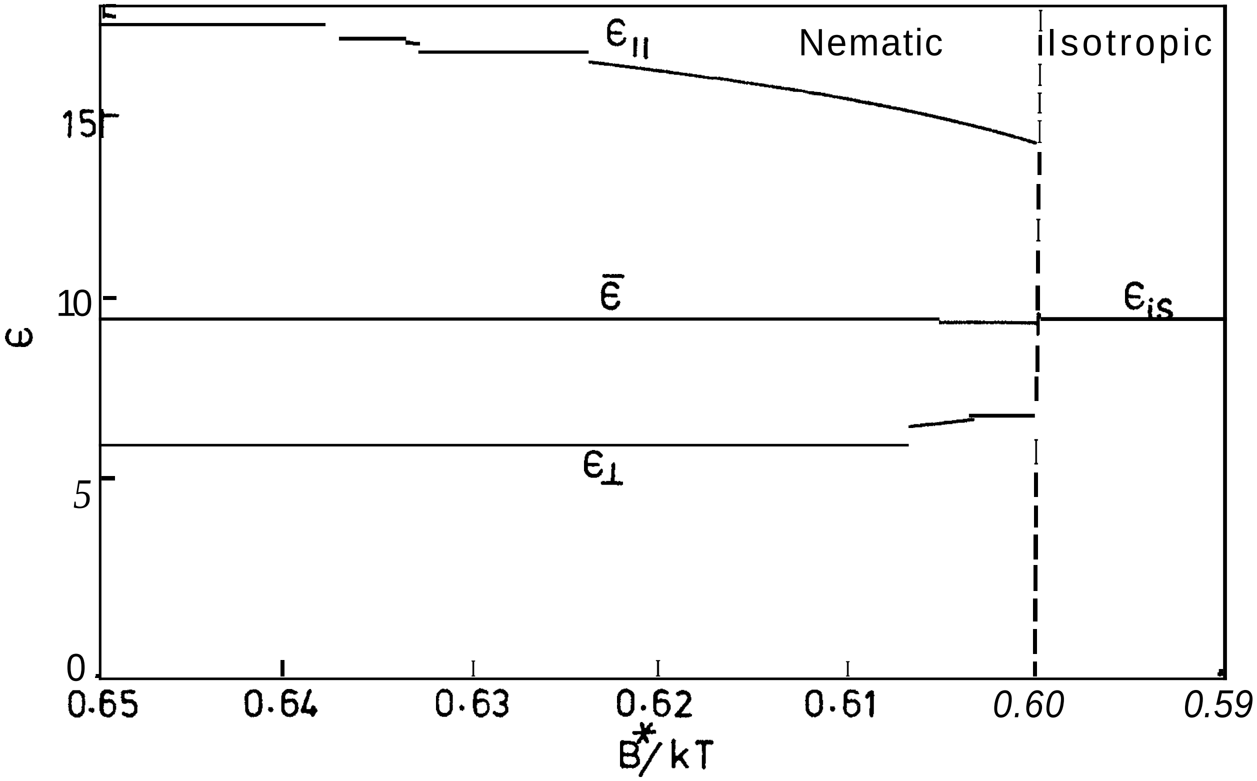

Figure 2.3

Theoretical variation of the dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, ε_{is} and $\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$ evaluated for $A^{*}/B^{*} = 0.5$. (After Madhusudana and Chandrasekhar[6]).

It was found that when $V(\theta_j)$ given by (2.24) was used the consistency relation was satisfied only to about 2-3% in the neighbourhood of $\theta_0 \simeq \pi/2$. In principle, this can be improved by including higher order terms in (2.24). Indeed, a marked improvement in the accuracy was observed[9] by taking

$$V(\theta_j) = -BP_2(\cos\theta_j) - CP_4(\cos\theta_j) . \qquad (2.35)$$

This satisfied the consistency relation to better than 0.1% at T_{NI} for $8 = 8$.

Derzhanski and Petrov[10] have also extended Maier-Meier theory by taking the anisotropic shape of the molecule into account, replacing the Onsager's spherical cavity by an ellipsoidal This leads to equations that are essentially the same as (2.13) and (2.15) except that h and f are now dependent an the order parameter and the ratio of the axes of the molecular ellipsoid.

It was suggested by Derzhanski and Petrov[11] that the difference between $\bar{\varepsilon}$ and ε_{is} observed by Maier and Meier[1] in PAA is probably due to piezoelectric clamping since the measurements were carried out in the radio frequency range. We now know that the difference exists even when the measuring frequency is as low as 1 KHz.

Bordewijk[12] extended the Kirkwood-Frohlich theory for isotropic liquids to nematics by taking into consideration the dielectric anisotropy. This model differs from that of Onsager's in that it includes the short range order effects via a correlation factor. The main drawback of this theory is that the polarisability anisotropy, which is an important property of a liquid crystal, has been ignored.

Dielectric relaxation

The dielectric constants of a liquid crystal are frequency dependent. All the theories discussed so far dealt with the behaviour of a nematic In the presence of a static electric field. When the applied static field is removed, the orientation polarization decreases exponentially with a characteristic time τ known as the relaxation time. Instead 14 we use an alternating field a time lag between the applied field and the orientation polarization will be introduced which becomes noticeable for frequencies of the order of τ^{-1}. When the frequency is greater than τ^{-1} the dipole moment will not be able to follow the field and the measured dielectric constant is due to the induced polarization only.

The mechanism of dispersion in a nematic is complicated. Due to the presence of the molecular order $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ have different frequency dependences $\varepsilon_{\perp}$ exhibits only the normal Debye relaxation which usually occurs in the GHz region. On the other hand, $\varepsilon_{\parallel}$ shows an additional dispersion in the MHz region or even in the KHz region. The low frequency relaxation of $\varepsilon_{\parallel}$ was first observed in alkoxyazoxybenzenes by Maier and Meier.[13] They also worked out theoretically the expected forms of the dispersion curves for nematics (figure 2.4) and showed that in the radio-frequency region $\varepsilon_{\parallel}$ exhibits a dispersion while $\varepsilon_{\perp}$ remains constant.

The low-frequency relaxation of $\varepsilon_{\parallel}$ is due to the reorientation of the parallel component of the dipole moment hindered by the nematic potential. Martin et al.,[14] extended the Debye model[15] for dielectric relaxation in isotropic liquids to nematics. They showed that the relaxation time (τ_R) corresponding to the reorientation of μ_l is larger than the relaxation time (τ_0) in the isotropic phase by a retardation factor 'g' and calculated 'g' as a function of the nematic potential 'q' by taking into account the strong intermolecular potential.

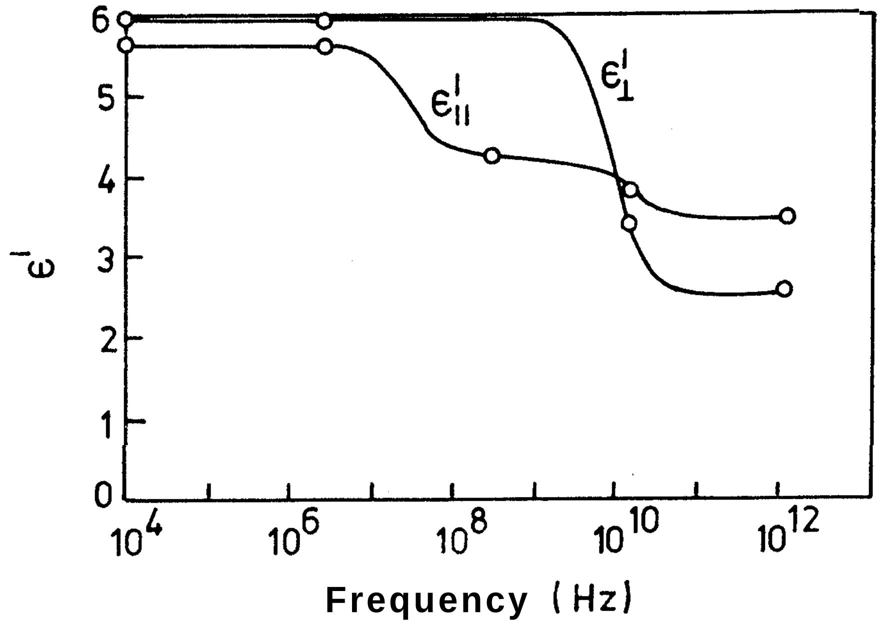

Figure 2.4

Expected forms of the dispersion curves for $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of 4,4'-di-n-alkoxyazoxybenzenes. (After Maier and Meier[13]).

In Debye's theory, which is based on Einstein's theory of Brownian motion, it is assumed that the rotation of a molecule due to an applied field is hindered by collisions with its neighbours. Consider a nematic in which the dipole moment μ is along the long molecular axis. In the presence of an external electric field E, the molecule rotates with an angular velocity

$$\left\langle \frac{\partial \theta}{\partial t} \right\rangle = \frac{M}{\gamma} , \qquad (2.36)$$

where $M = -\frac{\partial U}{\partial \theta}$ is the torque acting on the molecule and γ is the resistive constant. U is the total potential energy given by

$$U = -\mu E \cos\theta - \frac{As}{V^2} (3\cos^2\theta - 1) . \qquad (2.37)$$

The first term is due to the applied field while the second term is the nematic potential given by (2.5).

The orientational distribution of the molecules at a time t can be described by a distribution function

$f(\theta,t)$ such that $dN = 2\pi f \sin\theta \, d\theta$ is the fraction of molecules having an orientation between θ and $\theta + d\theta$. The orientation of the molecules changes continuously due La diffusion as well as the applied field till an equilibrium state is reached. If J is the number of molecules going through θ-orientation in unit time then

$$J = -K \frac{\partial f}{\partial \theta} + f \left\langle \frac{\partial \theta}{\partial t} \right\rangle , \qquad (2.38)$$

where the first term represents the diffusive process and the second term is the effect of the applied field. Substituting for $\left\langle \frac{\partial \theta}{\partial t} \right\rangle$ from (2.36) and solving the differential equation we get the diffusion constant

$$K = kT/\gamma .$$

The rate of increase in the number of molecules having orientations between θ and $\theta + d\theta$ is given by the difference in the number of molecules crossing orientations θ and $\theta + d\theta$, i.e.,

$$\frac{\partial}{\partial t}(2\pi \sin\theta \, d\theta \, f) = -\frac{\partial}{\partial\theta}(2\pi \sin\theta \, J)d\theta$$

or

$$\frac{\partial f}{\partial t} = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta \, J) .$$

Substituting for J from (2.38) we get the Debye differential equation

$$\frac{\partial f}{\partial t} = \frac{1}{2\tau_0 \sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\left(\frac{\partial f}{\partial t}\overset{\frac{\partial f}{\partial\theta}}{\wedge} - \frac{M}{kT}f\right)\right\} , \qquad (2.39)$$

where $\tau_0 = \gamma/2kT$ is the Debye relaxation time.

In order to solve this differential equation Meier and Saupe[16] made the simplifying assumption that the electric field E applied along $\underline{n}$ is turned off at a time t_0 and that the perturbation of the angular distribution function by E has the form of a cosine at all times after the field is switched off. This is mathematically represented by

$$f(\theta,t) = f_0\left(1 + \frac{a(E,t)}{kT}\cos\theta\right) , \qquad (2.40)$$

where f_0 is the undisturbed distribution of the nematic order. Let us assume the same form of f_0 taken in long range order theory^3, i.e.,

$$f_0(\theta) = c\, e^{-(q/kT)\sin^2\theta} . \qquad (a.41)$$

Let us now calculate the rate at which the electric polarization P decays after the removal of the external electric field. If N_0 in the number of molecules per cubic cm, the electric polarization

$$P = N_0 \bar{\mu} = N_0 \mu \int_0^{\pi} f \cos\theta \sin\theta \, d\theta .$$

Using the distribution function given by (2.40) we can arrive at the differential equation

$$\frac{\partial P}{\partial t} = -\frac{1}{\tau_0} \frac{f_0(\pi/2)}{\left\langle \left|\cos\theta\right| \right\rangle} P , \qquad (2.42)$$

where $\left\langle \left|\cos\theta\right| \right\rangle$ is the expectation value of the absolute value of cos θ in the undisturbed distribution f_0.

The solution of this differential equation is

$$P = P_0 e^{-t/\tau} , \qquad (2.43)$$

where
$$\tau = \frac{\langle|\cos\theta|\rangle}{f_0(\pi/2)} \tau_0 .$$

According to the definition of the retardation factor

$$\tau = g \tau_0 . \qquad (2.44)$$

Therefore

$$g = \frac{\langle|\cos\theta|\rangle}{f_0(\pi/2)} . \qquad (2.45)$$

In the isotropic phase, the value of both $f_0(\pi/2)$ and $\langle|\cos\theta|\rangle$ is 0.5 giving a value of unity for g. In the nematic phase, where the molecular order is between complete disorder and perfect order the value of $\langle|\cos\theta|\rangle$ is between 0.5 and 1.0. On the other hand $f_0(\pi/2)$ is a very small quantity less than 0.5 since the number of molecules having a 90°-orientation with respect to the direction of the applied field is a very small fraction of the total number of molecules. Thus the value of g is always greater than 1 in the nematic phase indicating that $\tau > \tau_0$. Using the form of f_0 given by (2.41) we can evaluate $f_0(\pi/2)$. The expectation value of $\langle|\cos\theta|\rangle$ can be obtained from

$$\langle|\cos\theta|\rangle = \frac{\int_0^{\pi}\cos\theta\, f_0 \sin\theta\, d\theta}{\int_0^{\pi} f_0 \sin\theta\, d\theta} .$$

Then we obtain the relation between g and q as

$$g = \frac{kT}{q}(\exp q/kT - 1) \simeq kT/q \exp(q/kT) . \qquad (2.46)$$

The Debye relaxation time in the isotropic phase can be determined by treating the molecule as a sphere of radius 'a' rotating in a viscous medium of viscosity η. According to Stoke's law the frictional resistance γ to rotation experienced by a molecule is

$$\gamma = 8\pi\eta a^3 ,$$

which gives

$$\tau_0 = \frac{1}{2kT} = \frac{4\pi\eta a^3}{kT} .$$

Expressing the temperature dependence of viscosity[17] as

$$\eta \propto \exp(q_\eta/kT) ,$$

where q_η is the activation energy due to viscosity effects, we get from (2.44) and (2.46)

$$\tau \propto \exp(q + q_\eta)/kT . \qquad (2.47)$$

This is a rate equation with the activation energy $(q + q_\eta)$, which can be determined by measuring the temperature variation of the relaxation time of $\epsilon_{\parallel}$.

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