Stochastic model for the reorientation of molecules around their long axes in a smectic C phase

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In smectic phases molecules can reorientate around their long and short axes. The motion of a molecule around its long axis is non-cooperative and influenced by both stochastic and deterministic forces exerted by neighbouring molecules. Solving the Smoluchovsky equation for such a reorientation process, two-time correlation functions are calculated which are related to frequency-dependent susceptibilities. The results are used for investigating how deterministic forces in higher ordered smectic phases have an effect on microwave spectra. It can be concluded that the quadrupolar ordering produces a splitting of the relaxation frequency. This splitting, which should occur at the transition from the smectic A to the smectic C phase, is only weakly influenced by an additional dipolar (ferroelectric) ordering.

1. Introduction

The reorientation of molecules in smectic phases is less restricted than in crystals. If the elongated molecules have a dipole, this process is detectable by using dielectric spectroscopy. In smectic A liquid crystals, the preferred direction (polar angle) of the molecular long axes strongly fluctuates near to the smectic A–smectic C phase transition temperature causing a soft-mode behaviour. Below the transition temperature, a Goldstone-mode additionally appears in the smectic C phase. This mode is caused by azimuthal angle fluctuations of the long molecules, which are tilted with respect to the normal to the smectic layers. Both the soft-mode and the Goldstone-mode are relatively slow cooperative motions observable by conventional dielectric spectroscopy [1–4]. Most known experimental and theoretical investigations refer to phases with a non-racemic mixture of chiral molecules forming a ferroelectric ordering in the smectic C phase.

The expected dielectric behaviour for low frequencies is qualitatively described correctly by the Landau theory, which is valid close to the smectic A–(ferroelectric) smectic C phase transition temperature [5]. Besides the soft-mode and the Goldstone-mode, the theory predicts a fast relaxation mechanism visible in the microwave regime. It results from the reorientation of molecules with a transverse dipole moment around their long axes. According to the Landau theory this mode should split into two branches below the smectic C–smectic A phase transition temperature.

The occurrence of such a splitting, however, is not yet experimentally clarified. Kremer et al., published a series of papers [6–8] which demonstrate that the fast reorientation mode does not split or broaden at the phase transition point, in contrast to the prediction of the Landau theory. Taking into account these experimental findings, Brand and Pleiner [9] proposed a slightly different formulation of the Landau theory

from that originally introduced by Blinc and Zeks [1]. On the other hand, Gestblom
et al. [10], suggested there could be a splitting in the high frequency relaxation spectrum,
but there is also a distribution of the relaxation times caused by libratory and
intramolecular motions. Then it would be hardly possible to obtain experimentally
resolved relaxation peaks, as the frequency differences are small.

In the present paper the reorientation of particles around their molecular long axes
is investigated from another point of view, using as a starting point, the microscopic
model proposed by Urbanc and Zeks [11]. Supposing a molecular-field-approximation,
the microscopic model defines an averaged potential energy for a single particle
surrounded by tilted neighbouring molecules in the ferroelectric smectic C phase,
namely

$$f(x) = h_1 \cos x + h_2 \cos 2x, \tag{1}$$

where x is the angle between a short particle axis and the direction perpendicular to the
tilt plane of the molecules ($0 < x < 2\pi$). The coefficients $h_1 \propto \theta$ and $h_2 \propto \theta^2$ depend on
the tilt angle θ. Then the single particle distribution is

$$P_e(x) = C \exp\left(-\frac{h_1 \cos x + h_2 \cos 2x}{kT} \right) \tag{2}$$

(C, normalization constant; T, temperature; k, Boltzmann constant). Fluctuations of the
long molecules around their short axes will be neglected.

Probably, the transverse molecular ordering does not originate from interactions
between electric dipoles even in the ferroelectric C phase, but is a local property of a
molecule which feels a rotation hindrance due to the tilted near neighbours. Hence the
assumption is reasonable that the main contribution in the anisotropic interaction is
caused by the shape of the molecules, whose cross-section deviates from a circle. The
order parameters $\langle \cos x \rangle$ for dipolar ordering and $\langle \cos 2x \rangle$ for quadrupolar ordering are
obtained by averaging

$$\langle \cos mx \rangle = \int_0^{2\pi} dx \cos mx \, P_e(x) \quad (m = 1, 2). \tag{3}$$

In the case of a weak periodic potential with $|h_1|, |h_2| \ll kT$, the results

$$\langle \cos x \rangle = -\frac{h_1}{2kT} \quad \text{and} \quad \langle \cos 2x \rangle = -\frac{h_2}{2kT} \tag{4}$$

are obtained. Actually, it has been found by measuring the spontaneous polarization,
which is proportional to $\langle \cos x \rangle$, and by recent ^{13}C and ^{14}N NMR and NQR experiments
[5,12, 13], that the conditions $|\langle \cos x \rangle| \ll |\langle \cos 2x \rangle| \ll 1$ are usually satisfied. Hence the
coefficients of potential (1) obey

$$|h_1| \ll |h_2| \ll kT. \tag{5}$$

The value of $|h_2|$ is seldom larger than $0.3kT$.

2.   Brownian motion around the molecular long axis

A frequently applied model which also seems to be applicable to reorientational
motions of liquid crystal molecules is based on the assumption of small step rotations
[14–19]. Before a full rotation around the long axis is accomplished, a particle is pushed
to and fro many times by its near neighbours. The resulting stochastic process is a
brownian motion described by a Langevin equation. In a smectic A phase, there does

not exist a preferred direction within the smectic planes and the potential energy is equal to zero ($h_1 = h_2 = 0$). Then the Langevin equation of an overdamped rotator, which describes the time dependence of the particle rotation angle x, has the simple form

$$\gamma \frac{dx}{dt} = \Gamma(t), \tag{6}$$

where γ is the viscosity coefficient and the stochastic torque obeying $\langle \Gamma(t) \rangle = 0$ is characterized by the two-time correlation function

$$\langle \Gamma(t)\Gamma(t') \rangle = 2\gamma k T \delta(t - t'). \tag{7}$$

The coefficient γ is expected to satisfy an Arrhenius law

$$\gamma = A \exp(E/kT), \tag{8}$$

with constants E and A. Considering higher ordered smectic phases, we assume that the stochastic motion is influenced by a deterministic periodic potential $f(x)$ for modelling the anisotropic environment of a particle. Furthermore, a time-dependent potential $f_1(x, t)$ is introduced on account of the interaction of a transverse dipole with an external electric field. Then the Langevin equation

$$\gamma \frac{dx}{dt} = -\frac{\partial f(x)}{\partial x} - \frac{\partial f_1(x, t)}{\partial x} + \Gamma(t) \tag{9}$$

is obtained. With regard to conditions (5), potential (2) can be simplified to

$$f(x) = h \cos(px), \tag{10}$$

with $p = 2$. But it will be instructive to suppose that p is an arbitrary integral number. It should also be noted that linear corrections (proportional to h_2/kT and h_1/kT) of the susceptibilities and relaxation times, which are separately obtained for the potentials $h_1 \cos x$ and $h_2 \cos 2x$ by a perturbation calculation, can be simply added, so that the result is valid for the combined potential (1).

The interaction energy of a transverse electric dipole μ with an electric field directed perpendicular to the long particle axis is

$$f_1(x, t) = \mu * \mathbf{E} \tag{11}$$

or written explicitly

$$f_1(x, t) = \mu(E_u(t) \cos x + E_v(t) \sin x), \tag{12}$$

where the axes u and v of a cartesian coordinate system are fixed in space (see figure 1). The angle x is enclosed by the axis u and the dipole vector μ, which is parallel to the short axis a. In § 5, the model will be modified by assuming that the dipole and the axis a can enclose a non-zero angle α.

Equation (12) motivates the introduction of two-time correlation functions for studying the linear response with respect to an applied electric field:

$$K_c(t - t') = \langle \cos x(t) \cos x(t') \rangle \quad \text{and} \quad K_s(t - t') = \langle \sin x(t) \sin x(t') \rangle. \tag{13}$$

The brackets $\langle \rangle$ define the averaging over a stationary ensemble, which means that the time-dependent electric field is switched off ($f_1(x, t) = 0$ in equation (9)). Obviously, if the system is isotropic in the u–v-plane, both functions (13) coincide.
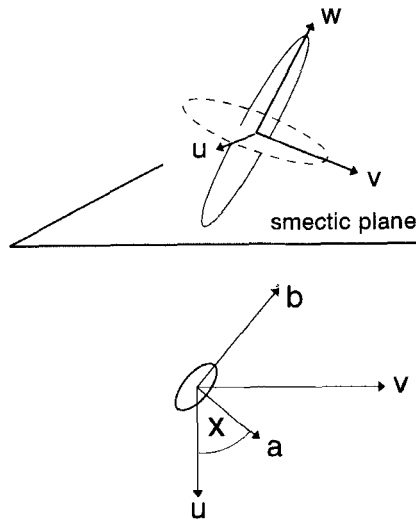
Figure 1.   In a smectic C phase long particles are tilted with respect to the normal to the smectic plane. A cartesian system u, v and w is assumed to coincide with the principal axes of the dielectric tensor. The angle x is enclosed by the short particle axis a and the axis u.

With the choice $t' = 0$ and the definition $x(0) = y$, the correlation functions (13) are expressed by [19]

$$\binom{K_c(t)}{K_s(t)} = \int_0^{2\pi} \int_0^{2\pi} dx\,dy\,P(x,t;y,0)\binom{\cos x \cos y}{\sin x \sin y}, \tag{14}$$

where the joint probability density ($t > 0$ in all further definitions)

$$P(x,t;y,0) = P(x,t|y,0)P_e(y) \tag{15}$$

is a product of the single particle distribution in equilibrium

$$P_e(y) = C\exp\left(-\frac{h\cos py}{kT}\right) \tag{16}$$

and the conditional probability density $P(x,t|y,0)$ obeying the initial condition

$$P(x,t|y,0) = \delta(x - y), \tag{17}$$

for $t = 0$. As is well known [19], the Langevin equation (9) is equivalent to a Smoluchovsky equation for the probability density $P(x,t)$ of particle orientation. Assuming $f_1(x,t) = 0$, we obtain

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(\gamma^{-1}P(x,t)\frac{\partial f(x)}{\partial x}\right) + D\frac{\partial^2 P(x,t)}{\partial x^2}, \tag{18}$$

with

$$D = \gamma^{-1}kT. \tag{19}$$

Equation (18) can be written in the symbolic manner

$$\frac{\partial P(x,t)}{\partial t} = LP(x,t) \tag{20}$$

where L is a linear differential operator. The transition probability $P(x,t|y,0)$ can be obtained by solving equation (18) with the initial condition (17).

2.1. *Correlation functions for* h = 0 (*smectic A phase*)

In the special case $h = 0$, equation (18) reduces to

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2} \tag{21}$$

and the transition probability $P(x, t | y, 0)$ is equal to Green's function of the diffusion equation (21), namely [20]

$$P(x, t | y, 0) = \frac{1}{2\pi} + \frac{1}{\pi} \sum_{n=1}^{\infty} \cos n(x - y) \exp(-n^2 Dt), \quad (\text{for } t > 0). \tag{22}$$

With $P_e(y) = (2\pi)^{-1}$, (15) and (14), the correlation functions (14) are given by

$$K_c(t) = \tfrac{1}{2} \exp(-Dt) \quad \text{and} \quad K_s(t) = \tfrac{1}{2} \exp(-Dt), \quad (\text{for } t > 0). \tag{23}$$

2.2. *Representation of the joint probability density for* h ≠ 0 (*ordered smectic phase*)

It is instructive to investigate how the correlation functions (23) are changed if a deterministic torque is acting ($h \neq 0$). Since $h \ll kT$, a perturbation approach is useful to obtain analytical results. Inserting the ansatz $P(x, t) = p_n(x) \exp(-\lambda_n t)$ into equation (20) leads to the eigenvalue problem

$$L p_n(x) = -\lambda_n p_n(x). \tag{24}$$

A transformation of the operator L into a hermitian operator [19]

$$H = \exp\left(\frac{f(x)}{2kT}\right) L \exp\left(\frac{-f(x)}{2kT}\right) \tag{25}$$

simplifies further calculations. As proved easily, the transformed differential equation

$$H \psi_n(x) = -\lambda_n \psi_n(x) \tag{26}$$

has the same eigenvalues λ_n as equation (24). The joint probability density has the representation [19]

$$P(x, t; y, 0) = \psi_0(x) \psi_0(y) \sum_n \psi_n^*(x) \psi_n(y) \exp(-\lambda_n t), \tag{27}$$

($\lambda_0 = 0$ is a single eigenvalue and $\psi_0(x)$ is chosen to be a real function),

with the normalization condition

$$\int_0^{2\pi} dx \psi_n^*(x) \psi_m(x) = \delta_{mn}. \tag{28}$$

For example, if $f(x) = 0$ equation (26) yields $\lambda_n = Dn^2$ and

$$\psi_n(x) = \frac{1}{\sqrt{(2\pi)}} \exp(Inx), \tag{29}$$

where n is an integer and $I = \sqrt{-1}$. Combining (29) with formulae (15) and (27), the Green's function (22) is rederived.

3. Application of Schrödinger's perturbation theory

For $f(x) \neq 0$, the operator (25) is determined by

$$H \psi \equiv D \psi'' + \gamma^{-1} \left[\frac{1}{2} f''(x) - \frac{1}{4kT} f'(x)^2 \right] \psi, \tag{30}$$

where the primes indicate the first and second derivative with respect to x, respectively. Taking into account that $\varepsilon = h/kT$ is a small parameter, H is a sum of three operators defined by

$$\left.\begin{aligned} H_0\psi &\equiv D\psi'', \\[2mm] H_1\psi &\equiv -\frac{Dp^2}{2}\frac{h}{kT}\cos px\,\psi \\[4mm] H_2\psi &\equiv -\frac{Dp^2}{8}\left(\frac{h}{kT}\right)^2(1-\cos(2px))\psi. \end{aligned}\right\} \tag{31}$$

and

The unperturbed equation

$$H_0\psi = -\lambda^0\psi \tag{32}$$

leads to $\lambda_n^\circ = Dn^2$ and the eigenfunctions (29). These functions, however, are not suitable for the present calculation, because the twofold degeneracy of the eigenvalues ($\psi_n(x)$ and $\psi_{-n}(x)$ have the same eigenvalue) requires a careful choice of the basis functions. The real basis with

$$\psi_0^\circ(x) = \frac{1}{\sqrt{(2\pi)}}, \quad \psi_n^\circ(x) = \frac{1}{\sqrt{\pi}}\cos nx \quad \text{and} \quad \varphi_n^\circ(x) = \frac{1}{\sqrt{\pi}}\sin nx, \quad (n=1,2,3,\ldots) \tag{33}$$

meets the requirement that divergent terms are avoided. Using Dirac's notation

$$\langle \psi(x)|\varphi(x)\rangle_q = \int_0^{2\pi} dx\,\psi(x)\varphi(x)$$

the basis functions (33) satisfy the conditions

$$\left.\begin{aligned} \langle\psi_m^\circ|\varphi_n^\circ\rangle_q &= 0 \\[2mm] \langle\psi_m^\circ|H_i|\varphi_n^\circ\rangle_q &= 0 \quad (i=1,2). \end{aligned}\right\} \tag{34}$$

and

As is also usual in quantum mechanics, the perturbation calculation is performed up to second order terms of magnitude for the eigenvalues and up to first order terms for the eigenfunctions. Taking into account (34), we obtain the formula

$$\left.\begin{aligned} \psi_n(x) &= \psi_n^\circ(x) - \frac{1}{D}\sum_{m\neq n}\frac{\langle\psi_m^\circ|H_1|\psi_n^\circ\rangle_q}{n^2-m^2}\psi_m^\circ(x), \\[4mm] \varphi_n(x) &= \varphi_n^\circ(x) - \frac{1}{D}\sum_{m\neq n}\frac{\langle\varphi_m^\circ|H_1|\varphi_n^\circ\rangle_q}{n^2-m^2}\varphi_m^\circ(x), \end{aligned}\right\} \tag{35}$$

and

for the eigenfunctions and

$$\lambda_n = Dn^2 - \langle\psi_n^\circ|H_1+H_2|\psi_n^\circ\rangle_q + \frac{1}{D}\sum_{m\neq n}\frac{|\langle\psi_m^\circ|H_1|\psi_n^\circ\rangle_q|^2}{n^2-m^2} \tag{36}$$

and

$$\xi_n = Dn^2 - \langle\varphi_n^\circ|H_1+H_2|\varphi_n^\circ\rangle_q + \frac{1}{D}\sum_{m\neq n}\frac{|\langle\varphi_m^\circ|H_1|\varphi_n^\circ\rangle_q|^2}{n^2-m^2} \tag{37}$$

for the corresponding eigenvalues. Formula (27) for the joint probability function is replaced by

$$P(x, t; y, 0) = \psi_0(x)\psi_0(y) \sum_{n=0}^{\infty} [\psi_n(x)\psi_n(y) \exp(-\lambda_n t) + \varphi_n(x)\varphi_n(y) \exp(-\xi_n t)]. \quad (38)$$

Elaborating the matrix elements in the expressions (35), (36) and (37) and inserting the results in (38) yields

$$P(x, t; y, 0) = P_{n \neq p/2}(x, t; y, 0) + P_{p/2}(x, t; y, 0), \quad (39)$$

with

$$P_{n \neq p/2}(x, t; y, 0) = \frac{1}{4\pi^2} \left[1 - \frac{h}{kT}(\cos px + \cos py) \right]$$

$$+ \frac{1}{2\pi^2} \left[1 - \frac{h}{2kT}(\cos px + \cos py) \right] \sum_{\substack{n=1 \\ \{n \neq p/2\}}}^{\infty} \cos n(x - y) \exp(-\lambda_n t)$$

$$+ \frac{1}{2\pi^2} \left(\frac{hp}{4kT} \right) \sum_{\substack{n=1 \\ \{n \neq p/2\}}}^{\infty} \left\{ \frac{\cos[n(x-y) - px]}{2n - p} - \frac{\cos[n(x-y) + px]}{2n + p} \right.$$

$$\left. - \frac{\cos[n(x-y) - py]}{2n + p} + \frac{\cos[n(x-y) + py]}{2n - p} \right\} \exp(-\lambda_n t).$$

The second term on the right hand side of (39) is determined by

$$P_{p/2}(x, t; y, 0) = \frac{1}{2\pi^2} \left\{ \left[\left(1 - \frac{h}{2kT}(\cos px + \cos py) \right) \cos \frac{p}{2} x \cos \frac{p}{2} y \right. \right.$$

$$\left. - \frac{h}{8kT} \left(\cos \frac{p}{2} x \cos \frac{3p}{2} y + \cos \frac{p}{2} y \cos \frac{3p}{2} x \right) \right] \exp(-\lambda_{p/2} t)$$

$$+ \left[\left(1 - \frac{h}{2kT}(\cos px + \cos py) \right) \sin \frac{p}{2} x \sin \frac{p}{2} y \right.$$

$$\left. \left. - \frac{h}{8kT} \left(\sin \frac{p}{2} x \sin \frac{3p}{2} y + \sin \frac{p}{2} y \sin \frac{3p}{2} x \right) \right] \exp(-\xi_{p/2} t) \right\}$$

if p is an even number; for odd p the term $P_{p/2}(x, t; y, 0)$ is defined to be zero. The decay rates λ_n and ξ_n are

$$\lambda_n = Dn^2 \left[1 + \frac{p^2}{2(4n^2 - p^2)} \left(\frac{h}{kT} \right)^2 \right]$$

and $\xi_n = \lambda_n$ for $n \neq p/2$,

$$\lambda_{p/2} = \frac{Dp^2}{4} \left[1 + \frac{h}{kT} + \frac{3}{8} \left(\frac{h}{kT} \right)^2 \right] \quad (40)$$

(for even p), and

$$\xi_{p/2} = \frac{Dp^2}{4} \left[1 - \frac{h}{kT} + \frac{3}{8} \left(\frac{h}{kT} \right)^2 \right]$$

(for even p).

The joint probability density (39) allows the calculation of correlation functions for the stochastic reorientation if $h \ll kT$.

4. Correlation functions

4.1. *Dipolar ordering*

We restrict our attention to the cases $p = 1$ and $p = 2$ corresponding to dipolar and quadrupolar ordering, respectively. Using (14), (39) and (40) the simple result

with
$$
\left.
\begin{array}{c}
K_c(t) = K_s(t) = \tfrac{1}{2}\exp\left(-\lambda t\right) + O(\varepsilon^2) \\[2mm]
\lambda = D\left[1 + \dfrac{1}{6}\left(\dfrac{h}{kT}\right)^2\right]
\end{array}
\right\}
\tag{41}
$$

and $\varepsilon = h/kT$ is derived. According to (41), the dipole ordering only weakly influences the decay constant λ, and the property $K_c(t) \approx K_s(t)$ is the same as for an isotropic system. This result is a little surprising, because a preferred direction of orientation exists which is accompanied by a non-zero order parameter $\langle \cos x \rangle$.

For comparison, an exactly solvable model [18] with the piecewise constant potential energy

$$
f(x) = \begin{cases} +h & \text{for} \ -\pi/2 + 2n\pi < x < +\pi/2 + 2n\pi \\ -h & \text{for} \ +\pi/2 + 2n\pi < x < +3\pi/2 + 2n\pi \end{cases}
\tag{42}
$$

(n, integer number) is considered, which also produces a dipolar ordering with non-zero $\langle \cos x \rangle$. In this case the correlation functions become

$$
K_c(t) = \frac{\exp\left(-Dt\right)}{2[\cosh\left(h/kT\right)]^2} + \frac{4}{\pi^2}[\tanh\left(h/kT\right)]^2\left\{1 + 2\sum_{n=1}^{\infty}\frac{1}{(4n^2 - 1)^2}\exp\left(-4Dn^2 t\right)\right\}
\tag{43}
$$

and

$$
K_s(t) = \tfrac{1}{2}\exp\left(-Dt\right).
\tag{44}
$$

The time independent contribution in (43) is due to the dipolar ordering accompanied by the order parameter

$$
\langle \cos x \rangle = -\frac{2}{\pi}\tanh\left(h/kT\right)
$$

which is proportional to a spontaneous polarization directed parallel to the axis u (see figure 1). Now $K_c(t)$ is expanded in a series up to second order with respect to ε

$$
K_c(t) = \frac{4}{\pi^2}\left(\frac{h}{kT}\right)^2 + \frac{1}{2}\left[1 - \left(\frac{h}{kT}\right)^2\right]\exp\left(-Dt\right) + \left(\frac{h}{kT}\right)^2 * \{\text{fast decaying terms}\}
\tag{45}
$$

and a comparison of (44) with (45) reveals that the anisotropy in the u–v-plane causes different correlation functions. In the present case with $\varepsilon \ll 1$, however, the difference between $K_c(t)$ and $K_s(t)$ is negligibly small.

4.2. *Quadrupolar ordering*

Applications of equations (14), (39) and (40) for $p = 2$ leads to two different correlation functions, namely

with

and

with

$$K_c(t) = \frac{1}{2} \left(1 - \frac{h}{2kT} \right) \exp(-\lambda t) + O(\varepsilon^2)$$

$$\lambda = D \left[1 + \frac{h}{kT} + \frac{3}{8} \left(\frac{h}{kT} \right)^2 \right] + O(\varepsilon^3)$$

$$K_s(t) = \frac{1}{2} \left(1 + \frac{h}{2kT} \right) \exp(-\xi t) + O(\varepsilon^2)$$

$$\xi = D \left[1 - \frac{h}{kT} + \frac{3}{8} \left(\frac{h}{kT} \right)^2 \right] + O(\varepsilon^3). \tag{46}$$

The quadrupolar ordering produces a more pronounced difference between $K_c(t)$ and $K_s(t)$ than the dipolar ordering, so that different susceptibilities and relaxation times are expected dependent on the electric field direction.

5. Susceptibilities in the case of quadrupolar ordering

The correlation functions $K_c(t)$ and $K_s(t)$ for the particle reorientation should allow the calculation of dielectric susceptibilities, provided that the electric field lies in the u–v-plane and there exists a non-zero transverse dipole moment. As shown previously, the dipolar term in potential (1) does not remarkably influence the two-time correlation functions even if the coefficient h_1 has the same magnitude as h_2. Thus, the simplified model with potential energy $f(x) = h \cos 2x$ ($h = h_2$) only needs to be considered neglecting the contribution $h_1 \cos x$.

Let us regard the simple case of particles which have only one transverse dipole firmly attached to the molecular long axis. The macroscopic dipole moment is equal to the sum

$$\mathbf{M}(t) = \sum_{i=1}^{N} \boldsymbol{\mu}_i(t)$$

over N particle dipole moments $\boldsymbol{\mu}_i(t) = (\mu_{iu}(t), \mu_{iv}(t))$. Macroscopic autocorrelation functions defined by [21]

$$\phi_a(t) = \frac{1}{V} \langle M_a(t) M_a(0) \rangle \quad (a = u, v) \tag{47}$$

(V, volume of the sample) are connected with the dielectric permittivities measured parallel to the axes u and v, respectively. The frequently used assumption for non-associated liquids $\langle \mu_{ia}(t) \mu_{ja}(t') \rangle = 0$ for $i \neq j$ should also be valid in the present case and (47) is transformed to

$$\phi_a(t) = \frac{N}{V} \langle \mu_a(t) \mu_a(0) \rangle.$$

The electric dipole is not always aligned parallel to the axis a of a sterically quadrupolar particle, but can enclose an angle α (see figure 2) as proposed in refs [11, 22]. In a smectic
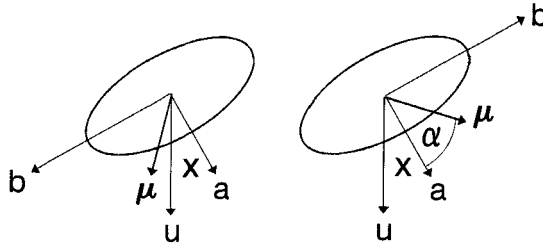
Figure 2.   One half of the particles is directed with their heads upwards and the other half downwards. The dipoles of the former particles enclose the angle $x + \alpha$ with the dielectric principal axis u, and the latter particles enclose the angle $x - \alpha$.

C phase, this angle is $+ \alpha$ for one half of the particles oriented with their heads upwards and $- \alpha$ for the other half of the particles, which are oriented downwards. Only in this case is the twofold rotation axis, which is both a symmetry element of the non-chiral and the chiral smectic C phase, preserved. Figure 2 shows that the angle α changes its sign when the head and tail of a long molecule are exchanged (by a rotation of $180°$ around the short axis a). An electric field directed parallel to the u axis and a dipole enclose either the angle $x + \alpha$ or $x - \alpha$. Then by averaging over all dipoles we obtain

$$\phi_u(t) = \tfrac{1}{2}\rho\mu^2 \langle \cos(x(t) + \alpha)\cos(x(o) + \alpha) + \cos(x(t) - \alpha)\cos(x(o) - \alpha)\rangle$$

where $\rho = N/V$ is the particle density. For a field parallel to the v axis the corresponding correlation function is

$$\phi_v(t) = \tfrac{1}{2}\rho\mu^2 \langle \sin(x(t) + \alpha)\sin(x(o) + \alpha) + \sin(x(t) - \alpha)\sin(x(o) - \alpha)\rangle,$$

$\phi_u(t)$ and $\phi_v(t)$ can be expressed by the previously defined correlation functions (14)

$$\phi_u(t) = \rho\mu^2[\cos^2\alpha K_c(t) + \sin^2\alpha K_s(t)]$$

and

$$\phi_v(t) = \rho\mu^2[\sin^2\alpha K_c(t) + \cos^2\alpha K_s(t)].$$

$$(48)$$

The principal values of the dielectric susceptibility tensor

$$\chi_a(\omega) = \chi_a'(\omega) + I\chi_a''(\omega) \quad (a = u, v) \tag{49}$$

obtained by a half-sided Fourier transformation

$$\chi_a(\omega) = \frac{1}{kT}\left[\phi_a(0) + I\omega \int_0^\infty \phi_a(t)\exp(I\omega t)\,dt\right] \quad (a = u, v) \tag{50}$$

refer to the dielectric response with respect to the local electric field **E** acting at the position of a dipole. Inserting (48) in (50) leads to the final results

$$\chi_u(\omega) = \frac{\rho\mu^2}{2kT}\left[\frac{1 + I\omega\tau_1}{1 + (\omega\tau_1)^2}\left(1 - \frac{h}{2kT}\right)\cos^2\alpha + \frac{1 + I\omega\tau_2}{1 + (\omega\tau_2)^2}\left(1 + \frac{h}{2kT}\right)\sin^2\alpha\right]$$

and

$$\chi_v(\omega) = \frac{\rho\mu^2}{2kT}\left[\frac{1 + I\omega\tau_1}{1 + (\omega\tau_1)^2}\left(1 - \frac{h}{2kT}\right)\sin^2\alpha + \frac{1 + I\omega\tau_2}{1 + (\omega\tau_2)^2}\left(1 + \frac{h}{2kT}\right)\cos^2\alpha\right],$$

$$(51)$$

with relaxation times

$$\tau_1 = \frac{1}{D[1 + (h/kT)]} \quad \text{and} \quad \tau_2 = \frac{1}{D[1 - (h/kT)]}, \tag{52}$$

which follow from relations (46), neglecting a term proportional to $(h/kT)^2$. Directly measurable dielectric permittivities

$$\varepsilon_a(\omega) = \varepsilon_a'(\omega) + I\varepsilon_a''(\omega) \quad (a = u, v), \tag{53}$$

are obtained from

$$\varepsilon_a(\omega) - n_a^2 = R_a(\omega)\chi_a(\omega), \tag{54}$$

where n_a is the infrared refractive index and $R_a(\omega)$ is the internal field factor connecting the local field and the applied electric field. There is no generally accepted procedure for calculating $R_a(\omega)$. Several approaches known from the literature are considered in [23].

6. Discussion

The model with the potential $f(x) = h \cos 2x$ refers to a quadrupolar ordering occurring in non-chiral and chiral smectic C phases. In the case of a chiral phase, the additional contribution $h_1 \cos x$ produces a ferroelectric ordering.

According to equations (41) and (45), the potential $h_1 \cos x$ produces corrections proportional to $(h_1/kT)^2$ for the susceptibilities and the relaxation time, which are very small since $|h_1/kT| \ll 1$. Therefore this potential has no remarkable influence on the dielectric spectrum, even if the coefficient h_1 is as large as $h = h_2$. This conclusion is supported by the molecular dynamics method applied to an array of rotators [24]. It was demonstrated that dipolar forces play little part in the dielectric relaxation spectrum. Angular potentials other than those resulting from dipole–dipole interaction were proved to be more effective. Thus the contribution $h_1 \cos x$ in potential (1) is negligible when dielectric susceptibilities are calculated.

Consequently, we only consider the potential $f(x) = h \cos 2x$ which produces more pronounced corrections proportional to h/kT in the formulae for τ and χ. Equations (51) and (52) are sufficient to demonstrate how the dipoles respond to an alternating local electric field. An additional consideration of the internal field factor $R_a(\omega)$ in (54) should not influence the general conclusions.

The potential barrier $h = h_2$ of the quadrupolar term is zero in a smectic A phase and grows linearly with decreasing temperature T in the smectic C phase. Close to the phase transition temperature T_{AC} the simple formula $h = c\theta^2 \sim T_{AC} - T$ is obeyed (c is a constant). In this case formulae (52) describe a splitting of the high frequency dielectric relaxation spectrum at the transition S_A–S_C as also predicted by the Landau theory of the version of Blinc and Zeks [1,5]. But there could be a difference in the interpretation of the splitting mechanism. In the framework of a Landau theory, the existence of a dipolar ordering and a spontaneous polarization seems to be essential for describing the high frequency spectrum. The model for a rotator in a single particle potential $f(x) = h \cos 2x$, however, only includes quadrupolar ordering of particles. In this case, the chiral smectic C phase with ferroelectric ordering and the non-chiral smectic C phase should not differ much in their high frequency dielectric spectra. Unfortunately, the splitting of frequencies in the smectic C phase is only a weak effect. Using formulae (52) and assuming $h \approx 0 \cdot 3kT$, we get the ratio $\tau_2/\tau_1 \approx 2$ for the relaxation times in the smectic C phase.
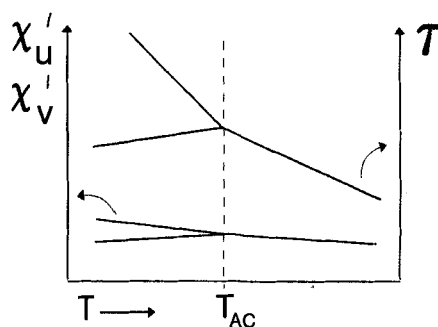
P. Schiller

Figure 3.   The temperature dependence of the relaxation time τ and the dielectric susceptibilities χ'_u and χ'_v concluded from equations (51), (52) and (8). The splitting of τ below the smectic C–smectic A phase transition temperature is similar to that predicted by the Landau theory for a chiral smectic C phase.

A comparison of theoretical and experimental results is difficult, since relaxation times must differ by at least one order of magnitude to resolve them uniquely [10]. Cole–Cole diagrams revealed that even in the smectic A phase, the spectrum is broadened, so that more than one relaxation frequency would be necessary to fit experimental data. A possible explanation for this behaviour is based on the occurrence of more than one electric dipole in molecules which form a ferroelectric smectic C phase. If two or more electric dipoles occur, intramolecular reorientations must be taken into account additionally. For example, motion around single bonds can lead to different relaxation times for two dipoles attached at the centre and a tail of a long molecule.

It seems that all known chiral molecules which form a ferroelectric smectic C phase have more than one electric dipole [25]. Perhaps a smectic A phase consisting of non-chiral molecules with only one electric dipole near the particle centre has a simple Debye spectrum in the high frequency regime. In this simple case, the splitting of the relaxation frequency in the smectic C phase could be detectable. Figure 3 shows the expected dielectric behaviour.

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