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LIQUID CRYSTAL OBSERVABLES: STATIC AND DYNAMIC PROPERTIES

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Abstract. In this Chapter we introduce the description of single and pair particle static properties of liquid crystals, and discuss their calculation from computer simulations. We also briefly describe the calculation of dynamic properties from molecular dynamics simulations using Linear Response theory.

1. Single particle properties

We consider a system of N molecules at certain specified thermodynamic conditions. Typically we shall consider that volume V and temperature T are fixed together with N (canonical conditions), but we shall also refer to the case where pressure P is fixed together with T (isobaric conditions). We assume the molecules to be classical, rigid particles with centre of mass at position $\mathbf{r}$ and orientation ω given for instance by a set of three Euler angles (α, β, γ), or only two angles (α, β) as illustrated in fig. 1 if we can assume that the molecules have cylindrical symmetry [1].

We shall discuss the calculation of observables in liquid crystals [2] in fairly general terms, but adopting a rather special point of view, that of computer simulations. As will be clear from the contributions in this book, computer simulations techniques [3] actually generate configurations of the system, i.e. sets of positions $\mathbf{r}_i = (x_i, y_i, z_i)$ and orientations ω_i of all the particles. In particular the Monte Carlo (MC) method generates equilibrium configurations, albeit non necessarily in the proper time order, while Molecular Dynamics (MD) actually generates configurations time step after time step in their natural time sequence. In this last case configurations consists not only of positions and orientations, but also of the full set of linear and angular velocities.

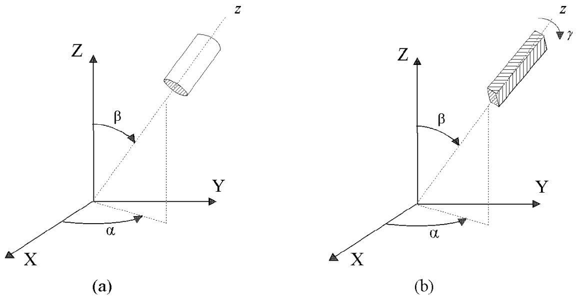

Figure 1. The two angles α, β defining the orientation of a cylindrically symmetric molecule (a) and the three Euler angles α, β, γ required for a generic rigid particle (b).

A complete static information about the system is represented by a sufficiently large set of M of its configurations. Indeed if we can calculate the value of a property dependent on molecular positions and orientations $A(\mathbf{r}_1, \omega_1, ..., \mathbf{r}_N, \omega_N)$ in each of these equilibrium configurations $(\mathcal{J})$, then the average value of A is

$$\langle A \rangle = \frac{1}{M} \sum_{\mathcal{J}}^{M} A(\mathbf{r}_1, \omega_1, ..., \mathbf{r}_N, \omega_N)^{(\mathcal{J})}. \tag{1}$$

The enormous number of positional and orientational coordinates specifying the various configurations is fortunately unnecessary if, as it is often the case, we are only interested in calculating average properties of single or pair molecule properties. In the next sections we shall discuss these two cases in turn.

1.1. THE SINGLET DISTRIBUTION AND ITS EXPANSION

Let us suppose that the probability density for a molecule to have a certain position $(\mathbf{r} + \mathrm{d}\mathbf{r})$ and orientation $(\omega + \mathrm{d}\omega)$ i.e. $P^{(1)}(\mathbf{r}, \omega)$ [4] is known. In this case the average of any property $A(\mathbf{r}, \omega)$ relating to a single molecule can be calculated as

$$\begin{aligned} \langle A \rangle &= \langle A(\mathbf{r}, \omega) \rangle_{\mathbf{r},\omega} \\ &= \int \mathrm{d}\mathbf{r} \mathrm{d}\omega A(\mathbf{r}, \omega) P^{(1)}(\mathbf{r}, \omega)/N, \end{aligned} \tag{2}$$

where we use the angular brackets $\langle ... \rangle$ to indicate a statistical average over the relevant degrees of freedom (here on positions and orientations), that we indicate explicitly only when needed. The volume elements $\mathrm{d}\mathbf{r}$, $\mathrm{d}\omega$ are respectively $\mathrm{d}x\mathrm{d}y\mathrm{d}z$ and $\mathrm{d}\alpha \sin\beta \mathrm{d}\beta$ or $\mathrm{d}\alpha \sin\beta \mathrm{d}\beta \mathrm{d}\gamma$ for a rigid molecule of arbitrary symmetry. Thus the integral over positions gives the volume

V of the sample: and that on orientations gives the total angular measure Ω ($\Omega = 4\pi$ for cylindrical symmetry and $\Omega = 8\pi^2$ for the general case). The factor $1/N$ in eq. 2 comes from the normalization of the distribution $P^{(1)}(\mathbf{r}, \omega)$. The singlet distribution $P^{(1)}$ therefore contains all the microscopic information necessary to calculate one particle properties and in turn the structure and ordering of the system will be reflected by $P^{(1)}$. $P^{(1)}(\mathbf{r}, \omega)$ counts the average number of particles that are found in a small volume element centred at $(\mathbf{r}, \omega)$. In practice having all the configurations at hand we could scan $\mathbf{r}$ and ω space adding one to a suitable multidimensional histogram bucket when we find a molecule with that $(\mathbf{r}, \omega)$. A useful way of writing this definition for the singlet distribution is through the introduction of Dirac delta functions. Indeed, since, for example, $\delta(\mathbf{r}_1 - \mathbf{r}'_1)$ is different from zero only when the position $\mathbf{r}_1$ of molecule 1 is at $\mathbf{r}'_1$ we can use a delta function as a device for counting the molecules at a certain position-orientation:

$$P^{(1)}(\mathbf{r}_1, \omega_1)/N = \langle \delta(\mathbf{r}_1 - \mathbf{r}'_1)\delta(\omega_1 - \omega'_1)\rangle_{\mathbf{r}'_1,\omega'_1}, \tag{3}$$

which gives the average number of molecules with the desired position-orientation. The formula, very useful in extracting distributions from simulated configurations, can be easily checked using the definition of single particle average eq. 2. Thus,

$$\begin{aligned}
\langle A(\mathbf{r}_1, \omega_1)\rangle_{\mathbf{r}_1,\omega_1} &= \left\langle \int \mathrm{d}\mathbf{r}'_1 \mathrm{d}\omega'_1 \delta(\mathbf{r}_1 - \mathbf{r}'_1)\delta(\omega_1 - \omega'_1) A(\mathbf{r}'_1, \omega'_1) \right\rangle_{\mathbf{r}_1,\omega_1} && (4)\\
&= \int \mathrm{d}\mathbf{r}'_1 \mathrm{d}\omega'_1 A(\mathbf{r}_1, \omega_1) \left\langle \delta(\mathbf{r}_1 - \mathbf{r}'_1)\delta(\omega_1 - \omega'_1)\right\rangle_{\mathbf{r}_1,\omega_1} \\
&= \langle A(\mathbf{r}'_1, \omega'_1)\rangle_{\mathbf{r}'_1,\omega'_1}, && (5)
\end{aligned}$$

giving eq. 3. We now concentrate on the description of long range orientational order. This is a central issue for liquid crystals, since this kind of order is common to all the various mesophases. In general we can obtain a purely orientational distribution $P(\omega)$ integrating out positions in eq. 3. For a uniform fluid, such as a nematic (but not a smectic), the singlet probability will be anyway independent of the position of molecules:

$$P^{(1)}(\mathbf{r}, \omega) = \rho P(\omega), \tag{6}$$

where $\rho \equiv N/V$ is the number density. In the limiting case of an ordinary isotropic liquid $P(\omega)$ will just be a constant.

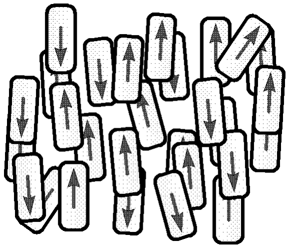

Figure 2. Schematic molecular organization for a system of polar molecules without overall polarization.

2. Orientational order of cylindrical molecules in uniaxial phases

2.1. EXPANSION OF THE ORIENTATIONAL DISTRIBUTION

We start by considering the simplest case of a molecule that can be considered of cylindrical symmetry, be it or rod-like or disc-like shape and that is embedded in uniaxial phase, $P(\omega) = P(\alpha, \beta)$. We do not distinguish by now if the molecule is a solute one or if it actually belongs to the mesophase.

If we take the laboratory Z axis parallel to the director and if the mesophase is uniaxial around the director then rotating the sample about $\mathbf{Z}$ should leave all observable properties unchanged. This means that the probability for a molecule to have an orientation (α, β) should be the same whatever the angle α [5]. More concisely

$$P(\alpha, \beta) = P(\beta)/2\pi. \tag{7}$$

Another experimental finding for nematics and some smectics is that nothing changes on turning the aligned sample upside down. Thus we should have

$$P(\beta) = P(\pi - \beta). \tag{8}$$

This is quite reasonable if we can think of the molecules of interest as spherocylinders or other cylindrically symmetric objects in which head and tail are not distinguishable. However, most mesogen molecules are not like this and for instance have dipole moments like *p-n* alkyl *p*'-cyano biphenyls (nCB). In practice the symmetry eq. 8, that is normally verified experimentally, means that the molecular arrangement will be such as to have on average no overall polarization (no *ferroelectricity*) as we show schematically in fig. 2. There is no fundamental argument that forbids uniaxial ferroelectric fluids and indeed these have been predicted by theory and simulations (see [6] and references therein), although not yet experimentally found. Notice that here we have used the same notation for $P(\beta)$ and $P(\cos\beta)$, that we assume to be renormalized to 1.

In a real experiment it will be extremely difficult to get this kind of complete information on the orientational distribution. A useful approach is, however, that of expanding $P(\beta)$ and approximating it in terms of a set of quantities that we can obtain from experiment. We need for this a set of functions that are orthogonal when integrated over $\mathrm{d}\beta \sin\beta$. Such a set of functions is that of Legendre polynomials $P_L(\cos\beta)$, for which we have

$$\int_0^{\pi} \mathrm{d}\beta \sin\beta \, P_L(\cos\beta) P_N(\cos\beta) = \frac{2}{2L+1}\delta_{LN}. \tag{9}$$

The explicit form of these Legendre polynomials is really very simple [7] and the first few terms are

$$\begin{aligned}
P_0(\cos\beta) &= 1 &(10)\\
P_1(\cos\beta) &= \cos\beta &(11)\\
P_2(\cos\beta) &= \frac{3}{2}\cos^2\beta - \frac{1}{2} &(12)\\
P_3(\cos\beta) &= \frac{5}{2}\cos^3\beta - \frac{3}{2}\cos\beta &(13)\\
P_4(\cos\beta) &= \frac{35}{8}\cos^4\beta - \frac{30}{8}\cos^2\beta + \frac{3}{8}. &(14)
\end{aligned}$$

Notice that $P_L(\cos\beta)$ is an even function of $\cos\beta$ if the rank L is even and an odd one if L is odd. Since $\cos(\pi-\beta) = -\cos\beta$ this means that in writing our even orientational distribution in terms of $P_L(\cos\beta)$ functions only even L terms need be retained. Clearly the odd terms will be present if $P(\beta)$ is not even, as for ferroelectric liquid crystal phases. Limiting ourselves to the more common even (see eq. 8) case we can write

$$P(\beta) = \sum_{L=0}^{\infty} \frac{2L+1}{2} \langle P_L \rangle P_L(\cos\beta); \quad L \quad \text{even}, \tag{15}$$

where the coefficients have been obtained exploiting the orthogonality of the basis set. The averages $\langle P_J \rangle$:

$$\langle P_J \rangle = \int_0^{\pi} \mathrm{d}\beta \sin\beta P_J(\cos\beta) P(\beta) / \int_0^{\pi} \mathrm{d}\beta \sin\beta P(\beta) \tag{16}$$

represent our set of orientational order parameters. The knowledge of the (infinite) set of $\langle P_J \rangle$ would completely define the distribution. From eq. 15 we can write

$$P(\beta) = \frac{1}{2} + \frac{5}{2}\langle P_2 \rangle P_2(\cos\beta) + \frac{9}{2}\langle P_4 \rangle P_4(\cos\beta) + \ldots \tag{17}$$

The first term contains the second rank order parameter

$$\langle P_2 \rangle = \frac{3}{2}\langle \cos^2 \beta \rangle - \frac{1}{2}. \tag{18}$$

It is easy to see that $\langle P_2 \rangle$ has the properties that we would intuitively expect an order parameter to possess and that can be identified with the empirical parameter introduced by Tsvetkov [8]. For a system of perfectly aligned molecules where $\beta = 0$ for every molecule $\langle P_2 \rangle$=1. At the other extreme, for a completely disordered system such as an ordinary isotropic fluid we have $\langle \cos^2 \beta \rangle = 1/3$ and thus $\langle P_2 \rangle = 0$. In general

$$-\frac{1}{2} \leq \langle P_2 \rangle \leq 1 \tag{19}$$

because $0 \leq \langle \cos^2 \beta \rangle < 1$. On going from an ordered to a disordered system the order parameter jumps discontinuously to zero if the transition is of the first order type, like the nematic–isotropic one. Notice that the same $\langle P_2 \rangle$ can be compatible with rather different molecular organizations and thus that it is important to try to determine $\langle P_4 \rangle$ or indeed as many as possible order parameters, to discriminate between alternative structural physical models [12]. The treatment has been generalized to molecules of arbitrary symmetry and to phases more complex than uniaxial by expanding $P(\alpha, \beta, \gamma)$ in a set of Wigner matrices $D^L_{mn}(\alpha, \beta, \gamma)$, orthogonal in (α, β, γ) space and systematically applying the symmetry properties of the molecule and of the phase [4].

2.2. EXPERIMENTAL DETERMINATION OF ORDER PARAMETERS. AN EXAMPLE

The order parameter $\langle P_2 \rangle$ is proportional to the anisotropy in experimentally measurable second rank properties. Just to make contact with real life measurements, we briefly consider as an example its determination from the *diamagnetic anisotropy* of liquid crystal materials.

When a diamagnetic material is placed in a sufficiently strong magnetic field a magnetization **M** is induced.

$$\mathbf{M} = \frac{1}{\mu_0} \boldsymbol{\chi} \mathbf{B}, \tag{20}$$

where **B** is the magnetic induction and $\boldsymbol{\chi}$ is the magnetic susceptibility. In a uniaxial liquid crystal two components $\chi_{ZZ} \equiv \chi_{\parallel}$ and $\chi_{XX} = \chi_{YY} \equiv \chi_{\perp}$ corresponding to the director parallel or perpendicular to the magnetic field direction, can in principle be determined. The trace of $\boldsymbol{\chi}$ is essentially temperature independent and can be taken to be the isotropic value

$\bar{\chi} = \mathrm{Tr}\boldsymbol{\chi}/3$. However, the difference between the parallel and perpendicular components changes significantly with temperature and is related to the ordering existing in the system. It is reasonable, for this property, to assume that the macroscopic diamagnetic susceptibility $\boldsymbol{\chi}$ is the average of independent molecular contributions corresponding to molecular magnetic polarizability $\boldsymbol{\chi}^{\mathrm{MOL}}$. Thus

$$\begin{aligned}
\chi_{\|} &= \langle \chi^{\mathrm{LAB}}_{ZZ} \rangle &(21)\\
&= \sum_{a,b} \langle R_{Za} \chi^{\mathrm{MOL}}_{ab} \tilde{R}_{bZ} \rangle &(22)\\
&= \langle R^2_{Zz} \rangle \chi^{\mathrm{MOL}}_{\|} + (\langle R^2_{Zx} \rangle + \langle R^2_{Zy} \rangle) \chi^{\mathrm{MOL}}_{\perp} &(23)\\
&= \langle \cos^2 \beta \rangle \chi^{\mathrm{MOL}}_{\|} + \langle \sin^2 \beta \rangle \chi^{\mathrm{MOL}}_{\perp} &(24)\\
&= \bar{\chi} + \frac{2}{3} \Delta\chi \langle P_2 \rangle, &(25)
\end{aligned}$$

where R_{ab} are elements of the cartesian rotation matrix [1] and $\bar{\chi}^{\mathrm{MOL}} = \frac{1}{3}(\chi^{\mathrm{MOL}}_{\|} + 2\chi^{\mathrm{MOL}}_{\perp})$ equals $\bar{\chi}$. Thus determining $\chi_{\|}$ and the isotropic value $\bar{\chi}$ gives $\langle P_2 \rangle$ if the molecular anisotropy $\Delta\chi \equiv \chi^{\mathrm{MOL}}_{\|} - \chi^{\mathrm{MOL}}_{\perp}$ is known. DeJeu and coworkers [9] have measured the diamagnetic susceptivity anisotropy in a series of Schiff's base nematics which include the popular mesogens n –(4 –methoxy benzylidene) –4′ –n –Butyl aniline (MBBA), p –methoxy benzylidene p –cyananiline (MBCA), anisylidene –p –aminophenyl acetate (APAPA), as well as o –hydroxy –p –methoxy benzylidene p' –Butyl aniline (OHMBBA). In fig. 3 we report the temperature dependence of $\langle P_2 \rangle$ for a few cases. We notice that the order decreases with increasing temperature and then suddenly jumps to zero, as expected for this first order phase transition. Plotting the results in terms of reduced temperature T/T_{NI} shows a similar trend for the different compounds, even though the detailed behaviour is not really universal. The temperature dependence of the order parameter is often found to be well represented by the so called Haller equation

$$\Delta\chi(T/T_{NI}) = \Delta\chi(0)(1 - T/T_{NI})^{\beta}, \tag{26}$$

where $\Delta\chi(0)$ and the exponent β are fitting parameters. The exponent β that describes the temperature dependence of $\langle P_2 \rangle$ when approaching the transition has values $\beta = 0.17 - 0.22$ for many liquid crystals [10]. For the materials in fig. 3 $\beta = 0.17$ (MBBA), 0.185 (APAPA), 0.198 (OHMBBA) while for MBCA the value is rather different: $\beta = 0.134$.

The experimental determination of second and fourth rank order parameter can now be achieved with a number of techniques, as discussed in detail in the various chapters of [11].

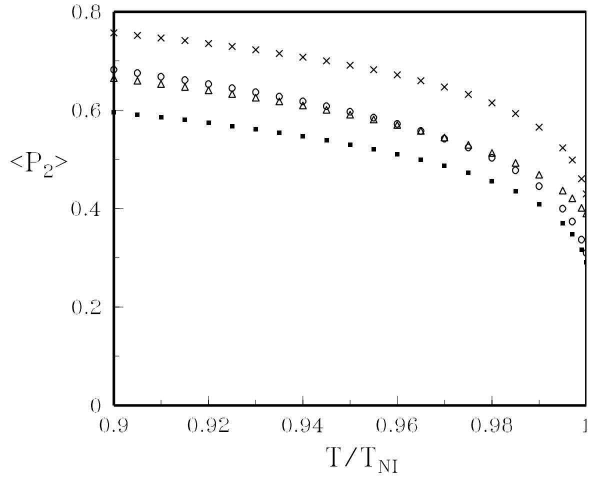

Figure 3. The second rank order parameter $\langle P_2 \rangle$ for MBBA (squares), OHMBBA (circles), MBCA (crosses), APAPA (triangles) obtained from diamagnetic anisotropy measurements as a function of temperature T/T_{NI} scaled with respect to the nematic–isotropic transition temperature [9].

2.3. GETTING ORDER PARAMETERS FROM SIMULATIONS

The calculation of orientational order parameters is clearly of particular importance in computer simulations of model liquid crystals. It also requires the development of some new algorithms as compared to simulations of isotropic fluids. We start by considering for simplicity a uniaxial mesophase formed of cylindrically symmetric particles, so that the description of ordering can be realized in terms of Legendre polynomial averages $\langle P_L \rangle$. In practice second and fourth rank parameters are particularly relevant and we shall consider their calculation in some detail.

2.4. SECOND RANK

The second rank order parameter $\langle P_2 \rangle$ can ideally be calculated by averaging $P_2(\cos\beta)$ over the probability $P(\beta)$ of finding the molecule at an orientation β with respect to the director, eq. 16.

This method can be used if the director orientation $\hat{\mathbf{n}}$ is known. This could in principle be achieved in MD, preparing a system with the director along Z, say, and exploiting the much slower time scale for director tumbling compared to molecular reorientation. Alternatively an attempt can be made, even in MC, of pinning the director along the z direction by an external field, for instance adding to the potential energy a term

$$U_{ext} = -\zeta \sum_{i=1}^{N} P_2(\cos\beta_i). \tag{27}$$

where the positive coupling parameter ζ determines the strength of interaction with the field and β_i measures the angle between the axis of the i-th molecule and the field. In these rather special cases $\langle P_2\rangle_{\rm LAB}$ can be simply calculated from an average over M equilibrium configurations of the sample order parameter $\langle P_2\rangle_S$. We have

$$\langle P_2\rangle_{\rm LAB} = \frac{1}{M}\sum_{\mathcal{J}}^{M} \langle P_2\rangle_S^{(\mathcal{J})}, \tag{28}$$

where

$$\langle P_2\rangle_S^{(\mathcal{J})} \equiv \frac{1}{N}\sum_{i=1}^{N} P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{n}})^{(\mathcal{J})} \tag{29}$$

is the order parameter computed for the $\mathcal{J}$-th configuration and $\hat{\mathbf{u}}_i \equiv (\sin\beta_i\cos\alpha_i, \sin\beta_i\sin\alpha_i, \cos\beta_i)$, defines the orientation of the i-th molecule in the laboratory frame. In this particular case it may be even simpler to calculate a histogram for the singlet orientational probability $P(\beta)$ and subsequently determine all the desired order parameters $\langle P_L\rangle_{\rm LAB}$ by integration.

The problem in using the simple method just described is that, at least in the ordinary MC method, we work in an arbitrary laboratory frame and we have no applied field. Thus we do not know the orientation of the director in each configuration and we have no a priori guarantee that it will remain the same during the simulation. This in turn means that we cannot normally calculate $\langle P_2\rangle$ as in eq. 16 in a configuration and then average the result over cycles. To find a way out [13] it is helpful to remember that computer simulations can be considered as experimental techniques where we can choose our observable at will. Thus we introduce a simple single molecule matrix property $\mathbf{A}$, whose only non vanishing component is along the molecule symmetry axis $\hat{\mathbf{u}}_i$:

$$A_{ab}^{\rm MOL} = \delta_{az}\delta_{bz}. \tag{30}$$

The sample average of $\mathbf{A}$ in our arbitrary laboratory frame is obtained relating the components of $\mathbf{A}$ to the molecule fixed components and summing over all particles:

$$\langle A_{ab}^{\rm LAB}\rangle_S \;=\; \frac{1}{N}\sum_{i=1}^{N}\{\sum_{a'b'}(R_i)_{aa'}(A_i)_{a'b'}^{\rm MOL}(\tilde{R}_i)_{b'b}\} \tag{31}$$

$$= \quad Q_{ab} + \frac{1}{3}\delta_{ab}. \tag{32}$$

Here we have defined the ordering matrix $\mathbf{Q}$ averaged over the sample (configuration) as

$$\mathbf{Q} = \frac{1}{N}\sum_{i=1}^{N} \begin{pmatrix} u_{i,x}^2 - \frac{1}{3} & u_{i,x}u_{i,y} & u_{i,x}u_{i,z} \\ u_{i,x}u_{i,y} & u_{i,y}^2 - \frac{1}{3} & u_{i,y}u_{i,z} \\ u_{i,x}u_{i,z} & u_{i,y}u_{i,z} & u_{i,z}^2 - \frac{1}{3} \end{pmatrix}. \tag{33}$$

since $(R_i)_{aZ} = u_{i,a}$. Notice that $\mathbf{Q}$ is symmetric and traceless. Diagonalization of $\langle \mathbf{A}^{\text{LAB}} \rangle_S$ with the rotation matrix $\mathbf{U}$ identifies the director frame where

$$\langle A_{ZZ}^{\text{DIR}} \rangle_S = \sum U_{aZ} U_{bZ} \langle A_{ab}^{\text{LAB}} \rangle_S \tag{34}$$

$$= \frac{2}{3}\langle P_2 \rangle_S + \frac{1}{3}. \tag{35}$$

The diagonalization procedure is equivalent to determining the order by maximizing the expression

$$\langle P_2 \rangle_S^{(\mathcal{J})} = \frac{1}{N}\sum_{i=1}^{N} P_2(\hat{\mathbf{u}}_{\mathbf{i}} \cdot \hat{\mathbf{n}}^{(\mathcal{J})}), \tag{36}$$

with respect to the unit vector $\hat{\mathbf{n}}^{(\mathcal{J})}$. Indeed in the special case that the director $\hat{\mathbf{n}}^{(\mathcal{J})}$ is parallel to the Z axis we see immediately that

$$\mathbf{Q} = \begin{pmatrix} -\frac{1}{3}\langle P_2 \rangle_S - \xi & 0 & 0 \\ 0 & -\frac{1}{3}\langle P_2 \rangle_S + \xi & 0 \\ 0 & 0 & \frac{2}{3}\langle P_2 \rangle_S \end{pmatrix}. \tag{37}$$

The sample biaxiality parameter ξ corresponds to different ordering with respect to the laboratory X and Y axis and will tend to zero at large sample sizes if the mesophase has uniaxial symmetry [14]. It is now obvious that the rotation diagonalizing $\langle \mathbf{A}^{\text{LAB}} \rangle$ or equivalently $\mathbf{Q}$ defines the orientation of the director frame in our laboratory frame. The director itself is defined by the eigenvector corresponding to the largest eigenvalue, λ_{max}, of $\mathbf{Q}$ [13, 15]. The second rank order parameter referred to the director in the sample, $\langle P_2 \rangle_\lambda$ is obtained from this λ_{max} as $\langle P_2 \rangle_{\lambda,S} = \frac{3}{2}\lambda_{max}$. Thus we can define a $\mathbf{Q}$ tensor for every configuration, say $\mathbf{Q}^{(\mathcal{J})}$ for the $\mathcal{J}$-th one. By diagonalizing $\mathbf{Q}^{(\mathcal{J})}$, we obtain an order parameter $P_2^{(\mathcal{J})}$ and a director $\hat{\mathbf{n}}^{(\mathcal{J})}$, that can change from one configuration to the next. Since $P_2^{(\mathcal{J})}$ is

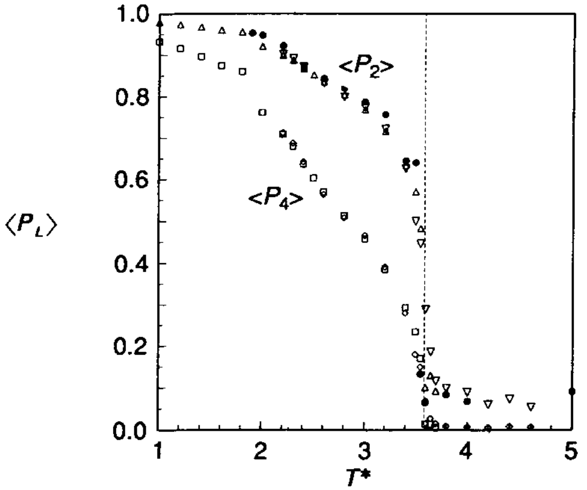

Figure 4. Orientational order parameters $\langle P_2 \rangle$, $\langle P_4 \rangle$ as a function of scaled temperature for a Gay–Berne system [17, 18]. We show results for a for N=512 (•) and N=1000 system in cooling ($\bigtriangledown$, $\diamond$) and heating ($\triangle$, $\Box$) sequences. The vertical dashed line indicates the nematic–isotropic transition.

obtained as an eigenvalue and the eigenvalues of a matrix are rotationally invariant (scalar), we then calculate

$$\langle P_2 \rangle_\lambda = \frac{3}{2M} \sum_{\mathcal{J}}^{M} (\lambda_{max})^{(\mathcal{J})}, \tag{38}$$

where $(\lambda_{max})_{\mathcal{J}}$ is the largest eigenvalue of the average tensor in configuration $\mathcal{J}$. The calculation of the orientational distribution with respect to the director strictly involves transforming the orientations, after each diagonalization, to the new director frame.

2.5. FOURTH RANK

We generalize the frame independent procedure by defining [16] a fourth rank molecular property as the direct square of the matrix **A** defined in eq. 30:

$$\mathbf{F} = \mathbf{A} \otimes \mathbf{A}. \tag{39}$$

We notice that in the molecule fixed frame the fourth rank property defined in this way has only one non vanishing component, F_{zzzz}, i.e.

$$F_{ijkl}^{\mathrm{MOL}} = \delta_{iz}\delta_{jz}\delta_{kz}\delta_{lz}. \tag{40}$$

The sample average of F is

$$\begin{aligned}
\langle \mathbf{F}^{\text{LAB}} \rangle_S &= \langle \mathbf{A}^{\text{LAB}} \otimes \mathbf{A}^{\text{LAB}} \rangle_S && (41)\\
&= \langle (\mathbf{U}\mathbf{A}^{\text{DIR}}\tilde{\mathbf{U}}) \otimes (\mathbf{U}\mathbf{A}^{\text{DIR}}\tilde{\mathbf{U}}) \rangle_S && (42)\\
&= (\mathbf{U} \otimes \mathbf{U}) \langle \mathbf{A}^{\text{DIR}} \otimes \mathbf{A}^{\text{DIR}} \rangle_S (\tilde{\mathbf{U}} \otimes \tilde{\mathbf{U}}) && (43)\\
&= (\mathbf{U} \otimes \mathbf{U}) \langle \mathbf{F}^{\text{DIR}} \rangle_S (\tilde{\mathbf{U}} \otimes \tilde{\mathbf{U}}), && (44)
\end{aligned}$$

where LAB,DIR indicate laboratory and director frame. We then relate the components in the director frame to those in the molecular frame

$$\begin{aligned}
\langle \mathbf{F}^{\text{DIR}} \rangle_S &= \langle (\mathbf{R}\mathbf{A}^{\text{MOL}}\tilde{\mathbf{R}}) \otimes (\mathbf{R}\mathbf{A}^{\text{MOL}}\tilde{\mathbf{R}}) \rangle_S && (45)\\
&= \langle (\mathbf{R} \otimes \mathbf{R}) \mathbf{A}^{\text{MOL}} \otimes \mathbf{A}^{\text{MOL}} (\tilde{\mathbf{R}} \otimes \tilde{\mathbf{R}}) \rangle_S && (46)\\
&= \langle (\mathbf{R} \otimes \mathbf{R}) \mathbf{F}^{\text{MOL}} (\tilde{\mathbf{R}} \otimes \tilde{\mathbf{R}}) \rangle_S. && (47)
\end{aligned}$$

The fourth rank order parameter $\langle P_4 \rangle$ can be obtained from

$$\begin{aligned}
\langle F^{\text{DIR}}_{ZZZZ} \rangle_S &= \langle (\mathbf{R}_{ZZ})^4 \rangle_S && (48)\\
&= \langle \cos^4 \beta \rangle_S && (49)\\
&= \sum_{a,b,c,d} U_{aZ} U_{bZ} U_{cZ} U_{dZ} \langle F^{\text{LAB}}_{abcd} \rangle_S && (50)
\end{aligned}$$

as

$$\langle P_4 \rangle_S = \frac{35}{8} \langle \cos^4 \beta \rangle_S - \frac{30}{8} \langle \cos^2 \beta \rangle_S + \frac{3}{8}. \qquad (51)$$

In fig. 4 we show, as an application of these techniques, the order parameters $\langle P_2 \rangle$, $\langle P_4 \rangle$ obtained from MC simulations for a Gay–Berne liquid crystal [18].

3. Biaxial order parameters

The determination of order parameters for different molecular and phase symmetries from computer simulations is far from simple. However, the idea, outlined above, of introducing suitable molecular observables and determining their average in the laboratory system as in a virtual experiment is quite helpful and has been used to determine the biaxial and uniaxial order parameters [19]. The minimum set of order parameters required to describe biaxial molecules in a biaxial phase is [20, 21, 12] $\langle P_2 \rangle$, $\langle R^2_{02} \rangle$, $\langle R^2_{20} \rangle$, $\langle R^2_{22} \rangle$. The R^L_{mn} are combinations of Wigner functions D^L_{mn} symmetry-adapted for the D_{2h} group of the two particles [4]. Their explicit expressions, for the even terms, are:

$$R^L_{mn} \equiv \frac{1}{2} \mathcal{R}e(D^L_{mn} + D^L_{m-n}) \qquad (52)$$

$$= \frac{1}{2}\Big[\cos(m\alpha)\cos(n\gamma)[d^L_{-mn}(\beta) + d^L_{mn}(\beta)] + \sin(m\alpha)\sin(n\gamma)[d^L_{-mn}(\beta) - d^L_{mn}(\beta)]\Big]. \tag{53}$$

Experimentally one would try to select a sufficiently high number of molecular properties A^{MOL}_{ij} and measure their average values $\langle A^{\mathrm{LAB}}_{ij}\rangle$. Then, through a diagonalization of these average tensors $\langle \mathbf{A}^{\mathrm{LAB}}\rangle$, one could determine the order parameters. The requirement that these order parameters are the same for different observables helps in assigning the correct principal laboratory frame. As an illustration the explicit expressions for the eigenvalues of a tensor $F_{ab} = \delta_{az}\delta_{bz}$ are

$$f_{XX} = \frac{1}{3} - \frac{1}{3}\langle P_2\rangle + \sqrt{\frac{2}{3}}\langle R^2_{20}\rangle \tag{54}$$

$$f_{YY} = \frac{1}{3} - \frac{1}{3}\langle P_2\rangle - \sqrt{\frac{2}{3}}\langle R^2_{20}\rangle \tag{55}$$

$$f_{ZZ} = \frac{1}{3} + \frac{2}{3}\langle P_2\rangle. \tag{56}$$

The non-trivial problem is finding a consistent way of assigning the three eigenvalues f_1, f_2, f_3 of the matrix $\mathbf{F}$ to the X,Y,Z axis. In the uniaxial phase or anyway when $\langle R^2_{20}\rangle \simeq 0$, and taking $\langle P_2\rangle > 0$, we have $f_{ZZ} > f_{XX} \simeq f_{YY}$ and letting $f_{ZZ} = \max(f_1, f_2, f_3)$ is sufficient to assign the axes except for an irrelevant exchange of X and Y. However, in the biaxial phase it may well happen that $f_{XX} > f_{ZZ}$, e.g. when $\langle P_2\rangle/\langle R^2_{20}\rangle < \sqrt{\frac{2}{3}}$, and, even if we assume that $\langle P_2\rangle$ and $\langle R^2_{20}\rangle$ are always positive, there is not a unique choice of axes other than assigning Y using $f_{YY} = \min(f_1, f_2, f_3)$. In particular the basic assumption used to calculate $\langle P_2\rangle$ in the uniaxial case, i.e. $\max(f_1, f_2, f_3) = f_{ZZ}$, breaks down. Fortunately in simulations we can perform more virtual experiments, determining the average of other probe properties sensitive to the alignment of the two other molecular axes. In practice, equations containing $\langle R^2_{02}\rangle$ and $\langle R^2_{22}\rangle$ as well as $\langle P_2\rangle$, $\langle R^2_{20}\rangle$ are constructed from the average of two other matrices, say $G_{ab} = \delta_{ax}\delta_{bx}$ and $H_{ab} = \delta_{ay}\delta_{by}$. The resulting expressions of the order parameters in terms of the average tensors are:

$$\langle P_2\rangle = \frac{3}{2}f_{ZZ} - \frac{1}{2} \tag{57}$$

$$= 1 - \frac{3}{2}(g_{ZZ} + h_{ZZ}) \tag{58}$$

$$\langle R^2_{20}\rangle = \sqrt{\frac{3}{8}}(f_{XX} - f_{YY}) \tag{59}$$

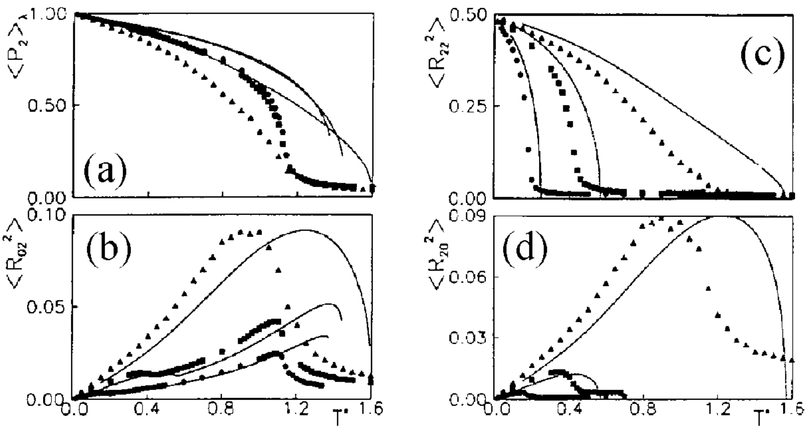

Figure 5. The second rank order parameter $\langle P_2\rangle$ (a), $\langle R^2_{02}\rangle$ (b), $\langle R^2_{20}\rangle$ (c), $\langle R^2_{22}\rangle$ (d) vs. temperature obtained from simulation: $\lambda = 0.2$ (circles), $\lambda = 0.3$ (squares) $\lambda = 0.40825$ (triangles) and from Mean Field Theory (lines) [19]

$$= \sqrt{\frac{3}{8}}(g_{YY} - g_{XX} + h_{YY} - h_{XX}) \tag{60}$$

$$\langle R^2_{02}\rangle = \sqrt{\frac{3}{8}}(g_{ZZ} - h_{ZZ}) \tag{61}$$

$$= \sqrt{\frac{3}{8}}(h_{XX} + h_{YY} - g_{XX} - g_{YY}) \tag{62}$$

$$\langle R^2_{22}\rangle = \frac{1}{2}(g_{XX} - g_{YY} + h_{YY} - h_{XX}). \tag{63}$$

The normalized eigenvectors of the matrices give the axes of the reference system, except for the sign, so there are $3! = 6$ different systems corresponding to the eigenvalue permutations. In [19] we have chosen the eigenvalue permutation which satisfies the following conditions: **a**) $\langle P_2\rangle > 0$; **b**) the same order parameters must have the same values in all the ways they are computed (here, e.g., $\langle P_2\rangle$ and $\langle R^2_{20}\rangle$ are computed in two different ways); **c**) for each configuration at one temperature the order parameters must be as close as possible to the mean value of the order parameters of the previous temperature (the sum of the differences is minimized). The above procedure effectively assigns the X and Y axes when the phase is biaxial. In the uniaxial phase X and Y are undistinguishable and the method, even though not needed, is not applicable because it forces a difference that is completely spurious. In a similar way, application of the algorithm previously described for finding $\langle P_2\rangle$ to an isotropic phase will give a spurious non-zero order parameter (decreasing with size). In fig. 5 we show a set of order parameters obtained from MC simulation of the simple second rank attractive pair potential [19, 22]:

$$\begin{aligned} U(\omega_{ij}) &= -\epsilon_{ij}\{P_2(\cos\beta_{ij}) + 2\lambda[R^2_{02}(\omega_{ij}) + R^2_{20}(\omega_{ij})] \\ &+ 4\lambda^2 R^2_{22}(\omega_{ij})\} \end{aligned} \tag{64}$$

with the biaxial molecules, or "spins", fixed at the sites of a three dimensional cubic lattice. The coupling parameter, ϵ_{ij}, is taken to be a positive constant, ϵ when particles i and j are nearest neighbors and zero otherwise. ω_{ij} is the relative orientation of the molecular pair. The biaxiality parameter λ accounts for the deviation from cylindrical molecular symmetry: when λ is zero, the potential reduces to the Lebwohl-Lasher P_2 potential, while for λ different from zero the particles tend to align not only their major axis, but also their faces. The value $\lambda = 1/\sqrt{6}$ marks the boundary between a system of prolate ($\lambda < 1/\sqrt{6}$) and oblate molecules ($\lambda > 1/\sqrt{6}$) [20].

We notice the different temperature dependence and the different magnitude of the four order parameters. Given the numerical errors inevitable in computer simulation results, e.g. those associated with finite size, the order parameter $\langle R^2_{22}\rangle$ can be recommended as a particularly effective monitor of the biaxial transition.

4. Pair properties

4.1. PAIR DISTRIBUTION

We can define a positional–orientational pair distribution using once more delta functions as counting devices:

$$P^{(2)}(\mathbf{r}_1\omega_1, \mathbf{r}_2, \omega_2)/[N(N-1)] = \langle\delta(\mathbf{r}_1 - \mathbf{r}'_1)\delta(\omega_1 - \omega'_1)\delta(\mathbf{r}_2 - \mathbf{r}'_2)\delta(\omega_2 - \omega'_2)\rangle. \tag{65}$$

As the separation between the particles becomes very large the probability of finding molecule 1 at $(\mathbf{r}_1, \omega_1)$ and molecule 2 at $(\mathbf{r}_2, \omega_2)$ will be the product of these two independent events and the pair distribution will tend to the product of two single particle ones.

$$\begin{aligned} &\lim_{r\to\infty} \langle\delta(\mathbf{r}_1 - \mathbf{r}'_1)\delta(\omega_1 - \omega'_1)\delta(\mathbf{r}_2 - \mathbf{r}'_2)\delta(\omega_2 - \omega'_2)\rangle \\ &= \langle\delta(\mathbf{r}_1 - \mathbf{r}'_1)\delta(\omega_1 - \omega'_1)\rangle\,\langle\delta(\mathbf{r}_2 - \mathbf{r}'_2)\delta(\omega_2 - \omega'_2)\rangle \end{aligned} \tag{66}$$

Thus it is convenient to write, for uniform systems

$$\begin{aligned} P^{(2)}(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2) &\equiv \rho^2 G(\mathbf{r}_{12}, \omega_1, \omega_2) \\ &= \rho^2 P(\omega_1)P(\omega_2)g(\mathbf{r}_{12}, \omega_1, \omega_2). \end{aligned} \tag{67}$$

The reduced pair distribution function $g(\mathbf{r}_{12}, \omega_1, \omega_2)$ introduced in eq.67 expresses a spatial - orientational correlation function or simply a *pair correlation function.* We have

$$\lim_{r_{12}\to\infty} g(\mathbf{r}_{12}, \omega_1, \omega_2) = 1 \tag{68}$$

i.e. the density of particles at large distances just becomes that of the bulk. This limiting value is often subtracted from the $g(\mathbf{r}_{12}, \omega_1, \omega_2)$ to define the *total correlation function*

$$h(\mathbf{r}_{12}, \omega_1, \omega_2) = g(\mathbf{r}_{12}, \omega_1, \omega_2) - 1 \tag{69}$$

or more generally

$$h(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2) = g(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2) - 1. \tag{70}$$

It is also clear that at large separations the only orientational correlation between particles will be that indirectly coming from the fact that both molecule 1 and 2 are separately parallel to the same director, if that exists. In particular no long range orientational correlations exist in a normal fluid.

Another limiting situation is obtained for very short distances. If the molecules have a hard impenetrable core, there is vanishing probability of finding a second particle nearer than a minimum approach distance $\sigma(\mathbf{r}_{12}, \omega_1, \omega_2)$ from the first one. Thus

$$g(\mathbf{r}_{12}, \omega_1, \omega_2) = 0, \quad \text{if} \quad r_{12} < \sigma(\mathbf{r}_{12}, \omega_1, \omega_2). \tag{71}$$

4.2. STONE EXPANSION OF THE PAIR DISTRIBUTION

We have seen earlier on, when discussing the calculation of $\langle P_2 \rangle$ from MC simulations, the advantages of using a rotational invariant description when calculating order parameters for a sample where no field is applied and the director could fluctuate from a configuration to the next. Here we wish to discuss the calculation of suitable rotationally invariant pair properties. The pair distribution can depend on orientations of the two molecules ω_1, ω_2 and on the intermolecular vector orientation (i.e. $\mathbf{r}_{12}$, not just r_{12}) but only through rotationally invariant combinations [23, 24, 25, 26, 4]. For example if we have linear molecules with orientation defined by unit vectors $\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2$ the distribution could depend on $\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2$, $\hat{\mathbf{u}}_1 \cdot \mathbf{r}_{12}$, $\hat{\mathbf{u}}_2 \cdot \mathbf{r}_{12}$ and their powers, but not on $\hat{\mathbf{u}}_1$, $\hat{\mathbf{u}}_2$, $\mathbf{r}_{12}$ by themselves. Let us now examine the general case

$$G(\mathbf{r}, \omega_1, \omega_2) = g(\mathbf{r}, \omega_1, \omega_2) P(\omega_1) P(\omega_2), \tag{72}$$

where $G(\mathbf{r}, \omega_1, \omega_2)$, $P(\omega_i)$ are the pair (cf. 67) and single particle distribution functions and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 = \mathbf{r}_{12}$ is the intermolecular vector with

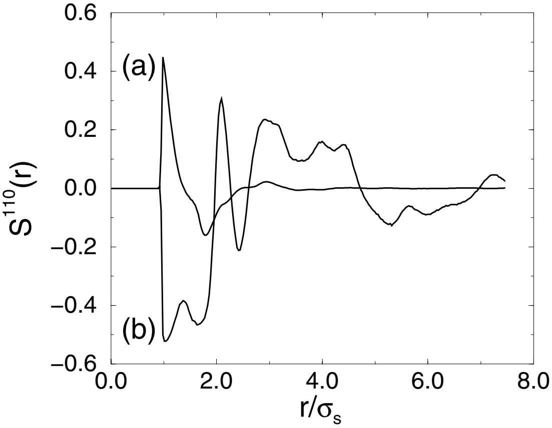

Figure 6. The dipole space correlation $S^{110}(r) = -\frac{1}{\sqrt{3}} \langle [\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2] \rangle_r$ for a system of Gay-Berne particles with dipoles. The curves refer to central (a) and shifted (b) dipoles. [27]

length r and orientation $\omega_r = (\alpha_r, \beta_r)$. The pair correlation (e.g. for uniaxial molecules) can be expanded in Stone invariants (cf. Appendix)

$$g(\omega_1, \omega_2, \mathbf{r}) = \sum_{L_1, L_2, L_3} g^{L_1, L_2, L_3}(r) S^{L_1, L_2, L_3}(\omega_1, \omega_2, \omega_r), \tag{73}$$

where the expansion coefficients are defined as

$$\begin{aligned} g^{L_1, L_2, L_3}(r) &= \int \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \; g(\omega_1, \omega_2, \mathbf{r}) S^{L_1, L_2, L_3 \, *}(\omega_1, \omega_2, \omega_r) \\ &= \frac{(2L_1 + 1)(2L_2 + 1)(2L_3 + 1)}{256\pi^5} S^{L_1, L_2, L_3 \, *}(r) \end{aligned} \tag{74}$$

Average rotational invariants as a function of inter-particle separation r are extremely useful to describe the molecular organization in a liquid crystal. As an example we show in fig. 6 the orientationally averaged rotational invariant $S^{110}(r)$ for a system of elongated Gay-Berne particles with an axial dipole at the center or near the end of the molecule [27]. The invariant shows that for central dipoles neighbouring dipoles tend to be antiparallel, while the opposite is true for shifted dipoles. Indeed monolayer smectic liquid crystals and modulated antiferroelectric bilayer stripe domains similar to the experimentally observed "antiphase" structures [28] are obtained in the two cases.

4.3. INTERMOLECULAR VECTOR CORRELATION FUNCTIONS

Given the anisotropy of liquid crystals, we can expect that pair distributions along the director or transversal to it, for instance, can be quite different.

More generally it is useful to define distributions along different orientations $\omega_{r_{12}}$ of the intermolecular vector relative to the director [29, 30, 18]:

$$g(r_{12}, \omega_{r_{12}}) = \int \mathrm{d}\mathbf{r}_1\, \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, g(\mathbf{r}_1, \omega_1, \mathbf{r}_1 + \mathbf{r}_{12}, \omega_2) / \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\omega_1 \mathrm{d}\omega_2. \quad (75)$$

This quantity gives the probability of finding a particle at a certain distance r_{12} from a particle chosen as origin when their intermolecular vector has an orientation $\omega_{r_{12}} = (\alpha_{r_{12}}, \beta_{r_{12}})$. For systems that are at most uniaxial, we can consider orientations defined with respect to a laboratory system with Z axis parallel to the director (perhaps after a suitable overall rotation of the sample) and we do not need to consider the angle $\alpha_{r_{12}}$, so that the intermolecular vector distribution reduces to $g(\mathbf{r}_{12}) = g(r_{12}, \beta_{r_{12}})/2\pi$. In fig. 7 we see an example of $g(r_{12}, \beta_{r_{12}})$ for a Gay-Berne system [18]. We notice that the radial distribution is not isotropic even in the nematic phase and that it changes quite significantly with temperature. The very low temperature one ($T^* = 1.8$) shows that as we move from a molecule along the z laboratory axis ($\cos\beta_r = 1$) a second molecule is found slightly below the particle length σ_e. However if we move transversally to the director ($\cos\beta_r = 0$) very sharp, well defined peaks appear, indicating structuredness in the layer. The characteristic double structure of the second peak indicates for this structure an hexagonal ordering, as expected in a smectic B or crystalline layer structure. It is convenient to expand $g(r_{12}, \beta_{r_{12}})$ as

$$g(r_{12}, \beta_{r_{12}}) = g_0(r_{12}) \sum_L (2L+1) g_L^+(r_{12}) P_L(\cos\beta_{r_{12}}), \quad (76)$$

where we have the standard radial distribution

$$g_0(r_{12}) = \frac{1}{2} \int \mathrm{d}\beta_{r_{12}}\, \sin\beta_{r_{12}} g(r_{12}, \beta_{r_{12}}). \quad (77)$$

This simple centre of mass, radial, distribution $g_0(r)$ on is very similar in the isotropic and in the nematic phase. This is because the $g_0(r_{12})$ are mainly structured at short range, and at short range liquid crystals are just like normal liquids.

The set of quantities $g_L^+(r_{12})$ associated to the intermolecular vector correlation function represent a sort of order parameters [29, 30]

$$\begin{aligned} g_L^+(r_{12}) &= \frac{1}{2\, g_0(r_{12})} \int \mathrm{d}\beta_{r_{12}} \sin\beta_{r_{12}} g(r_{12}, \beta_{r_{12}}) P_L(\cos\beta_{r_{12}}) && (78) \\ &= \langle P_L(\cos\beta_{r_{12}}) \rangle_{r_{12}}. && (79) \end{aligned}$$

We can also define a pair density function along the director

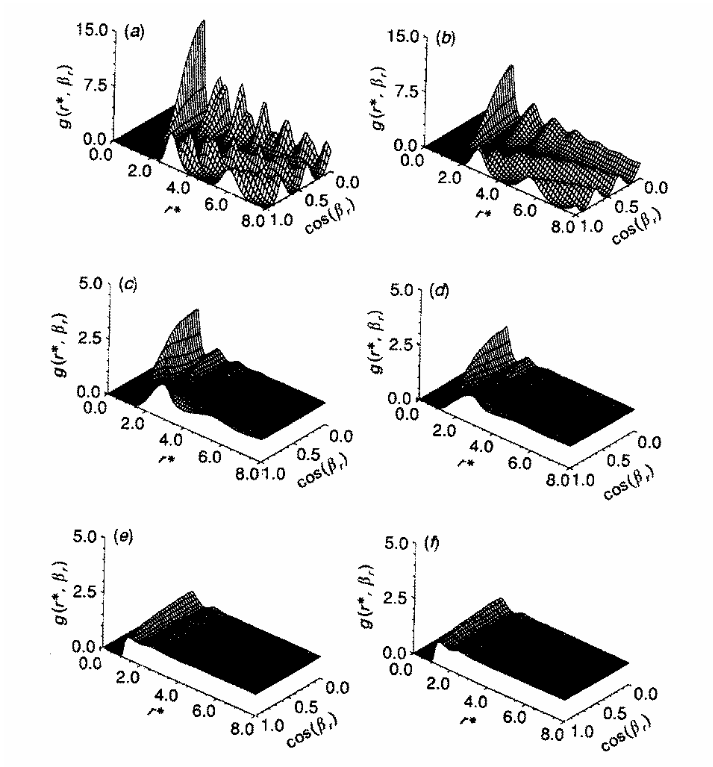

Figure 7. The intermolecular vector distribution $g(r^*, \beta_r)$ for a Gay-Berne potential at various dimensionless temperatures T^* in the crystalline, smectic: $T^* = 1.80$ (a), 2.00 (b), nematic: $T^* = 2.80$ (c), 3.50 (d) and isotropic: $T^* = 3.80$ (e), 4.00 (f) phase [18].

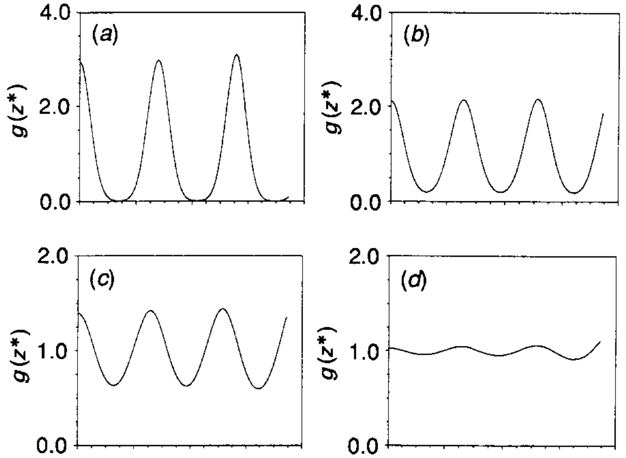

Figure 8. The pair density $g(z^*)$ for a Gay-Berne system [18].

$$g(z)=\frac{\int \,\mathrm{d}r\ r^2\mathrm{d}\beta_r\ \sin\beta_r\delta(r\cos\beta_r-z)g(r,\beta_r)}{\int \,\mathrm{d}r\ r^2\mathrm{d}\beta_r\ \sin\beta_r\delta(r\cos\beta_r-z)}. \tag{80}$$

The density $g(z)$ will be sinusoidally varying in a smectic and essentially constant in a nematic, as we see for a Gay-Berne fluid of elongated particles in fig. 8 [18].

5. Thermodynamic observables

The distribution functions introduced earlier on can be used to write down expressions for the various thermodynamic functions. Quite often these will be too complicated to be practically applicable as such but they nevertheless constitute the basis for approximate formulations or for algorithms to be used in computer simulations. Some relevant formulas are given here.

5.1. ENERGY

The total configuration energy of a system of N particles is most often assumed to be a sum of pairwise intermolecular contributions, and in turn the observed average can be written in terms of the pair distribution. Using the definition of pair correlation

$$\begin{aligned} U &= \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\langle U(\mathbf{X}_i,\mathbf{X}_j)\rangle && (81)\\ &= \frac{1}{2}\rho^2\int \mathrm{d}\mathbf{r}_1\mathrm{d}\omega_1\mathrm{d}\mathbf{r}_2\mathrm{d}\omega_2 G(\mathbf{r}_1\omega_1,\mathbf{r}_2,\omega_2)U(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2) && (82)\end{aligned}$$

and for a uniform system

$$U=\frac{V}{2}\rho^2\int \mathrm{d}\mathbf{r}_{12}\mathrm{d}\omega_1\mathrm{d}\omega_2 P(\omega_1)P(\omega_2)g(\mathbf{r}_{12},\omega_1,\omega_2)U(\mathbf{r}_{12},\omega_1,\omega_2). \tag{83}$$

5.2. HEAT CAPACITY

If we differentiate the microscopic expression for the energy we can show that the constant volume heat capacity is related to the mean square fluctuations in the energy:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V && (84)\\ &= \frac{1}{k_B T^2}\left(\langle U^2\rangle-\langle U\rangle^2\right) && (85)\\ &= \frac{1}{2}\rho^2\int \mathrm{d}\mathbf{r}_1\mathrm{d}\omega_1\mathrm{d}\mathbf{r}_2\mathrm{d}\omega_2 U(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2)\,\frac{\partial}{\partial T}G(\mathbf{r}_1\omega_1,\mathbf{r}_2,\omega_2), && (86)\end{aligned}$$

where k_B is the Boltzmann constant and the last equation applies to temperature independent potentials. Eq. 85 shows that the heat capacity is a non-negative quantity.

Notice that the heat capacity is not a pairwise quantity, even if the potential is a pairwise one. C_V does not depend only on the pair distribution at a given temperature but on its derivative. If we try to perform the derivative we see that the microscopic expression depends on more than two particles simultaneously. Thus the specific heat is really a collective property and it is reasonable that it can change significantly and diverge at a phase transition where the collective organization changes.

5.3. PRESSURE

The calculation of pressure provides an important observable and is also essential for implementing proper isobaric control, e.g. in NPT MC simulations. To derive a molecular expression for the pressure we start from the thermodynamic definition as a volume derivative of the free energy $\mathcal{A}$ [31, 32]

$$\begin{aligned} P &= -\left(\frac{\partial \mathcal{A}}{\partial V}\right)_T && (87) \\ &= k_B T \left(\frac{\partial \ln Q_N}{\partial V}\right)_T . && (88) \end{aligned}$$

We can render the volume dependence of the configurational integral Q_N an explicit one by changing the positional variable $\mathbf{r}_i$ to dimensionless units $\mathbf{s}_i$. Thus we let

$$\mathbf{r}_i = V^{\frac{1}{3}} \mathbf{s}_i. \tag{89}$$

and find

$$Q_N = \frac{V^N}{N!} \int \{\mathrm{d}\mathbf{s}\}^N \{\mathrm{d}\omega\}^N e^{-U(\{\mathbf{s},\omega\}^N)/k_B T}, \tag{90}$$

which gives

$$\begin{aligned} P &= \frac{N k_B T}{V} - \frac{V^N}{Z_N} \int \{\mathrm{d}\mathbf{s}\}^N \{\mathrm{d}\omega\}^N \frac{\partial U(\{\mathbf{s},\omega\}^N)}{\partial V} e^{-U(\{\mathbf{s},\omega\}^N)/k_B T} \\ &= \frac{N k_B T}{V} - \langle \frac{\partial U(\{\mathbf{r},\omega\}^N)}{\partial V} \rangle. && (91) \end{aligned}$$

The volume derivative of the potential energy is

$$\frac{\partial U(\{\mathbf{r},\omega\}^N)}{\partial V} = \sum_i \frac{\partial}{\partial \mathbf{r}_i} U(\{\mathbf{r},\omega\}^N) \cdot \frac{\partial \mathbf{r}_i}{\partial V}, \tag{92}$$

where $\partial/\partial\mathbf{r}_i U$ is the potential gradient. Since

$$\frac{\partial \mathbf{r}_i}{\partial V} = \frac{1}{3V}\mathbf{r}_i, \tag{93}$$

we find the *virial* equation [31, 4]

$$P = \frac{Nk_BT}{V} - \frac{1}{3V}\langle \sum_i \mathbf{r}_i \cdot \nabla_i U(\{\mathbf{r},\omega\}^N)\rangle. \tag{94}$$

For the special case of a pairwise potential the volume derivative of the potential energy in eq. 91 is

$$\frac{\partial U(\{\mathbf{r},\omega\}^N)}{\partial V} = \frac{1}{3V}\sum_{i<j}\frac{\partial}{\partial \mathbf{r}_{ij}}U(\mathbf{r}_{ij},\omega_i,\omega_j)\cdot \mathbf{r}_{ij} \tag{95}$$

Notice that these expressions have to be modified is the potential energy also depends directly on the volume, as is the case for instance of long range Coulomb interactions summed with Ewald or reaction field formulas [33].

5.4. SURFACE TENSION

We consider two coexisting phases with a plane interface separating them localized around $z = 0$. The thermodynamic definition relates the surface tension γ to the variation in free energy as the area A is changed [3, 34]:

$$\begin{aligned} \gamma &= -\left(\frac{\partial \mathcal{A}}{\partial A}\right)_{TV} && (96) \\ &= k_BT\left(\frac{\partial \ln Q_N}{\partial A}\right)_{TV}. && (97) \end{aligned}$$

To derive a molecular expression for the surface tension we can proceed as we did for the pressure to get the a virial type expression, by making the surface dependence of the configurational integral Q_N an explicit one by changing the positional variable to dimensionless units. In practice we can use

$$\begin{aligned} r_x &= A^{\frac{1}{2}}s_x, & \frac{\partial r_x}{\partial A} = \frac{r_x}{2A} && (98) \\ r_y &= A^{\frac{1}{2}}s_y, & \frac{\partial r_y}{\partial A} = \frac{r_y}{2A} && (99) \\ r_z &= \frac{V}{A}s_z, & \frac{\partial r_z}{\partial A} = -\frac{r_z}{A}. && (100) \end{aligned}$$

The surface tension can be written in terms of the average derivative of the potential energy with respect to the area is, for a pairwise potential:

$$\begin{aligned}
\gamma &= \left\langle \frac{\partial U(\{\mathbf{r},\omega\}^N)}{\partial A} \right\rangle_{TV} && (101) \\
&= \frac{1}{2A} \sum_{i<j} \left\langle \mathbf{r}_{ij} \cdot \frac{\partial U(\mathbf{r}_{ij},\omega_i,\omega_j)}{\partial \mathbf{r}_{ij}} - 3 z_{ij} \frac{\partial U(\mathbf{r}_{ij},\omega_i,\omega_j)}{\partial z_{ij}} \right\rangle_{TV} && (102) \\
&= \frac{1}{4V_z} \int_{-z}^{z} \mathrm{d}z \sum_{i<j} \left\langle \left(x_{ij} \frac{\partial U_{ij}}{\partial x_{ij}} + y_{ij} \frac{\partial U_{ij}}{\partial y_{ij}} \right) - 2 z_{ij} \frac{\partial U_{ij}}{\partial z_{ij}} \right\rangle_{TV}, && (103)
\end{aligned}$$

where $U_{ij} = U(\mathbf{r}_{ij},\omega_i,\omega_j)$ and V_z is the volume of a thin layer $\mathcal{L}$ containing the interface of thickness $2z$ and with area A equal to the sample cross section [35].

6. Dynamic evolution of a molecular property

We now turn to briefly considering the calculation of dynamic properties [36, 37, 38, 39, 40]. We start considering once more a system of N molecules at equilibrium in a volume V at temperature T. The full distribution of the system is

$$\rho_0(\mathbf{\Gamma}) \equiv \frac{1}{Z_N} \exp[-\beta \mathcal{H}_0(\mathbf{\Gamma})], \qquad (104)$$

where $\beta \equiv 1/(k_B T)$ and $\mathbf{\Gamma} \equiv (\{\mathbf{q},\mathbf{p}\}^N) = (\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_2,\mathbf{p}_2,\ldots,\mathbf{q}_N,\mathbf{p}_N)$ is the set of coordinates and momenta needed to specify a point in phase space and the unperturbed hamiltonian $\mathcal{H}_0$, is the sum of the potential $U(\{\mathbf{q}\}^N)$ and kinetic $K(\{\mathbf{p}\}^N)$ contributions:

$$\mathcal{H}_0(\{\mathbf{q}\}^N,\{\mathbf{p}\}^N) = U(\{\mathbf{q}\}^N) + K(\{\mathbf{p}\}^N) \qquad (105)$$

and correspondingly

$$\begin{aligned}
\rho_0(\mathbf{\Gamma}) &= \frac{1}{Z_N} \exp[-\beta U(\{\mathbf{q}\}^N)] \exp[-\beta K(\{\mathbf{p}\}^N)] && (106) \\
&= P(\{\mathbf{q}\}^N) P_M(\{\mathbf{p}\}^N), && (107)
\end{aligned}$$

where $P(\{\mathbf{q}\}^N)$ is the configurational probability studied earlier in this chapter, where we have considered, $\{\mathbf{q}\}^N = (\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, and each $\mathbf{q}_i$ can depend on a set of positions and orientations, $\mathbf{X}_i$. $P_M(\{\mathbf{p}\}^N)$ is the Maxwell distribution of linear and angular momenta.

For a system described by an hamiltonian $\mathcal{H}$ the equations of motion for coordinate and momenta are [41]

$$\frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} = \dot{\mathbf{q}}_i, \quad \frac{\partial \mathcal{H}}{\partial \mathbf{q}_i} = -\dot{\mathbf{p}}_i. \qquad (108)$$

The time derivative of a function A that depends on generalized coordinates $\mathbf{q}_i$ and momenta $\mathbf{p}_i$ i.e. of the state point $\mathbf{\Gamma}$, will be

$$\dot{A}(t) = \frac{\partial A}{\partial t} + \sum_i \left(\frac{\partial A}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial A}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right) \tag{109}$$

$$= \frac{\partial A}{\partial t} + \mathcal{H}^{\times} A. \tag{110}$$

The differential Liouville operator or evolution operator $\mathcal{H}^{\times}$ is defined as

$$\mathcal{H}^{\times} \equiv -\sum_i \left(\frac{\partial \mathcal{H}}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{q}_i} \right) \tag{111}$$

$$= \sum_i \left(\mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} + \frac{1}{m_i} \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} \right), \tag{112}$$

where $\mathbf{F}_i$ is the force acting on molecule i. If $\partial A / \partial t = 0$, the evolution of $A(t)$ is formally given by the so called Heisenberg evolution equation

$$A(t) = e^{\mathcal{H}^{\times} t} A(0). \tag{113}$$

In particular the evolution of the probability distribution $\rho(\mathbf{\Gamma})$ at equilibrium is

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial \rho}{\partial t} + \mathcal{H}^{\times} \rho, \tag{114}$$

but the total density must be conserved in time ($\dot{\rho}_0(\mathbf{\Gamma}) = 0$) so that evolution takes place through the Liouville equation

$$\frac{\partial \rho}{\partial t} = -\mathcal{H}^{\times} \rho, \tag{115}$$

where we have written

$$\rho \equiv \rho(\mathbf{\Gamma}) = \frac{1}{Z_N} \exp[-\beta \mathcal{H}(\mathbf{\Gamma})]. \tag{116}$$

Thus if the hamiltonian is the unperturbed one $\mathcal{H}_0$, it does not modify the equilibrium distribution ρ_0

$$\mathcal{H}_0^{\times} \rho_0 = \mathcal{H}_0^{\times} \frac{1}{Z} e^{-\beta \mathcal{H}_0} = -\beta \frac{1}{Z} e^{-\beta \mathcal{H}_0} \mathcal{H}_0^{\times} \mathcal{H}_0 = 0. \tag{117}$$

In other words ρ_0 is an eigenvector of the operator $\mathcal{H}_0^{\times}$ corresponding to a zero eigenvalue. Correspondingly for such a stationary system $\mathcal{H}_0^{\times} \langle A \rangle = 0$. The evolution operator is a combination of derivatives and thus it follows the standard rules of derivatives. For instance

$$\mathcal{H}^{\times}(AB) = (\mathcal{H}^{\times} A)B + A(\mathcal{H}^{\times} B). \tag{118}$$

In particular, given the average of two properties A,B, we have $\mathcal{H}_0^\times \langle AB \rangle = 0$ and the antisymmetric relation

$$\begin{aligned} \langle A\mathcal{H}_0^\times B\rangle &= \int \mathrm{d}\mathbf{\Gamma}\rho_0 A\mathcal{H}_0^\times B \\ &= -\langle (\mathcal{H}_0^\times A)B\rangle. \end{aligned} \tag{119}$$

More generally

$$\langle A e^{t\mathcal{H}_0^\times} B\rangle = \langle (e^{-t\mathcal{H}_0^\times} A)B\rangle. \tag{120}$$

The quantity just introduced is called an equilibrium time correlation function for properties A and B, $C_{AB}(t)$. In general it corresponds to an average of a property A taken at a certain time t_0 with the complex conjugate of a property B taken at time $t_0 + t$

$$C_{AB}(t) = \langle A(t_0)B^*(t_0 + t)\rangle \tag{121}$$

$$= \langle A(0)B^*(t)\rangle \tag{122}$$

$$= \langle A(0)e^{t\mathcal{H}_0^\times} B^*(0)\rangle \tag{123}$$

$$= \int \mathrm{d}\mathbf{\Gamma} A(\mathbf{\Gamma}) e^{t\mathcal{H}_0^\times} B^*(\mathbf{\Gamma})\rho_0(\mathbf{\Gamma}). \tag{124}$$

Time correlation functions can be calculated from the sequence of instantaneous values of the observables taken along a Molecular Dynamics generated trajectory. Thus

$$C_{AB}(t) \approx \frac{1}{M-n} \sum_{k=1}^{M-n} A(k\Delta t)B^*([k+n]\Delta t), \quad t = n\Delta t. \tag{125}$$

Since our system should be independent on where we start measuring the time, there is no dependence on t_0. We shall see in the next section that correlation functions are directly linked to observable dynamic properties. In this context it is useful to introduce also the Fourier-Laplace transform of a correlation function is called spectral density

$$j_{AB}(\hat{\omega}) = \int \mathrm{d}t\, e^{i\hat{\omega}t} C_{AB}(t) \tag{126}$$

$$= \langle A(0) \frac{1}{\mathcal{H}^\times - i\hat{\omega}} B^*(0)\rangle. \tag{127}$$

Here for simplicity we assume real quantities A, B.

7. Contact with experiment. Linear response theory

Let us consider the measurement of a property A of a molecular system through the application of a weak measuring field $f(t)$ [36, 37, 39, 40]. We assume that the field is switched on a time $t = 0$ and that it interacts with the system through a perturbation hamiltonian

$$\mathcal{H}_1 = -B(\mathbf{\Gamma})f(t). \tag{128}$$

The property coupling to the field B depends in the most general case on the coordinates and the momenta of all molecules, $B \equiv B(\mathbf{\Gamma})$. We assume that the observed value of property A changes from its static equilibrium value in the absence of the field $\langle A \rangle_0$. Since the applied field is weak the observed non equilibrium value in the presence of the field at time t, $\langle \delta A(t) \rangle_f$, should be linear in the field strength. Considering that the system may not react instantaneously to the field, what we observe at time t is a sum of the contributions from all possible time lags τ between application and observation

$$\begin{aligned} \langle \delta A(t) \rangle_f &= \sum_{\tau_i} K_{AB}(\tau_i) f(t - \tau_i) & (129) \\ &= \int_0^\infty \mathrm{d}\tau K_{AB}(\tau) f(t - \tau). & (130) \end{aligned}$$

The observed value is a *convolution* of the field function f with a “ kernel” K_{AB} whose functional form depends on the type of applied field and the observable property. The dynamics of molecular phenomena is most often explored as a frequency dependence of a certain observable property rather than a direct time dependence from a given starting event (there are exceptions of course, e.g. time domain fluorescence depolarization experiments). We can write the Fourier-Laplace transform of the time dependent response as

$$\begin{aligned} \langle \delta \tilde{A}(\hat{\omega}) \rangle_f &\equiv \int_0^\infty \mathrm{d}t\, e^{i\hat{\omega}t} \langle \delta A(t) \rangle_f & (131) \\ &= \chi_{AB}(\hat{\omega}) \tilde{f}(\hat{\omega}), & (132) \end{aligned}$$

where the Fourier-Laplace transform

$$\chi_{AB}(\hat{\omega}) = \int_0^\infty \mathrm{d}\tau K_{AB}(\tau) e^{i\hat{\omega}\tau} \tag{133}$$

is called a *susceptibility.* Thus the Fourier transform of a convolution integral of two functions is the product of the Fourier transform of the functions, and this useful result is called the *convolution theorem.* The equation we have just seen is macroscopic, but it is clear that if we could obtain a microscopic expression for the susceptibility we could be able to calculate the response to a measuring field. The importance of Linear Response Theory is that it gives a molecular interpretation to the susceptibility in terms of fluctuations of the unperturbed system.

8. Evolution in the presence of a perturbation

When the time dependent perturbation $\mathcal{H}_1(t) = -B(\mathbf{\Gamma})f(t)$ is added, so that

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t), \tag{134}$$

the perturbation produces an evolution of ρ_0:

$$\begin{aligned} \mathcal{H}_1^\times(t)\rho_0 &= -\beta\frac{1}{Z}e^{-\beta\mathcal{H}_0}\mathcal{H}_1^\times(t)\mathcal{H}_0 && (135)\\ &= -\beta\rho_0\dot{B}f(t) && (136) \end{aligned}$$

since using the definition of $\mathcal{H}^\times$

$$\begin{aligned} \mathcal{H}_1^\times(t)\mathcal{H}_0 &= -\mathcal{H}_0^\times\mathcal{H}_1(t) && (137)\\ &= f(t)\mathcal{H}_0^\times B(\mathbf{\Gamma}) \\ &= f(t)\dot{B}. && (138) \end{aligned}$$

In the presence of $\mathcal{H}_1(t)$ the distribution becomes at first order

$$\rho(t) = \rho_0 + \delta\rho(t) \tag{139}$$

and the non equilibrium value is

$$\langle\delta A(t)\rangle_f = \int \mathrm{d}\mathbf{\Gamma} A(\mathbf{\Gamma})\delta\rho(t). \tag{140}$$

From the Liouville equation we have substituting eq. 139 and keeping only linear terms

$$\begin{aligned} \dot{\delta\rho}(t) &= -\mathcal{H}_0^\times\delta\rho - \mathcal{H}_1^\times(t)\rho_0 \\ &= -\mathcal{H}_0^\times\delta\rho + \beta\rho_0 f(t)\dot{B}. && (141) \end{aligned}$$

This is a simple first order linear equation whose general solution is available[1]

---

[1] *The known differential equation is* $\dot{y}(t) + Py = Q(t)$ *if* $P = \mathcal{H}_0^\times$, $Q(t) = -\beta\rho_0\dot{\mathcal{H}}_1$ *that with* $y = y_0$ *when* $t = t_0$ *has the solution*

$$e^{Pt}y - e^{Pt_0}y_0 = \int_{t_0}^{t} e^{Pt'}Q(t')\mathrm{d}t'$$

$$\delta\rho(t) = \beta \int_{-\infty}^{t} \mathrm{d}t' e^{[(t'-t)\mathcal{H}_0^{\times}]} \rho_0 \dot{B} f(t'). \tag{142}$$

Substituting in eq. 140

$$\begin{aligned}
\langle \delta A(t) \rangle_f &= \beta \int_{-\infty}^{t} \mathrm{d}t' f(t') \int \mathrm{d}\mathbf{\Gamma} A(\mathbf{\Gamma}) e^{[(t'-t)\mathcal{H}_0^{\times}]} \dot{B}(\mathbf{\Gamma}) \rho_0(\mathbf{\Gamma}) \\
&= \beta \int_{-\infty}^{t} \mathrm{d}t' f(t') \int \mathrm{d}\mathbf{\Gamma} A(0) \dot{B}(t'-t) \rho_0(\mathbf{\Gamma}) \\
&= \beta \int_{-\infty}^{0} \mathrm{d}\tau f(\tau + t) C_{A\dot{B}}(\tau),
\end{aligned} \tag{143}$$

where we have shifted the time origin ($\tau = t' - t$). We can do one further manipulation noticing that

$$C_{A\dot{B}}(t) = \frac{d}{dt} C_{AB}(t) \tag{144}$$

and that the correlation $C_{AB}(t)$ is invariant for time reversal

$$C_{AB}(t) = C_{AB}^{*}(-t) \tag{145}$$

and then

$$C_{A\dot{B}}(t) = -C_{A\dot{B}}(-t). \tag{146}$$

We can then write our final result

$$\langle \delta A(t) \rangle_f = -\beta \int_{0}^{\infty} \mathrm{d}\tau f(t - \tau) C_{A\dot{B}}(\tau). \tag{147}$$

Thus Linear Response theory shows that the change observed in a property A when the perturbation $-Bf(t)$ is switched on at time 0 can be obtained simply from equilibrium time correlation functions $\langle A(0) B^{*}(t) \rangle$ that we can calculate in the absence of the perturbation, for instance from molecular dynamics simulations of the unperturbed system. Taking the Fourier transform and comparing with eq. 132

$$\chi_{AB}(\hat{\omega}) = -\beta \int_{0}^{\infty} C_{A\dot{B}}(\tau) e^{i\hat{\omega}\tau} \mathrm{d}\tau. \tag{148}$$

The resulting expression for the susceptivity is quite simple:

$$\chi_{AB}(\hat{\omega}) = \beta C_{AB}(0) + i\hat{\omega}\beta \int_{0}^{\infty} C_{AB}(\tau) e^{i\hat{\omega}\tau} \mathrm{d}\tau, \tag{149}$$

where $C_{AB}(\tau)$ is the *correlation function* for the two properties A, B.

9. Theory of dielectric response

As an example of application of Linear Response theory we obtain equations for the dielectric response of a material [42], for an idealized case where the problem of connecting the applied external field with that felt by the molecules [43] can be ignored. Let us consider a system of N molecules with permanent dipole moments μ_i to which a uniform external electric field i.e. $\mathbf{E}(t) = \mathbf{E}_0 \exp(i\hat{\omega}t)$ is applied. The system has a total dipole moment

$$\mathrm{M} = \frac{1}{N}\sum_{i}^{N} \mu_i, \tag{150}$$

while the general perturbation hamiltonian $\mathcal{H}_1 = -B(\mathbf{\Gamma})f(t)$ becomes

$$\mathcal{H}_1 = -\mathbf{M}(\{\omega_i\}^N) \cdot \mathbf{E}(t). \tag{151}$$

Notice that molecular positions have not been included since the field is assumed to be the same at every position. The expression for the dielectric susceptivity follows from general linear response theory as:

$$\chi_{\mathbf{MM}}(\hat{\omega}) = -\frac{1}{kT_B}\int_0^\infty C_{\mathbf{M}\dot{\mathbf{M}}}(\tau)e^{i\hat{\omega}\tau}\mathrm{d}\tau \tag{152}$$

$$\chi_{\mathbf{MM}}(\hat{\omega}) = \frac{1}{kT_B}\left(\langle\mathbf{MM}\rangle + i\hat{\omega}\int_0^\infty C_{\mathbf{MM}}(\tau)e^{i\hat{\omega}\tau}\mathrm{d}\tau\right), \tag{153}$$

where $C_{\mathbf{MM}}(\tau)$ is the dipole correlation function

$$C_{\mathbf{MM}}(t) = \langle\mathbf{M}(0)\mathbf{M}(t)\rangle \tag{154}$$

and we assume $\langle\mathbf{M}(t)\rangle = 0$.
A large number of dynamic properties and transport coefficients can be formulated in a similar way in terms of equilibrium correlation functions [44, 37, 38].

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Appendix

ROTATIONAL INVARIANTS

We often need to consider invariant functions of the position and orientation of two molecules $f(\mathbf{r}_1\omega_1, \mathbf{r}_2\omega_2)$. We assume that the function should be translationally invariant

$$f(\mathbf{r}_1\omega_1, \mathbf{r}_2\omega_2) = f(\mathbf{R} + \mathbf{r}_1\omega_1, \mathbf{R} + \mathbf{r}_2\omega_2). \tag{155}$$

This implies that the most general function will be

$$f(\mathbf{r}_{12}, \omega_1, \omega_2) = f(r_{12}, \omega_r, \omega_1, \omega_2), \tag{156}$$

where $\mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_2$ is the inter-centre vector with orientation ω_r. The function should also be invariant for an arbitrary rotation of the laboratory frame. General rotationally invariant combinations can be constructed following Blum and Torruella [24] and Stone [25]. $f(r_{12}, \omega_r, \omega_1, \omega_2)$ can be expanded in a basis of products of three Wigner rotation matrices

$$D^{J_1 *}_{m_1 n_1}(\omega_{1L'}) D^{J_2 *}_{m_2 n_2}(\omega_{2L'}) D^{J}_{m0}(\omega_{rL'}), \tag{157}$$

where the last subscript is zero because only the two angle α_r, β_r are needed to specify the intermolecular vector orientation. Thus we proceed to a symmetrization of these products by performing first an arbitrary rotation $\omega_{LL'}$ from L' to L. Using the closure relation of Wigner matrices [1] the original rotation from the laboratory can be rewritten starting from an arbitrary auxiliary frame L

$$D^{J*}_{m,n}(\omega_{1L'}) = \sum_{q=-J}^{J} D^{J}_{qm}(\omega_{L'L}) D^{J*}_{q,n}(\omega_{1L}). \tag{158}$$

Summation on all possible orientations $(\omega_{LL'})$ using the integral of three Wigner rotation matrices (Gaunt formula)[1] :

$$\begin{aligned} &\int \mathrm{d}\omega_{LL'} D^{J*}_{qm}(\omega_{LL'}) D^{J_2}_{q_2 m_2}(\omega_{LL'}) D^{J_1}_{q_1 m_1}(\omega_{LL'}) \\ = \; & \frac{8\pi^2}{(2J+1)} \delta_{q_1+q_2,q} \delta_{m_1+m_2,m} C(J_1 J_2 J; q_1 q_2) C(J J' J''; m_1 m_2) \end{aligned} \tag{159}$$

gives

$$\begin{aligned} &\mathcal{R} D^{J}_{m0}(\omega_{rL}) D^{J_2 *}_{m_2,n_2}(\omega_{2L}) D^{J_1 *}_{m_1,n_1}(\omega_{1L}) \\ &= \frac{8\pi^2}{(2J+1)} C(J J' J''; m_1 m_2) \\ &\sum_{q_1,q_2} C(J_1 J_2 J; q_1 q_2) D^{J_1 *}_{q_1,n_1}(\omega_{1L}) D^{J_2 *}_{q_2,n_2}(\omega_{2L}) D^{J}_{q,0}(\omega_{rL}). \end{aligned} \tag{160}$$

The quantity on the right is a rotationally invariant combination of the three orientations and could be used to define, apart from a constant, a useful invariant basis. In particular we use the rotationally invariant functions $S^{k_1 k_2}_{J_1 J_2 J}(\omega_1, \omega_2, \omega_r)$, as defined by Stone [25], which read in our notation

$$
\begin{aligned}
&S^{k_1,k_2}_{J_1,J_2 J}(\omega_1, \omega_2, \omega_r) = \frac{(i)^{J_1-J_2-J}}{\sqrt{2J+1}} \\
&\times \sum_{m_1,m_2} C(J_1 J_2 J; -m_1 - m_2) D^{J_1 *}_{m_1,k_1}(\omega_1) D^{J_2 *}_{m_2,k_2}(\omega_2) D^{J}_{-m_1-m_2,0}(\omega_r).
\end{aligned}
\tag{161}
$$

Using this definition and the properties of Clebsch - Gordan coefficients, we find the complex conjugate of the rotational invariant as

$$
S^{k_1,k_2 *}{}_{J_1,J_2 J}(\omega_1, \omega_2, \omega_r) = (-1)^{k_1+k_2} S^{-k_1,-k_2}_{J_1,J_2 J}(\omega_1, \omega_2, \omega_r). \tag{162}
$$

The rotational invariants form an orthogonal basis of functions for the space $\{\omega_1, \omega_2, \omega_r\}$:

$$
\begin{aligned}
\int \mathrm{d}\omega_1 \mathrm{d}\omega_2 \mathrm{d}\omega_r \quad & S^{k_1 k_2 *}_{J_1,J_2,J}(\omega_1, \omega_2, \omega_r) S^{k_1' k_2'}_{J_1',J_2',J'}(\omega_1, \omega_2, \omega_r) \\
= \quad & \frac{256\pi^5 \delta_{J_1,J_1'} \delta_{J_2,J_2'} \delta_{J,J'} \delta_{k_1,k_1'} \delta_{k_2,k_2'}}{(2J_1+1)(2J_2+1)(2J+1)}
\end{aligned}
\tag{163}
$$

and can be used to expand the intermolecular potential [25, 26] or the pair correlation function[24, 15]. The expansion of an arbitrary function will be

$$
f(r_{12}, \omega_1, \omega_2, \omega_r) = \sum_{\substack{J_1,J_2,J \\ k_1,k_2}} f^{J_1,J_2 J}_{k_1,k_2}(r_{12}) S^{k_1,k_2}_{J_1,J_2 J}(\omega_1, \omega_2, \omega_r). \tag{164}
$$

Since the expansion is valid in an arbitrary frame, we can in particular adopt the intermolecular frame, with z axis along the inter-centre axis and $\omega_r = (000)$. Thus $D^{J *}_{-m_1-m_2,0}(\omega_r) = \delta_{m_1,m_2}$

$$
\begin{aligned}
f(r_{12}, \omega_1, \omega_2, \omega_r) &= \sum_{\substack{J_1,J_2 J \\ k_1,k_2}} f^{J_1,J_2 J}_{k_1,k_2}(r_{12}) \frac{(i)^{J_1-J_2-J}}{\sqrt{2J+1}} \\
&\times \sum_{m_1} C(J_1 J_2 J; -m_1 - m_1) D^{J_1 *}_{m_1,k_1}(\omega_1) D^{J_2 *}_{m_1,k_2}(\omega_2) \\
&\equiv \sum_{\substack{J_1,J_2,J \\ k_1,k_2,m_1}} f^{J_1,J_2,J}_{k_1,k_2,m_1}(r_{12}) D^{J_1 *}_{m_1,k_1}(\omega_1) D^{J_2 *}_{m_1,k_2}(\omega_2).
\end{aligned}
\tag{165}
$$

Thus we can switch from a space fixed to a molecule fixed expansion writing the expansion coefficients of one representation in terms of those of the other:

$$f^{J_1,J_2J}_{k_1,k_2}(r_{12}) = \sum_{m_1} \frac{(i)^{J_1-J_2-J}}{\sqrt{2J+1}} C(J_1J_2J;-m_1-m_1) f^{J_1,J_2}_{k_1,k_2,m_1}(r_{12}). \tag{166}$$

For uniaxial molecules we only need the subset

$$\begin{aligned} S^{J_1,J_2,J}(\omega_1,\omega_2,\omega_r) \equiv & \quad S^{00}_{J_1,J_2,J}(\omega_1,\omega_2,\omega_r) \\ = & \quad \frac{i^{J_2-J_1-J}}{(2J+1)^{1/2}} \sum_{m_1,m_2} (-)^{m_1+m_2} C(J_1,J_2,J;m_1,m_2) \\ \times & \quad D^{J_1\,*}_{m_1,0}(\omega_1) D^{J_2\,*}_{m_2,0}(\omega_2) D^{J\,*}_{-m_1-m_2,0}(\omega_r). \end{aligned} \tag{167}$$

The first few rotational invariants for uniaxial molecules are, in cartesian terms, and using the unit vectors $\hat{\mathbf{u}}_1$, $\hat{\mathbf{u}}_2$ along the z axis of the two molecules [25]

$$S^{000} = 1 \tag{168}$$

$$S^{110} = -\frac{1}{\sqrt{3}} \hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2 \tag{169}$$

$$S^{101} = -\frac{1}{\sqrt{3}} \hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12} \tag{170}$$

$$S^{011} = +\frac{1}{\sqrt{3}} \hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12} \tag{171}$$

$$S^{112} = \frac{1}{\sqrt{30}} \left[\hat{\mathbf{u}}_1 \cdot \mathbf{z}_2 - 3(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})\right] \tag{172}$$

$$S^{121} = \frac{1}{\sqrt{30}} \left[(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12}) - 3(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})\right] \tag{173}$$

$$S^{211} = -\frac{1}{\sqrt{30}} \left[(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12}) - 3(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})\right] \tag{174}$$

$$S^{220} = \frac{1}{2\sqrt{5}} [3(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)^2 - 1] \tag{175}$$

$$S^{202} = \frac{1}{2\sqrt{5}} [3(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})^2 - 1] \tag{176}$$

$$S^{022} = \frac{1}{2\sqrt{5}} [3(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})^2 - 1] \tag{177}$$

$$\begin{aligned} S^{222} = & \frac{1}{\sqrt{70}} [2 - 3(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)^2 - 3(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})^2 - 3(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})^2 \\ & +9(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})] \end{aligned} \tag{178}$$

$$\begin{aligned} S^{224} &= \frac{1}{4\sqrt{70}}[1 + 2(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)^2 - 5(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})^2 \\ &\quad -5(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})^2 - 20(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12}) \\ &\quad +35(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})^2(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})^2] \qquad (179) \\ S^{242} &= \frac{1}{4\sqrt{70}}[1 - 5(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)^2 + 2(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})^2 - 5(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})^2 \\ &\quad -20(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12}) + 35(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)^2(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}}_{12})^2]. \qquad (180) \end{aligned}$$

Higher invariants can be generated e.g. using the coupling formula of two rotational invariants, obtained from the coupling formulae for Wigner rotation matrices [26].

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