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Flow birefringence at the sol-gel transition

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Résumé. — On discute les informations que pourrait fournir une expérience de biréfringence d'écoulement à la transition sol-gel en phase sol. Deux effets sont en compétition, la rotation des amas et la déformation élastique des amas. En régime stationnaire ce sont les effets de rotation qui dominent. A faible gradient de vitesse S on prévoit un angle d'extinction χ tel que $\pi/4 - \chi$ diverge avec un exposant de l'ordre de 3,4 c'est-à-dire un effet très important. Au voisinage de la transition, la biréfringence Δn a la même divergence que la viscosité macroscopique.

Abstract. — The information provided by a flow birefringence experiment at the sol-gel transition in the sol phase is discussed. There are two competing effects : cluster rotations, and cluster elastic deformation. In a steady state, rotational effects turn out to be dominant. For small velocity gradients S we predict an extinction angle χ such that $\pi/4 - \chi$ diverges with an exponent roughly equal to 3.4 i.e. a very strong effect. In the vicinity of the transition, the birefringence Δn has the same divergence as the macroscopic viscosity.

1. **Introduction.** — The singularities of various mechanical properties at the sol-gel transition are now quite well understood in the vicinity of the transition. In the sol phase, the macroscopic viscosity $\bar{\eta}$ diverges : $\bar{\eta} \sim \varepsilon^{-s}$ (where ε measures the distance to the critical threshold). The critical exponent s is experimentally of order 0.7 to 1 [1, 2]. On the other hand, in the gel phase the elastic modulus scales like $\bar{E} \sim \varepsilon^t$. In certain radical polymerization experiments the exponent t has been measured $t \approx 1.9$ [3], in a polycondensation t has been shown to be approximately 3 [4]. On the theoretical side it may be possible to relate the gel elasticity problem to the conductivity of random resistor networks [5] and the viscosity to the conductivity of superconducting grains [2].

Here, we discuss another kind of experiment which seems to provide useful information : the dielectric tensor anisotropy $D_{\alpha\beta}$ induced by a velocity gradient $S_{\alpha\beta}$. In a simple shear flow $v_x = Sy$ one essentially measures the extinction angle χ and the difference Δn between the ordinary and extraordinary indices. For small shears these two quantities are related to the dielectric tensor $D_{\alpha\beta}$ by

$$\frac{\pi}{4} - \chi \simeq \frac{D_{yy} - D_{xx}}{D_{xy}} \Delta n = D_{xy}. \quad (1)$$

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In a macromolecular solution such as the sol phase, there are two different contributions to the birefringence :

- a local contribution proportional to the polarizability anisotropy of the individual monomer $\alpha_{\parallel} - \alpha_{\perp}$,
- a shape contribution which exists even for isotropic monomers due to double scattering in the anisotropic macromolecules and thus proportional to the square of the monomer polarizability α^2

$$(\alpha = \frac{2}{3} \alpha_{\parallel} + \frac{1}{3} \alpha_{\perp}).$$

For linear flexible chains the shape contribution is usually negligible and the local contribution is always dominant.

There is however an important difference between a dilute linear solution and a sol just below the gelation point. In a dilute linear solution the characteristic relaxation times of the first mode of deformation of the individual chains and of the rotation of a chain on itself turn out to be nearly identical and one does not have to distinguish between the two effects. In our sol phase these two times are actually different; one has to study separately the influence of the rotation and of the chain deformation on the local contribution to the flow birefringence.

In order to have a better understanding of the relative importance of these two effects, we study in

the next section the flow birefringence induced by a simple shear on a solution of quenched or frozen Gaussian chains where only rotation effects are present. We can then generalize the result to a dilute solution of frozen randomly branched trees which we consider as closer to the gelation clusters. In section 3, we use these results to make reasonable conjectures for the flow birefringence at the sol-gel transition. In conclusion we qualitatively discuss the cross-over of these properties of the sol phase to the one of the gel phase where the presence of an infinite cluster prevents any rotation.

2. Flow birefringence for a solution of frozen chains.

— 2.1 FROZEN OR QUENCHED CHAINS. — We consider a linear chain of N monomers. A monomer i is represented by a bead \mathbf{b}_i . The angles between consecutive vectors \mathbf{b}_i and \mathbf{b}_{i+1} are fixed but random (Fig. 1).

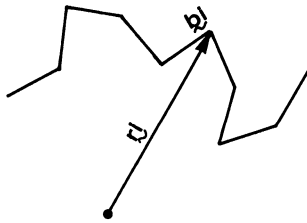


Fig. 1. — Frozen chains.

The only allowed motions for the chain is an overall translation and a rotation around its centre of mass. Such a rotation can be characterized by the 3 Euler angles : the precession ψ , the polar angle θ and the azimuthal angle ϕ (Fig. 2).

After a rotation $R(\psi, \theta, \phi)$ each bead of the chain is characterized by a vector \mathbf{a}_i so that $\mathbf{a}_i = R(\psi\theta\phi) \mathbf{b}_i$ or denoting by Greek subscripts the cartesian coordinates in a fixed frame (ijk)

$$a_i^\alpha = R_\beta^\alpha b_i^\beta. \tag{1}$$

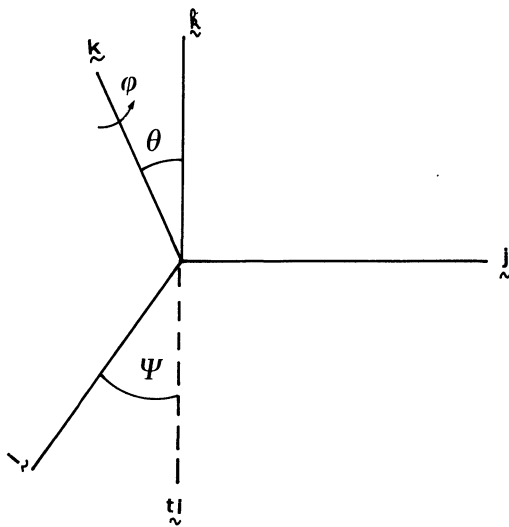


Fig. 2. — Euler angles.

Such frozen chains might be physically realizable. One can for instance imagine linear chains with big side groups; in certain conditions, at least at short times these side groups could quench the configuration of the chain [6].

2.2 EQUATIONS OF MOTION OF THE CHAIN IN A ROUSE APPROXIMATION. — We now consider the motion of our frozen chain in a simple shear flow $\mathbf{v}(r) = (Sy, 0, 0)$. The centre of mass of the chain is assumed to be at the origin, the position of monomer i is given by a vector \mathbf{r}_i . The force on monomer i is, neglecting all the hydrodynamic interactions

$$\mathbf{f}_i = \zeta \left(\mathbf{v}(\mathbf{r}_i) - \frac{d\mathbf{r}_i}{dt} \right). \tag{2}$$

In a steady state the total torque on the chain vanishes

$$\sum_i \mathbf{r}_i \times \left(\mathbf{v}(\mathbf{r}_i) - \frac{d\mathbf{r}_i}{dt} \right) = 0. \tag{3}$$

We just consider here over all rotations $R(\psi, \theta, \phi)$ of the chain. Each of these rotations is associated to a rotation vector $\boldsymbol{\omega}$

$$\left(\boldsymbol{\omega} = \frac{d\psi}{dt} \mathbf{k} + \frac{d\theta}{dt} \mathbf{u} + \frac{d\phi}{dt} \mathbf{K} \right)$$

such that for every monomer

$$\frac{d\mathbf{r}_i}{dt} = \boldsymbol{\omega} \times \mathbf{r}_i. \tag{4}$$

Introducing (4) in (3) one gets an implicit relation giving $\boldsymbol{\omega}$ as a function of ψ, θ and ϕ :

$$(R_G^2 - Q) \boldsymbol{\omega} = \mathbf{A}. \tag{5}$$

For simplicity we have introduced here the radius of gyration

$$R_G^2 = \frac{1}{N^2} \sum_i r_i^2$$

the quadrupolar tensor Q ,

$$Q_{\alpha\beta} = \frac{1}{N} \sum_i r_i^\alpha r_i^\beta$$

and a vector

$$\mathbf{A} = (0, Q_{yz}, -Q_{yy}).$$

In the following, we are interested only in small velocity gradients S and chains very close to a spherical shape (the other configuration will have a negligible weight when averaging over the angles between consecutive beads). In a first approximation we can then replace $(R_G^2 - Q)$ by its average value for an ideal gaussian chain. This tensor becomes diagonal and equal to $\frac{2}{3} R_G^2$ leading to

$$\boldsymbol{\omega} = \left(0, \frac{3}{2} \frac{Q_{yz}}{R_G^2}, \frac{3}{2} \frac{Q_{yy}}{R_G^2} \right). \tag{6}$$

In this formula Q_{yz} and Q_{yy} are functions of the Euler angles.

The next step amounts to writing a continuity equation for the probability $f(\psi, \theta, \phi)$ that the chain has rotated of (ψ, θ, ϕ) . For a small time interval dt we can call $d\chi$ the vector ωdt . The probability current associated with the rotation is $\omega \cdot f$. There is also a diffusion current given by $(D_{rot} L f)$ where we call L the operator $d/d\chi$. The continuity equation in a steady state reads then :

$$L(\omega f + D_{rot} L f) = 0. \tag{7}$$

The first term is the convection term driven by the velocity gradient. The second term is a diffusion term ; in a first approximation we can use for D_{rot} the average rotational diffusion constant of an ideal chain.

For zero velocity gradient S the probability f_0 is constant, we show in appendix B that up to first order in S , $\delta f = f - f_0$ is given by

$$\delta f = - \frac{3 f_0 S}{4 D_{rot} \langle R_G^2 \rangle} Q_{xy}. \tag{8}$$

One can express Q_{xy} as a function of the vectors \mathbf{a}_i

$$Q_{xy} = \frac{1}{2 N^2} \sum_{ij} (x_i - x_j)(y_i - y_j) = \frac{1}{2 N^2} \sum_{ij} \sum_{\substack{k \in [ij] \\ l \in [ij]}} a_k^x a_l^y. \tag{9}$$

2.3 FLOW BIREFRINGENCE FOR A DILUTE SOLUTION OF FROZEN CHAIN. — Up to first order in the velocity gradient, the dielectric tensor D is given by

$$D_{\alpha\beta} = \frac{c}{N} (\alpha_{\parallel} - \alpha_{\perp}) \left\langle \sum \frac{a_m^{\alpha} a_m^{\beta}}{a^2} - \frac{1}{3} \delta_{\alpha\beta} \right\rangle. \tag{10}$$

α_{\parallel} and α_{\perp} are respectively the polarizability of the monomers parallel and perpendicular to their symmetry axis.

The averaging denoted by the brackets consists first in an averaging over the Euler angles and then in an averaging over all the frozen configurations of the chain i.e. over all the orientations of the vectors \mathbf{b}_i .

Inserting the value (8) of δf we get

$$D_{\alpha\beta} = \frac{c}{N a^2} (\alpha_{\parallel} - \alpha_{\perp}) \frac{3 S}{4 D_{rot} R_G^2} \frac{1}{2 N^2} \times \sum_{ij} \sum_{\substack{k \in [ij] \\ l \in [ij]}} \langle a_k^x a_l^y (a_m^{\alpha} a_m^{\beta} - \frac{1}{3} \delta_{\alpha\beta}) \rangle_0. \tag{11}$$

The 0 subscript means that the averaging over the angles has to be done with the zeroth order distribution function f_0 which means that the Euler angles ψ, θ, ϕ are now randomly distributed.

For random distribution of the Euler angles and of the frozen vectors \mathbf{b}_i the orientation of the vectors \mathbf{a}_i is also random and thus :

$$\langle a_k^x a_l^y a_m^{\alpha} a_m^{\beta} \rangle_0 = \frac{1}{9} \delta_{\alpha x} \delta_{\beta y} \delta_{mk} \delta_{ml}.$$

The only non vanishing components of the dielectric tensor is then D_{xy}

$$D_{xy} = - \frac{c}{N} (\alpha_{\parallel} - \alpha_{\perp}) \frac{S}{12 D_{rot}}. \tag{12}$$

The most interesting feature is that apart from numerical constants the flow birefringence for a dilute solution of frozen linear chains behaves exactly the same way as the flow birefringence of a dilute solution of ideal flexible chains [7]. This result was not *a priori* obvious : for instance the N dependence of the dielectric tensor of a rod like macromolecule is not correctly given by (12), (17-18).

In the frame work of a mean field theory of branching (Zimm, Stockmayer) and in the Rouse limit one can also calculate the flow birefringence for a dilute solution of *frozen randomly branched* polymers. The calculation is exactly similar to that of linear chains and the flow birefringence is also given by equation (12). (The diffusion constant D_{rot} being of course different for a linear and a branched macromolecule of same molecular weights.) The reason is that both for linear and branched molecules the relative orientation of different beads is completely random. Of course the summation over the different monomers in equation (11) is different but in both cases it gives the mean square radius of gyration leading to identical results.

3. Flow birefringence at the sol-gel transition. —

We now come back to a sol phase close to the sol-gel transition. We assume that in the vicinity of the gel point the sol phase is well described by a percolation model [9]. We focus on a given cluster of p monomers. This cluster has two characteristic relaxation times.

- i) A time $T_{rot}^{(p)}$ characteristic of the rotation of the cluster.
- ii) The first relaxation time of the deformation modes of the cluster $T_{el}^{(p)}$.

Any individual cluster looks roughly like an ellipsoid and its characteristic rotation time is given by a Zimm formula.

$$T_{rot}(p) = \frac{6 \pi \eta_p}{kT} r_p^3 \tag{13}$$

r_p is the longest axis of the cluster and η_p is the viscosity « seen by the cluster » i.e. the viscosity for a perturbation of size r_p . The structure of this viscosity has been studied by De Gennes [2] with 3 basic assumptions.

- 1) For clusters of very small size the effective viscosity η_1 is equal to the solvent viscosity η_0 .
- 2) For large clusters of size ξ (the correlation length) the viscosity becomes equal to the macroscopic viscosity $\bar{\eta}$.
- 3) The viscosity is written as a scaling law

$$\eta_p = \eta_0 f\left(\frac{r_p}{\xi}\right).$$

One is then lead to $\eta_p = \bar{\eta}(r_p/\xi)^{s/\nu}$,

$\xi = a\varepsilon^{-\nu}$ being the correlation length .

The first deformation relaxation time is given by a Maxwell-type relationship

$$T_{el} = \frac{\eta_{(p)}}{E_p}. \quad (14)$$

E_p being the elastic modulus of a cluster of size p which can be derived by scaling arguments

$$E_p \simeq \bar{E} \left(\frac{\xi}{r_p} \right)^{t/\nu} \quad (15)$$

insuring that E_p is ε independent in the critical region. \bar{E} being the elastic modulus of the gel phase at the same distance of the gel point.

A comparison between the two times for the larger clusters ($r = \xi$) gives

$$\frac{T_{rot}}{T_{el}} = \frac{\bar{E}\xi^3}{kT} \simeq \varepsilon^{-3\nu+t}. \quad (16)$$

We shall assume in what follows that $3\nu > t$ (this agrees with certain data [3, 5] but not all). With this assumption, equation (16) shows that rotations are slower; the individual clusters behave as *stiff objects* and the flow birefringence is actually dominated by rotational effects.

The local contribution of the flow birefringence might then be calculated by assuming for the dielectric tensor a structure similar to that of quenched linear chains.

$$\Delta n = (\alpha_{\parallel} - \alpha_{\perp}) \sum n_p ST_{rot}(p) \quad (17)$$

n_p is the density of clusters of p monomers and of size r_p [9] (it plays the role of c/N in equation (12)). This quantity is normalized so that the total monomeric density is c i.e.

$$\sum pn_p = c.$$

This leads to

$$\Delta n \sim c(\alpha_{\parallel} - \alpha_{\perp})(S\tau_0) \varepsilon^{-s}. \quad (18)$$

$\tau_0 = \eta_0 a^3/kT$ being a microscopic rotation time. The slope of the local birefringence as a function of velocity gradient thus diverges with an exponent approximately equal to 0.8 to 1.

In order to determine the extinction angle χ one would have to calculate the dielectric tensor of a dilute solution of frozen chain up to second order, it would give a scaling law for D_{xx} or D_{yy}

$$D_{xx} \sim \frac{c}{N} (\alpha_{\parallel} - \alpha_{\perp}) \left(\frac{S}{D_{rot}} \right)^2.$$

With the same conjectures as for η the extinction angle given by (1) is

$$\frac{\pi}{4} - \chi = \frac{\sum n_p [ST_{rot}(p)]^2}{\sum n_p ST_{rot}(p)} \sim ST_{rot}(\xi) \sim (S\tau_0) \varepsilon^{-s-3\nu}. \quad (19)$$

The divergence here is very strong (with an exponent equal to 3.4-3.6) and experimentally one should be able to measure such a big effect.

One now has to look at the shape birefringence [10]. On the average the clusters of p monomers have a spherical shape but if we look at a given cluster of the solution, it looks rather like an ellipsoid of long axis r_p and excentricity $e \sim 1$ (we make here a conjecture of self similarity of the clusters and assume thus an excentricity independent of the polymerization index p).

For a dilute solution of ellipsoids of concentration C/N and long axis R , each of them containing N diffusive centres of polarizability α , we show in the appendix that the shape birefringence is

$$\Delta n \sim C\alpha^2 \frac{N}{R^3} (ST_{rot}) e^2 \quad (20)$$

e being the excentricity and T_{rot} the rotation time of the ellipsoid.

Assuming such a law for the gelation clusters and summing over all the cluster sizes would lead to a divergence $\Delta n \sim C \frac{\alpha^2}{a^3} \varepsilon^{-s+3\nu-2/\sigma} \sim \varepsilon^{-3.3}$ σ being a

critical exponent characteristic of the molecular weight of clusters of size ξ [9] ($\sigma = 0.4$ in 3 dimensions). However, this double diffusion process is much dependent on concentration. At very low concentrations the second diffusion is done by a monomer of the same cluster and the birefringence is correctly given by (20). When the concentration increases, the second diffusion can be done by a monomer of another cluster, the distribution of these other clusters around a given cluster will compensate somehow the anisotropy of the cluster and the shape birefringence is much smaller than that given by (20). In the limit of a melt (no solvent) the concentration is uniform all over the sample and this shape effect disappears. At the sol-gel transition, the solution is just at its overlapp concentration and the shape birefringence has to be strongly reduced⁽¹⁾.

4. Discussion. — When the polymer system is concentrated, we expect the rotational part of the local birefringence to be the dominant

$$\eta \sim \varepsilon^{-s} S$$

$$\frac{\pi}{4} - \chi \sim \varepsilon^{-s-3\nu} S.$$

⁽¹⁾ As pointed out by a referee this conjecture should be true only in the vicinity of the gel point. Above the gel point the excentricity of very large cluster should be zero.

If the birefringence Δn shows a rather small divergence ($s \approx 0.8$) the divergence of $\frac{\pi}{4} - \chi$ is very strong ($s + 3\nu \approx 3.4$) and one should be able to see it experimentally.

It is interesting to compare the value of the birefringence Δn to the shear stress $\sigma_{xy} = \bar{\eta}S$. We predict a ratio σ_{xy}/D_{xy} independent of ϵ . This ratio often called stress optical coefficient (S.O.C.) is well known to be both molecular mass and velocity gradient independent for solutions of linear chains in a very large velocity gradient domain and even in concentrated solutions. Our stress optical theorem is here more restricted, it is true only in the limit of small velocity gradients ($S \rightarrow 0$). This means however that in this regime the dominant contribution to the stress is due to rotations and not to the elastic properties of the clusters. De Gennes has proposed a parallel between the viscosity of a sol phase at the sol-gel transition and the conductivity of percolating superconducting grains. For this percolation problem dissipation occurs mainly in the normal fluid which would correspond here to the rotational effect we are talking about.

It is also interesting to discuss the cross-over properties between the sol and the gel phases. In the gel phase we expect any measure to be sensitive to the properties of the infinite cluster which does not have any rotational effects. Considering now experiments in an oscillatory velocity gradient of pulsation ω . In the sol phase we distinguish three regimes in a (ω, ϵ) plane (Fig. 3).

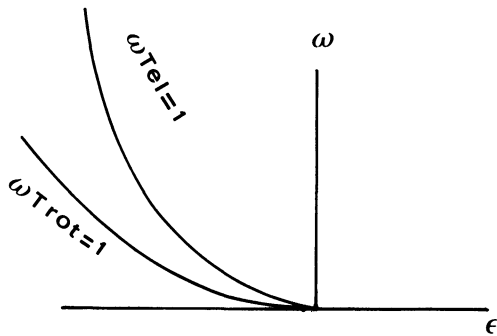


Fig. 3. — Cross-over from the gel phase properties to the sol phase properties.

For small ω , $\omega T_{rot} < 1$ the oscillatory effects are not important and we expect the static results to hold.

For intermediate pulsations $\omega T_{rot} > 1$, $\omega T_{el} < 1$ we expect the elastic effects to be dominant with small rotation contributions coming from the small clusters (clusters of size p so that $\omega T_{rot}(p) < 1$). The mechanical properties of the gel phase are expected to be determined by the mechanical properties of the infinite cluster.

For large ω we expect the birefringence to behave as a decaying power of ω the only contributing clusters

being those clusters for which $\omega T_{el}(p) < 1$ leading to a birefringence

$$\Delta n = (\alpha_{||} - \alpha_{\perp}) \sum_{\omega T_{el}(p) < 1} n_p [ST_{el}(p)] = c(\alpha_{||} - \alpha_{\perp}) \omega^{\left[\frac{3\nu}{s+\nu} - 1\right]}$$

According to a conjecture by Straley $t + s = 3\nu$ [12]. This would lead to a birefringence independent both on ω and ϵ .

Acknowledgments. — I acknowledge interesting discussions with P. G. de Gennes, T. Witten and the «Groupe d'hydrodynamique Physique» in Ecole Supérieure de Physique et Chimie (Paris) especially with A. Ambari.

Appendix A

Quenched chain in two-dimensional flow birefringence (cf. [16]). — Before going to the rather complicated problem of three-dimensional quenched chain it might be more pedagogical to study the flow birefringence of a two-dimensional frozen chain in a simple shear flow $v_x = Sy$. The overall rotation of the chain is characterized by a single angle α and the configuration of the frozen chain by the set of angles ψ_i that each frozen vector \mathbf{b}_i makes with the x axis. After a rotation of angle α the vectors \mathbf{a}_i make thus an angle $\alpha + \psi_i$ with the x axis.

The rotation vector $\omega = \partial\alpha/\partial t$ can be calculated as in equation (6), we find

$$\frac{\partial\alpha}{\partial t} = -S \frac{Q_{yy}}{\langle R_G^2 \rangle} \tag{A.1}$$

The continuity equation (7) is very simple in two dimensions

$$\frac{d}{d\alpha} \left(D_{rot} \frac{df}{d\alpha} + \frac{\partial\alpha}{\partial t} f \right) = 0 \tag{A.2}$$

At zeroth order in S , f is a constant f_0 .

Up to first order $\delta f = f - f_0$ is such that

$$\frac{d\delta f}{d\alpha} = + \frac{Sf_0}{D_{rot}} \left[\frac{Q_{yy}}{\langle R_G^2 \rangle} + \text{constant} \right] \tag{A.3}$$

δf has to be a periodic function of the angle α . The integration constant has to be chosen equal to

$$- \frac{Sf_0 a^2}{2 D_{rot}} \sum_{k \in \{i, j\}} \cos(\psi_k - \psi_{k'})$$

$$Q_{yy} = \frac{1}{2 N^2} \sum_{ji} \sum_{kk'} \sin(\alpha + \psi_k) \sin(\alpha + \psi_{k'}) a^2$$

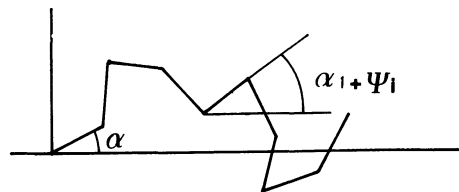


Fig. 4. — Frozen chain in 2 dimensions.

$$\frac{df}{d\alpha} = \frac{Sf_0 a^2}{2 D_{\text{rot}}} \frac{1}{N^2 \langle R_G^2 \rangle} \left\{ \sum_{ij} \sum_{kk'} \sin(\alpha + \psi_k) \sin(\alpha + \psi_{k'}) - \cos(\psi_k - \psi_{k'}) \right\}. \quad (\text{A.4})$$

The only non vanishing term of the dielectric tensor is then

$$D_{xy} = \frac{C}{Na^2} (\alpha_{\parallel} - \alpha_{\perp}) \sum_I a_I^y a_I^x = \frac{C}{N} (\alpha_{\parallel} - \alpha_{\perp}) \sum_I \frac{1}{2} \sin 2(\alpha + \psi_I).$$

In order to take the average we just have to weight each configuration by δf sum over α and average over all the ψ values

$$D_{xy} = \int f(\alpha) \frac{C}{2Na} \left[\sum_I \sin 2(\alpha + \psi_I) \right] d\alpha \quad (\text{A.5})$$

integrating by parts :

$$D_{xy} = \int \frac{-\partial \delta f}{\partial \alpha} \frac{C}{4N} \left[\sum_I \cos 2(\alpha - \psi_I) \right] d\alpha.$$

Summation over α then averaging over the ψ_i gives

$$D_{xy} = -\frac{C}{16N} (\alpha_{\parallel} - \alpha_{\perp}) \frac{S}{D_{\text{rot}}}. \quad (\text{A.6})$$

This has the same structure as the three-dimensional result proposed in equation (12).

Appendix B

Solution of the continuity equation (7). — 1) OPERATOR \mathbf{L} . — The components of the operator L can be expressed as functions of ψ, θ and ϕ

$$\begin{aligned} L_x &= \cos \psi \frac{\partial}{\partial \psi} - \frac{\sin \psi}{\text{tg } \theta} \frac{\partial}{\partial \psi} + \frac{\sin \psi}{\sin \theta} \frac{\partial}{\partial \phi} \\ L_y &= \sin \psi \frac{\partial}{\partial \theta} + \frac{\cos \psi}{\text{tg } \theta} \frac{\partial}{\partial \psi} - \frac{\cos \psi}{\sin \theta} \frac{\partial}{\partial \phi} \\ L_z &= \frac{\partial}{\partial \psi}. \end{aligned} \quad (\text{B.1})$$

The operator $\mathbf{J} = \mathbf{L}/i$ verifies the usual commutation rules for the kinetic momentum operator in quantum mechanics.

$$[J_\alpha, J_\beta] = \varepsilon_{\alpha\beta\gamma} J_\gamma,$$

$\varepsilon_{\alpha\beta\gamma}$ is the completely antisymmetric tensor. The operators J^2 commute with

$$J_z = \frac{1}{i} \frac{\partial}{\partial \psi} \quad \text{and} \quad J_z = \frac{1}{i} \frac{\partial}{\partial \phi}$$

the eigenvalues of which are integral numbers.

One can then find a set of eigenfunctions of the three

operators J^2, J_z and J_z with the respective eigenvalues $l(l+1), m$ and $p \mid l, m, p \rangle l$ being an integer such that $m < l, p < l$ (Cohen-Tannoudji, Chapter 9).

For $m = 0$ one can check directly that

$$\mid l, 0, p \rangle = Y_{lp}(\theta, \phi),$$

Y_{lp} being a spherical harmonic. The other eigenfunctions can be got by successive action of $J = J_x \pm iJ_y$.

2) ACTION OF \mathbf{L} ON $Q_{\alpha\beta}$. — We first study the action of a component L_y of \mathbf{L} on an element of the rotation matrix $R_\beta^\alpha(\psi, \theta, \phi)$. For a small variation $\partial\psi, \partial\theta, \partial\phi$ of the angles :

$$R_\beta^\alpha(\psi + \partial\psi, \theta + \partial\theta, \phi + \partial\phi) = \delta R_\beta^\alpha \times R_\beta^\alpha(\psi, \theta, \phi)$$

δR is a small rotation and can thus be written as a cross product

$$\delta R_\beta^\alpha = \delta_{\alpha\delta} + \varepsilon_{\alpha\gamma\delta} (\delta\chi)^\gamma,$$

$\delta\chi$ being the rotation vector $\delta\chi = \boldsymbol{\omega} dt$ we thus get :

$$R_\beta^\alpha(\psi + \delta\chi, \theta + \delta\theta, \phi + \delta\phi) = R_\beta^\alpha(\psi, \theta, \phi) + \varepsilon_{\alpha\gamma\delta} \delta\chi^\gamma R_\beta^\delta.$$

Which means that

$$L^\gamma R_\beta^\alpha = \varepsilon_{\alpha\gamma\delta} R_\beta^\delta. \quad (\text{B.2})$$

Using (1) and (9) one is lead to

$$L^\gamma Q_{\alpha\beta} = \varepsilon_{\gamma\alpha\alpha'} Q_{\alpha'\beta} + \varepsilon_{\gamma\beta\beta'} Q_{\alpha\beta'}. \quad (\text{B.3})$$

3) SOLUTION OF EQUATION (7). — Application of (B.3) gives

$$\mathbf{L}\boldsymbol{\omega} = \frac{-9 Q_{xy}}{2 \langle R_G^2 \rangle}. \quad (\text{B.4})$$

One can then check that Q_{xy} is an eigenfunction of L^2 for $l = 2$ leading to

$$\delta f = \frac{-3}{4} \frac{Sf_0}{D_{\text{rot}} \langle R_G^2 \rangle} Q_{xy}. \quad (\text{B.5})$$

Appendix C

Shape birefringence for a dilute solution of ellipsoids.

— We generalize here a problem studied in Landau and Lifshitz, *Electrodynamique des milieux continus*, p. 69.

For a dielectric ellipsoid in an electric field E_{ext} due to external charges, the field inside the ellipsoid E_{int} is

$$\mathbf{E}_{\text{int}} = \frac{\mathbf{E}_{\text{ext}}}{1 + \left(\frac{\varepsilon}{\varepsilon_0} - 1 \right) n} \quad (\text{C.1})$$

ε being the dielectric constant and n the demagnetizing tensor of the ellipsoid.

For p ellipsoids one can calculate the average value of the electric excitation

$$\langle \mathbf{D} \rangle = \varepsilon \langle \mathbf{E} \rangle + \frac{1}{V} \int (\mathbf{D} - \varepsilon_0 \mathbf{E}_{\text{ext}}) dv. \quad (\text{C.2})$$

V being the volume of the sample.

In all the medium outside the ellipsoids $\mathbf{D} = \varepsilon_0 \mathbf{E}$ and there is no contribution to the integral. Inserting (C.1) in the integral (C.2)

$$\varepsilon_{ij} = \varepsilon_0 + \frac{\varepsilon - \varepsilon_0}{1 + \left(\frac{\varepsilon}{\varepsilon_0} - 1\right) n_{ij}} \Phi \quad (\text{C.3})$$

Φ being the volume fraction occupied by the ellipsoids.

For revolution ellipsoids

$$n_{ij} = \frac{n_1 + 2n_2}{3} + (n_1 - n_2) \left(u_i u_j - \frac{1}{3} \delta_{ij} \right),$$

n_1 and n_2 being the principal demagnetizing factors and \mathbf{u} a unitary vector in the direction of the long axis.

For small $\left(\frac{\varepsilon}{\varepsilon_0} - 1\right)$, the off diagonal part of ε_{ij} is

$$\delta\varepsilon_{ij} = \Phi \frac{(\varepsilon - \varepsilon_0)^2}{\varepsilon} (n_1 - n_2) \left(u_i u_j - \frac{1}{3} \delta_{ij} \right). \quad (\text{C.4})$$

Averaging over the orientation of \mathbf{u} brings in a factor ST_{rot} [15] for $\delta\varepsilon_{xy}$. If every ellipsoid contains N diffusive centres of polarizability α , the radius of gyration of an ellipsoid being R , we obtain

$$\delta\varepsilon_{xy} \sim C \frac{N}{R^3} \alpha^2 ST_{\text{rot}}(n_2 - n_1) \quad (\text{C.5})$$

where C is the concentration of diffusive centres.

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