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► **To cite this version:**

S. Patlazhan, Patrick Navard. A Light Scattering Theory for Filled Diluted Polymer Solution under Flow. Journal de Physique II, 1995, 5 (7), pp.1017-1033. 10.1051/jp2:1995227 . jpa-00248208

HAL Id: jpa-00248208

<https://hal.science/jpa-00248208>

Submitted on 4 Feb 2008

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Classification
Physics Abstracts
61.25Hq — 82.70-y

A Light Scattering Theory for Filled Diluted Polymer Solution under Flow

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(Received 23 November 1993, revised 17 March 1995, accepted 27 March 1995)

Résumé. — La diffusion de lumière par des solutions de polymères flexibles chargées de particules sphériques est étudiée grâce à l'approximation théorique de Rayleigh-Gans-Debye. L'idée de base du travail est que les perturbations des lignes de courant et des taux d'écoulement dues à la présence des particules vont changer la conformation locale des chaînes, entraînant une diffusion de la lumière. Traitant ces perturbations comme des fluctuations de viscosité, le rapport de Rayleigh est calculé en tenant compte de la fonction de corrélation des fluctuations de viscosité pour les quatre orientations principales des polariseurs, HH, VV, HV et VH, et pour des écoulements de cisaillement et d'élongation. Les clichés de diffusion de lumière sont calculés en considérant une distribution aléatoire de particules.

Abstract. — Light scattering by dilute flexible polymer solutions filled with spherical particles is studied theoretically within the framework of the Rayleigh-Gans-Debye approximation. The basic idea of our work is that the perturbation of stream lines and flow rates due to the presence of the particles will change the local conformation of the chains, thus inducing a light scattering contribution. This is treated by considering viscosity fluctuations. The Rayleigh ratio is derived as a function of the viscosity fluctuation correlation function for the four major polarization configurations (HH, VV, HV and VH) in shear and elongational flow. Considering a random distribution of the particles, the small angle light scattering patterns are calculated

1. Introduction

Small-angle light scattering is a powerful method for analysing the structure of polymer liquids submitted to a flow (flow SALS). Several new shear-induced structural phenomena were found by the method in various polymer systems (semi-dilute solutions of worm-like macromolecules [1–3], lyotropic liquid crystalline polymers [4, 5] and polymer blends [6]). The scattered light forms patterns with complex dependence of the intensity on the azimuthal angle in

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all of these cases. These optical phenomena result from spatial modulations of density and/or orientational fluctuations of polymer during the flow. These structural changes are associated with different physical reasons. A theoretical analysis for semi-dilute polymer solutions under shear flow [7–9] showed that it may be accounted for by the coupling between the concentration fluctuations and polymer elastic stress. In the case of sheared liquid crystalline polymer solutions, the flow light scattering may be caused by the resulting domain structure [10].

A common feature of most of the flowing polymer systems with complex structure is the heterogeneity of the medium viscosity. Fluctuations of the viscosity will disturb stream lines and induce specific orientation effects in the polymer. This can generate an additional contribution to the light scattering. To take this specific effect into account, we will study the flow SALS from polymer suspensions composed of a diluted polymer solution filled with rigid spherical particles. In contrast to the above mentioned systems, the heterogeneity of viscosity in the latter case is induced solely by the presence of the particles. Since the viscosities of the polymer solution and the particles are different, local perturbations of the velocity gradient in the polymer liquid is generated. As a consequence, polymer chains in different points will experience different levels of stretching. This in turn will result in a heterogeneous distribution of polarizability which can give a specific scattering. The objective of this paper is to study this effect for a diluted polymer solution filled with undeformable spherical particles submitted to shear or elongational flows.

In Section 2 of the paper, a general representation of the Rayleigh ratio and reference coordinate system are given. In Section 3, the equations for local polarizability of the suspension are discussed in the framework of the Zimm and Rouse models of polymer dynamics for shear and elongational flows. The fluctuation of the velocity gradient tensor are considered in Section 4 of the paper. In Section 5, the expressions for the flow light scattering from the polymer suspension are derived. In Section 6, the results of the theory are applied to the analysis of the flow SALS patterns for shear and elongational flows for different positions of polarizer and analyzer.

2. Basic Relationships

For the sake of simplicity, the refractive index of the suspension at rest will be considered as homogeneous. If needed, the effect of light scattering due to a difference between the refractive indices of particles and solution can be taken into account independently. It is also assumed that the polymer chains are monodisperse and comprise N segments, that the particles are spherical and do not deform during the flow. This restricts the approach to rigid particles, either solid particles or mixture with highly viscous minor phase and a large interfacial tension between the two phases. The Rayleigh ratio of the polarised light scattering from the suspensions can be written in the framework of the Rayleigh-Gans-Debye approximation as follows [11]:

$$R = \frac{I r^2}{I_0 V} = k^4 c^2 P(q) F_{\mathbf{q}} \{ \langle \alpha'_{ik} \alpha'_{mn} \rangle \} O_i O_m t_k t_n \quad (1)$$

Here I is the far field light scattering intensity from a scattering volume V which contains a large number of particles, I_0 is the intensity of the incident light, c is the particle concentration, $P(q) = \chi^2(q)$, where $\chi(q)$ is the form factor of the particle. For monodisperse particles with a radius a , $\chi(q)$ is [12]:

$$\chi(q) = \frac{4\pi}{q^3} (\sin aq - aq \cos aq) \quad (2)$$

The value $F_{\mathbf{q}}\{\langle \alpha'_{ik} \alpha'_{m'n} \rangle\}$ is the Fourier transform of the correlation function $\langle \alpha'_{ik} \alpha'_{m'n} \rangle$ of polarizability fluctuations in the space of the scattering vector $\mathbf{q} = q\mathbf{s} = \mathbf{k}_0 - \mathbf{k}$ and \mathbf{k}_0 are the wave vectors of incident and scattered light; $k = |\mathbf{k}_0| = |\mathbf{k}| = \frac{2\pi}{\lambda}$, where λ is the average wavelength in the medium. The value of vector \mathbf{q} is equal to $q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$, where θ is the polar scattering angle. The unit vector \mathbf{t} gives the polarization direction of the incident wave. The unit vector \mathbf{O} is perpendicular to the vector \mathbf{k} and lies in a plane containing the transmission direction of analyzer and perpendicular to the analyzer plane [13].

To set the angular dependence of the unit vectors \mathbf{s} , \mathbf{t} and \mathbf{O} , we will use the Cartesian reference system with the x_1 -axis directed along the wave vector \mathbf{k}_0 of incident beam and the x_3 -axis parallel to the direction of the macroscopic velocity. In this reference system, the components of the unit vector \mathbf{s} are

$$s_1 = -\sin \frac{\theta}{2}, \quad s_2 = \cos \frac{\theta}{2} \sin \varphi, \quad s_3 = \cos \frac{\theta}{2} \cos \varphi \quad (3)$$

where the azimuthal angle φ is measured relatively to the x_3 -axis.

There are four relative positions of polarizer and analyser: HH, VV, HV and VH where the letters H and V denote the horizontal and vertical position of polarization directions, respectively. The first letter gives the orientation of the analyzer and the second letter the orientation of the polarizer. The vertical orientation is the one parallel to the x_3 -axis and the horizontal one is parallel to the x_2 -axis. The values of components of the vector \mathbf{t} for the vertical position of the polarizer are:

$$t_1 = 0, \quad t_2 = 0, \quad t_3 = 1 \quad (4)$$

For the horizontal position, they are:

$$t_1 = 0, \quad t_2 = 1, \quad t_3 = 0 \quad (5)$$

Components of the vector \mathbf{O} can be obtained from reference [13] as a function of analyzer transmission positions and polar θ and azimuthal φ scattering angles. It is useful to rewrite them as a function of the components of the unit vector \mathbf{s} . For the vertical position of the analyzer, it becomes:

$$O_1^v = 2s_1s_3(1 - 4s_1^2s_2^2)^{-1/2}, \quad O_2^v = 0, \quad O_3^v = (1 - 2s_1^2)(1 - 4s_1^2s_2^2)^{-1/2} \quad (6)$$

For the horizontal position of the analyzer, we have:

$$O_1^h = 2s_1s_2(1 - 4s_1^2s_3^2)^{-1/2}, \quad O_2^h = (1 - 2s_1^2)(1 - 4s_1^2s_3^2)^{-1/2}, \quad O_3^h = 0 \quad (7)$$

From equations (1-7) it follows that in order to calculate the light scattering intensity from a flowing heterogeneous medium, it is necessary to derive the dependence of polarizability fluctuations α'_{ik} on the dynamical properties of the suspension. The type of macroscopic flow must be specified at this stage.

3. Local Polarizability of Flowing Polymer Suspension

Consider a suspension composed of a diluted polymer solution and spherical rigid particles. Without any loss of generality we can consider the same concentration of polymer inside the particles as in the surrounding solution. Since we are interested in the change of the chain

polarizability under flow, this assumption will not contribute to the final result: the conformation is fixed inside the rigid spheres. At the same time, this approach provides a way of using the distribution function $\Phi(x^1, x^2, \dots, x^N; r)$ for chains located at an arbitrary point r of the suspension (x^1, x^2, \dots, x^N are the coordinates of the segments and r is the position of the chain centre of gravity).

First we consider the Zimm model for the chain dynamics. In this case the Smoluchowski equation for $\Phi = \Phi(x^1, x^2, \dots, x^N; r)$ in the steady-state local flow can be written as follows [14]:

$$\sum_{\mu=1}^N \left\{ \frac{\partial}{\partial x_i^\mu} (\kappa_{ik}(r) x_k^\mu \Phi) - D(r) \sum_{\nu=1}^N H_{\mu\nu} \left[\frac{\partial^2 \Phi}{\partial x_k^\mu \partial x_k^\nu} + \frac{3}{b^2} \sum_{\beta=1}^N A_{\nu\beta} \left(x_k^\beta \frac{\partial \Phi}{\partial x_k^\mu} + 3\Phi \delta_{\beta\mu} \right) \right] \right\} = 0 \quad (8)$$

Here summation over the repeated Latin indices from 1 to 3 is implied. $\kappa_{ik}(r)$ is the local velocity gradient tensor. The components of the matrix $H_{\mu\nu}$ of segment hydrodynamic interactions are equal to $H_{\mu\nu} = 1$ at $\mu = \nu$ and $H_{\mu\nu} = \langle b/r_{\mu\nu} \rangle_{\text{eq}}$ at $\mu \neq \nu$, where $r_{\mu\nu}$ is the distance between μ and ν segments and b is the size of one segment. The notation $\langle \dots \rangle_{\text{eq}}$ denotes the preaveraging over the non-perturbed segment distribution function. This approximation gives a reasonable accuracy of about 10% in the calculation of the polarizability and flow birefringence of diluted polymer solution [16]. A closer examination of the hydrodynamic interactions gives the same quantitative results [15]. The matrix $A_{\mu\nu}$ in equation (8) is the Rouse matrix whose components are equal to $A_{\mu\nu} = 2\delta_{\mu\nu} - \delta_{\mu-1,\nu} - \delta_{\mu+1,\nu}$. $D(r)$ is the local segment diffusion coefficient taking on different values for particles and polymer solution: $D(r) \cong 0$ inside the particles and $D(r) = D_s$ in the solvent. Using normal coordinates $\xi^1, \xi^2, \dots, \xi^N$ of the chain segments such that the matrices $H_{\mu\nu}$ and $\sum_{\sigma=1}^N H_{\mu\sigma} A_{\sigma\nu}$ are diagonal, equation (8) takes the following form:

$$\sum_{\mu=1}^N \left\{ \kappa_{ik}(r) \xi_k^\mu \frac{\partial \Phi}{\partial \xi_i^\mu} - D(r) \left[\nu_\mu \frac{\partial^2 \Phi}{\partial \xi_k^\mu \partial \xi_k^\mu} + \frac{3}{b^2} \lambda_\mu \left(\xi_k^\mu \frac{\partial \Phi}{\partial \xi_k^\mu} + 3\Phi \right) \right] \right\} = 0 \quad (9)$$

where ν_μ and λ_μ are the eigenvalues of the matrices $H_{\mu\nu}$ and $\sum_{\sigma=1}^N H_{\mu\sigma} A_{\sigma\nu}$, respectively.

The polarizability of a small region of the polymer suspension at the point r is the sum of the effective polarizability of suspension in absence of polymer α_{ik}^0 and of the polarizabilities $\alpha_{ik}^{\text{chain}}(r)$ of chains in this region (here we consider the case of equal polarizabilities of the solvent and the particles):

$$\alpha_{ik}(r) = \alpha_{ik}^0 + n_p \alpha_{ik}^{\text{chain}}(r) \quad (10)$$

where n_p is the average number of chains in the suspension per unit volume. Polarizability of the single polymer chain depends on the chain distribution function as follows [14]:

$$\alpha_{ik}^{\text{chain}}(r) = N\alpha_{\perp} + \frac{\Delta\alpha}{b^2} \sum_{\nu=1}^N \mu_\nu \Lambda_{ik}^{\nu\nu}(r) \quad (11)$$

$$\Lambda_{ik}^{\mu\nu}(r) = J \int \xi_i^\mu \xi_k^\nu \Phi(\xi^1, \xi^2, \dots, \xi^N; r) d\xi^1 \dots d\xi^N \quad (12)$$

where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, α_{\parallel} and α_{\perp} are the longitudinal and the transversal components of segment polarizabilities. J is the Jacobean of normal coordinate set and μ_{ν} is the eigenvalue of the matrix $A_{\mu\nu}$.

Since the particles and polymer solution have different viscosities, the structure of the suspension can be described in terms of viscosity random field, $\eta(r)$. It brings to the random behavior of the local diffusion coefficient, $D(r) = k_B T / (6\pi b \eta(r))$, and the velocity gradient tensor, $\kappa_{ik}(r)$ (see next Section). As is obvious from equations (9-12), this would provide in turn the dependence of segment distributions function $\Phi(\xi^1, \xi^2, \dots, \xi^N; r)$ and hence the polarizability tensor $\alpha_{ik}(r)$ on the structure of suspension in a flow mode. The fluctuation part of the polarizability is equal to the difference between the local and volume average values:

$$\alpha'_{ik}(r) = \alpha_{ik}(r) - \langle \alpha_{ik} \rangle = \frac{\Delta\alpha}{b^2} \sum_{\nu=1}^N \mu_{\nu} \tilde{\Lambda}_{ik}^{\nu\nu}(r) \tag{13}$$

where the tensor $\tilde{\Lambda}_{ik}^{\mu\nu} \Lambda_{ik}^{\mu\nu} - \langle \Lambda_{ik}^{\mu\nu} \rangle$ is the fluctuation part of the tensor $\Lambda_{ik}^{\mu\nu}$. In equation (13) we take into account the fact that the suspension under consideration is optically homogeneous in the state at rest.

In order to calculate the tensor $\tilde{\Lambda}_{ik}^{\mu\nu}$ the equation for the full tensor $\Lambda_{ik}^{\mu\nu}$ must be written. Using equations (9) and (12) we obtain:

$$t_{\nu}^{-1} \Lambda_{ik}^{\nu\nu} - \kappa_{p(i} \Lambda_{k)p}^{\nu\nu} - D \nu_{\nu} \delta_{ik} = 0 \tag{14}$$

The brackets at indices mean operation symmetrization over these indices: $\kappa_{p(i} \Lambda_{k)p}^{\nu\nu} = \frac{1}{2} (\kappa_{pi} \Lambda_{kp}^{\nu\nu} - \kappa_{pk} \Lambda_{ip}^{\nu\nu})$; $t_{\nu} = \frac{b^2}{3D\lambda_{\nu}}$ are the local relaxation times of the polymer chain which take different values in the particles and solvent.

Splitting the values κ_{ik} , $\Lambda_{ik}^{\nu\nu}$ and D into average and fluctuation parts in equation (14) and neglecting the terms which contain products of fluctuation part, we obtain after some algebra two equations for $\langle \Lambda_{ik}^{\nu\nu} \rangle$ and $\tilde{\Lambda}_{ik}^{\nu\nu}$:

$$\tau_{\nu}^{-1} \langle \Lambda_{ik}^{\nu\nu} \rangle - \langle \kappa_{p(i} \rangle \langle \Lambda_{k)p}^{\nu\nu} \rangle - \langle D \rangle \nu_{\nu} \delta_{ik} = 0 \tag{15}$$

$$\tau_{\nu}^{-1} \Lambda_{ik}^{\nu\nu} - \langle \kappa_{p(i} \rangle \tilde{\Lambda}_{k)p}^{\nu\nu} - \kappa'_{p(i} \langle \Lambda_{k)p}^{\nu\nu} \rangle + \frac{D'}{\langle D \rangle} (\langle \Lambda_{ik}^{\nu\nu} \rangle \tau_{\nu}^{-1} - \langle D \rangle \nu_{\nu} \delta_{ik}) = 0 \tag{16}$$

where $\kappa'_{ik} = \kappa_{ik} - \langle \kappa_{ik} \rangle$ and $D' = D - \langle D \rangle$ are the fluctuation parts of the velocity gradient tensor and diffusion coefficient respectively, $\tau_{\nu} = \langle t_{\nu}^{-1} \rangle^{-1} = \frac{b^2}{3 \langle D \rangle \lambda_{\nu}}$ are the average relaxation times of the chains in the suspension. In our case, $\langle D \rangle = (1 - c) D_s$ hence $\tau_{\nu} = \frac{1}{1 - c} \tau_{\nu}^Z$, where $\tau_{\nu}^Z = \frac{b^2}{3 D_s \lambda_{\nu}}$ are the Zimm relaxation times of the chain in the solvent. (The eigenvalue problem was discussed in Ref. [14]).

For the Rouse model of polymer chain the hydrodynamic interaction between the segments is ignored and the matrix $H_{\mu\nu} = \delta_{\mu\nu}$ in equation (8). This means that the eigenvalues of the matrix $H_{\mu\nu}$ are $\nu_{\nu} = 1$ in this case. Consequently we have $\lambda_{\nu} = \mu_{\nu}$, where μ_{ν} are the eigenvalues of the matrix $A_{\mu\nu}$. It follows that equations (15) and (16) hold the same form for the Rouse model and for the Zimm model except that the relaxation times must be changed to

$\tau_{\nu} = \frac{1}{1 - c} \tau_{\nu}^R$, where $\tau_{\nu}^R = \frac{b^2}{3 D_s \mu_{\nu}}$ are the Rouse relaxation times of the chains in the solvent.

Equations (15) and (16) will now be solved for two different types of macroscopic flows, shear and elongation, in the following two paragraphs.

3.1. SHEAR FLOW. — There are two main orientations of the velocity gradient relative to the direction of incident light which can be obtained by modern rheo-optical equipment: (i) velocity gradient parallel to the wave vector \mathbf{k}_0 of incident beam and directed along x_1 -axis (this type of arrangement will be called shear 1) and (ii) velocity gradient orthogonal to the wave vector \mathbf{k}_0 and directed along x_2 -axis (this type of arrangement will be called shear 2).

Let us first consider the case of shear 1. In this situation, the non-zero component of the average velocity vector is equal to $\langle v_3 \rangle = \kappa x_1$. The corresponding value of the macroscopic velocity gradient is $\langle \kappa_{ik} \rangle = \frac{\partial \langle v_i \rangle}{\partial x_k} = \kappa \delta_{i3} \delta_{k1}$. Substituting it into equations (15) and (16), we obtain:

$$\tau_\nu^{-1} \langle \Lambda_{ik}^{\nu\nu} \rangle - \kappa \delta_{1(i} \langle \Lambda_{k)3}^{\nu\nu} \rangle - \langle D \rangle \nu_\nu \delta_{ik} = 0 \quad (17)$$

$$\tau_\nu^{-1} \tilde{\Lambda}_{ik}^{\nu\nu} - \kappa \delta_{1(i} \tilde{\Lambda}_{k)3}^{\nu\nu} - \kappa'_{p(i} \langle \Lambda_{k)p}^{\nu\nu} \rangle + \frac{D'}{\langle D \rangle} (\langle \Lambda_{ik}^{\nu\nu} \rangle \tau_\nu^{-1} - \langle D \rangle \nu_\nu \delta_{ik}) = 0 \quad (18)$$

The solution of equation (17) for the tensor $\langle \Lambda_{ik}^{\nu\nu} \rangle$ can be written as follows:

$$\langle \Lambda_{ik}^{\nu\nu} \rangle = \nu_\nu \langle D \rangle \tau_\nu (\delta_{ik} + \kappa \tau_\nu \delta_{1(i} \delta_{k)3}) \quad (19)$$

Substituting equation (19) into equation (18) we can rewrite equation (18) in matrix form:

$$\Delta_{ikmn}^\nu \tilde{\Lambda}_{ik}^{\nu\nu} = \tilde{\Gamma}_{ik}^\nu \quad (20)$$

where

$$\Delta_{ikmn}^\nu = \tau_\nu^{-1} I_{ikmn} - \kappa \delta_{1(i} I_{k)3mn} \quad (21)$$

and

$$\tilde{\Gamma}_{ik}^\nu = \nu_\nu \langle D \rangle \tau_\nu \left[\varepsilon'_{ik} + \kappa \left(\tau_\nu \kappa'_{1(i} \delta_{k)3} - \frac{D'}{\langle D \rangle} \delta_{1(i} \delta_{k)3} \right) \right] \quad (22)$$

where $\varepsilon'_{ik} = \kappa'_{(ik)}$ is the fluctuation part of the rate strain tensor and $I_{ikmn} = \delta_{i(m} \delta_{n)k}$ is a fourth rank unit tensor.

We shall consider the small shear rate limit for which the condition $\kappa \tau_\nu \ll 1$ takes place. In this case the solution of equation (20) can be found by reversing the matrix Δ_{ikmn}^ν and conserving only the terms which are proportional to the first order of production of the velocity gradient and relaxation time:

$$\tilde{\Lambda}_{ik}^{\nu\nu} = (\Delta^{-1})_{ikmn}^\nu \tilde{\Gamma}_{ik}^\nu \cong \nu_\nu \langle D \rangle \tau_\nu^2 \left[\varepsilon'_{ik} - \frac{D'}{\langle D \rangle} \delta_{1(i} \delta_{k)3} \right] \quad (23)$$

Using the relation $D = k_B T / (6\pi b \eta)$, we can rewrite the ratio $D' / \langle D \rangle$ in terms of viscosity: $D' / \langle D \rangle = -\eta' / \langle \eta \rangle$ which is valid since we are dealing with a small concentration of particles. After substituting this solution into equation (13) and taking into account equation (22), the fluctuation of suspension polarizability at the point r can be found:

$$\alpha'_{ik}(r) = \frac{1}{3} n_p \Delta \alpha \tau \left[\varepsilon'_{ik}(r) + \kappa \frac{\eta'(r)}{\langle \eta \rangle} \delta_{1(i} \delta_{k)3} \right] \quad (24)$$

Here $\tau = \sum_{\nu=1}^N \tau_{\nu}$. The derivation of the equation (24) required the known relation between the eigenvalues: $\nu_{\nu} \mu_{\nu} = \lambda_{\nu}$ [14].

For the shear 2, the velocity gradient is directed along the x_2 -axis and average velocity is $\langle v_3 \rangle = \kappa x_2$. In this case it is easy to show that the fluctuation part of the polarizability can be written as:

$$\alpha'_{ik}(r) = \frac{1}{3} n_p \Delta \alpha \tau \left[\epsilon'_{ik}(r) + \kappa \frac{\eta'(r)}{\langle \eta \rangle} \delta_{2(i} \delta_{k)3} \right] \tag{25}$$

This expression differs from equation (24) only by changing index 1 into index 2.

3.2. ELONGATIONAL FLOW. — In this case the components of the average velocity vector are equal to $\langle v_i \rangle = \kappa_{(i)} x_i$. For an incompressible fluid, the macroscopic velocity gradient tensor is then equal to $\langle \kappa_{ik} \rangle = \kappa_{(i)} \delta_{ik}$ where $\kappa_1 = \kappa_2 = -\frac{\kappa}{2}$ and $\kappa_3 = \kappa$ (there is no summation over the repeated Latin indices if one of them is inside brackets). Substituting this expression for the velocity gradient tensor into equations (15) and (16) and taking into account the inequality $\kappa \tau_{\nu} \ll 1$, we find the following solutions for the tensors $\langle \Lambda_{ik}^{\nu\nu} \rangle$ and $\tilde{\Lambda}_{ik}^{\nu\nu}$:

$$\langle \Lambda_{ik}^{\nu\nu} \rangle = \Lambda_{(i)}^{\nu} \delta_{ik}, \Lambda_i^{\nu} = \frac{\langle D \rangle \nu_{\nu}}{\tau_{\nu} - 1 - \kappa_i} \tag{26}$$

$$\tilde{\Lambda}_{ik}^{\nu\nu} = \nu_{\nu} \langle D \rangle \tau_{\nu}^2 \left[\epsilon'_{ik} + \frac{\eta'}{\langle \eta \rangle} \kappa_{(i)} \delta_{ik} \right] \tag{27}$$

The expression of the tensor of polarizability fluctuation in an elongational flow is obtained after inserting equation (27) into equation (13):

$$\alpha'_{ik}(r) = \frac{1}{3} n_p \Delta \alpha \tau \left[\epsilon'_{ik}(r) + \frac{\eta'(r)}{\langle \eta \rangle} \kappa_{(i)} \delta_{ik} \right] \tag{28}$$

From the above analysis and equations (24), (25) and (28), it appears that for all considered modes of flow the polarizability fluctuations are linear functions of the strain rate and viscosity fluctuations for both the Zimm and Rouse models of polymer chains.

4. Hydrodynamic Fluctuations in a Diluted Polymer Suspension. Low Reynolds Number Limit

Here we shall derive the dependence of the velocity gradient fluctuations in the suspension upon the fluctuations of the viscosity for shear and elongational flows in a low Reynolds number limit. In this case, the Navier-Stokes equation of incompressible heterogeneous liquid at steady-state flow can be written as follows:

$$\eta v_{i,kk} + \eta_{,k} (v_{i,k} + v_{k,i}) - p_{,i} = 0 \tag{29}$$

Here p is a pressure which depends on the boundary conditions. Splitting the values v_i , η and p into average and fluctuation parts we obtain the hydrodynamic equation for the velocity fluctuation:

$$v'_{i,kk} = \frac{1}{\langle \eta \rangle} (p'_{,i} - 2\eta'_{,k} \langle \epsilon_{ik} \rangle) \tag{30}$$

In general the solution of equation (30) may be written with the help of a Green function $G(r)$ of the equation $G_{,kk} = -\delta(r)$ where $\delta(r)$ is a delta-function. We get:

$$v'_i = -\frac{1}{\langle \eta \rangle} G * (p'_{,i} - 2\eta'_{,k} < \varepsilon_{ik} >) \quad (31)$$

where the asterisk denotes the integral convolution. Using the incompressibility condition ($v'_{i,i} = 0$) to exclude the pressure p' and making differentiation of v'_i over the x_k in equation (31) we obtain the expression for the fluctuation part of the velocity gradient tensor:

$$\kappa'_{ik} = \frac{2}{\langle \eta \rangle} (\delta_{ip} G_{,kq} * \eta' + G_{,ik} * G_{,pq} * \eta') < \varepsilon_{pq} > \quad (32)$$

It is necessary to note that the second derivation of the Green function is the homogeneous generalised function of the (-3) degree. It has a singularity at the origin of coordinates which can be regularised as follows [17]:

$$G_{,ik}(r) = g_{ik}\delta(r) + G^f_{,ik}(r) \quad (33)$$

where $G^f_{,ik}(r)$ is the formal second derivation of the Green function (out of singular point). In the case of spherical shape of the particle the tensor $g_{ik} = \int G_{,i} dS_k = \frac{1}{3}\delta_{ik}$ [18].

It can be easily checked that the value of the velocity gradient inside the sphere is controlled by the first term in the right-hand side of equation (33), whereas κ'_{ik} outside the particle is determined by the second term. Substituting equation (33) into equation (32) we obtain

$$\kappa'_{ik} = \frac{2}{\langle \eta \rangle} \left[\frac{1}{3}\delta_{ip}\delta_{kq}\eta' + (\delta_{ip}G^f_{,kq} + G^f_{,ik} * G^f_{,pq}) * \eta' \right] < \varepsilon_{pq} > \quad (34)$$

Here we used up the incompressibility condition. Further on we have to know the Fourier transform of the tensor κ'_{ik} . For arbitrary value of $< \varepsilon_{ik} >$, it is equal to

$$F_{\mathbf{q}}\{\kappa'_{ik}\} = \frac{2}{\langle \eta \rangle} \left[\frac{1}{3}\delta_{ip}\delta_{kq} - \delta_{ip}s_k s_q + s_i s_k s_p s_q \right] < \varepsilon_{pq} > F_{\mathbf{q}}\{\eta'\} \quad (35)$$

where $F_{\mathbf{q}}\{\eta'\}$ is the Fourier image of the viscosity fluctuation. In the particular case of *shear 1* the velocity gradient tensor of the suspension is $< \kappa_{ik} > = \kappa\delta_{i3}\delta_{k1}$. Hence the average strain rate tensor is equal to $< \varepsilon_{ik} > = \kappa\delta_{1(i}\delta_{k)3}$. Substituting this $< \varepsilon_{ik} >$ into equation (35) we obtain:

$$F_{\mathbf{q}}\{\kappa'_{ik}\} = \frac{2\kappa}{\langle \eta \rangle} \left[\frac{1}{3}\delta_{i(1}\delta_{3)k} - \delta_{i(1}s_3)s_k + s_i s_k s_1 s_3 \right] F_{\mathbf{q}}\{\eta'\} \quad (36)$$

In the case of *shear 2* the average strain rate tensor is equal to $< \varepsilon_{ik} > = \kappa\delta_{2(i}\delta_{k)3}$. Substituting it into equation (35) we obtain:

$$F_{\mathbf{q}}\{\kappa'_{ik}\} = \frac{2\kappa}{\langle \eta \rangle} \left[\frac{1}{3}\delta_{i(2}\delta_{3)k} - \delta_{i(2}s_3)s_k + s_i s_k s_2 s_3 \right] F_{\mathbf{q}}\{\eta'\} \quad (37)$$

For the *elongation flow* we have $< \varepsilon_{ik} > = \kappa_{(i}\delta_{k)}$. The Fourier image for the fluctuation of the gradient tensor in the case is equal to

$$F_{\mathbf{q}}\{\kappa'_{ik}\} = \frac{2}{\langle \eta \rangle} \left[\frac{1}{3}\kappa_{(i}\delta_{k)} - \kappa_{(i}s_i s_k + \kappa_{(p)}s_i s_k s_p^2 \right] F_{\mathbf{q}}\{\eta'\} \quad (38)$$

Hence the Fourier transformation of the velocity gradient fluctuations are proportional to the Fourier image of the viscosity fluctuations in all the cases discussed.

5. General Expressions for Light Scattering by Diluted Polymer Suspension at Shear and Elongational Flow

To derive the reduced light scattering intensity according to equation (1), the relationship between the Fourier transforms of the correlation function of the polarizability fluctuations and of the viscosity fluctuations must be found. Using equations (24), (25), (28), (36-38) we can see that the tensor of the polarizability fluctuations can be written in the following general form:

$$F_{\mathbf{q}}\{\alpha'_{ik}\} = \frac{1}{3 \langle \eta \rangle} \Delta \alpha n_p B_{ik} F_{\mathbf{q}}\{\eta'\} \quad (39)$$

where the tensor B_{ik} depends on the types of macroscopic flow. Equations (1) and (39) give the general expression for the Rayleigh ratio at an arbitrary polaroid position:

$$R = \left(\frac{1}{3} \Delta \alpha n_p c k^2 \right)^2 P(q) (B_{ik} O_i t_k)^2 \overline{K}(q) \quad (40)$$

Here the value $\overline{K}(q) = \frac{1}{\langle \eta \rangle^2} F_{\mathbf{q}}\{\langle \eta' \eta' \rangle\}$ is an evaluation of the heterogeneity of viscosity and consequently is the structure function of the suspension. The dependence of light scattering intensity upon the viscosity-viscosity correlation function is the main physical result of this work. For HH, VV, HV and VH orientations of polaroids, R can be expressed as follows:

$$R_{\text{HH}} = A^2 P(q) (B_{12} O_1^h + B_{22} O_2^h)^2 \overline{K}(q) \quad (41)$$

$$R_{\text{VV}} = A^2 P(q) (B_{13} O_1^v + B_{33} O_3^v)^2 \overline{K}(q) \quad (42)$$

$$R_{\text{HV}} = A^2 P(q) (B_{13} O_1^h + B_{23} O_2^h)^2 \overline{K}(q) \quad (43)$$

$$R_{\text{VH}} = A^2 P(q) (B_{12} O_1^v + B_{23} O_3^v)^2 \overline{K}(q) \quad (44)$$

where $A^2 = \left(\frac{1}{3} \Delta \alpha n_p c k^2 \right)^2$. The expressions for the intensity of the reduced light scattering of such polymer suspensions in shear (of the two types) and in elongational flows can now be derived.

5.1. SHEAR 1. — The expression of the tensor B_{ik} in this case can be obtained by using equations (24) and (36) and taking into account the fact $\varepsilon'_{ik} = \kappa'_{(ik)}$:

$$B_{ik} = \kappa \tau \left[\frac{5}{3} \delta_{1(i} \delta_{k)3} - 2 \delta_{i(1} s_3) s_k + 2 s_i s_k s_1 s_3 \right] \quad (45)$$

By introducing the components of this tensor into equation (41)-(44) and utilizing the dependence of the vector \mathbf{O} on the component of the unit vector \mathbf{s} (see Eqs. (6) and (7)) the four Rayleigh ratios can be found:

$$R_{\text{HH}} = (A \kappa \tau)^2 P(q) \frac{s_1^2 s_2^4 s_3^2}{1 - 4 s_1^2 s_3^2} \overline{K}(q) \quad (46)$$

$$R_{\text{VV}} = \frac{1}{9} (A \kappa \tau)^2 P(q) \frac{s_1^2 s_3^2 (5 - 3 s_2^2)^2}{1 - 4 s_1^2 s_2^2} \overline{K}(q) \quad (47)$$

$$R_{\text{HV}} = \frac{1}{36} (A \kappa \tau)^2 P(q) \frac{s_1^2 s_2^2 (7 + 6 s_3^2)^2}{1 - 4 s_1^2 s_3^2} \overline{K}(q) \quad (48)$$

$$R_{\text{VH}} = \frac{1}{4}(A\kappa\tau)^2 P(q) \frac{s_1^2 s_2^2 (1 - 2s_2^2)^2}{1 - 4s_1^2 s_2^2} \overline{K}(q) \quad (49)$$

5.2. SHEAR 2. — In this case, the direction of velocity gradient is directed along x_2 -axis and the expression for B_{ik} can be obtained from equations (25) and (36):

$$B_{ik} = \kappa\tau \left[\frac{5}{3} \delta_{2(i} \delta_{k)3} - 2\delta_{i(2} s_{3)} s_{(k} + 2s_{i s_k} s_2 s_3 \right] \quad (50)$$

The Rayleigh ratios at the four positions of polarizer and analyzer are:

$$R_{\text{HH}} = (A\kappa\tau)^2 P(q) \frac{s_2^2 s_3^2 (s_3^2 - s_2^2)^2}{1 - 4s_1^2 s_3^2} \overline{K}(q) \quad (51)$$

$$R_{\text{VV}} = (A\kappa\tau)^2 P(q) \frac{s_2^2 s_3^2 (s_3^2 - s_2^2)^2}{1 - 4s_1^2 s_2^2} \overline{K}(q) \quad (52)$$

$$R_{\text{HV}} = \frac{1}{36} (A\kappa\tau)^2 P(q) \frac{(2 + 12s_2^2 s_3^2 + 6s_1^2 s_3^2 - 7s_1^2)^2}{1 - 4s_1^2 s_2^2} \overline{K}(q) \quad (53)$$

$$R_{\text{VH}} = \frac{1}{36} (A\kappa\tau)^2 P(q) \frac{(2 + 12s_2^2 s_3^2 + 6s_1^2 s_2^2 - 7s_1^2)^2}{1 - 4s_1^2 s_2^2} \overline{K}(q) \quad (54)$$

5.3. ELONGATION FLOW. — For this type of flow (along the x_3 -axis), B_{ik} , is obtained from equations (28) and (38):

$$B_{ik} = \tau \left\{ \frac{5}{3} \kappa_{(i} \delta_{ik} - s_i s_k [(\kappa_{(i} + \kappa_{(k)}) - 2\kappa_p s_p^2] \right\} \quad (55)$$

Substituting components of this tensor into equations (41-44), the following expressions of the Rayleigh ratios can be found:

$$R_{\text{HH}} = \frac{1}{36} (A\kappa\tau)^2 P(q) \frac{(18s_2^2 s_3^2 + 10s_1^2 - 5)^2}{1 - 4s_1^2 s_3^2} \overline{K}(q) \quad (56)$$

$$R_{\text{VV}} = \frac{1}{9} (A\kappa\tau)^2 P(q) \frac{(9s_2^2 s_3^2 + 10s_1^2 - 5)^2}{1 - 4s_1^2 s_2^2} \overline{K}(q) \quad (57)$$

$$R_{\text{HV}} = \frac{9}{4} (A\kappa\tau)^2 P(q) \frac{(s_2^2 s_3^2 (1 - 2s_3^2))^2}{1 - 4s_1^2 s_3^2} \overline{K}(q) \quad (58)$$

$$R_{\text{VH}} = \frac{9}{4} (A\kappa\tau)^2 P(q) \frac{(s_2^2 s_3^2 (1 - 2s_2^2))^2}{1 - 4s_1^2 s_2^2} \overline{K}(q) \quad (59)$$

It has to be stressed that the results obtained in this section are adaptable to both Zimm and Rouse models of polymer chains. The difference between them is only in different values of the relaxation times, τ . The relationships for the Rayleigh ratios are valid at arbitrary values of the scattering angle. In the next section we shall discuss their consequences for special cases of the flow SALS.

6. Numerical Predictions and Discussion

Provided that the reduced viscosity-viscosity correlation function $\overline{K}(q)$ is known, equations (45-59) give the flow SALS patterns for shear and elongational flows. The analysis of these

patterns is performed for the four classical orientations of the polarizer and analyzer, HH, VV, HV and VH.

The present theory being restricted to a random distribution of particles, the correlation function depends only on the value (not on the direction) of the scattering vector. In the simplest case of an ideal random two-phase structure which is under consideration, $\overline{K}(q)$ has the following form [19]:

$$\overline{K}(q) = \frac{\pi^2 a^3}{(1 + q^2 a^2)^2} \frac{\langle \eta'^2 \rangle}{\langle \eta \rangle^2} \quad (60)$$

where a is the size of the particles. Since the value of the scattering vector depends only on the scattering angle, the azimuthal dependence of the scattering patterns is assigned by the components of the tensor B_{ik} (see Eq. (40)).

The four sets of calculated SALS patterns (HH, VV, HV and VH) which are limited by 15° of scattering angle are given for the three types of flow conditions (shear 1, shear 2 and elongation) in Figures 1, 2, 3, and 4 in units of $(A\kappa\tau)^2$ and at $a/\lambda = 1$.

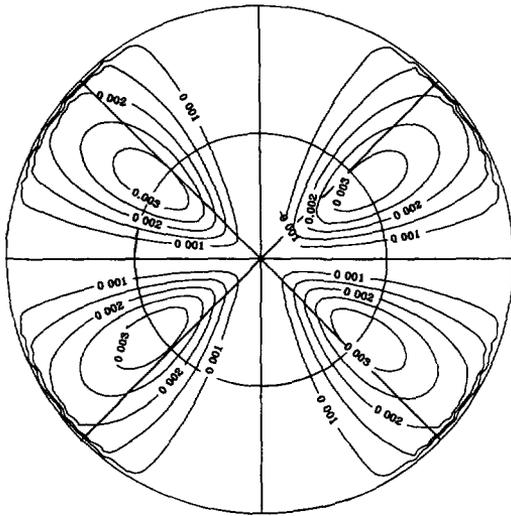
Figure 1 gives the predicted HH patterns. Let's recall that HH is defined as having the polarizer parallel to the analyzer, both perpendicular to the macroscopic flow direction. They are parallel to the vorticity axis in the case of shear 1 and to the shear gradient axis for shear 2. We can see that for shear 1 the light scattering pattern have a four-leaf structure, for shear 2 it is eight-leaf pattern with zero intensity at the azimuth angle equal to 0° and 90° and for the elongational flow the pattern has four leaves which are parallel and orthogonal to the flow direction. The last one is in qualitative agreement with known results for stretched filled polymer networks [20–22]. The HH scattering of shear 1 is also characterized by a non-monotonical dependence on the scattering angle that is in a contrast with shear 2 and elongation.

The very weak intensity in the case of shear 1 is due to the fact that the gradient is directed along the incident beam. The effect of flow field distortions due to the shear gradient on the scattering is minimised in this condition. In the case of shear 2 and elongation, the flow is mainly perturbing the shear rate distribution in a plane perpendicular to the incident beam, maximising its effect for the light scattering.

Figure 2 gives the predicted VV patterns. Again, a large difference between considered flows is found. Two leaves with no intensity at 90° azimuthal angle are found for shear 1 while shear 2 and elongation exhibit eight- and four-leaf patterns, respectively. A large difference in scattering intensity between shear 1 and the other two is also found. The reason is similar to the case of HH. For shear 2, it must be noted that HH and VV are very similar. It means that the fluctuations in this geometry have a symmetry of revolution around the beam. (Note that to have a symmetry of revolution around the incident beam is not enough to give $HH = VV$, see polymer spherulites for example). The flow field distribution around each particle has also a circular symmetry.

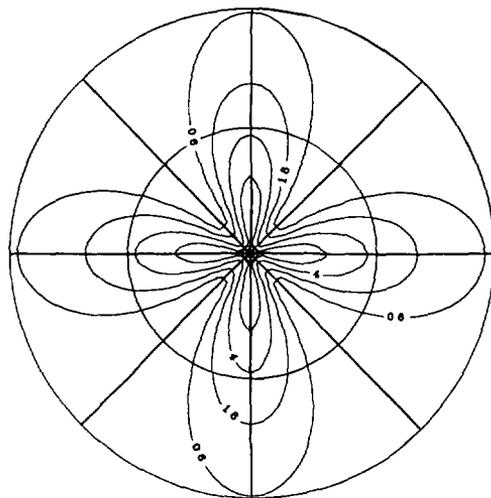
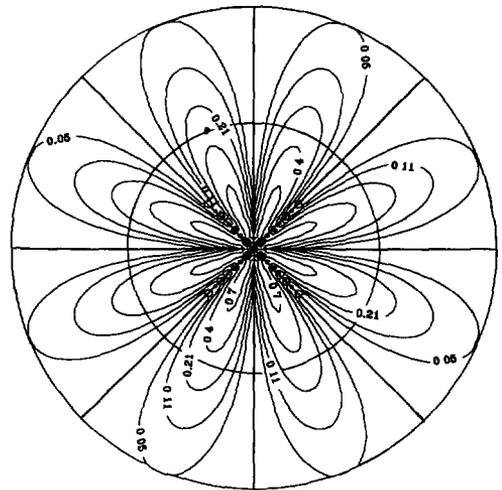
Figure 3 gives the predicted HV patterns. Shear 1 and shear 2 show different four-leaf patterns and elongation of the eight-leaf pattern. The total intensity at shear 1 is weak due to the small depolarisation of the scattering light in this configuration. As for VV and HH, there is no scattering intensity at zero-angle for shear 1. Such an eight-leaf pattern in the elongation case has been experimentally found and theoretically predicted for stretched filled elastomers [11,20–22]. To find a similar result is not surprising since hydrodynamic and elastic equilibrium equations have a very close structure.

Figure 4 gives the predicted VH patterns. There is a difference between VH and HV patterns: in the last case we obtained a six-leaf pattern with maximum intensity distribution along 90° azimuthal angle. Both patterns are exactly similar for shear 2, which correlates with the fact



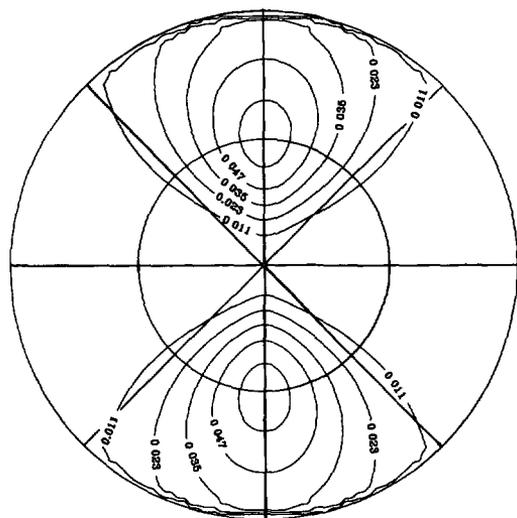
Shear 1. HH-scattering.

Shear 2. HH-scattering.

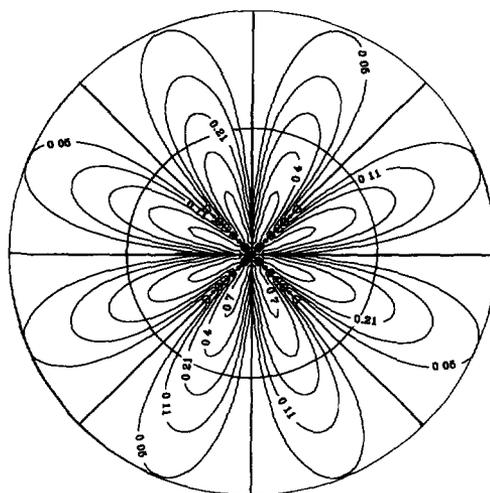


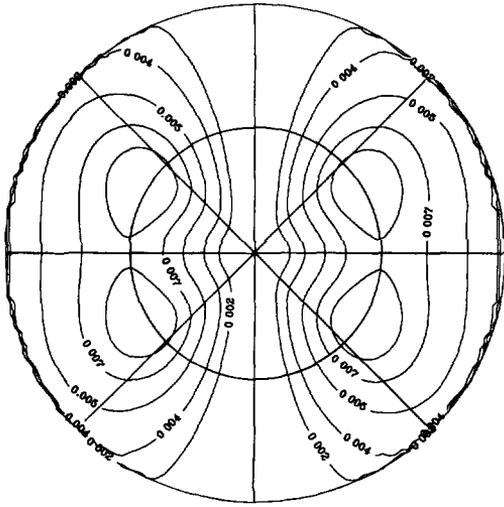
Elongation. HH-scattering.

Fig 1. — Contours of light scattering intensity from polymer suspensions at shear 1, shear 2 and elongational flow under the HH position of polarizer and analyzer.



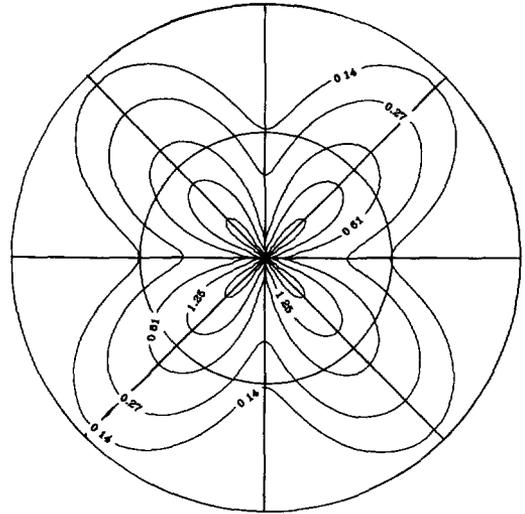
Shear 1. VV-scattering.





Shear 1. HV-scattering.

Shear 2. HV-scattering.



Elongation. HV-scattering.

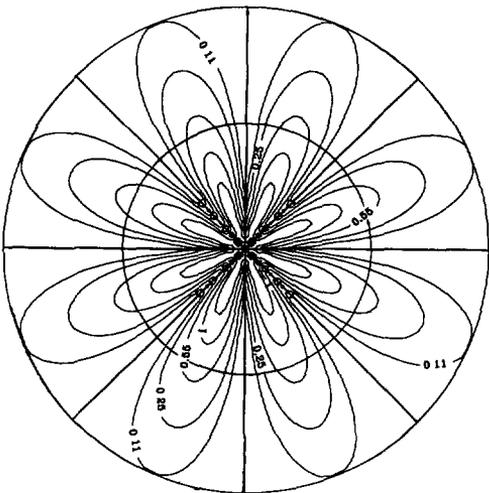


Fig. 3 — Contours of light scattering intensity from polymer suspensions at shear 1, shear 2 and elongational flow under the HV position of polarizer and analyzer.

that VV and HH are similar in this case. HV and VH patterns are also similar in the case of elongation due to reasons of symmetry.

7. Conclusion

The flow light scattering by a diluted polymer suspension is induced owing to the difference between particle and solvent viscosities. The scattering intensity is proportional to the Fourier transform of viscosity-viscosity correlation function in the case of equal refractive indices of the components at rest. This result does not depend on details of hydrodynamic interactions of chain segments. The angular behavior of flow SALS patterns depend on a flow mode and position of polarizer and analyzer.

Before extending the theory, the next step will be to compare it to experiments. In this context, the case of shear 1 is very interesting since the non-monotonical behaviour of the light intensity versus scattering angle allows a quantitative comparison to be made. Moreover, shear 1 is a simple geometry as far as rheo-optical experiments are concerned.

Acknowledgments

S.P. acknowledges the support of DRET ("Soutien à la Recherche" Program) during his stay at CEMEF.

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