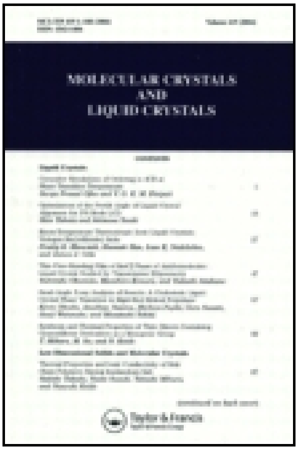

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Simulation of the Molecular Dynamics of Rod-Like Molecules in Semidiluted Solution: A Dielectric Relaxation Study

Maciej Wnęk [a] & Jozef K. Moscicki [a]
[a] Institute of Physics, Jagiellonian University, 31-059 Krakow, Reymonta, 4, Poland

Version of record first published: 22 Sep 2006.

To cite this article: Maciej Wnęk & Jozef K. Moscicki (1990): Simulation of the Molecular Dynamics of Rod-Like Molecules in Semidiluted Solution: A Dielectric Relaxation Study, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 192:1, 119-123

To link to this article: http://dx.doi.org/10.1080/00268949008035617

Mol. Cryst. Liq. Cryst. 1990, Vol. 192, pp. 119–123
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SIMULATION OF THE MOLECULAR DYNAMICS OF ROD-LIKE MOLECULES IN SEMIDILUTED SOLUTION: A DIELECTRIC RELAXATION STUDY.[1]

MACIEJ WNĘK and JOZEF K. MOSCICKI

Institute of Physics, Jagiellonian University,
31-059 Krakow, Reymonta 4, Poland.

(Submitted for publication September 14, 1989)

The dielectric relaxation of a model solution of polydisperse rods is studied numerically, using a modified Doi-Edwards model. A new model of the dielectric relaxation in the biphasic range of concentration is proposed.

INTRODUCTION.

It is characteristic of the lyotropic liquid crystalline (*lLC*) behavior of rodlike polymers that on the concentration-temperature phase diagram the low-concentration pure isotropic phase and the high-concentration pure anisotropic phase are separated by a significant transition region in which different phases coexist [1].

The rodlike character of *lLC* macromolecules is not only responsible for the phase behavior but also has a dramatic influence on their mobility in concentrated solutions. At concentrations typical for lyotropic behavior, the particles are so densely packed that any significant displacement or reorientation must result from a cooperative process involving the neighbors. These restrictions are manifested in the dramatic variation of the viscosity, and of the complex dielectric permittivity, on going from the isotropic phase through the biphasic phase to the anisotropic phase [1].

To explain these variations, we have studied numerically the zero-shear viscosity μ, and the complex dielectric permittivity $\hat{\varepsilon}$, of a model solution of polydisperse rods, over a wide range of concentration and temperature. Our model was based on the original theory of Doi [2]. Numerical results

---

[1] Supported by the Polish Academy of Sciences under project CPBP 01.12.

showed satisfactory agreement with the experimental data [3]. However, in the course of the model development, we made a number of simplifying assumptions [1], which limit the universality of the results. We decided, therefore, to reconsider these assumptions. The present paper reports on an improvement in the model for dielectric relaxation of the solution.

THEORY

The basic assumption of the Doi theory is that due to entanglement of rodlike macromolecules (≡ rods), the only unrestricted motion of a rod is translation along its length. A network of neighbors prevents both translation perpendicular to the long axis and large-angle reorientation of the long axis. The rod can escape from this trap only by translational diffusion along the long axis, or if the trap relaxes as the result of similar diffusional process in the neighborhood [2]. As a result, rotational diffusion of the rods and, in turn, the rotational relaxation time are strongly dependent on the rod concentration, the axial ratio (the length-to-diameter ratio), and on the orientational order of rods.

We have shown that $\hat{\varepsilon}$ of the isotropic and nematic phases of the solution of rods having permanent dipole moment proportional to the rod length can be written as [cf. Ref. 1, Eqs.(54) and (64)]:

$$\text{isotropic} \qquad \frac{\hat{\varepsilon}\,(f) - \varepsilon_\infty}{\varepsilon_0 \; - \varepsilon_\infty} = \frac{v_p^o}{3kT} \sum^{m} \frac{x_m P(x_m)}{1 + j2\pi f \tau_m} \,, \tag{1}$$

$$\text{nematic} \qquad \frac{\hat{\varepsilon}\,(f) - \varepsilon_\infty}{\varepsilon_0 \; - \varepsilon_\infty} = \frac{v_p^o}{3kT} \sum^{m} \frac{x_m P(x_m)\delta_m}{1 + j2\pi f \tau_m \, g_m} \,, \tag{2}$$

where ε_∞ and ε_0 are the dielectric constant of induced polarization and the static dielectric constant, v_p^o is the concentration of rods in solution, $P(x_m)$ is the rod length distribution function, and $x_m = L_m/d$ is the axial ratio (L_m is the length, all rods have the same diameter d). τ_m is the rotational relaxation time of m-type rods. Factors $\delta_m \ll 1$ and $g_m \ll 1$ reflect the presence of the nematic potential, and their dependence on the nematic order parameter S, can be found in [1]. f is a frequency of the probing electric field, T is the absolute temperature, and k is the Boltzmann constant.

For the pure isotropic or nematic material, Eqs.(1) or (2) can be used to calculate the dielectric relaxation spectrum. However, since the biphasic material is a heterogeneous mixture of both phases [1], the resultant dielectric relaxation spectrum of the biphasic sample depends heavily on the particular model of the mixture employed. In the past we have used a simplified bricklike sandwich model, based on an assumption that due to the gravity both phases separate into two well defined layers [1]. Such an assumption is justified if the biphasic solution is left to separate for a long time. When measurements are performed shortly after preparation of the solution, then the solution is most probably a suspension of one phase in the another in a form of more or less spherical droplets.

The dielectric permittivity of a lattice of identical spherical droplets of a guest phase in a host phase, has been considered by a number of authors [4]. We have applied a number of these models of the dielectric permittivity to calculate $\hat{\varepsilon}$ of the biphasic material, and full discussion of results will be given elsewhere [5]. Here we show results obtained with a simple model of Rayleigh [6], since we consider it the most representative.

Generalizing the formula of Rayleigh to the case of a cubic array of spherical droplets with dielectric constant of $\hat{\varepsilon}_g$ in a medium with dielectric constant of $\hat{\varepsilon}_h$, one obtains the effective dielectric permittivity of the suspension:

$$\hat{\varepsilon}_* = \hat{\varepsilon}_h \left[1 + \frac{3\phi_g(\hat{\varepsilon}_g - \hat{\varepsilon}_h)}{2\hat{\varepsilon}_h + \hat{\varepsilon}_g - \phi_g(\hat{\varepsilon}_g - \hat{\varepsilon}_h)} \right] , \tag{3}$$

where ϕ_g is the volume fraction of the quest phase. Note that since the Rayleigh model neglects the interaction between the dielectric moments induced in the droplets by the external electric field, it essentially should work satisfactorily only at low volume fractions of the guest phase, i.e., close to the isotropic-biphasic and biphasic-nematic transition concentrations.

RESULTS

To simulate the dielectric properties of a real solution of polydisperse rods, we assumed that the rod length distribution function is of the form of a skewed gaussian :

$$P^o(x_\alpha) = x_\alpha / x_p^o \exp\{-4 \ln 2[(x_\alpha - x_o)^2/\sigma_i^2]\} , \tag{4}$$

where the variance σ_i^2 takes different values for rods shorter ($i = 1$) and longer ($i = 2$) than x_o, in particular $\sigma_1^2 < \sigma_2^2$. A similar distribution was already employed in the past to describe properties of polyalkylisocyanates in solution [1]. Detailed calculations were performed for the distribution with $x_o = 15, \sigma_1 = 10$, and $\sigma_2 = 30$. Calculated values of the maximum of the dielctric loss factor, ε''_{max}, the dielectric increment, $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, and the frequency at the dielectic loss factor maximum, f_m, as a function of rod concentration in solution are shown in Fig. 1. For comparison, in the biphasic concentration range results are given for the new "array-of-droplets" and the old "sandwich" models of a heterogeneous mixture.

Results in Fig. 1 can be compared with experimental data for polyalkylisocyanates, *cf.* Fig. 4 in Ref.[3]. In all aspects the array-of-droplets model gives more realistic behavior of all dielectric parameters as a function of concentration; variation of the parameters in the biphasic range qualitatively closely resembles experimental results for polyhexylisocyanate, Figs. 1*a*-*c*, and copolymer of octyl and nonylisocyanates, Figs. 1*d*-*f*. In particular, this model reproduces the rapid decrease of the dielectric loss factor

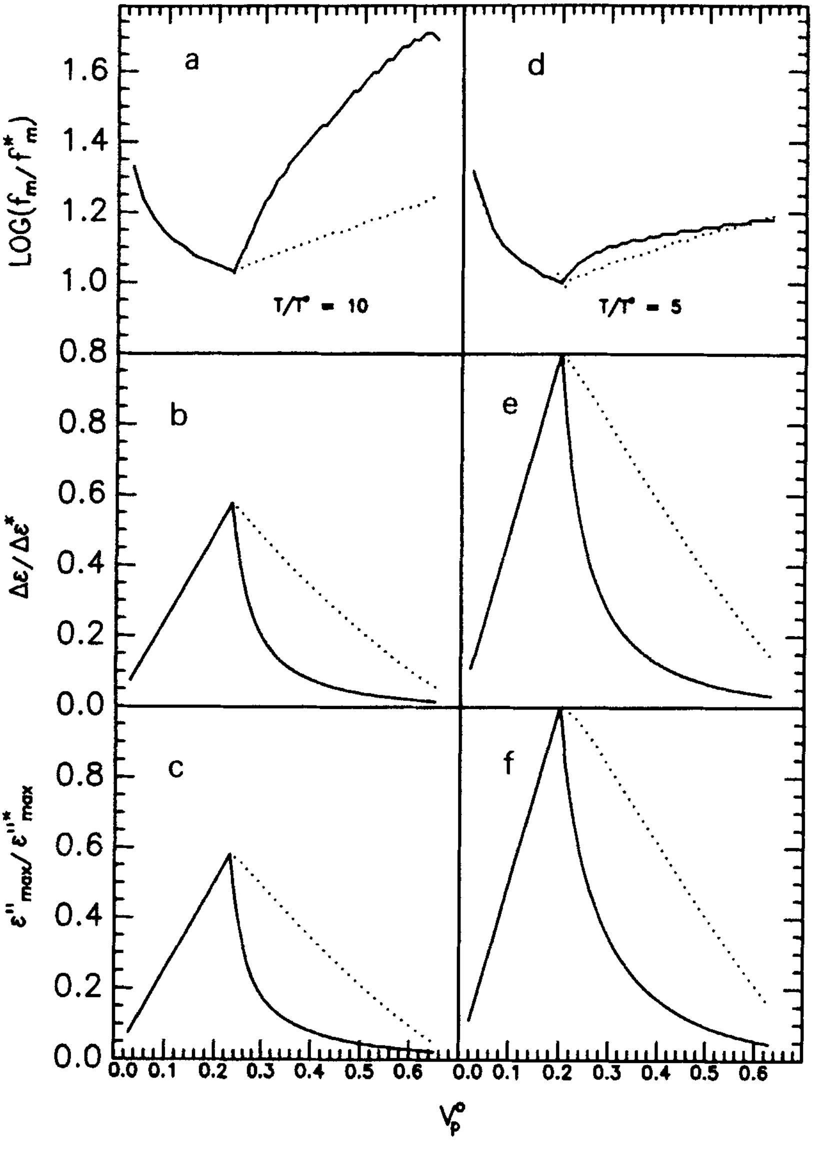

Figure 1. Simulated dielectric relaxation parameters for a concentrated solution of a polydisperse system of rods, calculated for two normalized temperatures (a), (b) and (c), $T/T^* = 10$, and (d), (e) and (f), $T/T^* = 5$ (T^* is the energy of interaction between rods in temperature units). All parameters are scaled by their values at the isotropic-biphasic transition concentration for $T/T^* = 5$.

and increment above the transition concentration, behavior not reproducable with the sandwich model. Also the concentration dependence of f_m more closely resembles that observed experimentally.

It has to be noted that results in Fig. 1 do not reproduce the deviation of ε''_{max} and $\Delta\varepsilon$ from linearity in v_p^o in the isotropic phase on approaching the transition concentration, a feature clearly visible in the experimental data. As we argued in [1], this is a result of neglecting in present calculations a "tail" of very long polymer chains in the distribution, which is probably present in polyalkylisocyanates samples. In a forthcoming publication we will account for the presence of very long chains in solution and discuss an effect of gelling of the solution on dielectric properties at high concentrations [5].

References

[1] J.K. Moscicki, *Adv.Chem.Phys.*, **63**, 631 (1985).

[2] M. Doi, *J. Physique*, **36**, 607 (1975); *J.Polym.Sci.Polym.Phys.Ed.*, **19**, 229 (1981).

[3] J.K. Moscicki, G. Williams, and S.M. Aharoni, *Macromolecules*, **15**, 642(1982).

[4] see, for example, L.K.H. van Beek, in "Progress in Dielectrics, vol VII", J.B. Birks, ed., Heywood Books, London 1967, pp. 69.

[5] M. Wnek, K. Rosciszewski, and J.K. Moscicki, to be published.

[6] J.W. Rayleigh, *Phil. Mag.*, **5-34**, 481 (1892).