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PRELIMINARY COMMUNICATIONS

Fractal-like scaling in liquid crystals

Odd–even effect of scaling exponents in the 4,4′-di-*n*-alkyloxyazoxybenzene homologous series

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A power law behaviour of dielectric loss versus frequency has been found in members of the 4,4′-di-*n*-alkyloxyazoxybenzene series. For each member the scaling of the data with respect to ν/ν_{max} is possible in the liquid-crystalline temperature range; this suggests a fractal-like geometry in nematic and smectic phases. The values of the scaling exponents, indicating a cooperativity of molecular reorientation around the short axes, exhibit an odd–even effect.

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Many representatives of soft matter exhibit a certain degree of order which being established at the molecular level hierarchically extends to the macroscopic scale. The existence of such a hierarchy stimulates the consideration of a possibility of fractal-like scaling of some physical properties. Thermotropic liquid crystals can be studied from this point of view.

It has been shown [1, 2] that one way to detect such fractal-like scaling arises from studies of dielectric relaxation phenomena, and in particular the relaxation connected with molecular reorientation around their short axes. This relaxation has to be sensitive to possible cooperativeness opened by the hierarchy of orders. The corresponding deviation from the Debye relaxation characteristic of disordered liquids may be derived from a departure of the relaxation function $\phi(t)$ from the exponential form. Now $\phi(t)$ is replaced by the two power laws with fractional exponents n and $1-m$ for short and long time intervals, respectively. Such asymptotic behaviour gives

$$\phi(t)=(2\pi\nu_{max}t)^{-n}\exp(-2\pi\nu_{max}t)\,{}_1F_1(1-m;\ 2-n;\ 2\pi\nu_{max}t), \tag{1}$$

which is the solution of the equation of motion for $\phi(t)$ proposed in the Dissado–Hill many body approach [3, 4]. The ν_{max} is the frequency of maximum dielectric loss and ${}_1F_1$ is the confluent hypergeometric function. From this we can obtain the asymptotic behaviour of the imaginary part of the electric susceptibility, i.e. of dielectric loss, $\varepsilon''(\nu)$

$$\varepsilon''(\nu)\sim(\nu/\nu_{max})^{n-1}, \qquad \text{for } \nu>\nu_{max}, \tag{2}$$

and

$$\varepsilon''(\nu)\sim(\nu/\nu_{max})^{m} \qquad \text{for } \nu<\nu_{max}. \tag{3}$$

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The scaling exponents n and $1-m$, which are fractional for various materials [3, 4], can be understood as measures of the strength of motional correlations (or degrees of order) at short and long range, respectively. The Debye relaxation process is recovered as n and $1-m$ tend to zero.

A plausible interpretation of the two crossover power laws pattern in the temporal evolution of $\phi(t)$ to equilibrium can be obtained by applying fractal models. Derivation of two different fractal regions of relaxation in a form which is the combination of equations (2) and (3) has been done analytically in a deterministic fractal circuit model [5]. All models based on a hierarchy of processes self-similar in time are also appropriate for the interpretation of the observed relaxation behaviour [6].

Previously published data [7–12] obtained in our group on the MHz electric susceptibility of aligned samples of the 4,4′-di-n-alkyloxyazoxybenzenes (denoted as kOAOB, where k is the number of carbon atoms in the alkyloxy chains) are now analysed in terms of the Dissado–Hill many body approach [3, 4]. As an example figures 1 and 2 present the relaxation observed at several temperatures for PAA (1OAOB) and 6OAOB nematic phases in compact $\log \varepsilon'' - \log \nu$ form for the scaling

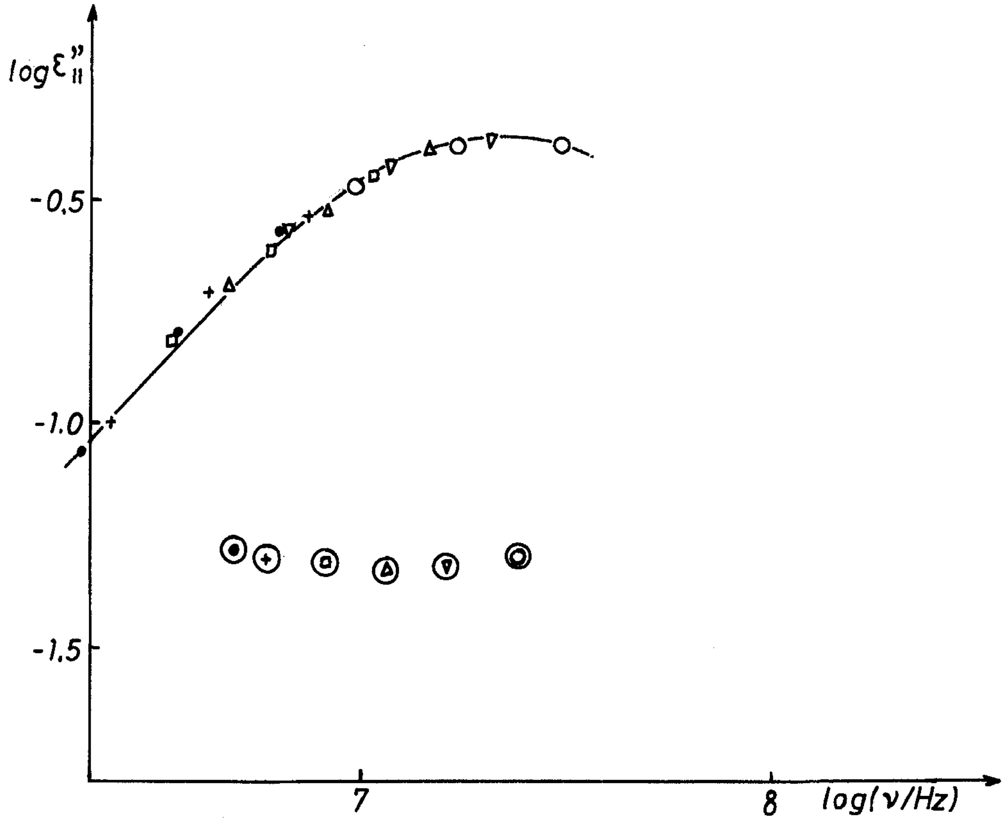

Figure 1. The master absorption curve for the nematic phase of PAA [10]. The points are in absolute scale only for the scaling temperature 389·1 K (○); (▽) 393·1 K, (△) 397·3 K, (□) 401·3 K, (+) 405·1 K and (●) 407·1 K. (The curve was obtained by appropriate shifting of $\log \varepsilon''$–$\log \nu$ curves for each temperature along both coordinates. The distance between the reference point ● and each encircled point shows the magnitude of the shift for each temperature).

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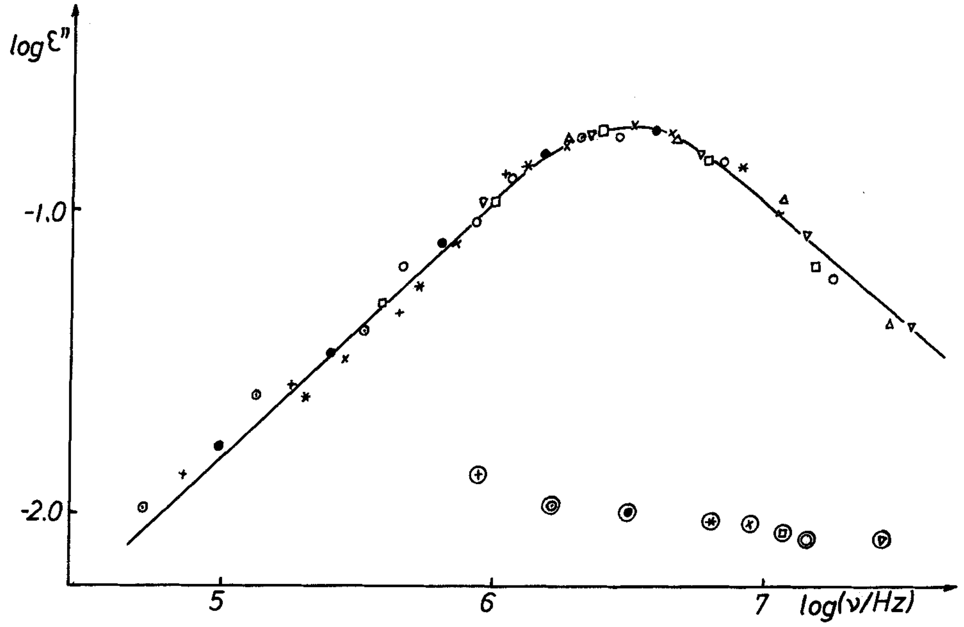

Figure 2. The master absorption curve for 6OAOB in the nematic and smectic phases [9]. The points are in absolute scale for the scaling temperature 385·1 K (●); (△) 350·6 K, (▽) 357·6 K (○) 363·1 K, (□) 368·0 K, (×) 372·1 K, (*) 377·1 K, (⊙) 393·1 K and (+) 399·1 K.

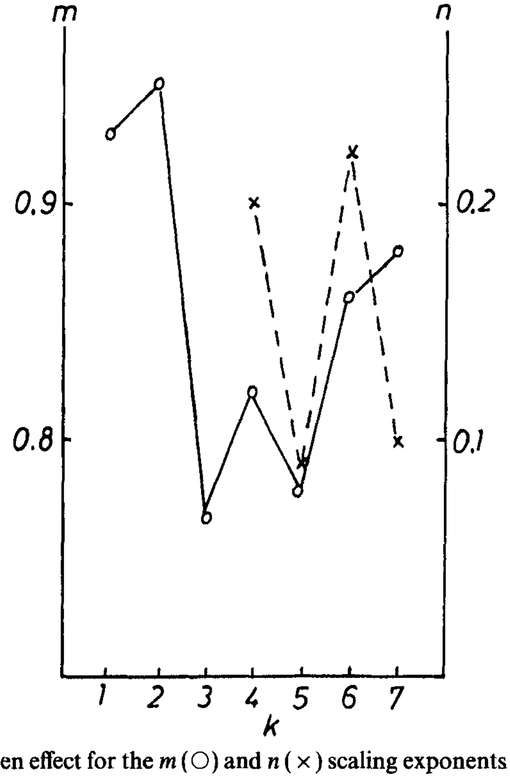

Figure 3. The odd–even effect for the m (○) and n (×) scaling exponents for 1 to 7 members of the 4,4′-di-n-alkyloxyazoxybenzenes.

The Dissado–Hill correlation parameters for seven members of 4-4′-di-*n*-alkyloxyazoxybenzenes.

Substance	Correlation parameters n	$1-m$	Relaxation time $\tau_{\parallel}$/ns at $T_{NI}-T=10$ K
1OAOB	—	0·07	4·3
2OAOB	—	0·05	7·5
3OAOB	—	0·23	34
4OAOB	0·2	0·18	15
5OAOB	0·09	0·22	42
6OAOB	0·22	0·14	25
7OAOB	0·1	0·12	37

temperature [13]. Deviations from the Debye process have been found for each member of the series (from $k=1$ to 7). The scaling exponents n and m are constant in a broad temperature region for each substance. Moreover, they exhibit an odd–even alternation, when k changes from 1 to 7 (see figure 3). The n and $1-m$ values evaluated from the slopes of the $\log \varepsilon'' - \log \nu$ plots for members of the homologous series are collected in the table together with the values of the relaxation rates characteristic of molecular reorientation around their short axes. It seems that the relatively low values of $1-m$ (i.e. values of m close to 1) for $k=1$ and 2 indicate that the two substances are essentially liquids, in which a fractal-like geometry is present only to a small extent. For $k=3$ to 7 the fractal-like character is more pronounced.

The existence of an odd–even effect in n and m indicates an alternation of the magnitude of the cooperative phenomena leading to fractal-like behaviour with increasing length of the alkyloxy chains. The degree of local order is larger in even than in odd members. Weak steric hindrances give good ordering and hence relaxation requires more cooperative adjustments than for strong steric hindrances. The behaviour of the n parameter, being a measure of a local order parameter as a function of the chain length, is found to be in agreement with the predictions of Marčelja [14].

There are several theoretical approaches useful in the description of non-Debye dielectric relaxation [15, 16]. However, for further consideration it seems important that the general behaviour of the observed dielectric response is independent of the details of the chemical and physical properties of the system. In some cases the fractional power law dependence of a physical property on a variable allowing for a scaling procedure could be understood as the macroscopic manifestation of the self-similarity, i.e. the scale invariance, existing on a certain interval of scale changes at the microscopic level of the system [4]. This suggests the introduction of fractal concepts into the description of dielectric relaxation in disordered materials. The aim of using the fractal philosophy is to find a quantitative relation between the dielectric response and the structure of the medium.

The advantage of admitting fractal concepts into the description of dielectric relaxation in materials with evident complexity lies also in the possibility of using theoretical models solved analytically for deterministic fractal constructions. Theoretical descriptions of AC conductivity have been performed on the self-similar circuit constructions of capacitors and resistors; this gives a qualitative electrical analogue of the dielectric medium [5, 17, 18]. A deterministic construction has to be a far simplification of any real system. However, for certain values of the parameters characterizing the composition of irreducible subcircuits the model [5] makes it

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possible to find the two power law regimes corresponding to relation (2) describing the constant phase angle region and to relation (3), respectively. The cluster model proposed by Dissado and Hill [19] to explain the power law frequency dependence of the electric susceptibility also gives the physical meaning of the two different fractal regimes observed [20]. The individual electric dipole moment is identified with the irreducible subcircuit. Clusters of different sizes correspond to the self-similar combinations of the various number of the smallest subcircuits. The intra and inter cluster interactions are introduced in the form of the electrical connections between the elements. Fifteen embeddings are enough to model the final relaxation in a form characteristic of the process where the particular relaxation in a given cluster influences the relaxation in another cluster effectively. Such a structure for the system reflects a contribution from both geometric and dynamic properties to the observed response. The spatial randomness of the system (defined by the fractal dimensionality d_f) makes it possible to create some chemical path [21] connecting the dipole displacements in the evolution to equilibrium. The dynamic interactions caused in the real medium by steric hindrances, structural strains, order defects, etc., spoil this process thus diminishing its contribution to the response.

There is a family of models regarding the temporal evolution of the sample towards equilibrium as a sequence of events distributed fractally in time [6, 22]. We can see the physical realization of these models by considering the relaxation in non-Debye systems in the way proposed by Palmer *et al.* [23], where interacting entities compose a hierarchy of degrees of freedom from fast to slow. The faster degrees, having the shorter waiting time [21, 24], successively constrain the slower ones. The set of moments in which subsequent dipoles of such a system make instantaneous jumps seems to correspond well to the random weighted Cantor set. In the model proposed by Niklasson [25] the m parameter is equal to the fractal dimensionality d_t characterizing the fractal time process. When d_t tends to unity there is a completely random contribution of independently reorienting dipoles to the relaxation process.

It is important to note that there are still controversies between models about the expression of correlation parameters in fractional dimensionality language. Reviews of the fractal aspects of the dielectric response in disordered materials have been presented by Niklasson [25] for charge carriers and by Dissado and Hill [20] mainly for polar materials.

The question as to whether there are any microscopic reasons for considering the members of the homologous series as random fractals, i.e. as fractal-like structures, seems open. Microscopic studies [26] and some hydrodynamic experiments [27] on liquid crystals provide evidence of their fractal-like peculiarities. For the substances presented in the table measurements of the fractal dimensionality d_f have not been made. Anyway it seems that the observed power laws from equations (2) and (3) can be understood as a result of a self-similar hierarchy of microscopic relaxation processes [5, 6] well grounded in so many disordered materials. The temperature independence of the n and m parameters observed for the substances under consideration points to the dominance of the geometric factor in the relaxational behaviour [20].

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References

[1] MASSALSKA-ARODŹ, M., and KRESSE, H., 1990, *Liq. Crystals*, **7**, 361.

[2] MASSALASKA-ARODŹ, M., STETTIN, H., and KRESSE, H., 1989, *Molec. Crystals liq. Crystals*, **177**, 155.

[3] DISSADO, L. A., and HILL, R., 1987, *J. chem. Phys.*, **111**, 193.

[4] Dissado, L. A., Nigmatullin, P. R., and Hill, R. M., 1985, *Advances in Chemical Physics*, Vol. 63, edited by M. R. Evans (Wiley), chap. 3.

[5] Dissado, L. A., and Hill, R. M., 1988, *Phys. Rev.* B, **37**, 3434.

[6] Chen Hog, Wu Xing, and Fang Jun-xin, 1986, *J. phys.* C, **19**, L499.

[7] Urban, S., Wróbel, S., Chłędowska, K., Chruściel, J., Janik, J. A., and Otnes, K., 1983, *Molec. Crystals liq. Crystals*, **100**, 57.

[8] Nguyen, X. P., Otowski, W., Chruściel, J., Kresse, H., Urban, S., and Wróbel, S., 1985, *Z. Naturf.* (*a*), **40**, 627.

[9] Maier, W., and Meier, G., 1961, *Z. Naturf.* (*a*), **16**, 1200.

[10] Weise, H., and Axmann, A., 1966, *Z. Naturf.* (*a*), **21**, 1316.

[11] Chłędowska, K., Chruściel, D., Janik, J. A., Janik, J. M., Kresse, H., Stettin, H., Otnes, K., Stanek, T., Urban, S., and Wróbel, S., 1988, *Liq. Crystals*, **3**, 1339.

[12] Nguyen, X. P., 1990, *Molec. Crystals liq. Crystals.*, **191**, 61.

[13] Masalska-Ardoż, M., 1988, *Acta phys. polo.*, **74**, 773.

[14] Marcelja, S., 1974, *J. chem. Phys.*, **60**, 3599.

[15] Nordio, P. L., Rigatti, G., and Segre, U., 1973, *Molec. Phys.*, **25**, 129.

[16] Davidson, D. W., and Cole, R. H., 1951, *J. chem. Phys.*, **19**, 1484.

[17] Clerc, J. P., Tremblay, A.-M. S., Albinet, G., and Mitescu, C. D., 1984, *J. Phys. Lett.*, **45**, L913.

[18] Clerc, J. P., Giraud, G., Laugier, J. M., and Luck, J. M., 1985, *J. Phys.* A, **18**, 2565.

[19] Dissado, L. A., and Hill, R. M., 1983, *Proc. R. Soc.* A, **390**, 131.

[20] Dissado, L. A., and Hill, R. M., 1989, *J. appl. Phys.*, **66**, 2511.

[21] Fu-siu Liu, and Wen Chao, 1989, *Phys. Rev.* B, **40**, 7091.

[22] Stanley, H. E., 1985, *Scaling Phenomena in Disordered Systems*, edited by R. Pynn and A. Skjeltorp (Plenum). Stanley, H. E., 1984, *Proceedings of International Conference on Kinetics of Aggregation and Gelation*, edited by F. Family and D. P. Landau (North Holland).

[23] Palmer, R. G., Stein, D., Abrahams, E. S., and Anderson, P. W., 1984, *Phys. Rev. Lett.*, **53**, 958.

[24] Weron, K. (private communication).

[25] Niklasson, G. A., 1987, *J. appl. Phys.*, **62**, R1.

[26] Bechhoefer, J., Simon, A., Libchaber, A., and Oswald, P., 1988, *Random Fluctuations and Pattern Growth: Experiments and Models*, edited by H. E. Stanley and N. Ostrowsky (Kluwer Academic).

[27] Buka, A., Kertesz, J., and Vicsek, T., 1986, *Nature, Lond.*, **323**, 424.

Downloaded At: 13:21 26 January 2011