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► **To cite this version:**

Helmut Brand, Kyozi Kawasaki. Mode coupling theory of the isotropic-nematic transition in sidechain liquid crystalline polymers. *Journal de Physique II*, 1994, 4 (4), pp.543-548. 10.1051/jp2:1994144 . jpa-00247978

**HAL Id: jpa-00247978**

**<https://hal.science/jpa-00247978>**

Submitted on 4 Feb 2008

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Classification  
*Physics Abstracts*  
64.70M — 05.70L — 61.30

Short Communication

## Mode coupling theory of the isotropic-nematic transition in sidechain liquid crystalline polymers

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*(Received 21 January 1994, accepted 1 March 1994)*

**Abstract .** — Using a mode coupling technique we investigate the dynamics near the isotropic-nematic transition in liquid crystalline sidechain polymers. While in mean field approximation one obtains  $z = 1$  for the dynamical critical exponent  $z$  for the relaxation time of the order parameter, we get from mode coupling the value  $z = 1.5$ , a result which is in agreement with recent experiments done in Martinoty's group on two different classes of sidechain liquid crystalline polymers using electric and acoustic birefringence measurements. An analysis of recent measurements of the dynamic stress-optical coefficient in sidechain elastomers shows that mode coupling effects are also important in that case.

### 1. Introduction and motivation.

Liquid crystalline sidechain polymers, which have been synthesized first in 1978 [1], have since been investigated in a rapidly growing number of papers (compare, for example, Refs. [2] and [3] for reviews). Most of these investigations were focusing either on the synthesis and the measurement of various physical static and dynamic properties in a specific liquid crystal phase or on the static properties near phase transitions such as, for example, the isotropic-nematic transition. Up to now much less work has been done on the dynamics of phase transitions and on the interaction between a phase transition and the dynamic glass transition. The latter term refers to the fact that below a certain frequency polymers behave macroscopically like a liquid whereas above this frequency the polymer reacts like a solid due to the transient network formed among the polymer chains.

To integrate the dynamic glass transition into the description of the macroscopic dynamics of polymers and liquid crystalline sidechain polymers, it has turned out to be crucial to incorporate the strain field associated with the transient network into the macroscopic dynamics

[4-7], when setting up a description in the spirit of irreversible thermodynamics [8]. Quite recently we have given the linearized macroscopic dynamics of the isotropic-nematic transition in sidechain polymers [9] generalizing earlier work on the isotropic-nematic transition in low molecular weight liquid crystals [10-14].

In two recent important experimental papers [15, 16], Martinoty's group has investigated, using electric and acoustic birefringence measurements, the static and the dynamic behaviour in two classes of sidechain liquid crystalline polymers. For the static behaviour of the modulus of the nematic order parameter as a function of temperature in the isotropic phase, Reys *et al.* [15, 16] find the same behaviour observed over two decades ago in low molecular weight materials [11, 17], namely mean field behaviour for the static susceptibility of the order parameter. It turns out that for liquid crystalline sidechain polymers the mean field exponent gives a satisfactory description over a temperature range of more than 20 K starting at about 1 K above the critical temperature of the nematic-isotropic transition. For the relaxation time of the induced nematic order parameter, however, Reys *et al.* find a result that is qualitatively different from that reported in low molecular weight materials. Measurements of the transient electrical birefringence yield for the order parameter relaxation time  $\tau$  an exponent  $z = 3/2$ , whereas one expects from the mean field description of the nematic-isotropic transition in low molecular weight materials the exponent  $z = 1$  with the divergence coming exclusively from the statics while the associated Onsager kinetic coefficient does not show any singular behaviour near the phase transition (in conventional notation our  $z$  is denoted as  $z\nu$ ). This is indeed what had been previously observed in acoustic birefringence measurements [18] in low molecular weight liquid crystals.

Naturally this qualitative difference in the dynamic behaviour between low molecular weight and polymeric systems triggers the question concerning its origin. Even taking into account reversible nonlinear terms in the macroscopic equations, as it has been done for low molecular weight systems e.g. in references [11, 19] and [20], one can convince oneself by straightforward analysis that such an approach does not give the experimentally observed exponents without additional considerations. Thus alternative explanations need to be found going beyond the mean field approximation.

Here we suggest that the observed lifetime enhancement of the order parameter fluctuations can be extracted from the mode coupling approach [21], a method that has since been generalized [22] and applied to a large number of physical systems including phase transitions in low molecular weight liquid crystals [23-25]. However, here we apply this technique to investigate the *life-time* renormalization arising from *dissipative* nonlinearities [26, 27, 22], whereas the usual mode coupling technique [21-25] dealt with the renormalization of kinetic coefficients arising from *reversible* nonlinearities. Note that the two types of nonlinearity act to modify the dynamics in opposite ways: the former slows down whereas the latter accelerates. Here we reformulate the theory by making use of the projector technique by Zwanzig and Bixon [28].

In the next section we present the model, sketch the ingredients of the method and give the results for the isotropic-nematic transition in liquid crystalline sidechain polymers. In section 3 we critically compare our model calculations with the experimental results and give a perspective for future directions of experimental and theoretical research. In this last section we will also discuss possible implications of our approach for the isotropic-nematic transition in liquid crystalline elastomers for which one has observed very recently [29], using dynamic stress-optical experiments, also a slowing down of the relaxation of the nematic order parameter that is different from classical mean field behaviour, while again the measured static properties show mean field behaviour.

## 2. Lifetime enhancement in liquid crystalline sidechain polymers.

In this section we present the model assumptions of our calculations of the lifetime enhancement, sketch the basic ingredients of the method used and give the results obtained. For a general exposition of the method as well as for the details of the calculations we refer to our forthcoming detailed paper [32]. We investigate a continuum model for liquid crystalline sidechain polymers expressed in terms of two field variables:  $\epsilon$  for the elastic strain and  $Q$  for the nematic order parameter. It is well-known [10] that the nematic isotropic phase transition in liquid crystals is weakly first order. We start out from the following functional for the generalized energy obtained by symmetry considerations [9, 31] above and near the critical point (for simplicity we suppress the tensorial character of  $Q(\mathbf{r})$  and  $\epsilon(\mathbf{r})$ ):

$$H(\{Q, \epsilon\}) = \int d\mathbf{r} \frac{1}{2} [L(\nabla Q)^2 + A Q^2 + c\epsilon^2 + 2UQ\epsilon + \zeta\epsilon^2 Q + \mu\epsilon Q^2] \quad (1)$$

where we have used the notation introduced in reference [9] for polymers and in reference [31] for elastomers. Since our main interest is in the effects of the coupling of the nematic order parameter  $Q$  to the strain field  $\epsilon$ , we have omitted higher order terms in  $Q$  in writing down equation (1). The equations of motion are taken to be (we suppress the arguments  $\mathbf{r}$  and  $t$  unless needed)

$$\nu^{-1} \dot{Q} = -\delta H / \delta Q + f_Q \quad (2)$$

$$\tau \dot{\epsilon} = -\delta H / \delta \epsilon + f_\epsilon \quad (3)$$

where a dot denotes time derivative. The  $f$ 's are thermal noise sources satisfying the fluctuation-dissipation (FD) theorem:

$$\langle f_Q(\mathbf{r}t) f_Q(\mathbf{r}'t') \rangle = 2k_B T \nu^{-1} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (4)$$

$$\langle f_\epsilon(\mathbf{r}t) f_\epsilon(\mathbf{r}'t') \rangle = 2k_B T \tau \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (5)$$

$$\langle f_Q(\mathbf{r}t) f_\epsilon(\mathbf{r}'t') \rangle = 0 \quad (6)$$

In writing down equations (4-6) we have neglected for simplicity the cross-coupling between  $\dot{Q}$  and  $\dot{\epsilon}$ , which is expected not to change the main conclusions.

We make now use of the formalism introduced in [26, 27] to calculate the lifetime renormalization based on an equation of motion for the correlation matrix thus also exploiting the projector approach of Zwanzig and Bixon [28]. This leaves us with (compare [32] for a detailed derivation) the following general expression for the frequency dependent renormalization  $\Delta \mathbf{R}(\omega)$  of the friction matrix  $\mathbf{R}$ , whose unrenormalized part is  $\begin{pmatrix} \nu^{-1} & 0 \\ 0 & \tau \end{pmatrix}$

$$\Delta \mathbf{R}(\omega) \equiv \int_0^\infty dt e^{i\omega t} \frac{1}{k_B T} \left\langle \left( \frac{\partial H}{\partial \mathbf{a}} \right)_{\text{NL}} e^{-t(1-\mathcal{P})\mathcal{L}} \left( \frac{\partial H}{\partial \mathbf{a}} \right)_{\text{NL}}^T \right\rangle \quad (7)$$

where  $\mathbf{a}$  is the set of variables considered, the subscript NL denotes the nonlinear part of the generalized energy derivative  $\partial H / \partial \mathbf{a}$  and where  $\mathcal{P}$  and  $\mathcal{L}$  are the projection on the linear  $\mathbf{a}$  variables and time displacement operator in the approach of [28], respectively.

We have in our model  $\mathbf{a} = (Q, \epsilon)$  and thus for the matrix of static susceptibilities

$$k_B T \langle \mathbf{a}_k \mathbf{a}_{-k} \rangle^{-1} = A_k \equiv \begin{pmatrix} A + Lk^2 & U \\ U & c \end{pmatrix} \quad (8)$$

The criticality is signalled by the vanishing of the smaller eigenvalue  $\alpha_k^{(1)}$  of  $\mathbf{A}_k$  at  $k = 0$  where the other one  $\alpha_k^{(2)}$  remains positive and non-critical. We can rewrite the nonlinear part of equation (1) as

$$H_{\text{NL}} = \frac{1}{3!} \int dV \sum_{\nu j l}^{1,2} B_{\nu j l} \phi^{(\nu)} \phi^{(j)} \phi^{(l)} \quad (9)$$

$$= \int dV \left\{ \frac{1}{6} B_{111} [\phi^{(1)}]^3 + \frac{1}{2} B_{112} [\phi^{(1)}]^2 \phi^{(2)} + \frac{1}{2} B_{122} [\phi^{(2)}]^2 \phi^{(1)} + \frac{1}{6} B_{222} [\phi^{(2)}]^3 \right\}$$

where  $\phi^{(1)}$  is the eigenvector in the space of  $\mathbf{a}$  associated with the critical eigenvalue  $\alpha_k^{(1)}$  and  $\phi^{(2)}$  with the noncritical eigenvalue  $\alpha_k^{(2)}$  and where the coefficients  $B_{\nu j k}$  are some linear combinations of  $\zeta$  and  $\mu$  and we neglect the dependence of  $B_{\nu j k}$  on  $k$  which is taken to be small near criticality. In the expansion in the second line of (9) the terms are ordered according to the strength of criticality.

$$\left[ \frac{\delta H_{\text{NL}}}{\delta \phi^{(\nu)}} \right]_k + \dots = \frac{1}{2} \sum_{j l} B_{\nu j l} (\phi^{(j)} \phi^{(l)})_k + \dots \quad (10)$$

We also note that the bilinear terms in  $H$  denoted as  $H_L$  become

$$H_L = \frac{1}{2} \int_k (\alpha_k^{(1)} |\phi_k^{(1)}|^2 + \alpha_k^{(2)} |\phi_k^{(2)}|^2) \quad (11)$$

We first consider the relaxation time renormalization of the critical mode which is signalled by  $\alpha_k^{(1)}$  with small  $k$  and thus we can take for small  $k$

$$\alpha_k^{(1)} = b(k^2 + \xi^{-2}) \quad (12)$$

$$\alpha_k^{(2)} \approx \alpha^{(2)} \equiv \alpha_0^{(2)} \quad (13)$$

where  $\xi$  is the correlation length of critical fluctuations which diverges as  $(T - T_c)^{-1/2}$  at criticality.

With this preparation and making use of equation (7) and the equation of motion for  $\mathbf{a}_k$  we find for the lifetime  $\tau_1$  of the critical mode

$$\tau_1 \sim B_{111}^2 \xi^5 \sim (T - T_c)^{-5/2} \quad (14)$$

On the other hand, the presence of the first term of equation (9) implies that the phase transition is first order. If the transition is second order or only weakly first order, the coefficient  $B_{111}$  must vanish or is at most very small. In this case the second term in equation (9) comes in and yields the contribution

$$\tau_1 \sim B_{112}^2 \xi^2 \sim (T - T_c)^{-1} \quad (15)$$

Next we proceed to look at the non-critical mode whose relaxation time  $\tau_2$  is calculated by the same procedure. We obtain

$$\tau_2 \sim B_{112}^2 \xi^3 \sim (T - T_c)^{-3/2} \quad (16)$$

Now, since both the critical and non-critical modes enter the coupled dynamics of  $Q$  and  $\epsilon$ , the strongest critical anomaly that can appear there arises from the non-critical mode whose relaxation time  $\tau_2$  behaves as  $(T - T_c)^{-3/2}$  in agreement with the experimental finding on the dynamics of  $Q$ . If this interpretation is correct, the same critical anomaly should appear in the dynamics of  $\epsilon$ , i.e. the elastic relaxation.

Here we presented the results of a perturbative calculation of relaxation time renormalization which gives the relaxation time diverging as  $\xi^3$  in the lowest order in agreement with the experiment. At this stage, however, we should point out the preliminary character of this conclusion. For a completely satisfactory calculation we need to go beyond the first order perturbation theory, for instance, by making the calculation self-consistent. These are the challenges left for future study.

### 3. Discussion and perspective.

In this paper we have indicated how the life-time enhancement with a critical exponent  $z = 3/2$  observed experimentally in liquid crystalline sidechain polymers near the isotropic-nematic phase transition can be extracted from a generalized mode coupling approach. The result obtained is due to cubic cross coupling terms between the strain field associated with the transient network and the nematic order parameter.

As expected on the basis of our model, the shear viscosity  $\eta$  showed no critical behaviour [15, 16] in the experiments. Also the experimental observation that the dynamic coefficient  $\mu$  coupling order parameter variations and flow diverges [15, 16] is consistent with our results. Furthermore we predict that the elastic relaxation time associated with the transient network must also show the same critical exponent for the singular behaviour as that of the nematic order parameter.

While we have considered up to this point the isotropic-nematic phase transition in sidechain liquid crystalline polymers, our analysis can be expected to carry over directly to this phase transition in sidechain liquid crystalline elastomers. In these systems it will actually be relevant for all finite frequencies, whereas for the polymeric case the analysis given only applies for frequencies above that for the dynamic glass transition for which a transient network exists. This expectation appears to have been confirmed by recent measurements of the dynamic stress-optical coefficient near the isotropic-nematic transition in liquid crystalline sidechain elastomers by Sigel *et al.* [29], who observed over a large temperature range a slowing down that is much stronger than that expected for mean field behaviour ( $z = 1$ ). For the sample called LCE-5 in [29] we extract from the data presented and plotted in figure 8c for the exponent  $z = 1.55 \pm 0.1$ . For the sample called LCE-1 [29] we deduce from figure 7c  $z = 1.65 \pm 0.2$ ; in this case it is rather difficult to get an exponent, since, as Sigel *et al.* noted, the data were obtained in two different sets of measurements, which were performed a considerable amount of time apart. Clearly the experiments described in reference [29] had not been done having in mind the possibility of a non-mean field behaviour. It appears therefore to be very important to repeat this type of experiments on new well characterized samples and to determine more precisely the value of the exponent  $z$ .

Motivated by experimental results, we have focused in this note exclusively on the dynamic exponents near the isotropic-nematic transition. In the future we will investigate how the presence of a transient or permanent (elastomers) network will change the critical dynamic behaviour near phase transitions between other liquid crystalline phases in both, polymeric and elastomeric materials, when compared to that obtained for low molecular weight systems. Clearly those phase transitions will be preferred in these studies that can be second order

or weakly first order including the nematic to smectic transitions and the uniaxial-biaxial transition in nematics.

### Acknowledgements.

It is a pleasure for us to thank Philippe Martinoty for stimulating discussions and his kind hospitality during our visit in Strasbourg.

Support of this work by the Yamada Foundation is gratefully acknowledged. H.R.B. thanks the Deutsche Forschungsgemeinschaft for partial support of his work through the Graduiertenkolleg "Nichtlineare Spektroskopie und Dynamik" and K.K. thanks the Humboldt Foundation for the award of a Humboldt Research Prize.

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