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Short Communication

Flow enhancement of electrical fluctuations in polymer solutions and melts

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Abstract. — We show that the origin of the enhanced electrical fluctuations under flow, observed over the last 15 years in polymer solutions, can be traced back to a dissipative cross coupling between the strain tensor (characterizing transient polymeric networks) and electric fields. Additional experiments to further test our picture are suggested.

1. Introduction.

In a series of papers over the last fifteen years Kubát and his group [1-7] have reported a number of features of a fascinating phenomenon, which has not been explained or cast into a proper framework up to now. In polymer solutions they have observed an enhancement of electrical fluctuations during flow when compared to those at rest. Without an external flow field the intensity of the electrical fluctuations corresponds to the value expected from thermodynamics [8, 9], and is in this case given by the Nyquist formula [10]. This situation changes drastically as soon as a flow of sufficient strength is imposed on the polymer solutions in question (for example, polyethylene oxide solutions). While we will not attempt here to explain the phenomena observed in all detail, especially not the nonlinear aspects, we think that the approach presented by us [11] in this journal recently, namely the linearized macroscopic dynamics of polymer solutions and melts, can provide a sensible framework to describe the experimental results. Our description is unique when compared to other approaches to polymer solutions, since it allows in a natural way to incorporate couplings between the transient network characterized by the strain tensor $\epsilon_{ij}$ and other macroscopic variables such as the temperature variations $\delta T$, the concentration $c$ and the electric field $\mathbf{E}$.
2. Experimental situation.

We first summarize briefly some important aspects of the experimental results [1-7]. As it has been found consistently in all experiments reported, there is a minimum flow rate, i.e. a threshold above which the electrical fluctuations are enhanced. In addition it has been observed that a certain degree of "elasticity" of the polymer solutions is necessary to obtain an enhancement. Very crudely speaking one could characterize this degree of "elasticity" by the relaxation constant \( \tau_2 \) of the transient network. For very small \( \tau_2 \), as for example in very dilute solutions, the enhancement of the electrical fluctuations observed is negligible, while for larger values of \( \tau_2 \) a strong enhancement is observed. In this picture the limit \( \tau_2 \to \infty \) corresponds to a genuine solid. In the experiments it has also been found that small scale flow structures, which occur as vortices or even turbulent flows near the inlet region of the capillaries, are important in getting a large effect. Thus, small length scales or large wavevectors are favourable for a big enhancement of the electrical fluctuations. In addition to these qualitative features just outlined, the experiments have revealed a number of phenomena that are clearly linked to strictly nonlinear properties.

Here we want to demonstrate that all the qualitative features outlined above result naturally from our macroscopic dynamic approach [11], which we have generalized meanwhile to liquid crystalline polymers [12-14] possessing additional degrees of freedom such as orientational order.

3. Elements of the macroscopic dynamic approach and its application to the experiments.

In macroscopic dynamics one keeps firstly all truly hydrodynamic degrees of freedom, which do not relax in the infinite wavelength limit [15, 16], and secondly those macroscopic degrees of freedom, which relax on a finite but sufficiently long time scale, i.e. long compared to the microscopic time scales. The classical example for this type of variable is the modulus of the order parameter near second order phase transitions such as for example near the \( \lambda \) transition in \( ^4\text{He} \) (compare Ref. [17]). Another example for a macroscopic variable in certain condensed systems (e.g. in complex fluids including liquid crystals) is the macroscopic electric polarization \( \mathbf{P} \) [18]. In reference [11] we have generalized further this approach and incorporated the strain tensor \( \epsilon_{ij} \) as a macroscopic variable to account for the fact that in polymer solutions and melts there exists a "transient network" [19, 20], i.e. for sufficiently small frequencies the polymer behaves like a simple liquid whereas for sufficiently large frequencies it reacts like a solid. Frequently this phenomenon is called the dynamic glass transition [21].

In this approach the additional dynamic equation for the strain tensor \( \epsilon_{ij} \) is coupled to the other macroscopic variables, namely to the conserved quantities density \( \rho \), energy density \( \epsilon \), density of linear momentum \( q \) and concentration \( c \) as well as to the macroscopic polarization \( \mathbf{P} \) making use of general symmetry arguments [15, 16] and irreversible thermodynamics [8]. The former include invariance under translations and rotations, Galilean invariance and the appropriate symmetries under parity and time reversal. In reference [11] we have given and discussed in detail the linearized macroscopic dynamic equations and we therefore concentrate in the following only on those aspects which are helpful in providing a framework for the experimental observations by Kubát's group. As we have pointed out there are static and dynamic couplings between the strain tensor \( \epsilon_{ij} \) and gradients of the electric field, where the latter coupling will turn out to be of crucial importance in our interpretation of the experimental results.

For the dynamic equations of the density of linear momentum, the strain tensor and the
polarization we have, including fluctuations

\[
\begin{align*}
\dot{g}_i + \nabla_j \sigma_{ij} + \nabla_j \Sigma_{ij} &= 0 \\
\dot{\xi}_{ij} + X_{ij} + \xi_{ij} &= 0 \\
\dot{P}_i + j_i^P + J_i^P &= 0
\end{align*}
\]

(1) (2) (3)

where the fluctuating currents \(\Sigma_{ij}, \xi_{ij},\) and \(J_i^P\) are introduced into the macroscopic dynamic equations along the lines pioneered by Landau and Lifshitz [22]. The reversible parts of the deterministic currents \(\sigma_{ij}, X_{ij}, \) and \(J_i^R\) are introduced into the macroscopic dynamic equations along the lines pioneered by Landau and Lifshitz [22].

\[
\begin{align*}
\sigma_{ij}^R &= \rho \delta_{ij} - \Phi_{ij} \\
X_{ij}^R &= -A_{ij} \\
J_i^R &= 0
\end{align*}
\]

(4) (5) (6)

where \(\Phi_{ij}\) is the thermodynamic conjugate to the strain tensor \(\epsilon_{ij}\) and where \(A_{ij} = \frac{1}{2}(\nabla_i v_j + \nabla_j v_i)\) with the velocity field \(v_i\). The relevant part of the dissipation function \(R\) reads

\[
2R = \int \text{d}r [.. + (1)_{ijkl} \Phi_{ij} \Phi_{kl} + \sigma^E E^2 + 2 \zeta^E E_i \nabla_j \Phi_{ij}]
\]

(7)

where \(\cdot\) indicate terms not relevant below, which are listed, together with the explicit form of the material tensors, in reference [11]. From the dissipation function we get the dissipative currents in equations (4-6) by taking a variational derivative of \(R\) with respect to the forces, for example

\[
j_i^{PD} = \frac{\delta R}{\delta E_i} = \sigma^E E_i + \zeta^E \nabla_j \Phi_{ij}.
\]

(8)

The fluctuating forces are linked to the dissipative transport parameters via the fluctuation dissipation theorem [8, 9, 23]

\[
\begin{align*}
\langle \Sigma_{ij}(r, t) \Sigma_{kl}(r', t') \rangle &= 2k_B T \eta_{ijkl} \delta(r - r') \delta(t - t') \\
\langle \xi_{ij}(r, t) \xi_{kl}(r', t') \rangle &= 2k_B T \frac{1}{\tau} \delta_{ijkl} \delta(r - r') \delta(t - t') \\
\langle J_i^P(r, t) J_j^P(r', t') \rangle &= 2k_B T \sigma^E \delta_{ij} \delta(r - r') \delta(t - t') \\
\langle \xi_{ij}(r, t) J_j^P(r', t') \rangle &= 2k_B T \zeta^E \delta_{ik} \nabla_j \delta(r - r') \delta(t - t').
\end{align*}
\]

(9) (10) (11) (12)

Combining equations (1-8) we find for the linearized macroscopic dynamic equations of the strain tensor \(\epsilon_{ij}\) and the macroscopic polarization \(P_i\)

\[
\begin{align*}
\dot{\epsilon}_{ij} - A_{ij} + (1)_{ijkl} \Phi_{kl} - \zeta^E \nabla_j E_i &= 0 \\
\dot{P}_i + \sigma^E E_i + \zeta^E \nabla_j \Phi_{ij} &= 0.
\end{align*}
\]

(13) (14)

From equations (13), (14) we read off immediately that the symmetrized velocity gradient \(A_{ij}\) drives the strain tensor \(\epsilon_{ij}\) and this in turn gives rise to variations in the polarization \(P_i\) via the dissipative cross coupling \(\zeta^E\). Since the strength of the velocity gradients and their fluctuations have not been measured quantitatively in the experiments described so far (cf. the discussion below), we will just take the intensity of the velocity variations as an input parameter and denote it by \(\Lambda\).
It is then straightforward using standard techniques [16] to get from equations (13), (14) the spectrum of the electric field fluctuations as a function of the wavevector $k$ and the frequency $\omega$. For the spectrum in the presence of flow we obtain after Fourier transformation in space and time, assuming incompressibility and neglecting crosscoupling effects in the denominator

$$\langle |E|^2 \rangle_{\text{flow}} = \frac{(2k^2\zeta^E)^2 \Lambda}{\omega^4(\chi/c_2)^2 + \omega^2[(4\chi/\tau_2)^2 + (\sigma^E/c_2)^2] + (4\sigma^E/\tau_2)^2}$$

(15)

where $\chi$ is the electric susceptibility and $c_2$ the elastic shear modulus [24]. This expression must be compared with the spectrum of thermal fluctuations of the electric field in the absence of flow, which is given neglecting crosscoupling effects by

$$\langle |E|^2 \rangle_{\text{th}} = \frac{\sigma^E}{(\omega\chi)^2 + (\sigma^E)^2}.$$

(16)

Taking the ratio of these two expressions we get the enhancement of the electric fluctuations without further simplifications

$$\frac{\langle |E|^2 \rangle_{\text{flow}}}{\langle |E|^2 \rangle_{\text{th}}} = \frac{(2k^2\zeta^E c_2)^2 \Lambda/\sigma^E}{\omega^2 + (4c_2/\tau_2)^2}.$$

(17)

Several remarks are to be made:

i) a large wavevector is favourable for getting a big enhancement, which is proportional to $k^4$;

ii) the enhancement is proportional to the square of the dissipative cross coupling $\zeta^E$ introduced in reference [11];

iii) taking the low frequency limit we also see that the enhancement is proportional to the square of $\tau_2$ characterizing the degree of “elasticity” of the polymer solution or melt;

iv) from a more general analysis, including all crosscoupling effects in equations (15) and (16), it follows that in equation (17) $\sigma^E$ is replaced by $\sigma^E + x F(x)$ with $x \equiv (\zeta^E k)^2$, where $F(x)$ depends in a very complicated manner on various hydrodynamic parameters as well as on the frequency $\omega$ and the wavevector $k$;

v) within our linearized description the enhancement is proportional to the intensity of the velocity variations. However, nonlinear effects are likely to change this proportionality and, in addition, the dependence on the wavevector and on the cross coupling $\zeta^E$ to noninteger powers.

Nevertheless the following picture emerges: an inhomogeneous hydrodynamic flow generates a strain tensor $\epsilon_{ij}$ in polymer solutions with a sufficiently large degree of “elasticity”. This strain increases if the lengthscale of the flow decreases. Such small scale, large wavevector flows can be obtained experimentally, for example, above the onset of an instability. This step has been suggested in a slightly different wording already in references [1-7]. But the decisive step to have a framework into which the observed effects can be incorporated is to realize that a transient network in the presence of small scale spatial variations gives rise invariably to enhanced electrical fluctuations via the dissipative cross coupling $\zeta^E$, whose existence has been pointed out first in reference [11]. From our analysis we see clearly the advantage of large wavevectors. We would like to stress that one would not know how to incorporate such a cross coupling into more conventional descriptions of polymer flows [19]. From the approach of macroscopic dynamics, however, such cross-couplings emerge quite naturally.
4. Suggested future experiments.

From the analysis given above quite a few possibilities for future experiments emerge immediately. First of all it would be very important to vary the diameter of the capillaries used to determine the precise dependence of the noise enhancement on the characteristic length scale of the flow. A second issue which clearly deserves further analysis is the measurement of the fluctuation spectrum of the velocity field. If the picture suggested is applicable, an enhancement of the intensity of the velocity variations should also give rise to an enhancement of the intensity of the electric fluctuations. From equations (13) and (14) it emerges that a time trace of the velocity and of the electric field are related. While these equations are strictly applicable only in the linearized domain, one might expect that even in the nonlinear regime the time series of velocity and electric field should show many qualitative similarities.

Finally we would like to point out that dissipative cross coupling terms to the strain tensor, similar to that of the electric field, also exist for temperature and concentration gradients. Thus, together with the fluctuations in the electric field, those in temperature and concentration are also generated by the small scale flow. While it might be difficult to detect the enhancement of the temperature fluctuations due to the cross coupling, because they are probably masked by Ohmic and viscous heating due to the flow, it could be possible to detect an enhancement in the concentration fluctuations of the polymer solutions studied, provided one finds a convenient experimental way to measure variations of the chemical potential.

5. Conclusions and perspectives.

In this note we have suggested a framework to account for experimental observations, which give enhanced electrical fluctuations in flowing polymer solutions when compared to thermodynamic fluctuations. We have traced this enhancement back to a dissipative cross coupling between the strain tensor associated with the transient polymeric network (generated by the small scale flow) and spatial variations of the electric field. This picture arises naturally only in the approach of macroscopic dynamics for polymer solutions, but is absent in the more conventional descriptions of polymer dynamics. We have also suggested several experiments to further test the given picture. In the future we hope to analyze the intrinsically nonlinear phenomena observed in the experiments.

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References

[24] Since we assumed incompressibility, the bulk elastic modulus $c_1$ (and $\tau_1$) did not occur in equation (15). We now believe that an additional restriction on $c_1$ and $c_2$ (Eq. (2.13) in [11]) is unnecessary (cf. Ref. [12] for a detailed discussion).