Mol. Cryst. Liq. Cryst., 1983, Vol. 101, pp. 301-313 0026-8941/83/1014-0301/\$18.50/0 © 1983 Gordon and Breach, Science Publishers, Inc. Printed in the United States of America

Transverse Viscous Forces in Carr Walls and Possible Dynamic Consequences[†]

DAN IGNER

Solid State Institute; Technion—Israel Institute of Technology, Technion City, Haifa 32 000, Israel and Baker Laboratory of Chemistry, Cornell University, Ithaca, N.Y. 14853 USA

and

JACK H. FREED

Baker Laboratory of Chemistry, Cornell University, Ithaca, N.Y. 14853 USA

(Received June 14, 1983)

Expressions for the anisotropic viscous forces transverse to a nematic flow confined in a straight splay-bend wall are derived under simplifying assumptions. Some possible dynamic consequences, such as longitudinal splitting of the walls and movement of asymmetric walls in electro-hydrodynamic instabilities, are suggested. The relevance to recent experimental observations is discussed.

I. INTRODUCTION

The existence of walls associated with flows was postulated by Carr on the basis of optical observations and magnetic resonance experiments.^{1a} In the following, we use "Carr walls" to imply nematic splay-bend walls associated with flows.^{1b} According to Carr's phenomenological model, the walls are formed in certain electrohydrodynamic and magneto-hydrodynamic instabilities (EHD and MHD) far above the threshold for instability. The walls have a width which is small

^{*}Supported in part by NSF Grant #DMR-81-02047.



FIGURE 1 Schematic of a Carr wall. The director field lines are drawn on the basis of optical observations on splay-bend walls which are thought³ to be associated with flows. The flow lines are drawn so as to be consistent with the Carr model and indirect experimental evidence.

compared to the characteristic wavelength of the instability and confine a strong flow of narrow delimitation. No adequate theoretical models for the nonlinear regime far above the threshold seem to be available yet for such instabilities. Further experiments seem to indicate existence of Carr walls in some other EHD's and MHD's,^{2,3} possibly in regimes close to the threshold for instability as well. A possible Carr wall formation very roughly consistent with experimental observations, so far, is schematically shown in Figure 1.

The present work was prompted by observations on the dynamical behavior of what could possibly be (asymmetric) Carr walls³ and represents an effort to examine if some of these observations can be explained by transverse anisotropic viscous forces (TAVF) in walls (see below). Section II of this work is devoted to derivation of formulae for transverse viscous forces in a model Carr wall as well as suggestions of possible dynamic consequences of these forces in EHD's. Section III is a discussion of the relevance of the suggested TAVF mechanisms to observed dynamic phenomena in some EHD's of Ref. 3 (below referred to as IF) and other instabilities.

II. TRANSVERSE BODY FORCES

In the presence of certain nonzero spatial derivatives of the velocity and director fields, anisotropic viscosity can cause body forces transverse to the direction of flows. These kinds of transverse forces are specific to anisotropic fluids, and their existence has been demonstrated in an experiment by Pieranski and Guyon in a Poisseuille flow of a nematic, with director orientation oblique to the flow.⁴ Below, we will try to find expressions for transverse forces in Carr walls as implied by the assumptions of the Carr model, and suggest mechanisms by which these forces are likely to cause longitudinal wall splitting, movement of asymmetric walls and other dynamic phenomena.

Since the anisotropic viscous forces tend to modify the assumed flows and director distributions, a more complete understanding of the phenomena we are dealing with can be gained in principle by an iterative process, in which one calculates the viscous forces in an assumed flow and director field configuration, then recalculates these fields (and possibly the charge distribution) taking into account the calculated forces, and then proceeds with new iterations. Although such an iterative procedure might prove useful, our aim at present is more modest. We only try to find qualitatively, under simplifying assumptions, the *first order* transverse forces which develop in a straight wall because of the flows assumed by the Carr model, and figure out possible dynamic consequences.

Let us look at a model Carr wall referred to coordinates as shown in Figure 2 and whose section is shown in Figure 3a for a symmetric wall and in 3b for an asymmetric one. The x axis is along the length of the wall, and the y axis along its height. The director distribution $\overline{n}(\vec{r})$ is planar, in the sense that although it can be distorted, \overline{n} always lies in a well-defined plane, viz. the yx' plane (the x' axis lies along the



FIGURE 2 Schematic wall referred to coordinates as used in text.



FIGURE 3 Symmetric (a) and asymmetric (b) model Carr walls consistent with the simplified assumptions under which expressions for transverse anisotropic viscous forces are derived in the text.

projection of $\bar{n}(\vec{r})$ in the *xz* plane). We let α be the angle between the wall and the *yx'* plane (i.e. $xox' = \alpha$).

In a real experiment the wall could be confined in a nematic layer parallel to the xz plane (e.g. with parallel plates located at y = 0 and y = l). Adjustment of the director field to the alignment at the top of the nematic layer and to the bulk surrounding the wall requires (mostly) splayed regions (cf. Figure 1). As required by continuity, at the bottom and the top of the wall, close to the surface of the nematic layer, the flow should divide into two parts along the z and -zdirections (cf. Figure 1). We neglect the effects of these flows.

In order to find the components F_x , F_z of the transverse forces in the walls we use

$$F_i = \frac{\partial t_{ji}}{\partial x_j} \tag{1}$$

(Summation over repeated indices is understood here and below.)

The t_{ji} are the components of the Leslie-Ericksen stress tensor for a nematic expressed in terms of the viscosity coefficients $\alpha_i (i = 1 \text{ to } 6)$:^{5,6}

$$t_{ij} = \alpha_1 n_i (n_k A_{ki} n_l) n_j + \alpha_2 n_i N_j + \alpha_3 n_j N_i + \alpha_4 A_{ij} + \alpha_5 n_i n_k A_{ki} + \alpha_6 n_j n_k A_{ki}$$
(2)

where

$$A_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right);$$

with v_i the *i*th components of flow velocity and

with
$$N_{i} = \dot{n}_{i} - \omega_{ik} n_{k}$$
$$\omega_{ij} = \frac{1}{2} \left(\frac{\partial v_{i}}{\partial x_{j}} - \frac{\partial v_{j}}{\partial x_{i}} \right);$$

 n_i are the director components. We find it convenient to express \bar{n} in spherical polar coordinates (r, θ, α) with r = 1, while θ is the angle between \bar{n} and the y axis, α as defined above is the angle between the projection of \bar{n} in the xz plane and the x axis. Thus $0 \le \alpha < 2\pi$ and $0 \le \theta < \pi$. In these coordinates:

$$\bar{n}(y,z) = \begin{pmatrix} \sin\theta\cos\alpha\\ \cos\theta\\ \sin\theta\sin\alpha \end{pmatrix}$$
(3)

where $\theta = \theta(y, z)$ and α is constant for a straight wall as is the case in the present treatment. The flow as shown in Figures 2 and 3 is along the y-axis and we assume its velocity varies only as a function of z. Thus

$$A = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{s}{2} \\ 0 & \frac{s}{2} & 0 \end{pmatrix}$$
(4)

with

$$s \equiv \frac{\partial v_y}{\partial z}; \qquad v_y = v_y(z)$$

In calculating N, we neglect $\dot{n} = \partial n_i / \partial t$, which is zero for static walls and introduces only a small renormalization of viscosities for walls of this kind moving at reasonable speeds.⁷ Thus:

$$N = \frac{s}{2} \begin{pmatrix} 0 \\ -\sin\theta\sin\alpha \\ \cos\theta \end{pmatrix}$$
(5)

D. IGNER AND J. FREED

We use Eqs. (1)-(5), the Parodi-Onsager relation: ^{5,6} $\alpha_6 - \alpha_5 = \alpha_2 + \alpha_3$, and also, we recognize that $t_{ij}(s, \theta, \alpha) = s(z)g_{ij}(\theta, \alpha)$, but α is independent of the x_i here as already noted. We find:

$$F_{x} = f_{1,x} \frac{\partial s}{\partial z} + f_{2,x} s \frac{\partial \theta}{\partial y} + f_{3,x} s \frac{\partial \theta}{\partial z}$$
(6)

$$F_{z} = f_{1, z} \frac{\partial s}{\partial z} + f_{2, z} s \frac{\partial \theta}{\partial y} + f_{3, z} s \frac{\partial \theta}{\partial z}$$
(7)

where

$$f_{1,x} = \frac{\alpha_1}{4} \sin^2\theta \sin 2\theta \sin \alpha \sin 2\alpha + \frac{\alpha_3 + \alpha_6}{4} \sin 2\theta \cos \alpha$$
$$f_{2,x} = \frac{\alpha_1}{4} \sin 4\theta \sin 2\alpha + \frac{(\alpha_6 - \alpha_3)}{4} \sin 2\theta \sin 2\alpha$$
$$f_{3,x} = \frac{\alpha_1}{4} (2\cos 2\theta \sin^2\theta + \sin^2 2\theta) \sin 2\alpha \sin \alpha + \frac{\alpha_3 + \alpha_6}{2} \cos 2\theta \cos \alpha$$

and

$$f_{1,z} = \frac{\alpha_1}{2} \sin^2\theta \sin 2\theta \sin^3\alpha + \frac{\alpha_6}{2} \sin 2\theta \sin \alpha$$
$$f_{2,z} = \frac{\alpha_1}{2} \sin 4\theta \sin^2\alpha - \frac{(\alpha_6 - \alpha_3)}{2} \sin 2\theta \cos^2\alpha$$
$$f_{3,z} = \frac{\alpha_1}{2} (2\sin^2\theta \cos 2\theta + \sin^2 2\theta) \sin^3\alpha + \alpha_6 \cos 2\theta \sin \alpha$$

The F_x , F_z components can be seen as composed of terms of two different origins: The terms in $(\partial s/\partial z) = (\partial^2 v_y/\partial z^2)$ can be nonzero in the presence of a uniform director distribution, the terms in $(\partial \theta/\partial x_i)$ require a distorted director distribution and just $s = (\partial v_y/\partial z) \neq 0$.

In a symmetric wall, the values of θ , α , s, $(\partial s/\partial z)$, $(\partial \theta/\partial y)$, $(\partial \theta/\partial z)$ in an element around x, y, z in one side of the wall relate to their values in the symmetry related element around x, y, -z by:

$$\begin{array}{ccc} \theta \to \theta; & \alpha \to \pi + \alpha; & s \to -s; \\ \frac{\partial s}{\partial z} \to \frac{\partial s}{\partial z}; & \frac{\partial \theta}{\partial y} \to \frac{\partial \theta}{\partial y}; & \frac{\partial \theta}{\partial z} \to \frac{-\partial \theta}{\partial z} \end{array}$$
(8)

Using (8) we find that TAVF in the two halves of a symmetric wall are

related by

$$F_{x}(x, y, z) = -F_{x}(x, y, -z)$$

$$F_{z}(x, y, z) = -F_{z}(x, y, -z)$$
(9)

and

 $F_z(x, y, z) = F_z(x + \delta, y, z)$

for any finite δ in an infinitely long wall. Also

$$F_x(x, y, z) = F_x(x + \delta, y, z)$$

To proceed further we note that $v_y(z)$ decreases rapidly to the sides in the +z and -z directions in the Carr model. This implies (in the absence of singularities) that $s \neq 0$ in at least part of the wall region with s > 0 for z < 0 and s < 0 for z > 0; we assume $(\partial s/\partial z) < 0$ corresponding to a maximum in v_y at z = 0. We shall also assume for simplicity that z = 0 is at the center of the wall.

Eq. 7 for F_{z} has a complex angular dependence, but we do note that as $\theta(y, z)$ varies as a function of coordinates within the wall, then it could be possible for F_{r} to change sign. This could be due to either sign change in $(\partial \theta / \partial y)$ and/or $(\partial \theta / \partial z)$ or else to the angular dependence of the $f_{i,z}$. In general, an overall negative F_z for z > 0(with a corresponding positive F_z for z < 0, cf. Eq. 9) would imply that the force components in the two sides of the wall point towards the interior of the wall (i.e. they are "focalizing"⁶ the flow toward the middle of the wall). While this is likely to be the dominant behavior in a stable wall, it could be that, as a wall grows, then in particular regions there would be a change of sign of F_z , which if large enough, could cause the flow to be pulled outward from the wall toward the sides before it reaches the top. We do wish to point out that in the case of an EHD the repulsive Coulombic forces associated with the charge flows, which we have not explicitly considered in our analysis, would tend to help this "outward refocussing." In an EHD, this could possibly cause a longitudinal splitting of the wall. The flows and the charges ejected out of the wall to the sides could interact with the director field and cause formation of two new splay-bend distortions on the sides, distortions which will focalize⁶ the flows and replace the central splay-bend "heap." One of the possible "scenarios" for such a mechanism is illustrated in Figure 4 together with a further possible step which could bring about formation of "core flow" [sec. III, B-2a in IF]. Other possible ways will be discussed in an example below. Static and dynamic splitting of what are thought to be Carr walls are actually seen in EHD's. For example, every second wall in the right



FIGURE 4 Suggested mechanism for Carr wall splitting in Electrohydrodynamic instabilities. The details of possible mechanisms are sensitive to the set of Leslie's viscosity coefficients α_i . Dominance of a positive α_1 is supposed in this simple example (vs. α_6 dominance in the example discussed in the text). (a) Unsplit wall. (b) Sharpening of the distortion (occuring during the wall growth, or under higher excitation voltages) can cause transverse viscous body forces on the flows to become directed toward the outside of the wall. These forces could cause flows to get out of the wall, on the sides, where they create new splay-bend distortions (broken lines). (c) The central heap is replaced by a double humped structure which focalizes a new flow configuration. (d) Sharpening of the two "humps" can bring creation of "core flow" (the flow between walls) in a way similar to transition from (a) to (b) and also because of continuity requirements.



FIGURE 5 A suggested interpretation of the VGMV instability³ showing (a) the director distribution in an *a*-type sample prior to application of an electric field; (b) the director distribution in the walls and surroundings in the presence of an electric field, in which the oblique boundaries are assumed to induce the asymmetry in the walls; (c) the flow lines and velocity profile; (d) "VGMV" schematic showing the outward flow lines from the wall.

"Flow figures"



FIGURE 6 A suggested interpretation of the "flow-figure" of the low voltage type a sample DC instability of Ref. (3). (a)–(d): similar to Figure 5 except for the flow-figure.

side of the photograph 5 plate 8 in IF showing a VGMV instability appears to be longitudinally split; (this is not very easily visible in the printed reproduction). Our suggested model for the VGMV is illustrated in Figure 5. The replication mechanism of the type **a** sample low voltage DC instability of IF (sec. III, B2a and plates 3, 4, 5, Ref. 3 and illustration in Figure 6 here) also involves a local or propagated splitting of the wall, leading to the formation of a core flow.³ "Bad" flow figures (IF, sec. III, B2a and photograph 1 plate 8) also possess double-walled "branches" apparently containing an elongated core flow in between. Splitting is also seen in Williams Domains lines above the threshold, in a regime in which the Carr wall model might apply (e.g. Figure 26b, Ref. 6).

In order to make further progress with Eq. 7 to illustrate the TAVF mechanism for wall splitting we need to know the relative magnitudes of the viscosity coefficients α_1 , α_3 , and α_6 . These are not known for nearly all liquid crystals. If we regard the set of values that have been fairly accurately determined for MBBA as indicative ($\alpha_1 = 6.5 \pm 4$, $\alpha_3 = -1.1 \pm 0.2$, and $\alpha_6 = -34 \pm 2$ in units of cp. at room temperature)^{8a} we would be led to conclude that α_6 is dominant and negative. It has been argued that α_1 should be small.⁸ Then we obtain:

$$f_{1,z} \approx \frac{\alpha_6}{2} \sin 2\theta \sin \alpha$$
$$f_{2,z} \approx -\frac{\alpha_6}{2} \sin 2\theta \cos^2 \alpha$$
$$f_{3,z} \approx \alpha_6 \cos 2\theta \sin \alpha$$

Experimentally, (for the Nematic Phase V) $\alpha \approx 20^{\circ} - 25^{\circ}$.³ Thus for $z > 0, f_{1z}(\partial s/\partial z)$ makes a positive contribution to F_z , while the sign of $f_{2,z}s(\partial\theta/\partial z)$ is opposite to the sign of $(\partial\theta/\partial z)$, and that of $f_{3,z}s(\partial\theta/\partial z)$ is the same as the sign of $(\partial\theta/\partial z)$ for $\theta < 45^{\circ}$ and opposite for $\theta > 45^{\circ}$. In Figure 3a we observe that for this symmetric director pattern: $(\partial \theta / \partial y) < 0$ and $(\partial \theta / \partial z) < 0$ for z > 0. Thus a "focalization" of flows in the wall would require that $f_{3,z}s(\partial\theta/\partial z)$ be dominant in F_z and $\theta(y, z) < 45^\circ$ over most of the wall. However, in a region of large $\theta(y, z)$ this term would become positive, and this would cause a change in sign of F. In Figure 2, θ will be large only near z = 0, but $s \approx 0$ for $z \approx 0$, so this may not be satisfactory to achieve a change of sign in F_r . But if the first two terms in Eq. 7 are making appreciable contributions, then it would only be necessary for the third term to decrease somewhat due to an increase in θ for F, to change sign. Another possibility is to note, in Figure 1, that there are upper splay regions shown [for which there is some experimental evidence, namely interference fringes contouring around the outer side of the A-shape form (cf. Figure 6) of the flow figures³]. In these regions $(\partial \theta / \partial z) > 0$ for z > 0, so they could be regions of "outward" refocussing" if $f_{3,z}s(\partial\theta/\partial z)$ is dominant. In concluding this example, we remind the reader that we do not yet know what the unique physical properties of Phase V are that lead to observations shown in IF but are not observed in MBBA. Thus this example is largely for illustrative purposes.

Perhaps an even more likely effect of TAVF could be the movement of asymmetric walls. Asymmetric Carr walls could be formed by oblique boundary conditions³ (cf. Figure 3b, 5 or 6), or close to places of irregularities in the preparation of planar samples (which induce some kind of asymmetry over regions of the nematic), or with arrangements which lead to creation of inhomogeneous electric fields in planar samples.⁹ For focalizing flows in a static wall the resultant TAVF, $F_x \mathbf{i} + F_z \mathbf{k}$ in the two sides of a symmetric wall are equal and opposite and balance to zero net transverse force (except perhaps for small regions at the ends of the walls). When the wall is asymmetric, the sum of the TAVF of the two halves of the wall could become nonzero. The net TAVF could cause the flow inside the wall to move in the xz plane. The nematic splay-bend distortion would tend to move to adjust to the shifting mass and charge flow as this moves in the xz plane. This is because flow, charge, and distortion are coupled: fluctuation in one of these quantities brings about the adjustment of the others. (This was shown to be the case close to the threshold for instability in simple EHD's,^{6,10} and we have no reason to suspect it

will not be the case in related EHD's and at higher excitation regimes.) In the experiments in IF^3 , movement of presumed asymmetric Carr walls was observed. For example, the flow figures with and without core flow of IF (sec. III, B2a and plates 3–6 of Ref. 3, illustrated here in Figure 6), interpreted in IF (sec. III, B4) in terms of Carr walls (but without mention of asymmetry) are examples of what could be asymmetric Carr walls moving under resultant TAVF.

Two other phenomena in which, we believe, TAVF could play a role, are the growth in length of the walls (e.g. growth of the "branches" of flow figures, sec. IIIB, 2a in IF) and the process of folding and unfolding (sec. IIIB, 2b in IF). Unbalanced F_x components due to asymmetry in (or end effects of) the walls might eject charged flows out of the open end of a growing wall. These charged flows could cause further splay-bend distortions and y axis oriented flows, thus elongating the wall.¹¹ We also suspect that the incipient stage of the folding process (sec. IIIB, 2b in IF) could be caused by the sudden growth of unbalanced F_x forces in (what we believe are) asymmetric Carr walls which will tend to take on the slope of a sine generated curve¹² under this stress, if the only constraint is a single fixed end toward which the F_x resultant is directed. The subsequent development of this process seems to be much more intricate.

III. DISCUSSION

While the above suggested mechanisms for phenomena in IF involving what are believed by the authors to be Carr walls might have a role to play in some of the EHD's of that study, further work will be needed to prove this. Explanations in terms of the Carr wall model were advanced in IF for the VGMV and the low voltage a- and p-type sample DC EHD's (sec. IIIB in IF). The experimental observations are compatible with the Carr wall explanation, but cannot, as yet, be regarded as providing firm proof of the existence of Carr walls in these instabilities. While the flows between the presumed Carr walls of the VGMV and the core flow surrounded by the presumed cylindrical Carr wall (of the low voltage a type cell DC instability) were established by observation of dust particle movement, the same kind of observation within the presumed walls themselves are still not conclusive.¹³ The sudden jump of a dust particle when it hits a "wall" could be of electrostatic or other origin than from encountering a strong flow; the behavior of a dust particle encountering a cylindrical wall is not always the same, and the observations of IF in this respect are still incomplete. The evidence for existence of flows in the "branches" of the flow figures (sec. IIIB, 2a IF) which are supposed to be Carr walls, too, is still only indirect.

The possibility that the Carr wall model could lead to an explanation of dynamical phenomena observed in IF, as we have suggested in Sect. II, may be regarded as further indication that these observed EHD's could possibly involve Carr walls. Certainly further work is necessary to prove this.

We also wish to remark that TAVF might play a role in some EHD's close to the threshold, too. This can happen in EHD where there exists a bend or a splay-bend mode associated with flows (like the case of Williams domains), if there is no symmetry about any plane perpendicular to the wavevector of the mode. Our arguments about movement of asymmetric Carr walls are not specific to the non-linear regime, narrow walls and flows etc., and could be adapted to apply to lower excitation regimes. Quite often at voltages slightly lower than the overall threshold for instability of Williams Domains,^{6,14} moving rolls are observed to originate at places of imperfection in the sample (of a quite common but yet unidentified kind¹⁵). The rolls are continuously emitted (i.e. not discretely) and the resulting undulating pattern fades away at a distance which grows with increasing voltage.

The movement of these rolls as well as the movement of the solitary vortices observed by Ribotta⁹ under conditions in which there is obvious asymmetry about any plane perpendicular to the direction of their movement, could also possibly be caused by unbalanced TAVF of the type we have suggested for movement of asymmetric Carr walls. Clearly, further experimental investigation of such phenomena under more controlled conditions is required before one can accept such a model.

Acknowledgment

We wish to thank Professor James T. Jenkins for a critical reading of the manuscript.

References

 E. F. Carr in Liquid Crystals and Ordered Fluids III, edited by J. F. Johnson and R. S. Porter (Plenum, New York, 1978), p. 165; b) C. E. Tarr and E. F. Carr, Solid State Commun., 33, 359 (1980). As described by Carr, the walls might involve some twist.

- 1b. Strictly speaking, walls that are not perpendicular to the plane of the splay and bend also involve twist. In keeping with tradition (cf. refs. 7) we also call these walls splay bend.
- (a) E. Guyon, R. Meyer and J. Salan, Mol. Cryst. Liq. Cryst., 54, 261 (1979);
 (b) E. F. Carr, Mol. Cryst. Liq. Cryst., 34, 159 (1977).
- 3. D. Igner and J. H. Freed, J. Chem. Phys., 76, 6035 (1982). Referred to as IF.
- 4. P. Pieranski and E. Guyon, Phys. Lett., 29A, 237 (1974).
- 5. J. T. Jenkins, Ann. Rev. Fluid Mech., 10, 197 (1978).
- E. Dubois-Violette, G. Durand, E. Guyon, P. Manneville and P. Pieranski in Solid State Physics, Supplement 14, Liquid Crystals, edited by L. Liebert, Academic Press, New York, 1978, pp. 147-208.
- 7a. F. Brochard, J. Phys. (Paris), 33, 607 (1972). b) L. Leger, Mol. Cryst. Liq. Cryst. 24, 33 (1973).
- 8. W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach, N.Y. (1980).
- 9. R. Ribotta, Phys. Rev. Lett., 42, 1212 (1979).
- 10a. P. G. de Gennes, Comments Solid State Phys., 3, 35, 148 (1970).
- 10b. P. G. de Gennes, The Physics of Liquid Crystals (Clarendon, Oxford, 1974).
- 11. A more obvious mechanism for growth of walls would be by propagation of splay-bend distortion from the end of the wall into the nematic bulk (since nematics transmit torques^{10b}). The prolongation of the splay-bend distortion will focalize new flows which in their turn will enhance the newly created distortion, etc.
- 12. L. B. Leopold and W. B. Langbein, Sci. Am., 214, 60 (1966).
- 13. Since the publication of Ref. 3 the authors have not carried out any more observations in this direction.
- 14. R. Williams, J. Chem. Phys., 39, 384 (1963).
- 15. D. Igner and J. H. Freed, unpublished results. These are SiO coated electrode samples. The authors believe that other researchers should have noted this kind of moving rolls, but no mention could be found in the literature.