

Shear thickening in dilute solutions of wormlike micelles

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Abstract. – A new mechanism is suggested for shear thickening in dilute solutions of wormlike micelles. According to this mechanism, there is an instability above a critical shear rate, $\dot{\gamma}_c$, by which micelles aggregate to form networks of bundles. We examine the first step of this instability by studying the aggregation of two micelles into a paired bundle. The model predicts that $\dot{\gamma}_c$ is given by the inverse of the time necessary for the two micelles to unbind from each other. The order of magnitude and temperature dependence of the predicted $\dot{\gamma}_c$ are in good agreement with experimental measurements. In addition, the model provides a natural explanation for the observation of coexistence between the shear-induced structure and a dilute phase at fixed shear stress.

Introduction. – Many surfactant molecules self-assemble in solution to form long cylindrical micelles. While great progress has been made in understanding the rheological behavior of such systems [1–3], some fundamental problems still remain to be understood. Some of the most intriguing phenomena are the shear thickening and rheopexy observed in a wide class of low-concentration wormlike micellar solutions. These solutions can exhibit a steep increase of the viscosity in shear flow as the shear rate exceeds a critical value, $\dot{\gamma}_c$, as well as a decrease of the drag in turbulent flow [4–6]. These phenomena are attributed to the formation of a shear-induced structure (SIS) [7–12, 20]. The following common characteristics are observed:

- Shear thickening occurs in solutions of cylindrical micelles made of cationic surfactants (*e.g.*, CTAB) with a strongly bound counterion (*e.g.*, the salicylate ion Sal^-). The counterion typically has a hydrophobic moiety and acts like a co-surfactant [13].
- The shear thickening transition is observed in the dilute regime, where the rodlike micelles are not entangled [8, 11].
- The critical shear rate exhibits an Arrhenius temperature dependence [8, 12, 14, 21]: $\dot{\gamma}_c \propto \exp[-E/k_B T]$, where E is an activation energy.

On the theoretical side, shear thickening has been attributed to shear-induced gelation into a network of long micelles [15–18]. In all these theoretical approaches, gelation occurs when the shear rate is high enough to overcome the rotational Brownian diffusion of the rodlike micelles. Thus, they predict a critical shear rate of the order of the rotational diffusion constant of a rod D_r [19]:

$$\dot{\gamma}_c \sim D_r \sim \frac{k_B T}{\pi \eta L^3}, \quad (1)$$

where L is the length of the rods and η is the viscosity of the solvent. However, several authors [8, 20, 21] have pointed out that this prediction (1) does not agree with experimental results. For average micellar lengths of several hundred angstroms, D_r is roughly 10^5 – 10^6 s $^{-1}$, several orders of magnitude higher than the measured critical shear rates of 1 s $^{-1}$ – 500 s $^{-1}$ [7–12, 21].

In this letter, we present a new mechanism for the formation of SIS in which the micelles collide under the shear flow and aggregate into bundles. In contrast to previous theoretical approaches, we attribute shear-induced gelation to inter-micellar interactions. Similar ideas are suggested in [20]. We argue that there is a metastable attractive minimum in the interaction potential when the two micelles are close together and nearly parallel and a stable repulsive minimum when the micelles are far apart and perpendicular. These two minima are separated by a barrier of height ΔE . In equilibrium, collisions at small angles can lead to aggregation of micelles, but the micelles can then unbind on some time scale τ set by the barrier height. Under shear flow, we assume that the collision rate is given by the shear rate $\dot{\gamma}$ [18, 22, 23]. When the shear rate is small compared to $1/\tau$, there is enough time between collisions for two aggregated micelles to unbind, so the shear flow has no effect on the structure of the solution. When $\dot{\gamma}$ exceeds $1/\tau$, however, there is not enough time for the micelles to unbind between the collisions, so bundles will form and grow in thickness. Thus, this simple analysis shows that the critical shear rate predicted by our model is given by the inverse of the unbinding time τ . For solutions of sufficiently high concentration that are still unentangled, the micelles should aggregate into a network of bundles instead of isolated bundles. This network is the shear-induced structure (SIS).

Calculation of inter-micellar interaction energy. – In order to estimate the unbinding time τ , we must calculate the barrier height. The wormlike micelles are composed of cationic surfactants with strongly bound anionic counterions that we will consider as cosurfactants. Both species can move freely along the micelles so that the local charge density and the position of the charges are not frozen. For entropic reasons, some counterions must stay free in the solution, so the fraction of bound counterions per surfactant, f , is below unity and each micelle carries a positive net charge. Thus, the micelles can be described as polyampholytes with a net charge. If the micelles were neutral ($f = 1$), they would attract each other even under quiescent conditions [24, 25]. This is because the charges within the micelles can rearrange and charge distributions on different micelles can become correlated so that a positive charge on one micelle is matched by a negative charge on the adjacent site of another micelle. This correlation attraction is similar in origin to the attraction between like-charged rods mediated by multivalent counterions [26–28], which leads to bundle formation. Because the micelles carry a total net charge ($f < 1$), they also repel each other. As f decreases from unity, the attraction should weaken relative to the repulsion and the attractive minimum should first become metastable and then disappear. We note that under quiescent conditions, micelles do not tend to form bundles, which implies that the attractive minimum is not the stable one.

Here we estimate the interaction potential between wormlike micelles. The electrostatic interaction energy can be obtained by summing up the screened Coulomb interaction between the charges on one rod with the charges on the other rod:

$$E_{\text{tot}} = l_B \sum_{1,2} q_1 q_2 \frac{\exp[-Kr_{12}]}{r_{12}}, \quad (2)$$

where K is the inverse Debye screening length, r_{12} is the distance between the ions on the first and the second rod. Here, q_1 and q_2 are the charges of the ions. In order to describe the experimental systems, we consider cylindrical rods of length L and radius $R = 22$ Å [10], which carry surface charges of both signs with a total net charge $Q = \frac{2\pi RL}{A}(1-f)e$, where A is the

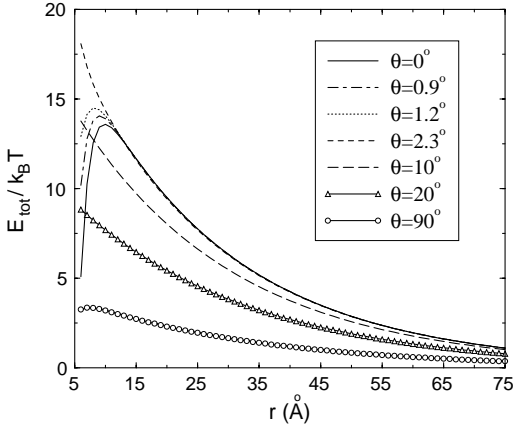


Fig. 1

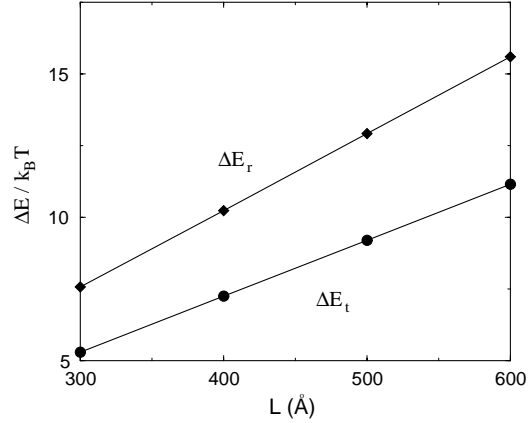


Fig. 2

Fig. 1 – Electrostatic interaction energy of two rods as a function of the separation r , with $L = 500 \text{ \AA}$ and $f = 0.94$, for different angles between the rods.

Fig. 2 – Dependence of barrier heights ΔE_t and ΔE_r on rod length L at $f = 0.94$.

area per charge ($\sim 90 \text{ \AA}^2$ [29]), e the elementary charge and f the fraction of counterions per surfactant molecule. We will consider the range $0.9 < f < 0.95$. The lower limit is given by the Manning calculation [30] and the upper one comes from light scattering measurements [31].

To obtain an upper bound on the strength of the attraction, we calculate the electrostatic interaction between two rods in the limit of maximum correlation [32]. Qualitatively similar results were obtained previously for a related model using a high-temperature approach [33]. At maximum correlation, there is perfect alternation of positive and negative charges on the surfaces of each rod, and the charge on one rod will be opposite in sign to the adjacent charge on the other rod. In our simple model, we assign a charge of 1 to the cationic surfactants and a charge of $-f$ to the counterions. (In reality, of course, the counterions carry a charge of -1 and there are f counterions per surfactant. Our simplification should have an insignificant effect compared to the assumption of maximum correlation.)

In fig. 1, we plot the interaction energy as a function of separation, r , for several different angles between the rods. The competition between the correlation attraction and the electrostatic repulsion leads to a potential with two minima: a metastable attractive minimum at $\theta = 0$ and small r corresponding to aggregation of two parallel rods (see the solid curve in fig. 1) and a stable repulsive minimum at $\theta = 90^\circ$ and large r corresponding to two separated perpendicular rods (see the circles in fig. 1). Note that we cut off the interaction below $r = 6 \text{ \AA}$ and assume a preferred separation of 6 \AA in the aggregated state because this is a typical intermolecule distance in a condensed DNA bundle [34]. The corresponding numbers for wormlike micelles are not known. We impose this cutoff because our simple model predicts that the interaction diverges at $-\infty$ in the limit $r \rightarrow 0$. In a more realistic model with short-ranged hard-core repulsions, we would obtain a minimum at small $r \simeq 6 \text{ \AA}$ and the potential would diverge to $+\infty$ in the limit $r \rightarrow 0$.

The metastable attractive minimum (at $r = 6 \text{ \AA}$ and $\theta = 0^\circ$) and stable repulsive minimum (at $r = \infty$ and $\theta = 90^\circ$) are separated by a barrier. In fig. 2 we plot the barrier heights ΔE_t (circles) and ΔE_r (squares) along two paths (fixed angle and fixed separation, respectively) as a function of micellar length L . Here, ΔE_t is the barrier encountered by two rods as

they unbind by translational motion at fixed parallel orientation ($\theta = 0^\circ$). Similarly, ΔE_r is the barrier encountered by two rods as they unbind by rotational motion at fixed separation ($r = 6 \text{ \AA}$). The barrier heights ΔE_t and ΔE_r both increase linearly with L , as shown in fig. 2. These results are in accord with earlier results using a high-temperature approximation [33], showing that qualitative trends are independent of the approximations used. However, the actual numbers are quite sensitive to the choice of cutoff at $r = 6 \text{ \AA}$. The barrier heights would be higher if the preferred intermicellar separation were smaller than 6 \AA .

We find that ΔE_t and ΔE_r depend only weakly on the bound counterion fraction f . The most important effect of f is to change the stability of the attractive minimum: for $f < 0.95$, the attractive minimum is metastable (the interaction energy at $r = 6 \text{ \AA}$ is positive), while for $f > 0.95$, the attractive minimum is stable. Note that we have overestimated the strength of the attraction by assuming maximum correlation, so the actual threshold in f may be somewhat bigger than $f = 0.95$.

In summary, for $0.9 < f < 0.95$ and $300 \text{ \AA} < L < 600 \text{ \AA}$, corresponding to the values measured in experiments, we estimate barrier heights in the following ranges: $5.5k_B T < \Delta E_t < 11k_B T$, $7.5k_B T < \Delta E_r < 16k_B T$. These are the barriers that must be overcome by translational or rotational motion in order for two rods to unbind.

Calculation of critical shear rate. – As discussed earlier, the critical shear rate in our model is given by $\dot{\gamma}_c \approx 1/\tau$, where τ is the time required for two micelles to unbind, or to cross the barrier from the metastable attractive minimum to the stable repulsive minimum. Because the interaction energy depends on both the angle between the rods and the separation between the rods, the time to cross the barrier depends on both the rotational and translational diffusion coefficients. We define two times: τ_r is the characteristic time to cross the barrier ΔE_r by rotating from a parallel configuration to a perpendicular one at fixed separation $r = 6 \text{ \AA}$, and τ_t is the characteristic time to cross the barrier ΔE_t by translating at parallel orientation. The unbinding time τ is approximately the smaller of these two times.

Based on Kramer's theory [36], we estimate the time scales τ_r and τ_t as follows:

$$\tau_r \simeq \frac{1}{D_r} \exp \left[\frac{\Delta E_r}{k_B T} \right] \quad \text{and} \quad \tau_t \simeq \frac{K^{-2}}{D_t} \exp \left[\frac{\Delta E_t}{k_B T} \right], \quad (3)$$

where $D_t \simeq k_B T / (\pi \eta L)$ is the translational diffusion constant in a dilute solution of rods of length L [19], and D_r is the rotational diffusion constant defined in eq. (1). For a millimolar ($\sim 10 \text{ mMol}$) solution (with $K^{-1} = 30 \text{ \AA}$, $\eta = 10^{-3} \text{ Pa s}$ and $T = 300 \text{ K}$) of rods of length $300 \text{ \AA} < L < 600 \text{ \AA}$, we find that it is faster for the rods to unbind by translation than by rotation ($\tau_t \ll \tau_r$). This implies that the critical shear rate is given by the following expression:

$$\dot{\gamma}_c \simeq \frac{1}{\tau_t} \simeq D_t K^2 \exp \left[-\frac{\Delta E_t}{k_B T} \right]. \quad (4)$$

For rods of length $L = 600 \text{ \AA}$, (4) predicts $\dot{\gamma}_c \simeq 40 \text{ s}^{-1}$ and for $L = 300 \text{ \AA}$, $\dot{\gamma}_c \simeq 10^4 \text{ s}^{-1}$. The lower estimate is in good agreement with experimental observations [7–12].

Note that (4) predicts the same temperature dependence (*e.g.*, Arrhenius law) as observed in the experiments. The barriers measured experimentally, however, tend to be somewhat higher than we have predicted. For systems with salt, the Arrhenius coefficient is approximately $20\text{--}30k_B T$ [14, 37], and for systems without salt, the Arrhenius coefficient is even bigger, approximately $100 k_B T$ [10, 21]. The Arrhenius coefficient is not the same as the energy barrier that we have calculated, because we have assumed that the micellar length L and bound counterion fraction f do not depend on temperature. In experiments, these parameters cannot be fixed and their temperature dependence will contribute to the Arrhenius coefficient.

The dependence of (4) on salt concentration is complex. The barrier height ΔE_t depends on salt in two ways: first, salt affects the electrostatic interactions, and second, salt affects the micellar length. Salt also controls the barrier thickness. Perhaps this is why trends of the critical shear rate with salt and with concentration vary so much from a system to another [7, 21].

Note that we have assumed that the critical shear rate is given by the rate for two rods to unbind. This is because the barrier height for a rod to unbind from an N -rod bundle increases with N as $N^{1/4}$ [35]. The characteristic time for a rod to escape from a 3-rod bundle is therefore longer than the time for two rods in a pair to unbind. As a result, once $\dot{\gamma}$ is high enough to form aggregated pairs ($\dot{\gamma} > \tau^{-1}$), there is an instability towards the formation of thick bundles.

Dynamical equilibrium between dilute and gel phases. – Our picture is consistent with experiments performed by Hu *et al.* [38, 39], in which they observe dynamical phase coexistence at fixed shear stress. At low shear stress, the solution has a low viscosity, η_d . Above a critical shear stress Hu *et al.* observe dynamical phase coexistence between the low-viscosity phase (dilute phase) and the SIS (gel phase). As the stress increases, they find that the volume occupied by the gel phase increases. We can understand this result within the context of our model in terms of a dynamical equilibrium between a dilute phase of isolated micelles and a network of bundles of micelles (the SIS or gel phase). Suppose the dilute phase has a viscosity η_d and the gel phase has a viscosity $\eta_g \gg \eta_d$. When the shear stress is below $\sigma_c = \eta_d \dot{\gamma}_c$, there is no bundle formation and shear flow has no effect on the structure of the solution, as we discussed earlier. For $\sigma > \sigma_c$, however, shear-induced collisions lead to bundle formation in the dilute phase and a gel phase begins to form. The rate at which micelles “condense” from the dilute phase into the gel phase, k_{cond} , depends on the shear rate in the dilute phase, σ/η_d , and is nonzero only above the critical shear rate, σ_c/η_d :

$$k_{\text{cond}} = (\sigma - \sigma_c)/\eta_d. \quad (5)$$

On the other hand, micelles can “evaporate” from the gel phase into the dilute phase by escaping over the barrier (by unbinding from bundles). Since the viscosity of the gel phase is very high, the shear rate in the gel phase is very small, below the critical shear rate $\dot{\gamma}_c$. Thus, micelles can unbind and “evaporate” from the gel with a rate

$$k_{\text{evap}} = 1/\tau_{\text{bundle}}, \quad (6)$$

where the time to unbind from a bundle of average thickness satisfies $\tau_{\text{bundle}} \gg \tau$, where τ was estimated earlier as the time for two rods to unbind from each other. The time scale τ_{bundle} is the time required for the SIS to disappear upon cessation of shear.

One can construct a phenomenological model for the kinetics of gel formation based on (5)-(6) that is similar to ref. [40]. The resulting model predicts dynamical coexistence at fixed stress and a discontinuity in the stress at fixed shear strain rate [41], as is observed [39].

Conclusion. – In this letter, we present a new mechanism to explain the formation of shear-induced structures in dilute solutions of wormlike micelles. We propose that electrostatic correlation attractions lead to the formation of metastable bundles. This is consistent with light scattering results [11]. We have calculated the first step of bundle formation, where two rods aggregate to form a pair. Once two rods aggregate, there is an instability to bundle formation because the barrier height increases with bundle size.

Isolated bundles of micelles would probably not lead to the substantial shear thickening observed experimentally. However, networks of bundles are a generic morphology in closely

related systems, namely solutions of DNA or F-actin with multivalent counterions. A similar electrostatic correlation attraction mediated by multivalent counterions is believed to lead to condensation of DNA or F-actin into bundles under quiescent conditions [34, 42]. In such solutions, isolated bundles form at sufficiently dilute concentrations, but networks of bundles tend to form at concentrations near but below overlap [34, 43]. In the case of micelles, it seems reasonable that polydispersity in the micellar length will further encourage network formation.

The above argument suggests that shear thickening may not occur in sufficiently dilute solutions of wormlike micelles. A very dilute solution might contain isolated bundles above some critical shear rate, but there may be no shear thickening. On the other hand, our picture can also explain why shear thickening is not observed in sufficiently concentrated solutions of wormlike micelles. In quiescent solutions above the entanglement concentration, the micelles will tend to cross each other at an angle of 90° because they repel each other. Since aggregation of micelles into bundles can only occur when micelles are nearly parallel, shear-induced bundling will be suppressed.

We note that the shear-induced structure (SIS) we have proposed, a network of bundles, is consistent with images obtained by freeze-fracture microscopy [44]. However, it is difficult to obtain a clear description of the SIS from experiments. Thus, it is difficult to test our picture by determining directly whether the SIS is indeed a network of bundles. Fortunately, our model can be tested indirectly in a number of ways that we list below.

First, the depth of the metastable attraction in our model depends sensitively on the net micellar charge. If the micelles are sufficiently close to neutral, we predict that the attractive minimum is stable, and that one should therefore observe bundles under quiescent conditions. It may be possible to decrease the net charge of the micelles by increasing the hydrophobicity of the counterion. Another possibility is to use divalent counterions, which would simultaneously increase the attraction and decrease the net charge of the micelle.

Second, several aspects of our model can be tested by using solutions of semiflexible polyelectrolytes, which should exhibit shear thickening when multivalent counterions are present. It is known that DNA condensation (*i.e.* bundle formation) does not occur below some threshold concentration of multivalent counterions. We speculate that shear might induce bundling in solutions below (but near) this threshold. There is some evidence that solutions of F-actin can shear-thicken by bundling [45]. Experiments on polyelectrolyte solutions would be particularly useful because the chain length does not vary with salt concentration or other parameters. One could test our prediction that the critical shear rate should depend exponentially on chain length. In addition, one should be able to alter the critical shear rate by varying the valency of the counterion.

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REFERENCES

- [1] CATES M. E., *Macromolecules*, **20** (1987) 2289.
- [2] TURNER M. S. and CATES M. E., *J. Phys. II*, **2** (1992) 503.
- [3] SPENLEY N. A., CATES M. E. and LEISH T. C. B., *Phys. Rev. Lett.*, **71** (1993) 939.
- [4] OHLENDORF D., INTERHAL W. and HOFFMANN H., *Rheol. Acta*, **25** (1986) 468.
- [5] SMITH B. C., CHOU L. C. and ZAKIN J. L., *J. Rheol.*, **38** (1994) 73.
- [6] HOFMANN S., STERN P. and MYSKA J., *Rheol. Acta*, **33** (1994) 419.

- [7] WUNDERLICH I., HOFFMANN H. and REHAGE H., *Rheol. Acta*, **26** (1987) 532.
- [8] HOFMANN S., RAUSCHER A and HOFFMANN H., *Ber. Bunsenges. Phys. Chem.*, **95** (1991) 153
- [9] BOLTENHAGEN P., HU Y., MATTHYS E. F. and PINE D. J., *Europhys. Lett.*, **38** (1997) 389.
- [10] BERRET J.-F., GAMEZ-CORRALES R., OBERDISSE J., WALKER L. M. and LINDNER P., *Europhys. Lett.*, **41** (1998) 677.
- [11] LIU C.-H. and PINE D. J., *Phys. Rev. Lett.*, **77** (1996) 2121.
- [12] HARTMANN V. and CRESSELY R., *J. Phys. II*, **7** (1997) 1087.
- [13] RAO U. R. K., MANOHAR C., VALAULIKAR B. S. and IYER R. M., *J. Phys. Chem.*, **91** (1987) 3286.
- [14] HU Y., WANG S. Q. and JAMIESON A. M., *J. Rheol.*, **37** (1993) 531.
- [15] CATES M. E. and TURNER M. S., *Europhys. Lett.*, **11** (1990) 681
- [16] TURNER M. S. and CATES M. E., *J. Chem. Soc. Faraday Trans.*, **87** (1991) 2073.
- [17] WANG S. Q., *Macromolecules*, **24** (1991) 3004.
- [18] BRUINSMA R., GELBART W. M. and BEN-SHAUL A., *J. Chem. Phys.*, **96** (1992) 7710.
- [19] DOI M. and EDWARDS S. F., *The Theory of Polymer Dynamics* (Oxford University Press, New York) 1986, p. 297.
- [20] ODA R., WEBER V., LINDNER P., PINE D.J., MENDES E. and SCHOSSELER F., *Langmuir*, **16** (2000) 4859.
- [21] GAMEZ-CORRALES R., BERRET J.-F., WALKER L. M. and OBERDISSE J., *Langmuir*, **15** (1999) 6755.
- [22] VON SMOLUCHOWSKI, *Z. Phys. Chem.*, **92** (1917) 129.
- [23] *The collision rate should be given by the shear rate when there are no inter-micellar interactions. The effect of interactions on the collision rate is complex, and is the subject of ongoing work.*
- [24] HIGGS P. G. and JOANNY J. F., *J. Chem. Phys.*, **94** (1991) 1543.
- [25] CORPART J. M. and CANDAU F., *Macromolecules*, **26** (1993) 1333.
- [26] GRONBECH-JENSEN N., MASHL R. J., BRUINSMA R. F. and GELBART W. M., *Phys. Rev. Lett.*, **78** (1997) 2477.
- [27] HA B. -Y. and LIU A. J., *Phys. Rev. Lett.*, **79** (1997) 1289.
- [28] SHKLOVSKII B. I., *Phys. Rev. Lett.*, **82** (1999) 3268.
- [29] IMAE T., KAMIYA R. and IKEDA S., *J. Colloid Interface Sci.*, **108** (1985) 215.
- [30] MANNING G. S., *J. Chem. Phys.*, **51** (1969) 924.
- [31] BELLOUR M., KNAEBLE A., MUNCH J.P. and CANDAU S.J., preprint.
- [32] ARENZON J. J., STILCK J. F. and LEVIN Y., *Eur. Phys. J. B*, **12** (1999) 79.
- [33] HA B.-Y. and LIU A. J., *Europhys. Lett.*, **46** (1999) 624.
- [34] BLOOMFIELD V. A., *Biopolymers*, **31** (1991) 1471.
- [35] HA B.-Y. and LIU A.J., unpublished. Note that the N -dependence of the barrier height quoted in ref. [33] is incorrect for a cylindrical bundle.
- [36] VAN KAMPEN N. G., *Stochastic Processes in Physics and Chemistry* (North-Holland Publishing Company, Amsterdam) 1981.
- [37] HU Y., RAJARAM C. V., WANG S. Q. and JAMIESON A. M., *Langmuir*, **10** (1994) 80.
- [38] BOLTENHAGEN P., HU Y., MATTHYS E. F. and PINE D. J., *Phys. Rev. Lett.*, **79** (1997) 2359.
- [39] HU Y. T., BOLTENHAGEN P. and PINE D. J., *J. Rheol.*, **42** (1998) 1185.
- [40] GOVEAS J. L. and PINE D. J., *Europhys. Lett.*, **48** (1999) 706.
- [41] BARENTIN C., LIU A. J., PINE D. J., unpublished.
- [42] TANG J. X. and JANMEY P. A., *J. Biol. Chem.*, **271** (1996) 8556.
- [43] STEVENS M. J., *Phys. Rev. Lett.*, **82** (1999) 101.
- [44] KELLER S. L., BOLTENHAGEN P., PINE D. J. and ZASADZINSKI J. A., *Phys. Rev. Lett.*, **80** (1998) 2725.
- [45] CORTESE J. D. and FRIEDEN C., *J. Cell. Biol.*, **107** (1988) 1477.