

Behaviour of materials in magnetic fields studied by small-angle X-ray scattering

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Traditionally the combination of electromagnetic fields and small-angle X-ray scattering has been mainly employed in the study of liquid crystals. However, with stronger magnetic fields becoming available owing to developments in superconductor technology it is possible to access a domain where larger macromolecular materials show, in some cases, a susceptibility to magnetic fields due to diamagnetic interactions. This effect can be used in several ways. The most obvious one is to use the alignment of the molecules to perform fibre diffraction experiments. Using an on-line split coil super-conducting magnet it is also possible to perform time-resolved studies on the re-orientation of, for instance, smectic liquid crystals under the influence of changing fields. In experiments where one is interested in the fundamental physics of liquid-crystal displays the use of magnetic fields often is preferred over the use of electric fields since there are fewer problems with ionic sample contaminations and temperature dependent susceptibilities.

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1. Introduction

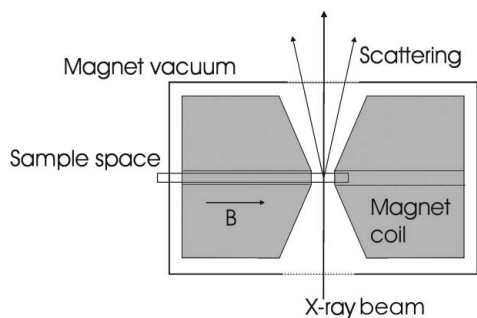
The use of strong magnetic fields as sample environment, in contrast to sample preparation, in small-angle scattering (SAS) has not found widespread use. This is understandable if we take into consideration that in the first place magnetic fields do not very often induce structural changes at length scales accessible with SAS if smaller fields (<1.5 T) have not been able to induce this already. In the second place, most often the construction of super-conducting magnets, which are the most convenient tools for the generation of strong fields outside of specialized high-magnetic field laboratories, is simplified when the sample can be kept at cryogenic temperatures and under vacuum, and thus can be mounted in the same enclosure as the magnet coils. There are only a few SAS experiments that are carried out on samples that are kept at cryogenic temperatures. The construction of split coil magnets with sample spaces that allow ambient pressures and temperatures, or even elevated temperatures, is technically feasible but also carries an elevated price ticket. Thirdly, we should keep in mind that the minimum path length which the X-rays have to be sent through the magnet is about 400 mm due to all the cryogenic shielding that is required for the magnet coils. This effectively limits use to synchrotron radiation or neutron laboratories where it is relatively easy to obtain highly collimated X-ray beams.

The range of available magnetic fields on beamlines can be coarsely divided in three regimes. The first range is below 2.5 T where either permanent- or electro-magnets can be used. The second regime roughly ranges $1.5 < B < 15$ T which can be covered by super-conducting magnets. Fields in excess of 15 T can, in specialized laboratories, be generated by resistive Bitter magnets but these require very large power supplies which, at present, are not available outside these specialized laboratories. Therefore one has to rely on pulsed magnets, which are fed by capacitor banks that are discharged *via* a resistive coil. These are capable of generating fields of $15 < B < 60$ T. However, the pulse duration is relatively short (10–50 ms) which

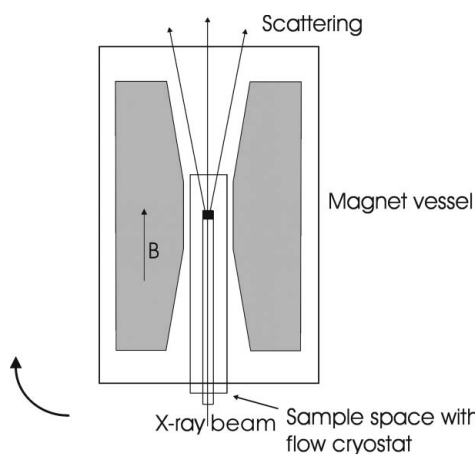
makes it less interesting for SAS experiments. It is worthwhile remarking that invariably the magnetic field interactions do not scale linearly with the magnetic field but quadratically. A change in field of 1.5 T to 15 T therefore means a gain of a factor of 100 in interaction strength.

The interaction of magnetic fields with macromolecules is diamagnetic in general and therefore rather weak (Maret & Dransfeld, 1985). Sometimes paramagnetism is observed but this tends to be the case in some liquid crystalline materials. So far the use of strong magnetic fields in soft condensed matter has been mainly limited to the preparation of samples suitable for fibre diffraction (Stubbs, 1999). One of the main sources of sensitivity to magnetic fields for biological molecules is the presence of α -helices in samples. The peptide bonds, which carry a diamagnetic moment (Pauling, 1979), are in this case all pointing in the same direction and one obtains a sizeable moment (Torbet, 1987). In the case of nematic liquid crystals one can use less strong fields. In this case not only the interaction of individual molecules with the field plays a role but also the even stronger effect is the collective effect. However, the weak interaction and small effects that have been shown so far with, for instance, synthetic polymers do not give the impression that magnetic fields will become a major processing tool in the near future (Ebert & Thurn-Albrecht, 2003; N. Vilaphiyou & E. Heeley, 2005, private communication).

The production of aligned macromolecular samples with even the strongest available magnetic fields generates in most cases only a partial alignment (Torbet & Dickens, 1984; Bras *et al.*, 1998). An improvement on this situation is possible when one enhances the effect by a secondary alignment mechanism like, for instance, shear or a slow reduction of that available sample volume, for instance, by slowly evaporating the solvent (Stubbs, 1999; Yamashita *et al.*, 1998). The disadvantage of this latter method is that one cannot study the sample in its original environment anymore. With biologically relevant molecules, for which the environment in which they are active is

**Figure 1**

Schematic top view of a scattering experiment in the Voigt geometry used in the experiments utilizing a super-conducting magnet. The field is at right angles with respect to the X-ray beam. This configuration is most useful for the study of alignment effects in macromolecules.

**Figure 2**

Schematic top view of the Faraday geometry used in the experiments described in this text when utilizing the 30 T pulsed magnet. The field is parallel with the X-ray access. This configuration is of limited use in the study of macromolecules but can be very useful in solid-state physics. The arrow indicates the rotation direction of the magnet when one wants to change the sample.

a watery solution, one cannot be sure anymore of the relevance of the found dehydrated structure in relation to the biological active form. The advantage over the use of electric fields is that ionic shielding does not counteract the magnetic field.

Most fibrous molecules align with their long axis parallel to the magnetic field. For structural studies the Voigt geometry, in which the field is at right angles with respect to the X-ray beam, is the most useful (Fig. 1). The Faraday geometry, *i.e.* beam parallel to field, is sometimes useful to study the interactions between the elongated molecules (Fig. 2). The latter configuration is fairly easy and relatively cheap to implement. The former one requires a split coil magnet. The requirement of having a fairly large scattering opening angle and a reasonably large sized magnet bore in order to be able to accommodate temperature control is making this more complicated and expensive although technically it is not difficult to build such magnets. Although for neutron scattering the issue of vacuum windows is not all that important it is very important in the case of X-ray scattering. The window material should be vacuum tight, should be strong enough to be able to construct windows of around 50 mm diameter and have a low scattering background.

Notwithstanding the fact that it is unlikely that there ever will be a very large demand for the use of strong magnetic fields in SAS experiments it is still worthwhile to spend some time and effort in

implementing this possibility in order to increase the tools available for experimenters. On the DUBBLE beamline at the ESRF (Bras *et al.*, 2003) we have been able to use both super-conducting as well as 30 T pulsed magnets.

2. Materials and methods

All experiments described here have been carried out on the Dutch-Belgian Beamline BM26B at the European Synchrotron Radiation Facility (ESRF) in Grenoble. This beamline has been described elsewhere (Bras *et al.*, 2003). The main relevant technical details are the photon flux, which are 10^{10} – 10^{11} photons s^{-1} (depending on the photon energy) and a beam size of 300 μm diameter. The useful energy range for SAXS experiments is between 5–20 keV.

The super-conducting magnet used in this work was a converted split coil magnet in which a sample space, that could be maintained at ambient pressure and temperature and with a free diameter of 12 mm, was inserted in the bore of the magnet. The X-ray access was along the split of the magnet thus leading to a configuration where the B-field vector and the X-ray beam have a perpendicular intercept. The maximum field strength that could be obtained was 10 T.

A problematic aspect of the use of super-conducting magnets is that in order to have a high field it is required to have a relatively small bore. If we keep in mind that one also requires a vacuum vessel and cryogenic shielding, one can understand that it is difficult to use elevated temperatures without transmitting heat to the magnet coils or expose the X-ray windows to temperature gradients that can lead to failure.

The second magnet that we have used is a pulsed resistive magnet. The coils are placed in liquid nitrogen to be able to dissipate the heat that is generated when a strong current is sent through the resistive coil. The high current required for this type of magnet (>10 kA) is generated by a capacitor bank that has to be charged between shots.

The maximum field that we have achieved so far has been 30 T with a pulse duration of 10 ms in which the field is above 27 T. The repetition rate between pulses can vary between 1–4 min and is determined by the time-averaged heating of the coils and the recharge time of the capacitor bank (Frings *et al.*, 2006).

The method described here is certainly not the only way in which one can generate pulsed fields in excess of 10 T. One can also revert to micro coils. The disadvantage of these is that control of temperature and pressure is, in general, very difficult. In the system described here it is possible to insert a flow cryostat, or even heaters, if one wants to work with more controlled sample conditions.

Technically the field that can be reached with an improved coil design but with the same capacity bank is about 60 T in the Faraday geometry and maybe 50 T in the more interesting Voigt layout where the field is perpendicular to the X-ray beam.

3. Results

In earlier work we have shown that it is possible to obtain relatively well aligned samples of microtubules, derived from pig brains, using an off-line magnetic field and that the orientation remained whilst the samples were transported to the X-ray beamline. However, the alignment was only partial and in the best of circumstances was never better than about 10° (Bras *et al.*, 1998). From magnetic birefringence measurements we could conclude that there was a slight loss of birefringence, and thus orientation, when the samples were taken out of the magnetic field. Therefore we have attempted to perform the

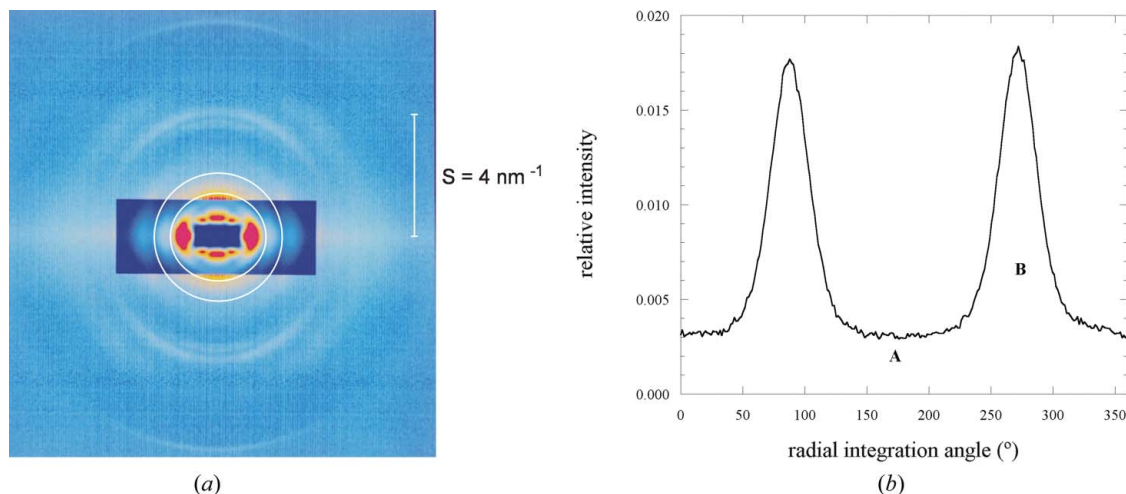


Figure 3 The X-ray fibre diffraction pattern of magnetically aligned microtubules. In (a) the intensity in the rectangular box is adapted for display purposes. Also indicated is the annulus over which one can perform a radial integration in order to establish the degree of alignment. In (b) the result of such an integration is shown.

same experiments with an on-line magnet so that we possibly could improve this.

In Fig. 3 we show the fibre diffraction pattern that we have been able to obtain in earlier experiments. Fig. 3(b) shows a typical result of an integration over an annulus, which is covering the strongest diffraction peaks. The width of the peak is an approximation of the final angular spread. If we calculate the intensity in an annulus covering the two strongest diffraction peaks we observe that in the case of the off-line experiment the difference between the intensities at positions A and B [as indicated in Fig. 3(b)] is less than in the case of the experiments with the on-line magnet but that the under similar conditions regarding biochemistry and concentration the degree of orientation is the same. However, with the on-line experiments the peak-to-background ratio is higher. This indicates that when using the on-line magnet the fraction of oriented material is increased even though the degree of alignment of the oriented fraction is not increased.

The result can be rationalized when one realises that microtubules are a prime example of large rigid rod polymers. The persistence length is reported to be over 5 μm whilst the average length, depending on the biochemical conditions, is in the region of 1 μm . Therefore we can apply rigid rod polymer theory to this sample (Onsager, 1949). This theory predicts that once the concentration and length exceed the limit of the semi-diluted to concentrated regime a phase separation will take place. Concentrated nematic and a diluted isotropic domains will be formed. The magnetic field will have a strong interaction with the nematic domains and a weaker interaction with the molecules in the isotropic phase. From these experiments we can derive that the intrinsic orientation inside the concentrated domains is about 10° . The order parameter, $\langle P_2 \rangle$, for the whole sample, *i.e.* nematic and isotropic phase together, is concentration dependent but is approximately $\langle P_2 \rangle = 0.8 \pm 0.05$. The order inside the nematic domains is higher. However, in diffraction experiments, which sample the whole sample, this can not be measured accurately since this would require microscopic beams aimed at a single nematic domain. The radiation damage thus inflicted would be too high to obtain reliable data.

In the diluted regions the rotational freedom of the molecules is increased, allowing single molecules to be rotated by the field but also to misalign under the influence of Brownian motion once the field is

removed. It will be virtually impossible to obtain a better alignment, not only for microtubules, but also for many other fibrous molecules, purely using magnetic fields. To overcome the repulsion owing to surface charges on the molecules would requires fields beyond what is feasible.

A second example that can be discussed is the rotational behaviour of smectic liquid crystals under the influence of magnetic fields. These materials are seen as possible candidates for a new generation of liquid crystal displays. Obviously these displays will not be operated with magnetic fields in this high field region. However, if we use electric fields the experiments are more difficult to interpret since the interaction parameters are temperature dependent and are more prone to influences due to ionic impurities. Therefore we have chosen to use the model liquid crystal 4-octyl-4'-cyanobiphenyl (8CB) and examine the rotational behaviour, not in relatively low electric fields, but in the required strong magnetic fields. 8CB has a smectic morphology in the temperature range $294.5 < T < 306.5$ K. Below this temperature it is crystalline and above it has a nematic morphology.

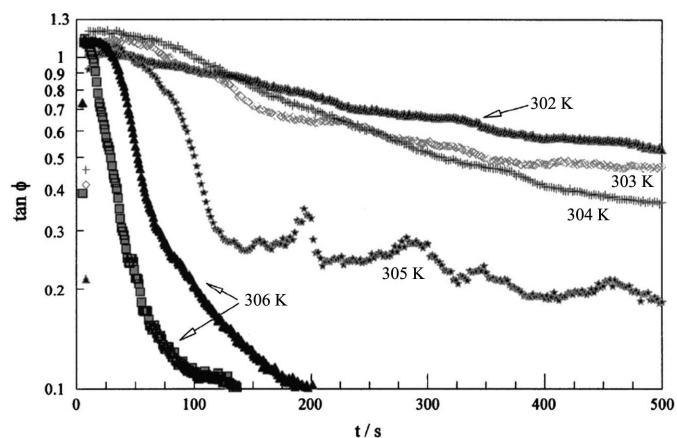


Figure 4 The angular dependence as a function of time of the centre of mass of the main diffraction peak expressed in the angle with respect to the original position of the sample after a rotation to 45° . The interaction with the magnetic fields is the reason for the rotation back to the original position. It is interesting that at some temperatures it is clear that this is not a homogeneous rotation since the data indicate a counter rotation.

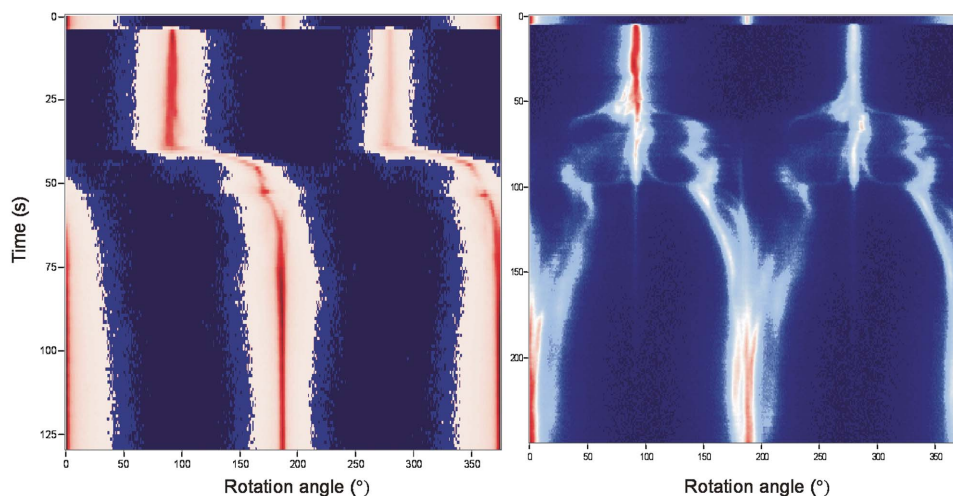


Figure 5

(a) The angular dependence of diffraction intensity as function of time is given for the case of a rotation over 45° . There is only a single diffraction peak that, after delay, starts to move back slowly to the original position. (b) shows an example which is representative of rotations of angles between 45 and 90° . It is clear that the behaviour is much more chaotic.

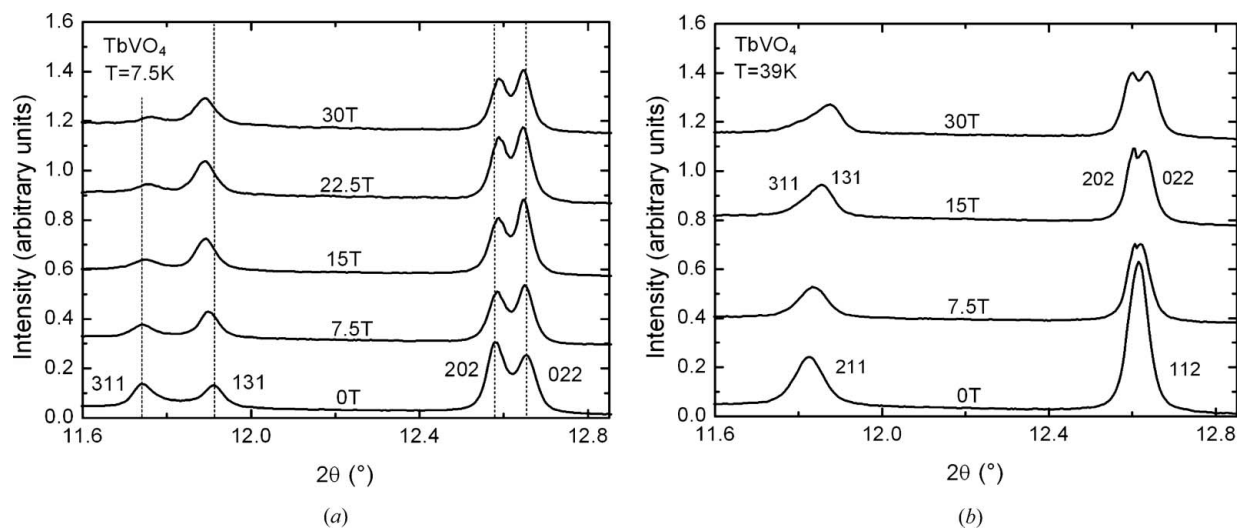


Figure 6

The powder diffraction pattern of TbVO_4 at different temperatures and magnetic fields. The phase transitions as function of temperature and the suppression of this phase transition owing to a strong applied field are clearly observed. The intensity is plotted on an arbitrary scale and an offset has been applied to the successive curves for clarity.

The question that we would like to have answered here is what the molecular behaviour is in a field-induced reorientation. This has been studied extensively in the case of nematic liquid crystals but little work has so far been done for smectic liquid crystals. Possible mechanisms are that a single liquid crystal can rotate or that it can break up in smaller domains, which then rotate. Other alternative pathways are a intermediate nematic phase or even a complete disordering and reordering in the direction imposed by the field (Bras *et al.*, 2004).

The samples were rotated in the (static) magnetic field. A full 90° turn could be made within 70 ms. The results of these experiments for rotations below 45° are that the sample more or less moves like a mono-domain. As expected the rotation velocity of this mono-domain is lower when one sets the sample temperature further below the smectic nematic transition. See Fig. 4.

However, there is clear evidence that the reorientation mechanism is more complicated than a simple rotation. In Fig. 4 we can see that

at some temperatures, around 3° below the smectic nematic transition (*i.e.* 305 K), the centre of mass of the main diffraction peaks moves against the restoring force. This can not be explained in terms of the rotation of a single domain since then this would mean a spontaneous increase in the magnetic energy of the system. Therefore we must assume that there are other factors that play a role.

With rotation angles above 45° the situation changes dramatically and becomes chaotic. Actually in such a way that quantitative analysis is rather difficult. An example of this is shown in Fig. 5.

In Fig. 5(a) the angular dependence of the diffraction intensity as a function of time is given for the case of a rotation over 45° . There is only a single diffraction peak that, after delay, starts to move back slowly to the original position. Fig. 5(b) shows an example, which is representative of rotations to angle between 45 and 90° . It is clear that the behaviour is much more chaotic.

The main conclusion that can be drawn from these experiments is that the reorientation process is not *via* a single pathway. There is

some rotation of small domains that retain their structural integrity but there is a second pathway in which material disorders and recombines in the direction dictated by the magnetic field. However, from these experiments we could conclude that there is a pathway that would involve a nematic or smectic C intermediate stage. The most likely mechanism is that under the stress of the magnetic field the initial large mono-domain breaks up into several smaller domains. At the fringes of these domains, the material starts to disorder and when sufficient material has become disordered the smaller domains can start to rotate.

The last example that will be discussed is the use of pulsed magnetic fields. So far this has not yet been used with experiments in SAS. However at several neutron and synchrotron radiation facilities there are plans to construct the required infrastructure that can be moved around to different beamlines for use with different experimental techniques. The first experiments, using the coils described here, at the ESRF were done on the SAXS/WAXS beamline BM26B since this beamline has the required large hutch to accommodate the rather bulky capacitor bank.

Terbium *ortho*-vanadate, TbVO₄, is an example of a material exhibiting a cooperative Jahn–Teller (JT) transition caused by quadrupolar interactions between the electrons in the 4*f* state. At ambient temperature, TbVO₄ has a tetragonal crystal structure [space group *I*4₁*amd*, *a* = *b* = 7.1841 (3), *c* = 6.3310 (4) Å]. Below *T* = 33 K, it undergoes a JT transition: the crystal distorts in the [110] direction to the orthorhombic space group *Fddd* [*a* = 10.239 (2), *b* = 10.029 (2) and *c* = 6.3154 (13) Å]. The distortion is relatively large, reaching $2(a - b)/(a + b) = 2\%$ at 22 K. It has been predicted that in strong magnetic fields the Jahn–Teller distortion can be suppressed. The most direct way of measuring this is using diffraction methods (see Fig. 6).

The magnet used in this work is less useful in, for instance, fibre diffraction measurements since the field is oriented parallel with the X-ray beam. However, with the same type of capacitor bank and using a different magnet coil it is possible to construct a split coil magnet, which can reach fields of about 40–45 T and at a reasonable cost.

4. Conclusions

We have shown several examples in which strong magnetic fields have been used on synchrotron radiation beamlines in combination with scattering and diffraction. The full results are published elsewhere. However, it will be clear that it is possible, using modern synchrotron beamlines, to add strong magnetic fields to the toolbox of the SAS user community.

This manuscript is an overview of work done in collaboration with three groups. The 30 T pulsed field experiments have been done in collaboration with P. Frings, J. Vanacken, C. Detlefs, F. Duc, J. E. Lorenzo, M. Nardone, J. Billette, A. Zitouni and G. Rikken. The liquid crystalline work was a collaboration with Y. K. Levine, G. R. Luckhurst, J. M. Seddon, B. A. Timimi and P. Christianen. The microtubule work is part of a long standing collaboration with G. P. Diakun and J. F. Diaz.

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