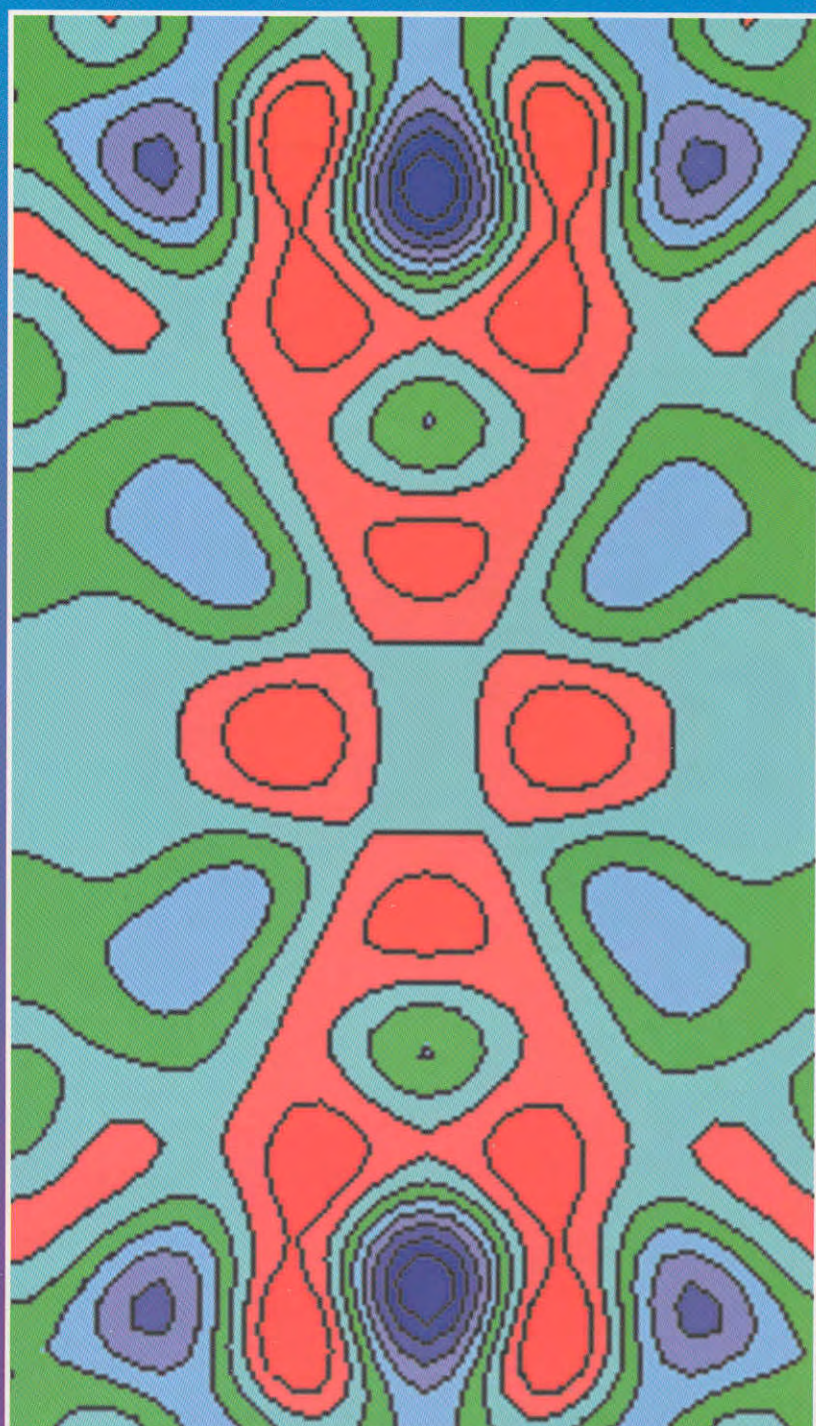


# *FIBRE DIFFRACTION*

## *REVIEW*

*THE CCP13 NEWSLETTER*  
*Software Development for Fibre Diffraction*

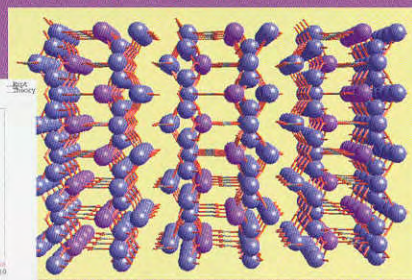
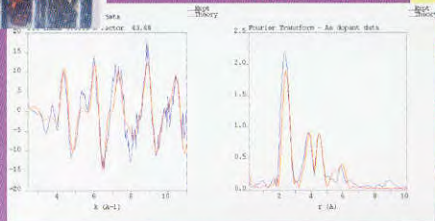
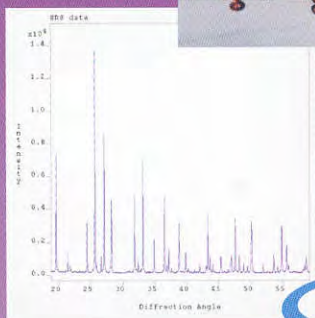


Issue 6

December 1997



# What can we do for you?



Daresbury Analytical Research and Technology Service

Now is your chance to access the benefits that your work may reap from the application of synchrotron radiation studies. EPSRC has awarded a grant to the CLRC Daresbury Laboratory to set up a national synchrotron radiation (SR) data collection and processing service. The Service, known as DARTS, is intended to support those inexperienced in the use of SR, and those whose work may benefit from small scale or infrequent use of SR as part of a wider research programme.

If you are unaware of how SR can help you, then please contact us and find out. As DARTS is aimed at inexperienced SR users, there is a level of consultancy inherent in the Service - and of course, it is absolutely free to qualified academics.

We look forward to hearing from you.

**DARTS**  
**CLRC Daresbury Laboratory**  
**Warrington WA4 4AD, UK**

phone +44 (0)1925 603141  
FAX +44 (0)1925 603124  
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SR techniques include:

- Powder X-ray diffraction, grazing incidence and reflectivity studies
- X-ray absorption spectroscopies
- Small and wide angle X-ray diffraction for non-crystalline samples (fibres, films, etc.)

<http://www.dl.ac.uk/SRS/DARTS>



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### Front Cover Image

*Contour plots of Fourier difference maps synthesized for mannan II at the level  $z=0$ . The left and right sections show density calculated from different conventional maximum a posteriori estimates of the coefficients while the central section is calculated from the minimum mean-square-error estimation of the coefficients. See the article by R.P.Millane and S.Baskaran for details.*

### Newsletter Production

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# Chairman's Message

## CCP13 News

This has been a good year for CCP13, with an excellent annual Workshop in May, a number of visits to outstanding meetings and conferences by people sponsored by CCP13 and with many interesting publications of work in which CCP13 software has played a central part. This, our 6th CCP13 Newsletter, is the second issue of the Newsletter under its new title: "The Fibre Diffraction Review". The main credit for the very nice presentation of the "Review" should go to Geoff Mant and Richard Denny at the Daresbury Laboratory who have put in a great deal of effort to make it look good. This new edition includes many interesting articles, some arising from the May Workshop, together with Meeting/Conference reports and progress reports on new and developing CCP13 software. In addition, the Fibre Diffraction Review is being incorporated as part of the CCP13 World Wide Web pages (as with the previous Newsletters: details elsewhere).

As detailed in the report by Geoff Mant, the 1997 Annual Workshop at Daresbury was, once again, a joint meeting, with an international flavour, of CCP13 and the UK Non-Crystalline Diffraction community. This year the Meeting was somewhat experimental in format in being held over two days rather than the usual three. It was an enormous pleasure to be able to welcome to the meeting an old, and very eminent, friend, Professor Don Caspar (Florida State). He gave a splendid talk on fibre diffraction studies of Tobacco Mosaic Virus. As usual we presented prizes to the best posters as judged by Don Caspar, together with two other of our distinguished visitors from overseas, Sanjay Rastogi and Ben Hsiao.

We hope that you will come along to the 1998 Workshop (May 12-14) at Daresbury. Remember not only that your poster could win a large cash prize (1st Prize £100; 2nd Prize £50), but also that abstracts will be included in this Annual "Fibre Diffraction Review" (also on the www) - your work will be available to a worldwide audience. As usual, there will be bursaries available for students and young scientists to attend the 1998 Workshop. Details of all these are given at the end of the Newsletter.

## About CCP13

CCP stands for Collaborative Computational Project. CCP13 is funded in the UK mainly by the Biotechnology and Biological Sciences Research Council (BBSRC). An additional grant comes from EPSRC to help fund meetings and travel for the "synthetic polymer" side of CCP13. CCP13 is one of 12 current CCPs run by BBSRC & EPSRC. Our current CCP runs to the end of September, 1998 with BBSRC support. The current BBSRC grant to CCP13 allows the continued employment of Richard Denny as the CCP13 RA and it provides funds towards Workshops, Newsletter Production and International Interactions. The funding by BBSRC and EPSRC also allows CCP13 to carry out "good works". Among these are schemes to fund a small number of "CCP13 Travelling Fellowships" and a "CCP13 Visiting Scientist Fellowship Program". Currently the CCP13 Committee is involved in drafting the next application to BBSRC for continued support. However, the importance of CCP13 in furthering non-crystalline diffraction applications of synchrotron radiation has been recognised by CLRC Daresbury Laboratory in that they have agreed to sponsor 50% of the Research Assistant position, currently tenanted by Richard Denny.

## Your Contribution

Interested groups or individuals are invited to contact any of the officers of CCP13 to obtain information about CCP13 Workshops, software developments, software standards and so on. Offers of home-written software that could be incorporated into the new CCP13 suite of programs would be much appreciated and will, of course, permanently carry the author's attribution. Make sure that you are on the CCP13 mailing list and you will be kept informed.

## Editorial Policy

Articles for inclusion in the Fibre Diffraction Review are welcome by the Editor at any time, but preferably items for the December 1998 issue should arrive before the end of November 1997. It is hoped that the Fibre Diffraction Review will become an Annual "essential" for fibre diffractionists. This is the place to advertise your fibre diffraction or NCD meetings, to report on new software or "hot" results obtained using the CCP13 or other fibre pattern processing

suites and to provide reports of meetings of interest, preferably together with one or two photographs. All technical articles will be scrutinised both for scientific content and presentational style by the Editor (or his nominee) together with at least one other member of the CCP13 Steering Panel. In this way we hope to maintain high standards. Remember that the Newsletter not only goes to other fibre diffractionists, but also to various members of the Research Council Secretariats and to other funding agencies.

### International Cooperation

Although these CCPs are UK funded projects, there is a very strong interest in making them international through cooperation with interested scientists in other countries. A natural link for CCP13, for example, exists with the Special Interest Group (SIG) in Fibre Diffraction of the American Crystallographic Association and possibly with some American synchrotron users (CHESS). Others exist

with the ESRF at Grenoble and with the Photon Factory in Japan.

### Retirements and New Elections

At the 1997 Annual General Meeting of CCP13, Professor Tony Ryan (Sheffield) was re-elected as a Committee member until the year 2000 and Dr. Bob Pendlebury (ICI, Wilton Centre) was elected as a replacement for Rob Rule who had resigned. This year sees the end of the periods of office of Mike Ferenczi and Trevor Forsyth. Both are prepared to stand for re-election. Other existing Committee members all continue at least until 1999. There are therefore two positions to be filled at the CCP13 Annual General Meeting in May. Any nominations for election to the Committee can be sent to the CCP13 Secretary, Dr. Geoff Mant, before the May 1998 meeting.

John Squire

**IF YOU ARE A FIBRE DIFFRACTIONIST STUDYING SYNTHETIC OR BIOLOGICAL POLYMERS. THIS CCP IS FOR YOU. PLEASE HELP TO MAKE IT WORK!**

## International Conference on Neutron Scattering Toronto, Canada, 17-21 August 1997

This meeting attracted approximately 700 delegates from all walks of the neutron scattering world, and included sessions on biology, polymers, materials, liquids, surfaces and industrial applications. The programme was diverse and highlighted the fact that there is enormous scope for the use of neutron scattering by the CCP13/NCD community. In the Biology sessions there were presentations on computational/neutron studies of protein folding and dynamics (Jeremy Smith, Commissariat a l'Energie Atomique), quasi-Laue crystallography (Dean Myles, ILL), membrane studies (Jeremy Bradshaw, ILL), small angle neutron scattering (S. Krueger, NIST), as well a lively poster session that included presentations on actin (Ivkov, University of Maryland), DNA hydration (Shotton, Pope, Keele University), and ribosomes. In the polymer session there were talks on block copolymer phase behaviour (Bates, Minnesota), relaxation processes in glass-



forming polymers (Richter, Julich), nucleation and growth in polymer mixtures (Balsara, Polytechnic University, New York).

As with all large meetings there is often a feeling that it will be impossible to remember all of the interesting work that was presented. However, the

highlight of the meeting, a trip across Lake Ontario from Toronto to Niagara, in a very odd way, helped with this problem. The boat was laid out with enormous quantities of exotic food and everybody duly filled themselves up. There then followed a crossing that was by anybody's standards horrendously rough. Most people on the boat were very ill and unfortunately three people were hospitalised after the journey. Some delegates felt well enough after getting off the boat to be amused by the name of the carrier (see photograph).

The idea was that after the crossing, delegates were to get on another boat (The Maid of the Mist) which was to give a unique approach to the base of Niagara Falls. Enthusiasm for this seemed to be low however,

and this part of the outing was cancelled. After a quick glimpse of the falls, everybody was bundled onto a coach and delivered straight back to Toronto where the conference dinner awaited them.

Whilst the outing did not quite work out as the organisers planned, most delegates (probably with at least three exceptions) were able to look back on the trip with some amusement, although tinged with concern for the more seriously affected. The meeting was an enormous success scientifically and the main entertainment event ensured that it will never be forgotten!

Trevor Forsyth

## **The Fourth Synchrotron Radiation School**

### **UMIST - Daresbury Laboratory - University of Wales**

### **5-17 January 1997**

A fresh winter's day in Manchester was the starting point for the fourth Synchrotron Radiation School this January. The only problem about repeating things is that you have to reconcile trying something new with undoing something that has already worked. The timing, location, organisation and expanded programme of the Synchrotron Radiation School constituted a new departure. It proved that students will come to a northern city in the UK in the first week of a new year and work solidly from 9 in the morning often until 9 at night. The reward of course is that one week later they can work even longer hours at the Synchrotron Radiation Source at Daresbury Laboratory coping with practicals and data analysis!

Where the previous three Synchrotron Radiation Schools have been held at Keele University, the University of Manchester Institute of Science and Technology hosted the first week of lectures and tutorials of SRSIV. These were given in the Manchester Materials Science Centre under the watchful eye of Tony Ryan (who also directed students to the bright lights of Manchester after hours). Once Storage Rings, Crystalline Symmetry and Disorder had been set aside, students were introduced to Diffraction Theory including Magnetic Diffraction, the basis of Small Angle Scattering and Fibre Diffraction, the theory of XAFS and of Photoemission. The course programme then moved

on to Synchrotron Radiation X-ray and UV optics (crystals, mirrors and gratings) and detectors (solid state, wire and also electron varieties). This comprehensive background of theory and instrumentation provided the natural lead-in to the formal experimental arrangements now found at most SR centres. Experiments covered X-ray Diffraction both from powders, protein crystals and microcrystals; X-ray Scattering from polymers and bio-fibres; XAFS from materials and SEXAFS from single crystal surfaces; and last but not least gas phase photoabsorption and photoemission spectroscopy.

By this time the School had moved on to Daresbury Laboratory via a short tour of the English Peak District. This included appropriately enough a visit to Styal Mill - one of the best preserved examples of intensive 19th century factory life from the height of the Industrial Revolution - surely a foretaste of the synchrotron radiation experience to come! Practical sessions at the SRS were brought together by Bob Bilsborrow and mirrored the principal diffraction, scattering and spectroscopy experiments featured previously in the lecture programme. Individual experiments were designed to introduce students to experimental procedure as well as to data handling. Following the example of a previous SR school, first thing each morning the SRS machine crew demonstrated the start up of the source from linac, to

synchrotron to storage ring. The final day of the Synchrotron School comprised research seminars from leading experimenters from throughout the UK SR community and concluded a series which had interspersed the course programme throughout the two weeks. Topics ranged from metal alloys to protein structures, from mineralogy to MBE microfabrication, from polymer chemistry to chemical crystallography and from Compact Storage Rings to the Future of Synchrotron Radiation.

All told, the fourth Synchrotron Radiation School

attracted between 40 and 50 students from the UK, the EU and from industry. Project leaders of most of the major SR teams currently exploiting the SRS - both from university and from Daresbury Laboratory - contributed to the lectures, tutorials and practicals. SRSIV was sponsored by EPSRC, CLRC and Oxford Instruments. It was organised by the University of Wales, Aberystwyth who also provided secretarial and administrative support.

Tony Ryan and Neville Greaves

## 6th Annual CCP13/NCD Workshop

The sixth annual workshop for the collaborative computational project for fibre diffraction (CCP13) and non-crystalline diffraction (NCD) was held at Daresbury on the 7th-8th of May. This year's meeting had a revised format, attracting 54 participants and retaining its high standard of presentations. Once again, the workshop covered the following major topics: synthetic polymers, hardware sources and detectors, software developments and biological systems. The talks were complemented with a poster session.

After the Chairman's introduction, Ben Hsiao (DuPont), the first keynote speaker, opened the meeting by describing the crystallisation of PET and a demonstration of the subsequent data analysis using the package XDPP. The session continued with Nick Terrill (UMIST) describing his latest work on the various structural intermediates during polymer extrusion, as studied by on-line SAXS/WAXS. Gareth Jones (Daresbury) then presented recent results on protein folding, using stopped flow processes, to measure the multi-wavelength CD, time resolved SAXS and time resolved fluorescence anisotropy, on millisecond time scales. Magdalena Ivanova (Florida State) concluded the session with a presentation on 2D background subtraction techniques on Filamentous Bacteriophage M13 patterns.

After lunch, Colin Nave (Daresbury) outlined a scenario of three possible station designs, for NCD, on Diamond by matching the source to the specimen. Richard Denny (Daresbury & Imperial College) then described the recent updates to the CCP13 programs and gave a live demonstration of the new graphical

user interfaces, XFIT, for 1D peak fitting and XFIX for 2D image manipulation. Dick Hilmer (dCode Software Tools) also presented an on-line demonstration of a software package for developing software graphically, using a combination of data flow and structure diagrams. Simon Dobson rounded off the day with an overview of the possibilities for the World Wide Web and the use of distributed objects, JAVA and CORBA. The day was concluded with a poster session followed by the conference dinner at the Daresbury Park Hotel.

The second day began with Sanjay Rastogi (Eindhoven) describing his work on enhanced chain mobility of UHMW-PE at low pressures and temperatures and its use for processing and welding. Norbert Stribeck (Hamburg) discussed the use of PV-WAVE in the analysis of image plate SAXS patterns of elongated fibres of thermoplastic elastomers. Michael Firenczi (NIMR) outlined his work on the molecular movement involved in muscle contraction using UV-light to photolyse caged-ATP and temperature jump to produce a tension change. Tony Ryan (UMIST) presented work on the crystallisation of cyclic ethers which gave crystals with an integral number of folds. Rob Lewis (Daresbury) explained the advantages of using SR for medical imaging compared to conventional radiography and went on to describe recent results on simultaneous X-ray diffraction and imaging. Ruth Cameron (Cambridge) then concluded the morning session by describing the importance of the biodegradable polymer polyglycolic acid in biomedical applications and the necessity of understanding its morphology.

After lunch, our final keynote speaker, Don Caspar



(Florida State), described a brief history of the development of the Tobacco Mosaic Virus structure which included cryoelectron microscopy, 3D image reconstruction and fibre diffraction using SR. Pierre Rizkallah (Daresbury) described his current work on the tetrameric/dimeric structure of Lectins and their importance in HIV research as anti-viral agents. Peter Williams (Kings College) gave the final talk by describing his work on the structure of PLB which has been identified as a convoluted bilayer in the form of a tetrapod, joined together as a diamond cubic lattice.

John Squire concluded the meeting by awarding the

prizes for the best poster presentations (as judged by D.Caspar, S.Rastogi and B.Hsiao) to Patrick Fairclough (UMIST) and Liam Welsh (Cambridge). A special vote of thanks was made to Val Matthews and Diane Travis for all the hard work and organisation that went into making the whole meeting run smoothly.

A fuller account of the talks/posters presented at this workshop may be read later in this volume or viewed on the World Wide Web at:

<http://www.dl.ac.uk/SRS/CCP13/workshop97>.

Geoff Mant

## **Third Fibre Diffraction Workshop Kentucky, USA, 5-8 October 1997**

A group of fibre diffractionists gathered at Jenny Wiley State Park, Kentucky, USA, during 5-8 October 1997, for the "Third Fiber Diffraction Workshop." This was the third in a series of highly successful workshops, the first being held in Tennessee in 1989 and the second in Indiana in 1993. The emphasis of the workshops has been on methodology, since this is often not emphasised at other crystallographic and specialist meetings. In addition to the U.S. participants, there was a rather large turnout from the U.K., as well as one participant (Consiglia Tedesco) from Italy. The workshop was sponsored, as were the previous ones, by the du Pont Company.

Highlights of the workshop were descriptions of the uses of neutrons to study water structure around DNA (Trevor Forsyth) and bacteriophage structure (Magdalena Ivanova), and X-ray synchrotron radiation for microfocus and time-resolved studies (Watson Fuller and A. Mahendrasingam); as well as a description of the instrumentation and facilities for fibre diffraction at the SRS (Elizabeth Towns-Andrews). Gerald Stubbs used examples from virus structures determined by fibre diffraction to address the question: What are the limits of fibre diffraction analysis? He concluded that recent successes have not yet defined the limits of molecular replacement approaches in fibre diffraction, and that continued vigilance is needed in assessing the accuracy of structural results.

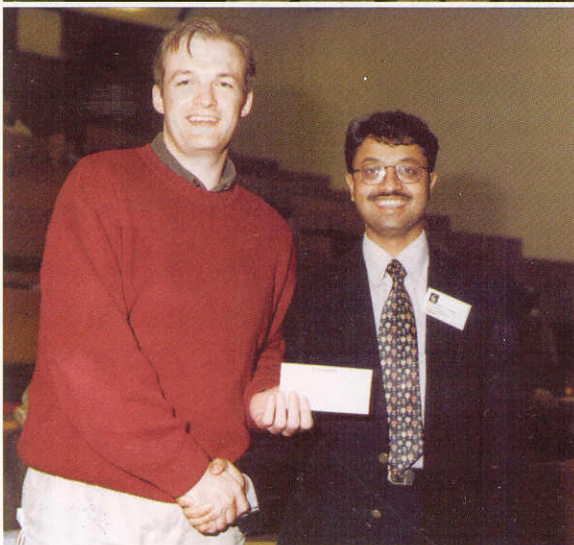
Hong Wang and Richard Denny updated us on software systems for processing fibre diffraction data. The various kinds and degrees of disorder present in fibre specimens, ways of modelling them, and their effects on diffraction data and structure determination were discussed by Rick Millane and Jon Eads.

The structures of a variety of synthetic polymers were described, including fluoropolymers (Soo-Young Park), polyamides (Kenn Gardner), and copolyester-amides (JaeDong Cho), as well as studies of variations in orientation and crystallinity of PET and LDPE both across container walls and during drawing.

The wide applicability of fibre diffraction techniques was illustrated by descriptions of various aspects of applications to viruses, bacteriophages, nucleic acids (Akella Radha), actin (Rebecca Page), amyloid (Mark Bartlam), polysaccharides (Victoria Finkenstadt), deoxy-hemoglobin (Xiang-Qi Mu), liquid crystals (George Mehl), and various synthetic polymer structures.

The meeting concluded with unanimous agreement to hold a fourth workshop, probably in the year 2000.

Rick Millane



## Photographs

*Bob Pendlebury describes a new ICI polymer fishing line suitable for mendacious anglers. Don Casper peruses this year's posters, while Norbert Stribeck reminisces with Greg Diakun about the SAS96 meeting in Campinas. Patrick Fairclough receives his prize, confirming the Ryan group domination of the polymer poster competition.*

## Perfect Plastic Products Need Good Crystal Management Proceedings of Royal Society 1997

It is all too easy to take for granted something as simple as plastic sachets used in coffee and tea machines. In reality, it can take some complex polymer science to get the right material properties for the sachets and, just as important, to maintain those properties from batch to batch. Polymer processors now have a better understanding of how they can achieve these goals thanks to a research project carried out by the Manchester Materials Science Centre at UMIST and the Daresbury Laboratory of the Council for the Central Laboratories of the Research Councils (CCLRC).

The ROPA project was on show at this summer's prestigious annual summer exhibition at the Royal Society. The exhibit was a 2/3 scale model of the experiment on beamline 16.1 at the SRS. To make the exhibit work visually the data was played back from video on screens placed in the detector housing. There were many other interesting exhibits at the exhibition but there was little time to enjoy them as the days were spent explaining the research to members of the public (mainly OAPs and schoolchildren) and the evenings dedicated to Fellows and their guests.

The UMIST team, Nick Terrill, Patrick Fairclough, Bob Young and Tony Ryan, in collaboration with Liz Towns and Ernie Komanschek of CLRC investigated the way in which polypropylene crystallises during extrusion to produce polymer films using 2D SAXS/WAXS during extrusion. Analysing the scattered radiation allowed the UMIST group to create what were in effect movies of what was happening inside polymers as films formed through extrusion.

Crystal growth itself is well understood. Indeed, as Tony Ryan points out, it is a part of undergraduate

teaching. Nucleation is another matter. "Understanding of the nucleation step is far from satisfactory" says Ryan, who has just moved to Sheffield University along with Fairclough and Terrill. So they decided to study this in a ROPA project.

The team made both small and wide angle scattering measurements on polypropylene and other polymers. The researchers built an extruder that let them study the polymer in conditions like those produced during commercial processing. Wide angle X-ray scattering (WAXS) allows researchers to study the development of structure at the atomic level while small angle X-ray scattering (SAXS) is suitable for studying the larger length scales associated with orientation of the polymer crystals. CCP13 software is used to extract the information from the noisy data. One surprise finding of the work on the SRS was that there were signs of long range order developing before crystallisation began and created short range order. There are two papers in press, one dealing with the experimental observations and the other outlining a phenomenological density of states theory for spinodally assisted crystallisation. These papers should provoke some controversy and energise the academic field of polymer crystallisation for some time.

The research has not only added to the understanding of the process of polymer crystallisation, it has already produced commercial benefits. A company making sachets for coffee vending machines has improved its products thanks to the better understanding of polymer processing. As a result of the UMIST work, the sachets now break and deliver the contents in a more controlled way.

Tony Ryan

## 50 Years of Synchrotron Radiation Grenoble November 1997

The 50th anniversary of the discovery of SR was celebrated in a conference hosted by the most recent SR machine in Europe. The meeting was organised by the ESRF and reflected their agenda. The subject of the main conference was condensed matter and there was an auxiliary symposium on structural biology, these of course being the subjects which have benefitted most from the development of the ESRF. The main meeting was organised around a series of plenary lectures and contributed posters.

Day one started with some historical lectures which were interesting in their perspective. Daresbury did not feature in any landmark discoveries according to Bob Barterman from CHESS at Cornell, we should invite him to the next user meeting! The rest of the day, and part of the following morning, was given over to studies of magnetic phenomena. Malcolm Cooper gave a good review of Compton scattering and flew the flag for the UK.

Soft condensed matter was the subject of the second day. Sunil Sinha gave an excellent exposition of the power of coherent and incoherent X-rays in studying fluctuations. This was followed by an excellent talk on X-ray photon correlation spectroscopy by Günther Gruebel. Polymers were covered by a general review by Manfred Stamm and a talk by Tony Ryan on fluctuation induced crystallisation in polymers. These were followed by talks on inelastic scattering and another poster session where there was

some interesting work on SAXS/WAXS from polymers, surfactants and lipids from Hamburg and excellent microfocus studies (including microfocus SAXS) on keratin (human hair and nails). The first results from RAPID were also presented in this poster session and aroused considerable interest from a wide variety of users.

The third day was a mixture of structural biology (MAD) and geophysics, with interesting work on the structure of the earth's core. The conference dinner, that night, was held in a delightful chateau about 30km out of Grenoble. With the participants suitably refreshed the final day was given over to biology and imaging. Sebastian Doniach gave a great talk on using flow kinetics to study protein folding and there were a number of illuminating talks on diffraction imaging. This session was also followed by a poster session but the highlight of the day was the presentation of the ESRS prize to Malcom McMahon who gave what was one of the best talks of the meeting on high pressure phase transitions.

There was a party that night, being the 3rd Thursday in November also the day that Beaujolais Nouveau was released, which meant there were a number of sore heads the following day at the ESRF Users meeting.

Tony Ryan

## Alpbach Workshop 1997 Coiled-Coils, Collagen and Co-Proteins

The second Alpbach Fibrous Protein Workshop was held from September 7th to 13th, 1997 at the Boglerhof Hotel, Alpbach, Austria. Alpbach is a beautiful Tyrolean town in a high valley surrounded by mountains and it provides a splendid venue for scientific meetings. The first of these fibrous protein meetings, in honour of Bruce Fraser and Tom MacRae, was held in the same place exactly four years before. Its tremendous success prompted the organisation of the 1997 meeting, this time honouring the achievements of Professor Carolyn

Cohen from The Rosenstiel Center for Basic Medical Sciences, Brandeis University, Massachusetts. The Workshop, organised jointly by Professor John Squire, from Imperial College, London, and Professor David Parry, from Massey University, New Zealand, was sponsored by Glaxo-Wellcome, by the Journal of Structural Biology, by CCP13 and by Imperial College. It involved about 100 participants, with a good mix of very eminent scientists together with young post-docs and some PhD students. The Workshop, launched by a splendid reception put on



**Figure 1:** The participants at the 1977 Alpach Workshop on 'Coiled-Coils, Collagen and Co-Proteins' standing in front of the hill behind the Bogelerhof Hotel, which lies about 10m to the left of this picture.

by the Hotel on the Sunday evening, was divided into 11 scientific sessions over five days.

**Monday:** Session 1, Chaired by Carolyn Cohen and David Parry, outlined the enormous progress in analysis of basic  $\alpha$ -helical coiled-coil structures with a seven residue (heptad) amino acid repeat and the effects of particular amino acids at specific points in the repeat. Talks were given by Tom Alber, Andrei Lupas, Derek Woolfson, Richard Kammerer, Robert Hodges and Norma Greenfield. Derek Woolfson showed that unusual coiled-coils with a repeat of 11 amino acids rather than 7, and sometimes occurring in series with normal heptads, could be found in some cytoskeletal proteins. In general it was concluded that we have a much better understanding of coiled-coil structure in terms of sequence than is currently possible with globular proteins.

The second session, Chaired by Don Caspar, included a talk by Jurgen Engel on a 5-stranded coiled-coil structure linking the five subunits of the cartilage oligomeric matrix protein COMP, a member of the thrombospondin family of extracellular matrix proteins. Keiichi Namba presented recent work on the molecular architecture of the bacterial flagellar filament and Don Caspar talked about the structure of Tobacco Mosaic Virus.

**Tuesday:** Day 2 had two muscle sessions: Session 3 on "Thin Filaments", chaired by Ken Holmes, and Session 4 on "Thick Filaments", chaired by John

Squire. In the morning, Ken Holmes outlined his latest ideas on the molecular interactions between myosin and actin involved in muscle contraction, based on the known crystal structures. There followed a number of papers related to thin filament regulation, especially a talk by Dmitry Vassilyev on the newly solved structure of troponin-C with an expressed peptide of troponin-I bound to it. The myosin session, with a plethora of speakers, started with a rapid introduction by John Squire on basic ideas on thick filament structure and the latest molecular modelling of myosin filament fibre X-ray diffraction patterns, and continued with a variety of talks on myosin head positions and backbone structures, but most notably on the enormous

progress that is being made in elucidating the structures and interactions of titin (particularly Siegfried Labeit, Wolfgang Linke and Larissa Tskhovrebova) and myosin binding protein C (C-protein), particularly Don Fischman.

**Wednesday:** Session 5, Chaired by David Parry, was a fascinating session on "Intermediate Filaments and Associated Proteins" including talks by Norbert Geisler, Ueli Aebi, Robert Goldman, Peter Steinert, Elizabeth Rugg, Kathy Green and David Parry himself. Considerable attention was paid to the structure of hard  $\alpha$ -keratins. David Parry summarised recent analysis of the four classes of intermediate filament: the hard  $\alpha$ -keratins, the epidermal keratins, the vimentin and neurofilament families, and the nuclear lamins. He showed that the number of chains in cross-section is probably the same in all of these classes, whereas the lateral packing in hard  $\alpha$ -keratins is different from the others, probably due to intermolecular disulphide bonding.

Wednesday afternoon not only saw the taking of the workshop photograph (see figure 1), but also provided a special highlight when Carolyn Cohen presented an invited overview on the "romance" of coiled-coils. Before she spoke she was honoured in a series of off-the-cuff tributes by David Parry, Ken Holmes, Andrew Szent-Gyorgyi, Hugh Huxley, Don Caspar and others and she was presented with a "coiled-coil" trophy by David Parry (figure 2).

Carolyn's talk was a masterful mix of science, philosophy and reflection, with considerable reference being made to the early fibre diffraction work of Astbury and others and the considerable clarification that is being made nowadays in understanding globular protein behaviour from knowledge of fibrous protein structures. Carolyn's own major contribution to the field was acknowledged by a standing ovation at the end of her talk. This occasion was a real treat for all those lucky enough to be present.

The evening session (6) on Wednesday carried the coiled-coil story from two chains to three. Fascinating talks on such molecules as fibrinogen,  $\alpha$ -actinin, dystrophin and utrophin were presented by, among others, John Weisel, John Kendrick-Jones, Paul Matsudaira, Stephen Winder and Mathias Gautel.

**Thursday:** Thursday saw a change of tack from alpha-proteins to the other sort of super-helical protein molecule, collagen. In two sessions (7,8) chaired by Barbara Brodsky and Darwin Prockop, collagen structure was described from the level of peptide crystal structure to fibril structure to larger scale assemblies. Speakers included Barbara Brodsky, Ruggiero Tenni, Helen Kramer, John Ramshaw, Hans-Peter Bachinger, Darwin Prockop, Tim Wess and Peter Fratzl, with the latter two concentrating on synchrotron radiation diffraction studies carried out at Daresbury Laboratory.

Thursday evening saw the "Romantik" dinner where the always superb cuisine of the Boglerhof Hotel was given full rein. The meal and company were excellent.

**Friday:** The last morning, Friday, saw a special session (9) on microtubules and associated proteins with a galaxy of stars: Linda Amos, Ekhard Mandelkow, Robert Hodges, Andreas Hoenger, Eva Mandelkow. Linda Amos presented the recent momentous work on the related structures of tubulin and FtsZ protein from bacteria. Papers on both of these have featured in a recent issue of *Nature* (Vol. 391, pp. 199 and 203 respectively). The tubulin study, using electron crystallography from 2-D crystals, was by a well-known "alumnus" of Daresbury Laboratory, Eva Nogales. The last talk by Eva Mandelkow was a lucid presentation on current ideas about Alzheimers Disease. Friday concluded with a very interesting session (10) on " $\beta$  helices,



**Figure 2:** Carolyn Cohen (centre), the guest of honour at the Coiled-Coil meeting, holding the coil-coil model that was presented to her by David Parry just before her 'Romantik' lecture. Left to right: John Squire, David Parry, Carolyn Cohen, Don Caspar, Susan Lowey.

amyloid and novel structures" with excellent talks on these unusual structures being given by Alasdair Steven, Fran Jurnak, John Jenkins and finally Dan Kirshner who spoke about amyloid proteins.

The Workshop finished with a brief general discussion in which a general, philosophical overview on where coiled-coil analysis is going was given by Tom Alber. As an example of what will be appearing in the near future in the muscle area, John Squire presented a movie of mass movements in the fish muscle unit cell during normal isometric contractions. This was based on time-resolved low-angle X-ray diffraction studies of active muscle using synchrotron radiation at Daresbury and is probably the first real time movie of dynamic changes at the molecular level in any intact tissue.

In an open discussion which followed it was agreed that these workshops are tremendously useful as a means of bringing together researchers in normally disparate disciplines. Such relaxed, informal workshops in agreeable surroundings, where considerable exchange of ideas can take place, are real promoters of good science. Alpbach is particularly suitable because of the beautiful hill/mountain walks that can be taken around the Hotel (or skiing in the winter!). These, and the relaxed atmosphere over meals, poster sessions or in the bar, all serve to provide excellent opportunities to get to know people and to exchange ideas. It was agreed that the third such fibrous protein workshop should be organised at Alpbach in another four years time, this time in 2001.

John Squire

## Summary of Available CCP13/NCD Software

Program	Description
XOTOKO	1-D data manipulation
BSL	2-D data manipulation
V2A	vax to unix data conversion
A2V	unix to vax data conversion
OTCON	ascii to otoko data conversion
RECONV	otoko to ascii data conversion
TIFF2BSL	image plate (tiff) to bsl conversion
I2A	ieeee to ansi data conversion (DEC only)
CONV	file format conversion
CORFUNC	correlation function
FD2BSL	intensity to bsl conversion
FDSCALE	scaling and merging of intensities
FIT/PGFIT	1-D fitting and plotting
FIX/PGFIX	preliminary fibre pattern analysis
FTOREC	reciprocal space transformation
LSQINT	2-D integration and background fitting
SAMPLE	Fourier-Bessel smoothing
XFIT	graphical user interface for fit
XFIX	graphical user interface for fix
BSL2TIFF	bsl to tiff conversion

The tables list the currently distributed CCP13/NCD programs, available as executable modules. The dates refer to the last creation of the executable. HP-UX version 10 executables should be available shortly.

A LOQ2BSL conversion program, for ISIS neutron data to BSL format, is also available for Solaris platforms.

Program	Solaris 2.5	Irix 5.4	Hp-UX 9.0	IBM AIX	Ultrix	OSF	Linux
XOTOKO	28/11/97	30/05/96	11/08/97	-	13/04/92	29/04/97	06/05/97
BSL	02/05/97	21/03/97	11/08/97	-	13/04/92	27/04/97	06/05/97
V2A	19/05/95	-	-	-	13/04/92	-	-
A2V	19/05/95	-	-	-	-	-	-
OTCON	06/06/95	08/07/94	-	-	-	-	08/05/97
RECONV	06/06/95	31/10/94	-	-	-	-	08/05/97
TIFF2BSL	17/03/97	-	-	-	-	-	-
I2A	n/a	n/a	11/08/97	n/a	09/10/92	29/04/97	02/05/97
CONV	05/11/96	04/11/96	05/04/95	18/05/95	04/11/96	04/11/96	04/11/96
CORFUNC	26/10/95	-	-	-	-	-	-
FD2BSL	05/11/96	04/11/96	01/12/95	18/05/95	04/11/96	04/11/96	04/11/96
FDSCALE	05/11/96	04/11/96	01/12/95	18/05/95	04/11/96	04/11/96	04/11/96
FIT/PGFIT	22/01/97	05/11/96	-	-	23/01/97	-	-
FIX/PGFIX	05/11/96	04/11/96	29/11/95	18/05/95	04/11/96	04/11/96	04/11/96
FTOREC	05/11/96	04/11/96	01/12/95	11/07/95	04/11/96	04/11/96	04/11/96
LSQINT	05/11/96	04/11/96	27/10/95	18/05/95	04/11/96	04/11/96	04/11/96
SAMPLE	05/11/96	04/11/96	01/12/95	24/05/95	04/11/96	04/11/96	04/11/96
XFIT	22/07/97	22/07/97	-	-	-	15/10/97	-
XFIX	22/07/97	22/07/97	-	-	-	15/10/97	-
BSL2TIFF	21/03/97	-	-	-	-	-	-

## Optimal Difference Fourier Synthesis in Fibre Diffraction

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*A weighting scheme for difference Fourier synthesis in fibre diffraction that yields a minimum mean-square-error estimate for the missing electron density is described. Simulations show the advantages of using the weighting scheme, and other applications in fibre diffraction are discussed.*

### 1. Introduction

Difference Fourier synthesis is an important technique in small molecule and protein crystallography, where it is used to locate missing components (*e.g.* counterions, or solvent or other bound molecules) or to correct errors (such as in side-chain positions), in crystal structures. Since difference Fourier synthesis involves using a partially determined structure to phase the diffraction data, it is also closely related to molecular replacement methods. For single crystal crystallography, difference Fourier methods are quite well established. The most straightforward approach is to synthesise a map of the difference electron density by inverse Fourier transforming the difference between the observed (measured) amplitudes  $|F_{\mathbf{h}}^o|$  and the calculated amplitudes (*i.e.* those calculated  $|F_{\mathbf{h}}^c|$  from the known part of the structure, or from a model structure), phased by the known part, *i.e.*  $\Delta\rho(x) = \mathcal{F}^{-1}\{|F_{\mathbf{h}}^o| - |F_{\mathbf{h}}^c| \exp(i\phi_{\mathbf{h}}^c)\}$ , where  $\mathcal{F}\{\cdot\}$  denotes the Fourier transform and  $\phi_{\mathbf{h}}^c$  denotes the phase of  $F_{\mathbf{h}}^c$ . This difference map can be improved upon by weighting the  $|F_{\mathbf{h}}^o|$  in accordance with the reliability of the  $\phi_{\mathbf{h}}^c$ , and by including the effects of errors in the partial structure [1,2]. Difference Fourier methods have also found significant application in fibre diffraction analysis since the early days for analysis of the symmetry of nucleic acids [3], through detailed visualization of solvent and cation interactions in polysaccharide systems [4] and applications to helical viruses [5]. However, the relatively straightforward approach to

difference synthesis in single crystal crystallography does not translate exactly to fibre diffraction analysis, and applications have involved approximations unless special symmetry was present. The difficulty arises because one needs to synthesise a three-dimensional electron density function but, whereas the model structure provides the quantities  $|F_{\mathbf{h}}^c|$  and  $\phi_{\mathbf{h}}^c$ , the two-dimensional diffraction data available from a fibre diffraction experiment do not generally provide the individual quantities  $|F_{\mathbf{h}}^o|$ . To calculate a fibre diffraction difference map, one must use the form

$$\Delta\rho(\mathbf{x}) = \mathcal{F}^{-1}\left\{\left(|F_{\mathbf{h}}^{o'}| - |F_{\mathbf{h}}^c|\right)\exp(i\phi_{\mathbf{h}}^c)\right\} \quad (1)$$

where the  $|F_{\mathbf{h}}^{o'}|$  are approximations to the  $|F_{\mathbf{h}}^o|$  that must be estimated from the fibre diffraction data.

Two approaches to this problem have traditionally been used in fibre diffraction analysis. For a polycrystalline specimen, the observed intensity of a diffraction spot  $I^o$  takes the form

$$I^o = \sum_{\mathbf{h}} |F_{\mathbf{h}}^{o'}|^2 \quad (2)$$

where the sum is over the reflections  $\mathbf{h}$  that overlap in the spot, as a result of either systematic or accidental overlap. One approach to approximating  $|F_{\mathbf{h}}^{o'}|$  is to assume that all the contributing reflections are of equal amplitude so that

$$|F_{\mathbf{h}}^{o'}| = \sqrt{\frac{I^o}{\mathcal{N}}} \quad (3)$$

where  $\mathcal{N}$  is the number of reflections contributing to  $I^o$ . This  $|F_{\mathbf{h}}^{o'}|$  is used in equation (1). This is a parsimonious choice as it uses phase information from the model (or known part of the structure), but does not make use of the relative values of the amplitudes  $|F_{\mathbf{h}}^c|$  from the model in estimating  $|F_{\mathbf{h}}^{o'}|$ . This is the approach usually taken as it reduces an overriding concern, that of biasing the result towards the model. The second approach is to make use of the structure amplitudes  $|F_{\mathbf{h}}^c|$  derived from the model to estimate  $|F_{\mathbf{h}}^{o'}|$  and assume that the observed amplitudes are distributed in the same ratios, but are constrained such that they satisfy equation (2), *i.e.*



$$|F_{\mathbf{h}}^{o'}| = \frac{|F_{\mathbf{h}}^c|}{\sqrt{I^c}} \sqrt{I^o} \quad (4)$$

where  $I^c$  represents the fibre diffraction intensities that would be observed from the partial structure, *i.e.*  $I^c = \sum_{\mathbf{h}} |F_{\mathbf{h}}^c|^2$ . This approach makes use of more information from the model (*i.e.* the amplitude ratios as well as the phases) and is therefore expected to be more reliable if the model is closer to the full structure (*i.e.*  $\phi_{\mathbf{h}}^c$  is closer to the phase of the full structure and  $|F_{\mathbf{h}}^c|$  is closer to  $|F_{\mathbf{h}}^o|$ ). However, if the model is not close to the full structure, this synthesis can introduce more bias towards the model structure than does the first approach described above. Therefore, one is generally cautious about using this synthesis unless one is confident that the partial structure is a good approximation to the full structure, *i.e.* the missing part constitutes a relatively small part of the full structure.

Returning to single crystal crystallography, in 1960 Sim [1] showed that an improved estimate for the missing structure can be obtained by using

$$\Delta\rho(\mathbf{x}) = \mathcal{F}^{-1} \left\{ \left( w |F_{\mathbf{h}}^{o'}| - |F_{\mathbf{h}}^c| \right) \exp(i\phi_{\mathbf{h}}^c) \right\} \quad (5)$$

where the weighting function  $w$  is given by  $w = I_1(2|F_{\mathbf{h}}^o||F_{\mathbf{h}}^c|/\Sigma)/I_0(2|F_{\mathbf{h}}^o||F_{\mathbf{h}}^c|/\Sigma)$  for the acentric reflections and  $w = \tanh(|F_{\mathbf{h}}^o||F_{\mathbf{h}}^c|/\Sigma)$  for the centric reflections.  $I_m(\cdot)$  is the modified Bessel function of the first kind,  $\Sigma = \sum_j f_j^2$  and the  $f_j$  are the scattering factors of the missing atoms in the unit cell. Since the missing atoms are generally not known,  $\Sigma$  must be estimated from the data. The Sim weighting function stems from minimizing the difference (in the least-squares sense) between the actual and estimated missing electron density, and is based on Wilson's statistics [6] for the distribution of the structure amplitudes for the missing electron density. Applying Sim weighting can give a significant improvement in the accuracy of a difference map. Further modifications can be made to the synthesis to take into account errors in the known part of the structure [2].

The amplitude of a difference map is scaled by approximately one-half (for the acentric reflections), so that a map of the full structure based on the coefficients  $(2w|F_{\mathbf{h}}^o| - |F_{\mathbf{h}}^c|)\exp(i\phi_{\mathbf{h}}^c)$  gives better relative peak heights than does one based on

$w|F_{\mathbf{h}}^o|\exp(i\phi_{\mathbf{h}}^c)$  [7]. Note, however, that for the centric reflections the coefficients  $w|F_{\mathbf{h}}^o|\exp(i\phi_{\mathbf{h}}^c)$  should be used. Namba and Stubbs [8] have shown that a (unweighted) synthesis of the full electron density based on the coefficients  $(m|F_{\mathbf{h}}^{o'}| - (m-1)|F_{\mathbf{h}}^c|)\exp(i\phi_{\mathbf{h}}^c)$ , where  $m$  is the number of degrees of freedom in the spot to which  $|F_{\mathbf{h}}^o|$  belongs (defined in the next section), gives the correct relative peak heights in the fibre diffraction case.

### Optimal fibre diffraction difference Fourier synthesis

We have carried out an analysis [9,10] analogous to that of Sim for the fibre diffraction case using the statistics for the fibre diffraction data  $I^o$  [11,12] (analogous to Wilson's statistics). Significant insight is obtained by formally posing the problem as a Bayesian estimation problem [9]. The synthesis that minimizes the mean-square-error (*i.e.* the MMSE estimate) to the actual electron density is derived as follows. The structure factors corresponding to the MMSE estimate of the missing electron density are given by using the *posterior mean*  $\langle F^o P(F^o|I, F^c) \rangle$  for  $F^{o'}$  in equation (1), where  $P(F^o|I, F^c)$  is the posterior (conditional) probability density for the observed structure factors given the intensity data and the structure factors of the partial structure. Bayes theorem is used to derive the posterior density from  $P(I|F^o, F^c)$  and a prior density for the structure factors of the missing part of the structure based on Wilson's statistics, and using equation (2). Evaluating the above expressions then shows that the MMSE is given by using [9,10]

$$F_{\mathbf{h}}^{o'} = w_m \frac{|F_{\mathbf{h}}^c|}{\sqrt{I^c}} \sqrt{I^o} \quad (6)$$

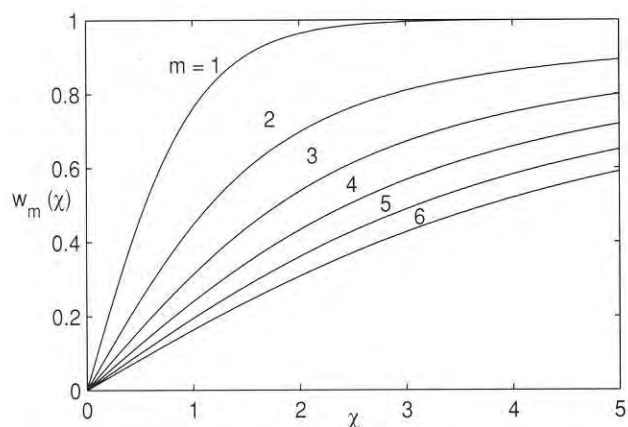
in equation (1), where

$$w_m = \frac{I_{m/2} \left( c\sqrt{I^o I^c} / \Sigma \right)}{I_{m/2-1} \left( c\sqrt{I^o I^c} / \Sigma \right)} \quad (7)$$

$m$  is the number of degrees of freedom in the datum  $I^o$  (twice the number of contributing acentric reflections or the number of contributing centric reflections),  $c = 1$  for centric reflections and 2 for acentric reflections, and  $\Sigma$  is defined as in the previous section. We have devised effective methods

for estimating  $\Sigma$  from fibre diffraction data [10]. We note that equation (7) is strictly correct only if the datum  $I^o$  contains only reflections of one type (either centric or acentric). The weighting function is considerably more complicated for mixed data [10]. Note that equation (6) takes the form of equation (4) except for the weight, *i.e.* the amplitudes are divided in the same proportion as the amplitudes from the known part, but are weighted down more, the more the known part deviates from the full structure (*i.e.* the more dissimilar are  $I^o$  and  $I^c$ ). The weights depend on the number of degrees of freedom of each datum, and reduce (as they must) to the Sim weights for  $m = 1, 2$ . The weighting function,  $w_m(\chi)$ , as a function of  $\chi = c\sqrt{(I^o I^c)}/\Sigma$ , for different numbers of degrees of freedom is shown in Fig. 1. As expected,  $w_m$  decreases as the derived  $F_{\mathbf{h}}^{o'}$  become less reliable, *i.e.* with decreasing  $\chi$  and increasing  $m$ . The effects of errors in the data and in the known part of the structure can also be included in the analysis [10].

Furthermore, we have also shown that the two currently used syntheses described above correspond to *maximum a posteriori* (MAP) estimates, *i.e.* estimates that are located at the maxima of certain posterior densities [9]. The estimate equation (3) corresponds to is the value of  $F_{\mathbf{h}}^{o'}$  that maximizes  $P(F_{\mathbf{h}}^{o'}|I, \phi_{\mathbf{h}}^c)$ , *i.e.* it uses the intensity data, and the phases (but not the amplitudes) derived from the partial structure. The second estimate, equation (4), utilizes both the amplitude and phase from the partial structure, and corresponds to the maximum of  $P(F_{\mathbf{h}}^{o'}|I, F_{\mathbf{h}}^c)$ . The MMSE estimate is generally better than the MAP estimates since it is based on the mean



**Figure 1:** The weighting function  $w_m(\chi)$  as a function of  $\chi = c\sqrt{(I^o I^c)}/\Sigma$ , for different values of  $m$ .

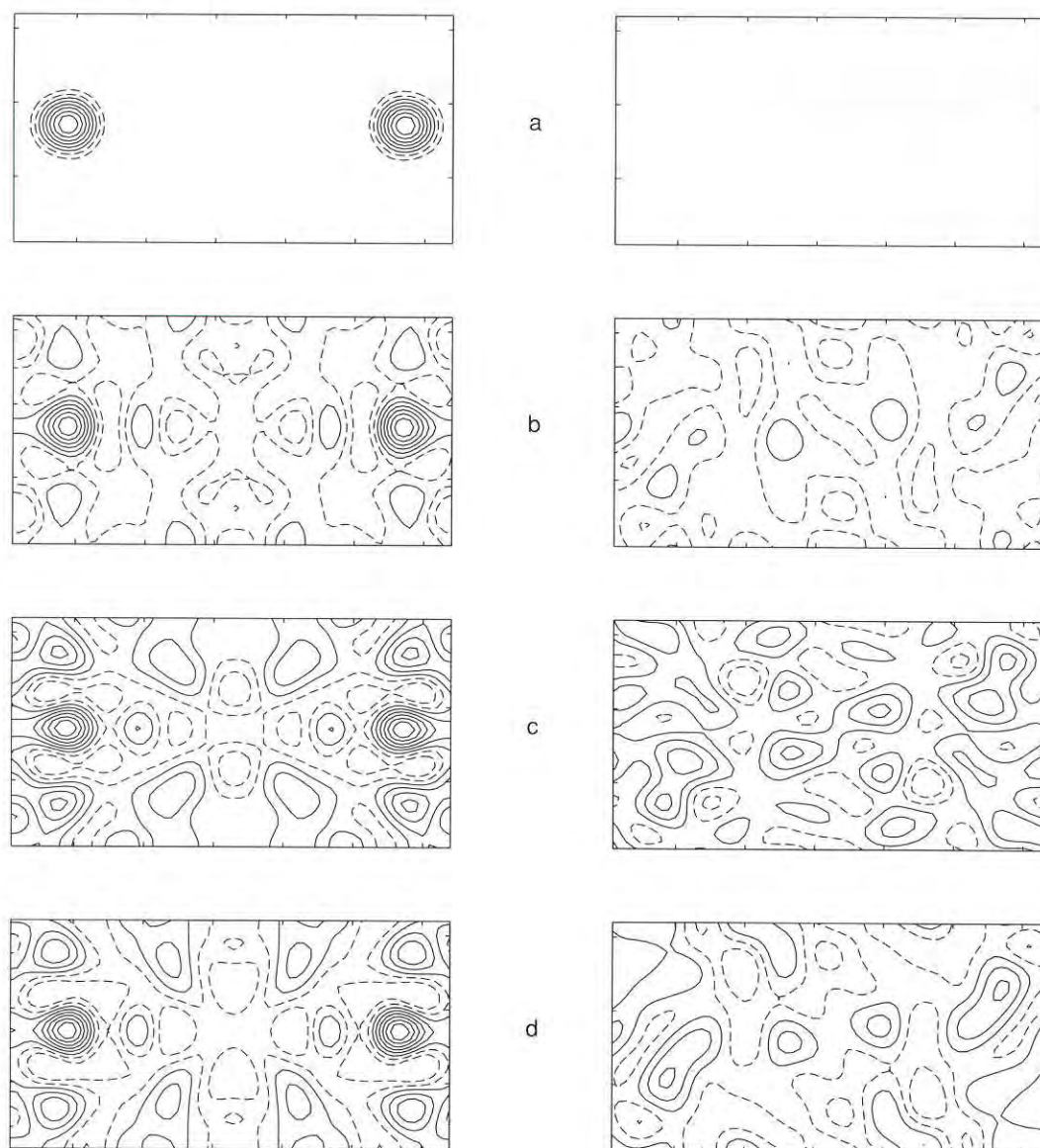
rather than the mode.

## Simulations

The performance of the various difference Fourier syntheses described above was investigated by calculating difference maps using simulated fibre diffraction data for mannan II, the structure of which is described by Millane and Hendrixson [13]. The unit cell is orthorhombic and the space group is  $I222$ . Four polymer chains pass through the unit cell with their axes at  $(1/4, 1/4)$ ,  $(1/4, 3/4)$ ,  $(3/4, 1/4)$  and  $(3/4, 3/4)$  in the  $a$ - $b$  plane. In determining this structure, conventional difference Fourier synthesis was used to locate an ordered water molecule in the crystal structure [13].

Synthetic fibre diffraction data  $I^o$  to  $2\text{\AA}$  resolution were calculated based on the crystal structure consisting of the polymer and water molecules (represented by oxygen atoms). The partial structure was taken to be that consisting of the polymer molecules only, from which the structure factors  $F_{\mathbf{h}}^c$  were calculated. The water molecule accounts for approximately 10% of the electrons in the unit cell. There are 71 unique reflections within this resolution limit, that give 51 fibre diffraction data as a result of both systematic and accidental overlaps. There are no mixed data, *i.e.* all data contain either centric or acentric reflections. For these simulations,  $\Sigma$  was calculated explicitly, as a function of resolution, using the atomic scattering factors of the missing atoms. Using these data, difference electron density maps for the water molecules were calculated using the three different methods described above.

Contour maps of the true difference electron density (calculated using the  $F_{\mathbf{h}}^o$ ) are shown in Fig. 2a at the  $z = 0$  level (left) where two water molecules are located as shown by two strong peaks, and at the  $z = 1/4$  level (right), which is between the water molecules and the difference map is relatively featureless (below the lowest contour level). Difference maps calculated based on equations (6) (MMSE), (4) and (5) are shown in Figs. 2b, c and d, respectively. Comparison of these maps with the true map (Fig. 2a) shows that the MMSE map (Fig. 2b) is superior to the other two maps in terms of a higher amplitude of the peaks corresponding to the water molecules, lower amplitudes of spurious peaks, and a smaller overall noise level. The improvement over the maps obtained using the conventional fibre



**Figure 2:** Contour plots of (a) the true difference electron density map, and estimated maps using (b) equation (6), (c) equation (3), and (d) equation (4), for mannan II. The maps are shown at levels  $z=0$  (left) and  $z=1/4$  (right). Dashed contours denote negative levels.

diffraction difference syntheses (Figs. 2c and d) is significant and is expected to improve map interpretability when real data are used and the missing structure is more complex than in this example. Note that in this example, the synthesis using equation (4) (Fig. 2d) is superior to that obtained using equation (3) (Fig. 2c). This is probably because the fraction of the total structure that is missing is rather small so that the ratios of the  $|F_{\mathbf{h}}^c|$  within a spot is a good approximation to the ratios of the  $|F_{\mathbf{h}}^o|$ .

## Discussion

A rigorous weighting scheme for difference Fourier synthesis in fibre diffraction has been derived, and is

a generalisation of Sim's weighting scheme. Simulations show the potential for significant improvements in the interpretability of difference maps using this scheme. Extensions to include the effects of errors in the diffraction data and in the partial structure, as well as the treatment of mixed (centric and acentric) data, are in progress. The weighting scheme, as well as traditional unweighted syntheses in fibre diffraction, can be neatly categorised in a Bayesian framework.

The analysis described above applies, strictly, to diffraction data from polycrystalline fibres. However, a very similar approach should be applicable to continuous diffraction data from non-crystalline fibres also. In the latter case, the problem is one of

estimating the difference electron density from the continuous diffraction data  $I_l^o(R)$  and the Fourier-Bessel structures  $G_{nl}^c(R)$  of a known partial structure. The traditional approach is to estimate the missing electron density as [8]

$$\Delta\rho(r, \theta, z) = \mathcal{FB}^{-1}\left\{\left(|G_{nl}^{o'}(R)| - |G_{nl}^c(R)|\right)\exp(i\phi_{nl}^c(R))\right\} \quad (8)$$

where  $\mathcal{FB}\{\cdot\}$  denotes the Fourier-Bessel transform,  $|G_{nl}^{o'}(R)|$  is an approximation to  $|G_{nl}^o(R)|$ , and  $\phi_{nl}^c(R)$  is the phase of  $G_{nl}^c(R)$ . The diffracted intensity  $I_l(R)$  is given by

$$I_l(R) = \sum_n |G_{nl}^o(R)|^2 \quad (9)$$

where the sum is over the values of  $n$  that satisfy the helix selection rule. In principle, the number of terms in the sum is infinite. However, for a particular molecule and value of  $R$ , the  $G_{nl}(R)$  are small for  $n$  larger than a fixed value, and the number of terms contributing to equation (9) is effectively finite [14]. Equation (9) is then of the same form as equation (2), and currently used methods to approximate  $|G_{nl}^o(R)|$  are analogous to those described in section 1, *i.e.* dividing  $I_l^o(R)$  up either equally among the contributing  $|G_{nl}^o(R)|^2$ , or in the same proportion as  $|G_{nl}^c(R)|^2$  divides  $I_l^c(R)$ . The  $G_{nl}(R)$  approximately follow Wilson's statistics [11] so that an identical approach to that described in section 2 leads to the same weighting scheme for continuous diffraction data. While this is likely to be effective in practice, a more rigorous study of the effects of a sharp cutoff in the order of the Fourier-Bessel terms that contribute to the right-hand-side of equation (9), and deviations from Wilson's statistics for the  $|G_{nl}(R)|$ , would be worthwhile.

Molecular replacement is becoming an increasingly important approach in fibre diffraction. This is particularly the case for large systems where isomorphous replacement is very demanding, but where structure determination by *ab initio* model building is not feasible. In such cases, the use of a related structure to phase, and separate the amplitudes of, the diffraction data, or to provide an initial model, is attractive. Since the model structure in molecular replacement can be considered a partial structure (with errors), molecular replacement can be considered as a problem of difference Fourier synthesis. In fact, current applications of molecular

replacement in fibre diffraction (almost exclusively with continuous diffraction data, e.g. [15]) use the model structure to phase and separate the structure factors contributing to the diffraction data from the unknown structure, in the same way as for traditional difference Fourier synthesis as described above. The weighting scheme described here is therefore expected to be useful in molecular replacement also. Two considerations will be important. Since the model structure is not strictly a part of the full structure, the effects of errors in the partial structure will be more important. And since one wishes to synthesise the full unknown structure, the effects of bias towards the model will be more important. Applications of the results presented in section 2 to molecular replacement, and investigation of the above considerations, would be worthwhile.

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## Couette Cell Commissioned

I.W.Hamley

School of Chemistry, University of Leeds, Leeds LS2 9JT.

A new Couette cell for use on NCD stations has been constructed in a collaboration between the School of Chemistry at the University of Leeds and the NCD group.

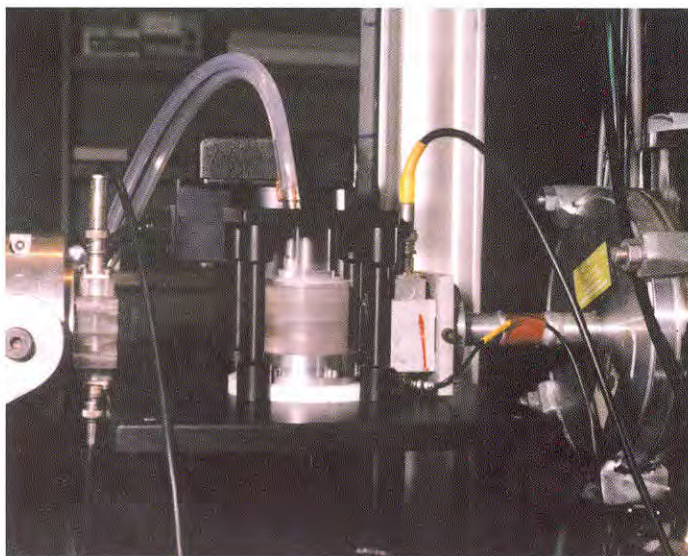


Figure 1: The Cell.



Figure 2: The Collaborators from left to right: John Pople, Ernie Komanschek, Ian Hamley, Mike Wardell and Greg Diakun.

This instrument has been designed for SAXS experiments on polymer and surfactant solutions or gels subjected to shear. It consists of a cylindrical outer rotor, machined from polycarbonate and an inner polycarbonate stator, which is cylindrical in the region through which the X-ray beam is incident, and tapered at the base. The sample gap is 0.5mm and approximately 3ml of sample is required to fill the cell. The rotor is driven by a programmable DC servo motor that can be operated in continuous or oscillatory mode. The motor is controlled from a PC.

The user can specify shear rates in the range  $0.05\text{-}1000\text{s}^{-1}$ , and for oscillatory shear the amplitude can be varied from 1 to  $1800^\circ$ . The system also comprises a refrigerated water bath for temperature control in the range  $0\text{-}85^\circ\text{C}$ . This is controlled from the software on the PC. The system was designed by John Pople, then working with Ian Hamley at the University of Leeds, and constructed in collaboration with Greg Diakun and Mike Wardell in the NCD group.

The capabilities of the instrument have recently been demonstrated on 8.2, where Ian Hamley and John Pople have been investigating the effect of shear on cubic phases formed in block copolymer and surfactant solutions. A representative diffraction pattern is shown in Fig.3. It was obtained from a gel of a poly(oxyethylene)-poly(oxybutylene) (EB) diblock copolymer in salt solution ( $0.2\text{ M K}_2\text{SO}_4$ , 30 wt% polymer) at room temperature, during continuous shear at a rate  $\dot{\gamma} = 100\text{s}^{-1}$ . The relative position of reflections, in the ratio  $1:\sqrt{2}:\sqrt{3}$ , indicates a body centred cubic structure. The pattern prior to shear was unoriented, but steady shear leads to macroscopic orientation of the gel as shown by the presence of Bragg reflections. This orientation was found to be retained upon cessation of shear.

Colleagues interested in using the device should contact Ian Hamley (I.W.Hamley@chem.leeds.ac.uk, tel: 0113 233 6430) or Greg Diakun (G.Diakun@dl.ac.uk, tel: 01925 603343) for further details.

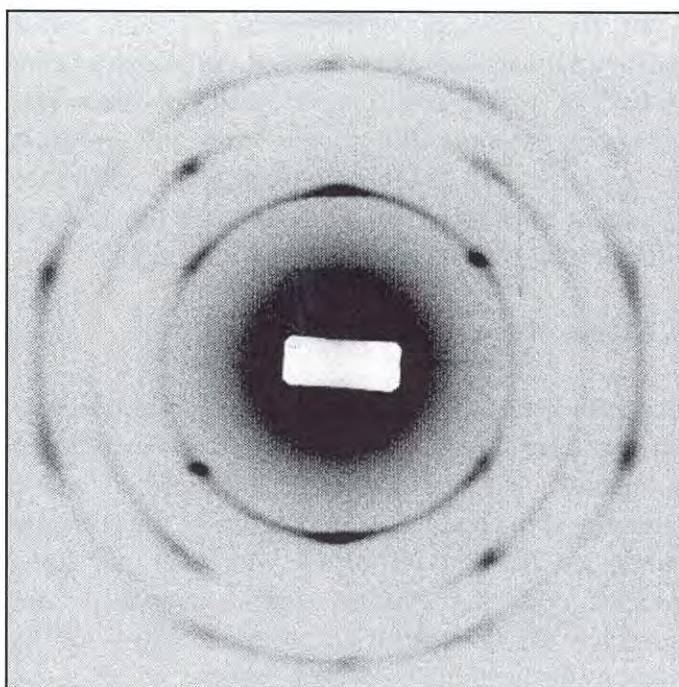


Figure 3: Diffraction pattern from a block copolymer gel oriented by steady shear.

## Data Analysis of 2D-SAXS Patterns with Fibre Symmetry from Some Elastomers

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Using a special programming tool for scientific use (PV-WAVE), a program is being developed in order to analyse quantitatively 2D SAXS patterns with fibre symmetry. As the first detectors for synchrotron radiation have become available which allow the recording of high resolution patterns with a good S/N ratio in a short time, there is an urgent need for such evaluation tools. Using data recorded during the straining of two thermoplastic elastomers, the program and the underlying concepts are presented.

### 1. Experimental

The soft/hard domain structures of two polyetheresters (Sample PBT/PEG from S. Fakirov's laboratory and the commercial product A2000/20 manufactured by DSM) are studied at HASYLAB, beamline A2 using small-angle X-ray scattering (SAXS). The samples are strained in the synchrotron beam and 2D scattering patterns are recorded on image plates. Additional data are recorded in order to eliminate the empty scattering background and to calibrate the intensity with respect to constant primary intensity and constant irradiated volume. The distance between sample and detector is about 1.8m. The usable area of the pattern is limited by the vacuum tube (10cm diameter) and the primary beam stop. The plates are scanned using a Molecular Dynamics model 400 scanner and the program ImageQuant (V3.3). It only requires a square of 12x12cm to be read for a 1.6MB data file in 16bit TIFF format ("gel format") to be generated.

### 2. Choice of the programming tool

Experience has shown that program code which is relevant for the technique of data evaluation comprises only a rather small part of the whole program, if the coding is done in one of the common languages like Pascal or C. Moreover, in some popular operating systems with a graphical user interface (GUI) one finds serious flaws in the routines for heap memory management, which cause extra programming work. I thus decided to use UNIX based versions of the programming tool

PV-WAVE, distributed by Visual Numerics Corp.

Presently my program is simply a collection of procedures and functions, which are called from the interpreter prompt. The advantages of PV-WAVE are, in particular, short development cycles, the extensive library and the close relation to the programming language IDL, another well-known programming tool for the scientist. In order to be able to write effective programs for PV-WAVE, one has to understand the paradigms of a programming language designed for the evaluation of vectors and matrices.

### 3. Data structure and file format

Basic decisions, such as how to define data structure and how to store data in a file, have far-reaching implications. Bad data structure design results in programs which force the user to process every single dataset sequentially. Good data structure design may allow the user to find his own path through the program without driving it into an inconsistent state. Thus pixel size and other parameters are stored inside each image structure, which may be extended.

Each of the evaluated patterns has to be archived. Each pattern is stored in a file of its own and the complete data structure (pixel values and pattern parameters) is mapped without any conversion into the file. Thus even large images can be read and stored fast. Representations of floating point numbers and even of integers (big-endian vs. little-endian) vary from platform to platform (e.g. UNIX on an Intel-based machine and UNIX on a Silicon Graphics workstation). In order to read files across platforms using PV-WAVE, the interpreter offers a special binary format named "exchange data format". This format enables any local PV-WAVE interpreter to convert foreign binary formats transparently into the local binary representations.

In fact, the achieved portability is not really far-reaching, since the algorithms rely on a particular data structure. Thus a new island solution is created. A major reason for this presentation was my interest in a discussion which may lead to a redesign according to a common proposal of an interchange data format for 2D scattering patterns.

Generation and definition of my image data structure can be extracted from the following:

```

; img=sf_structure( $
; 'Sample', '19961001', $
; 500, 450 )
; Generates a
; sf_structure with
; img.Width = 500
; img.Height = 450
; img.map (all zero
; floating point matrix)
; img.BoxLen = (0, 0)
; (floating point vector)
; img.Center = (0, 0)
; (integer vector)
; img.Title = 'Sample'
; img.Date = '19961001'
;
FUNCTION sf_structure, $
  name, stamp, x, y
; Generate structure and
; fill in parameter values
RETURN, $
  { , Width:x, $
    Height:y, $
    map:FLTARR(x,y), $
    BoxLen:FLTARR(2), $
    Center:INTARR(2), $
    Title:name, $
    Date:stamp }
END ; Func sf_structure

```

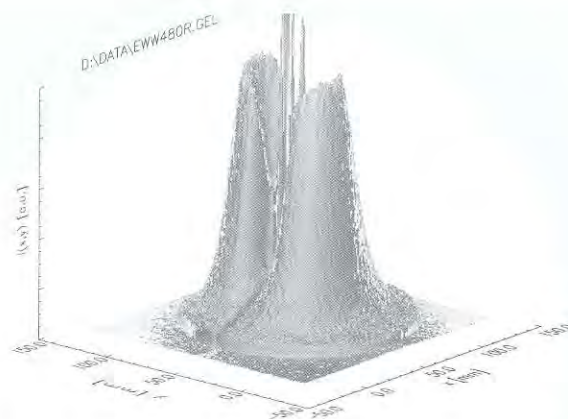
#### 4. Raw data features

The scanned scattering pattern is given in a gel format file (eww480r.gel) and must be mapped onto an image structure (e.g. r480) in computer memory (r480 = sf\_gelread( 'sbb20\_4a.gel' ) ). Then library functions of PV-WAVE can be used to display a topographical plot of the pattern on the screen. The features of the pattern determine the first steps of data evaluation (see figure 1).

##### 4.1 Shade of vacuum tube and background fog

A relatively large area outside a circle is shaded by the vacuum tube. Here we lose information on the scattering, but gain information on the height of the background fog level. Thus background fog can easily be subtracted from every pattern.

The sharp shadow boundary can be used to align sample scattering and empty scattering before correction. This is necessary, since the positions of



**Figure 1:** Raw SAXS data of a PBT/PEG, 1min after recovering from an elongation  $\epsilon=1.48$ . Image plate exposure: 2min.

the patterns vary from gel file to gel file. By extrapolating a surface into the blind outer region it may be possible to extend information on the shape of the scattering.

##### 4.2 Pattern tilt

In general, the main axis of the straining stage is not parallel to the y-direction of the scanned image. Thus provisions must be made which allow correction for a tilt angle from symmetry considerations.

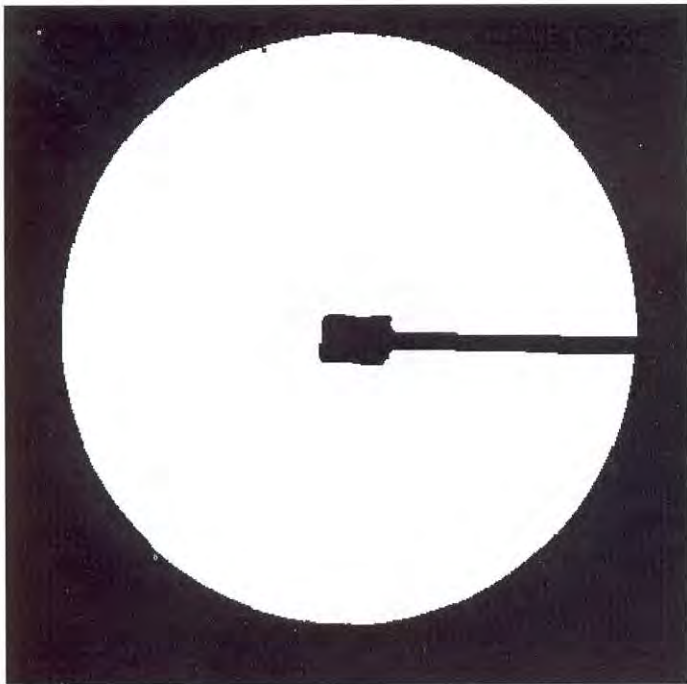
##### 4.3 Area shaded by beam stop

Information lost in the stem of the beam stop area may be reconstructed from symmetry considerations. In the centre, information is lost without any possibility to recover it. When integrals are to be computed from the pattern, it will be useful to fill the blind hole in the middle by an extrapolated surface in order to minimise systematic errors.

#### 5. Concept of masks

The evaluation steps discussed in Section 4 are coded as procedures for PV-WAVE. By my convention the names of these procedures begin with the characters "sf\_". Some of the procedures need additional information, which must be supplied by the user. Information such as a mask is frequently requested. A mask is a special image, which only contains pixel values of *true* (1) or *false* (0).

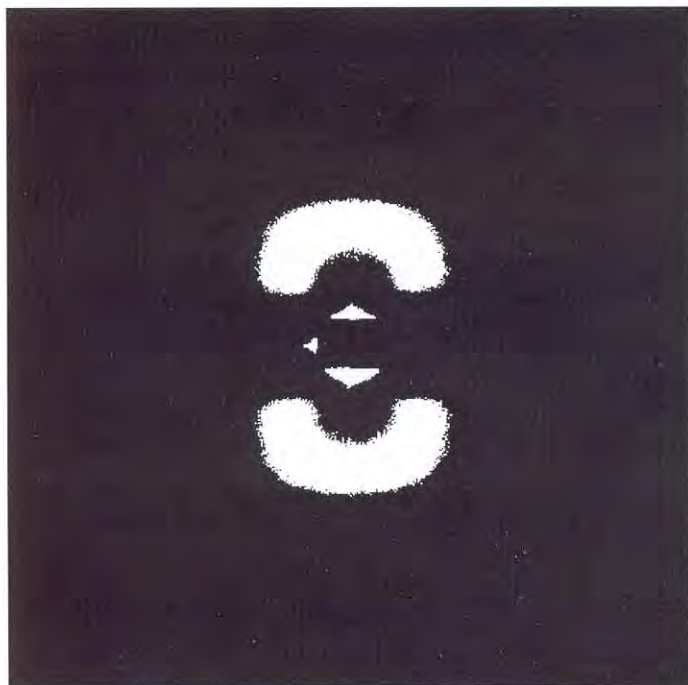
Figure 2 shows the mask which can be generated by first copying the image ( $m = r480$ ) to a mask image and then setting all intensities to *true*, which are greater than 300 counts ( $m.map=r480.map > 300$ ). In order to see the result as presented in figure 2 the



**Figure 2:** Example of a mask extracted from a SAXS pattern with fibre symmetry.

user types `tvsc1, m.map`. This mask is good for the determination of the position of the scattering pattern on the image plate. Moreover, it can be used to set the noisy blind area to zero intensity (`r480.map = r480.map * m.map`).

Before the program can start to fill information into zero intensity pixels, the image must be centred and aligned. Masking `m.map = r480.map GT 8000` yields the mask shown in figure 3. After manual erasure of the three fragments near the beam stop this mask can



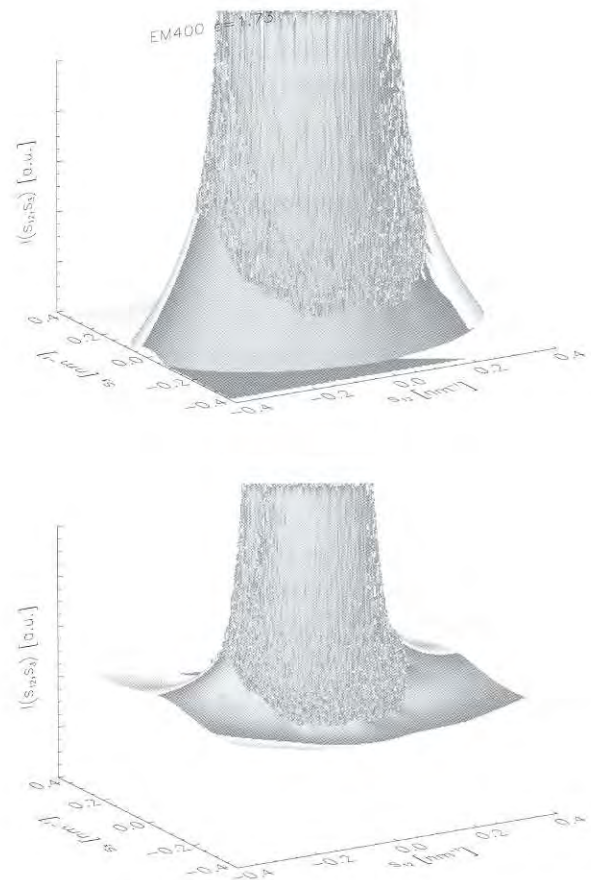
**Figure 3:** Mask for the alignment of SAXS patterns with fibre symmetry.

be used by an alignment procedure, which starts by computing centres of gravity from both the contiguous regions in the mask.

## 6. Filling in missing information

Now symmetry considerations can be used to fill some part of the blind area of the image, and the remaining part of the image may be filled with extrapolated surfaces using procedures provided in the IMSL library of PV-WAVE. A fair understanding of the advanced matrix operations built into PV-WAVE is essential for generating economical code for these algorithms. PV-WAVE code is interpreted, so there is considerable time penalty for inefficiency.

In particular, the 2D extrapolation of a surface into the outer blind area will be demonstrated. It is well known from quantitative analysis of 1D SAXS data that one should gather information on the shape of the SAXS curve over a wide angular range including



**Figure 4:** Examples of extrapolated aprons using 2D-SAXS data from different polyetheresters. Top: Arnitel A2000/20. Here the sample-detector distance is too long to give a reasonable 2D extrapolation. Bottom: PBT/PEG. In this series all the extrapolated aprons show the expected shape of a SAXS fluctuation background.



the beginning of the WAXS curve [1]. This ensures that the determination of the electron density fluctuation background is possible. If the measured data do not extend far enough into the region of Porod's law, one will have to guess the fluctuation background and information on the size distribution of domains is inaccessible.

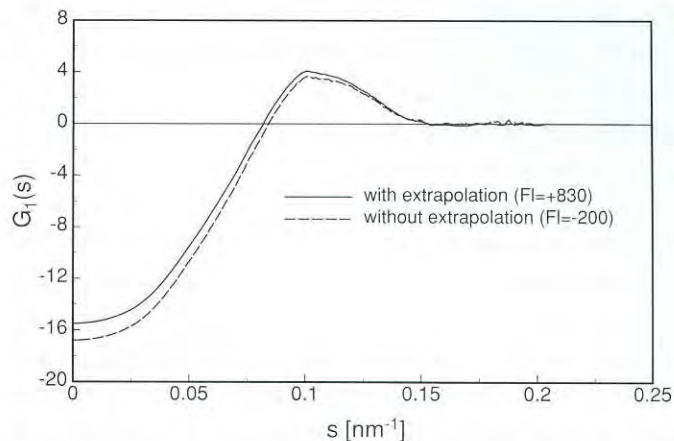
An extrapolation may be superfluous, either if the vacuum tube can be widened without risking failure of the vacuum window, or if the distance between sample and detector can be shortened without loss of information in the central part, or if it is possible to measure the same state of the sample with two different instrument adjustments. The special benefit of a 2D extrapolation may result from the fact that the fitting of a surface to given points is stiffer than the 1D fitting of a curve. Thus it might follow the expected shape of a 2D SAXS pattern, if only the measured data are sufficient for a prediction. Since we generally record patterns from a series of states, we can compare the extrapolated aprons and thus obtain some heuristic measure on the validity of the extrapolations. Examples are shown in figure 4.

## 7. Evaluation of the patterns

In order to perform a qualitative evaluation of the patterns, one does not need to work through all the stages of preprocessing, which have been demonstrated here. Thus information on several general features of the domain structure and its response on straining can be obtained from simply picking the positions of peak maxima and plotting them versus the sample elongation [2].

Modelling of the 2D scattering pattern as a whole is a challenging task for future quantitative evaluation methods. But in analogy to the one-dimensional case, a quantitative evaluation can be performed on curves, which can be extracted from the scattering patterns by projection operations. Thus the "longitudinal structure" and the "transverse structure" of the fibre may be studied [3] by application of models which describe the hard domains and the soft domains in the elastomer by 1D or 2D models in real space. The scattering intensity of the longitudinal structure  $I_1(s_3)$  is given by the projection

$$I_1(s_3) = \int_0^{\infty} s_{12} I(s_{12}, s_3) ds_{12}$$



**Figure 5:** Interference function  $G_1(s_3)$  computed from vertical projections  $I_1(s_3)$  after correction for the scattering effects of non-ideal multiphase systems. Data from sample PBT/PEG at an elongation of  $\varepsilon=1.48$ .

of the pattern intensity  $I(s_{12}, s_3)$  and the scattering intensity of the transversal structure  $I_2(s_{12})$  is defined by the projection integral

$$I_2(s_{12}) = \int_{-\infty}^{\infty} I(s_{12}, s_3) ds_3$$

The latter can be treated like any SAXS curve measured with the Kratky camera. Each of the two projections from the same scattering pattern has its own Porod law, and if the range of the measured data is insufficient for a complete evaluation of  $I_1(s_3)$ , the data in  $I_2(s_{12})$  may still suffice for a quantitative evaluation of the transverse structure.

The effect of an insufficient measuring area can easily be demonstrated by comparing different evaluations of the same sample. One of the evaluations relies on the measured pattern, the second is based on the same data after extrapolation of an apron. In order to find Porod's law in the projection  $I_1(s_3)$  obtained from the narrow area data, one has to assume a negative fluctuation background, which is of no physical sense. The corresponding projection from the wide area data shows a well expressed Porod law with a positive fluctuation background, if the shape of the apron made physical sense (as found for patterns from the sample PBT/PEG). Quantitative evaluation of the longitudinal structure is based on the analysis of an interference function  $G_1(s_3)$  [4], in which the heights of the soft domains and the heights of the hard domains are given by attenuated cosine functions. The frequency of the cosine is related to the average domain height; the attenuation factor is related to the width of the domain height distribution. An example

is shown in figure 5. The position of the peak and the general shape of the interference function are not altered by missing data and thus the average domain heights should be extractable even if the measured area is rather narrow. On the other hand, the attenuation is considerably higher in the curve obtained from the narrow scattering pattern. Thus the determination of the width of domain height distributions becomes wrong. Model fitting on several series of straining data from thermoplastic elastomers confirm this assessment. They show that determined distribution widths as a function of elongation can only be connected by a smooth curve, if the previous analysis of the Porod region has been performed in a sufficiently long angular interval.

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### Chain Mobility in Polymer Systems; Lamellar Doubling during Annealing of Polyethylene

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The motion of chains in quiescent polymer melts is confined to a reptative diffusion along the contour length as proposed by De Gennes [1,2]. In the constitutive equations based on the concept of chain reptation, it is assumed that the longest relaxation times in polymer melts correspond to the reptative motion of complete chains [3]. In the case of ultra-high molecular weight polyethylene, UHMW-PE, the experimentally determined [4,5] longest relaxation times exceed  $10^4$  seconds.

Processing of UHMW-PE via conventional routes is virtually impossible due to the high molar mass and the excessive high melt-viscosity. The viscosity of

polymer melts, above a certain threshold value for the molar mass  $M_c$ , is given by  $\log \eta_0 = C + 3.4 \log M_w$ , where  $\eta_0$  is the zero-shear viscosity. The strong increase in the melt-viscosity with increasing molar mass is related to entanglement coupling [6] and the presence of a physical entanglement network.

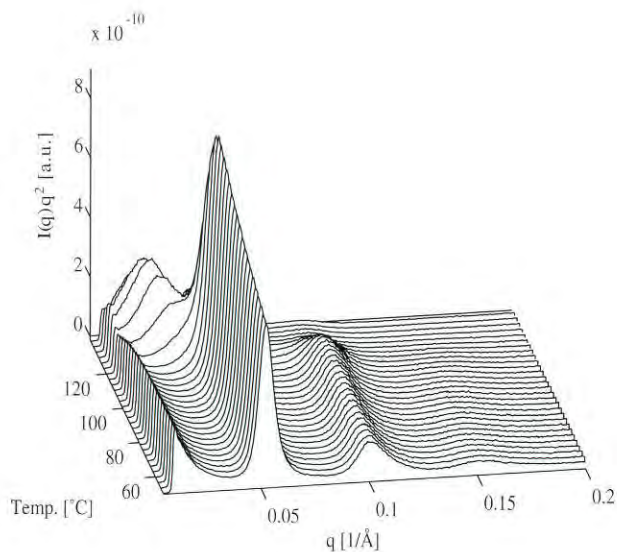
Despite many efforts in the past, no advantage could be gained by processing disentangled solution-crystallised UHMW-PE via the melt. We anticipated an initial lower melt-viscosity upon heating disentangled UHMW-PE above the melting temperature in view of the fact that a certain time period is needed to form an equilibrium melt starting from (completely) disentangled systems.

Since the long chains in UHMW-PE have to reptate into each other and the tube renewal time is expected to be relatively long, in the order of a few hours [6], welding or sintering of the UHMW-PE is practically not feasible via conventional routes. In this letter, we present a summary of our recent study on enhanced chain mobility during annealing in a temperature range close to, but below the melting point of solution-crystallised UHMW-PE. The achieved chain mobility is used in welding of the two UHMW-PE films.

### Characterisation techniques

By proper crystallisation from semi-dilute solutions of UHMW-PE ( $M_w \sim 3 \times 10^3$  kg mol, Hoechst GUR 2122), we could make films possessing well stacked lamellar crystals. By combining small-angle X-ray scattering (SAXS), Transmission Electron Microscopy (TEM) and Low-frequency Raman spectroscopy the confined motion of the polymer chains along the chain axis has been traced.

The SAXS/WAXS studies were performed at station 8.2 of the synchrotron radiation facility available in Daresbury, U.K. [7]. A Linkam THMS 600 hot-stage mounted on the optical bench with a sample holder (capillary/film) was used to perform heating, cooling or annealing experiments. The SAXS and WAXS detectors were calibrated using the usual standards. Experimental data were normalised for the transmitted intensity and corrected for detector response and the background scattering.



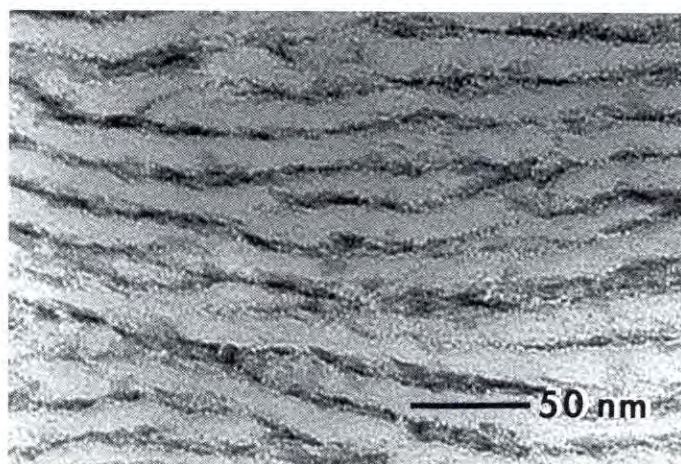
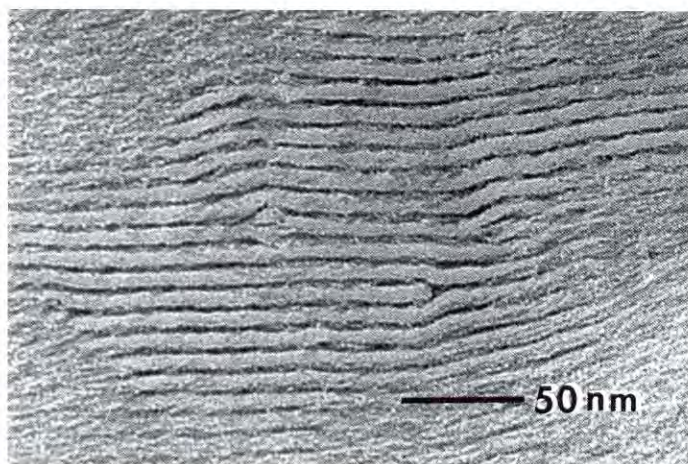
**Figure 1:** SAXS patterns of the solution-crystallised UHMW-PE film during a heating scan from 25 to 140°C at 10°C/min.

Raman spectra were obtained in-situ using a Dilor XY triple monochromator spectrometer. An Argon laser was used. The frequency shift of a peak with respect to the excitation line, denoted by  $\Delta\nu$ , expressed in  $\text{cm}^{-1}$  throughout the text, can be converted into values for the chain length within the crystalline region using the relationship derived by Schaufele and Schimanouchi [8] for paraffins. For Polyethylene, a Raman chain length,  $L_R$ , can be calculated directly from the first order by using the expression  $L_R = 3169/\Delta\nu$ . The morphology of the unannealed and annealed solution-crystallised films was examined using a Jeol JEM 2000FX transmission electron microscope.

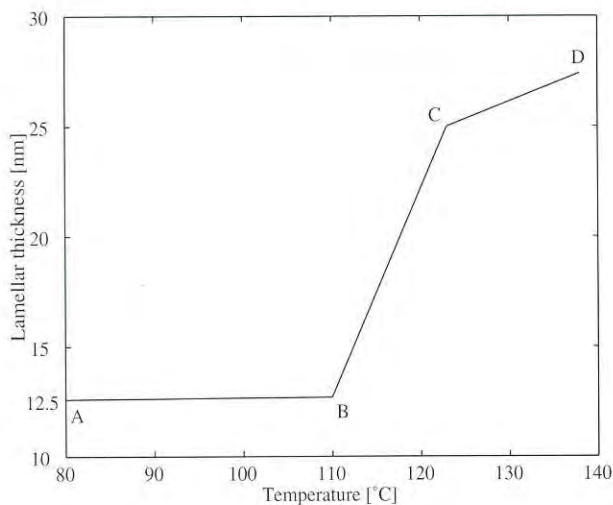
### Chain mobility below the melting temperature: Lamellar doubling

We have investigated the chain mobility during

heating in a regularly stacked solution-crystallised UHMW-PE film. Figure 1 shows the time resolved SAXS patterns while heating at a rate of 10°C/min. At low temperatures, the SAXS patterns show three peaks with decreasing intensity along the scattering wavenumber  $q$ , satisfying the Bragg's condition for the first ( $q = 0.052 \text{ \AA}^{-1}$ ), second ( $q = 0.104 \text{ \AA}^{-1}$ ), and third ( $q = 0.156 \text{ \AA}^{-1}$ ) order of an average lamellar thickness of 12nm. The higher orders and sharp peaks in SAXS patterns suggest regular stacking of lamellae with nearly constant thickness. This is confirmed by TEM (figure 2a). On heating above the threshold temperature of 110°C, initially a broad weak peak at  $q = 0.0262 \text{ \AA}^{-1}$  ( $d = 24\text{nm}$ ) appears, which becomes sharper and more intense, with diminishing intensities of the second and third orders of the 12nm crystals, and a simultaneous decrease in intensity of the first order for the 12nm crystals. The increase in lamellar thickness corresponds to a major rearrangement of chains, as confirmed by TEM in the annealed sample, figure 2b. It is evident that the thickness of the majority of the lamellar crystals increases to twice the initial value. Such a quantum increase in thickening is rather surprising and would require a proper register of lamellae with the same thickness. During heating, the loss in long range order is observed by the loss of the peaks for the second and third order. Simultaneously, the appearance of a comparatively broad peak, corresponding to a lamellar thickness of 24nm, indicates that after the quantum increase in lamellar thickness, the lamellae are no longer in perfect register as observed before heating, figure 2b. Moreover, it is intriguing to observe that after doubling, lamellae melt without substantial further thickening. Figure 3 shows a schematic representation of the increase in lamellar thickness

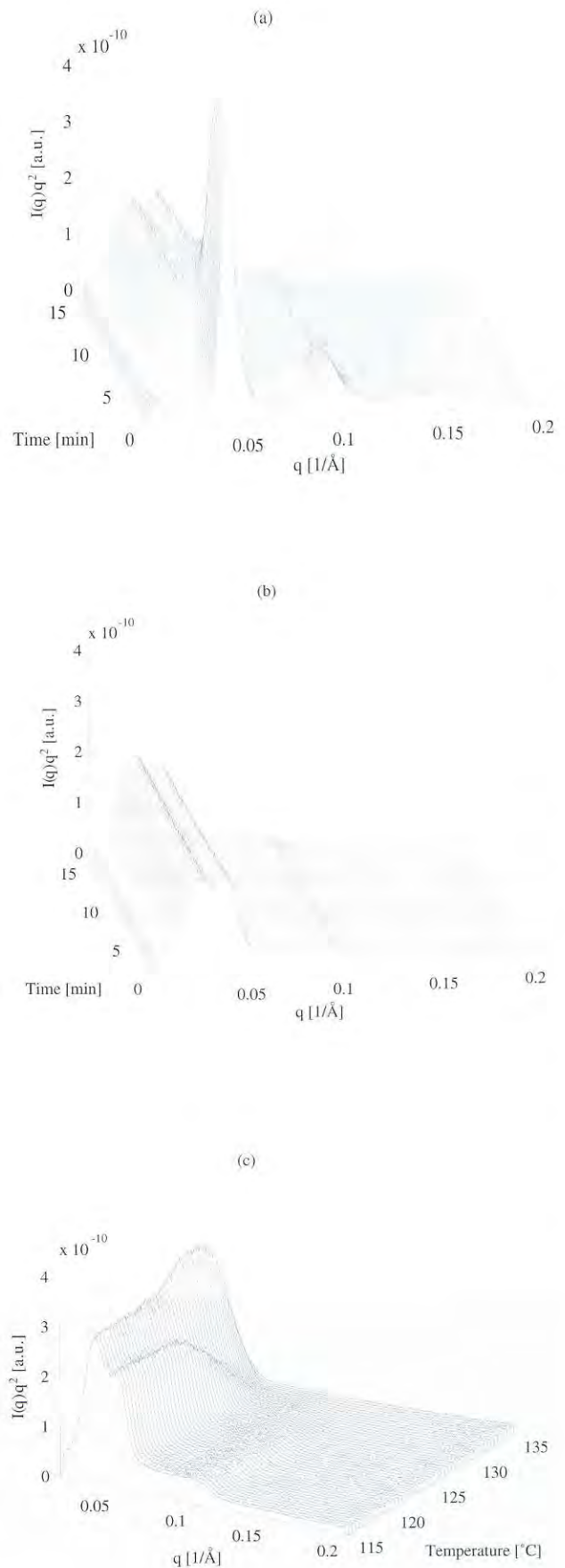


**Figure 2:** (Left) TEM of solution crystallised UHMW-PE film. (Right) TEM of the film annealed at 125°C for 15 minutes. Bands are lamellae as viewed edge-on.



**Figure 3:** A schematic representation of the increase in the lamellar thickness as function of temperature.

with temperature. Lamellae start to thicken to double the initial value above point B, 110°C. Figure 3 may be divided into three different regions, AB, BC and CD. Within region AB, the lamellar thickness is constant, whereas in region BC, two different populations in terms of lamellar thicknesses, *i.e.* 12 and 24nm, co-exist. CD is the region where the logarithmic increase in lamellar thickness occurs during annealing or heating. Region BC in figure 3, which lies between 110°C to 120°C, is of significance in evaluating the mechanism involved in lamellar thickening. Therefore, it is of interest to investigate the influence of annealing within this region. A heating scan of the sample from 75°C to 115°C at the rate of 5°C/min is shown in figure 4a. Above 110°C, a few lamellae in the bulk thicken to double the initial value, while the remaining crystals do not change in terms of thickness. Thus, in the bulk of the sample two distinct populations of lamellar thickness exist. When the sample is left to anneal at 115°C, the peak intensity for the 12nm crystals decreases, while a simultaneous increase in the peak intensity for the 24nm crystals occurs (figure 4b). The rate of increase depends on the annealing temperature. When the sample is heated further beyond the annealing temperature at a rate of 1°C/min, an increase in the peak intensity for 24nm lamellar thickness occurs with the disappearance of the peak for the 12nm lamellar thickness (see figure 4c). The lamellae melt at ~135°C without substantial thickening beyond 24nm. These results clearly demonstrate that within region BC of figure 3 only two distinct populations of the crystals exist, favouring the quantized thickening in the regularly



**Figure 4:** Time resolved SAXS patterns obtained during: (a) a heating scan from 75 to 115°C at 5°C/min (0-8 minutes) and left to anneal (8-15 minutes), (b) annealing for 15 minutes at 115°C, and (c) a heating scan from 115 to 140°C at 1°C/min.