

Second International Small-Angle X-ray Scattering Conference

The *Second International Conference on Small-Angle X-ray Scattering* was held at the Institut für Physikalische Chemie, University of Graz, Graz, Austria, from 26 to 29 August 1970. Chairman of the meeting was Professor O. Kratky, Graz, and the Co-chairman was Professor H. Brumberger, Syracuse, New York, U.S.A. Other members of the conference committee were: G. W. Brady, Murray Hill, New Jersey, U.S.A.; R. W. Hendricks, Oak Ridge, Tennessee, U.S.A.; R. Kriste, Mainz, Germany (BRD); K. Krajnc, Zagreb, Yugoslavia;

W. Ruland, Brussels, Belgium; G. G. Shipley, Welwyn, Herts. England; and P. W. Schmidt, Columbia, Missouri, U.S.A.

The meeting was sponsored by the International Union of Crystallography and the Deutsche Biologische Gesellschaft. Representing the hosts were Dr Hertha Firnberg, Austrian Federal Minister for Science and Research; Dr h.c. Josef Krainer, Governor of Styria, Dipl.-Ing. Gustav Scherbaum, Mayor of Graz; and Professor Karl Lechner, President of the University of Graz.

Following are the abstracts of the 64 papers actually presented. The author index is on p. 426. Some post-conference editing has been done by the Chairman in order to assure that each abstract fairly represents the author's position after his paper had been presented and had been discussed by the participants.

Where a paper has been presented by more than one author, the lecturer is denoted by an asterisk.

A critical review of the meeting, by A. Guinier and H. Brumberger, appears on pages 405-407.

Opening lecture

1. Small-angle scattering in crystals.

By A. GUINIER, *Service de Physique des Solides, Faculté des Sciences, Université de Paris, Orsay, France*

A crystal perturbed by inhomogeneities gives rise to a diffuse scattering, eventually in particular in the domain of small angles. This SAS may be treated either by the general theory in some cases or must be considered merely as part of the general scattering. Examples are given chosen in pre-precipitated alloys, doped ionic crystals, radiation damaged crystals and imperfectly crystallized substances as cellulose or carbon.

Theory of small-angle scattering

2. **Interpartikuläre Interferenzen in dichtgepackten Systemen.** Von G. POROD, *Physikalisches Institut, Universität Graz, Österreich*

Wie P. Debye [*Physik. Z.* (1927). 28, 135] zeigen konnte, führt bei einem Kugelgas bereits die Undurchdringlichkeit allein zu einem Interferenzeffekt von der Art eines Flüssigkeitsdiagramms. Auch abgeänderte Stati-

stiken [A. Guinier & G. Fournet, *Small-Angle Scattering of X-rays*. New York: John Wiley (1955); G. Porod, *Kolloid.-Z.* (1951). 124, 83; (1952). 125, 51] ergeben im wesentlichen ähnliche Ergebnisse. Experimentell findet man aber in der SAXS dichtgepackter Systeme den Typ der Partikelstreuung mit besonders steilem Anstieg gegen den Winkel 0.

Die Diskrepanz erklärt sich dadurch, dass die Nahordnung der Teilchen besonders empfindlich gegen Feinheiten der Form ist. Kugeln führen immer zum liquid-type, eben begrenzte Körper wie etwa Würfel können auch das entgegengesetzte Verhalten zeigen. Mathematisch lässt sich die Streuung des Systems zerlegen [G. Porod, *Int. Conf. El. magn. Scattering*, Amherst (1955)] in eine Partikelstreuung und einen Anteil, der durch den Formfaktor der gemittelten Umgebung, nämlich die Abweichung von der mittleren Elektronendichte beschrieben wird. Dieser Formfaktor muss grundsätzlich eine steilere Winkelabhängigkeit haben als der Formfaktor der Teilchen. Das Vorzeichen kann positiv oder negativ sein. Das führt zu zwei qualitativ verschiedenen Streudiagrammen, mit positiver Wechselwirkung (cluster type) und mit negativer Wechselwirkung (liquid type). Diese beiden Fälle können

durch stochastische Modellsysteme demonstriert werden.

In der Natur wird offenbar der cluster type häufiger realisiert. Er darf nicht mit der Partikelstreuung der Cluster verwechselt werden, wie an Hand der Modellsysteme gezeigt werden kann.

3. **Theory and application of an analytical method for the evaluation of polydisperse particle systems.** By M. TEICHGRÄBER* & E. WALENTA, *Institut für Faserforschung, Abt. Physik, Deutsche Akademie der Wissenschaften zu Berlin, Teltow-Seehof, Germany (DDR)*

As a preliminary step, a relationship is derived for the trigonometric Fourier coefficients, b_n , of a special correlation function

$$b_n = b_{N_0} + \frac{\pi}{R_w} \int_{u_n}^{u_{N_0}} t \cdot I(t) dt, \quad n=1, 2, \dots, N_0. \quad (1)$$

$I(u)$ is the experimental scattering curve with $u = 2 \sin \theta / \lambda$, $u_n = n / 2R_w$ and R_w is the 'radius of the interaction zone' [R. Hosemann, *Kolloid.-Z.* (1950). 117, 13].

The correlation function introduced implicitly by equation (1) is immediately related to the convolution square of the electron density in the particle system. For diluted particle

systems the coefficients b_n of equation (1) are simply related to the Fourier coefficients p_n of a distribution function $H(L)$ by

$$1 - p_n = \frac{\pi^2 n^2}{NR_w^2} b_n. \quad (2)$$

$H(L)$ represents the length distribution of those sections of a straight line arbitrarily placed in the system which are located within intersected particles. This function depends in an intricate way on the size distribution and the shape of the particles. Particularly, for monodisperse systems of spheres having the diameter D , $H(L)$ adopts a triangular shape. The corresponding Fourier coefficients $p_{n,D}$ are given by

$$p_{n,D} = 2R_w \left[2 \frac{\sin 2\pi n \delta}{2\pi n \delta} - \frac{\sin^2 \pi n \delta}{\pi^2 n^2 \delta^2} \right], \delta = \frac{D}{2R_w}. \quad (3)$$

Thus, the more general case of a polydisperse system will obviously be described by

$$1 - p_n = \int_0^{D_{\max}} P(D) \cdot (1 - p_{n,D}) dD, \quad (4)$$

where $P(D)$ is the distribution function of the particle diameter, $P(D) \equiv 0$ when $D \gtrsim D_{\max}$.

For solution, the integral equation (4) is reduced to the solution of a system of linear equations by replacing $P(D)$ by a step function

$$\frac{\pi^2 n^2}{NR_w^2} \cdot b_n = \sum m P_m a_{mn}. \quad (5)$$

P_m is the mean value of $P(D)$ in the m th partial interval and a_{mn} are coefficients which are independent of $P(D)$ and can be easily calculated.

Equations (5) are principally devoid of termination effects even though their application requires in any case only the knowledge of the scattering curve in a finite region that can be covered experimentally. The solution of $P(D)$ is represented by a histogram, the line number of which can easily be adapted to the experimental conditions while deducing the scattering curve and the experimental error.

The analytical method presented involves as a special case, equations of the theory of monodisperse systems. Likewise, the evaluation of synthetic scattering curves with $P(D)$ given led to satisfying results as well.

As examples of application to experimental results the scattering curves of various lattices and poly-

acrylonitrile fibres having different void content were evaluated and the $P(D)$ functions were compared with corresponding distributions observed by electron microscopy.

To be published in *Faserforschung u. Textiltechnik*.

4. On the solution of the equation for slit correction in small-angle scattering. By J. MAZUR, *Institute for Materials Research, National Bureau of Standards, Washington, D.C., U.S.A.*

A novel approach to the problem of the slit correction in small-angle X-ray scattering is presented, based on the matrix inversion method. The integral equation for the slit correction is written as a Volterra-type equation of the first kind. This equation is reduced to a system of simultaneous equations, expressed in matrix form. The order of the matrix is equal to the number of experimentally determined points. To obtain these equations, one has to expand the unknown function in Taylor series around each point to be subsequently determined. There is, however, a difficulty inherent in this method owing to the fact that most of the series expansions of the function to be determined lead to a strong numerical instability. However, a general method is developed, which enables us to find shifting operators leading to numerically stable systems of equations. The 'unsmearing' of the experimental data is then performed by standard matrix inversion procedures.

A general computer program (in Fortran language) was developed. In this program, no *a priori* assumption is made about the functional form for the set of experimental data. We considered four different forms for the slit weighting function:

- (1) Constant weighting function (infinite slit),
- (2) Gaussian,
- (3) Trapezoid, and
- (4) Data weighting function.

The results of the computations were subsequently tested by an inversion of the calculation procedures. The accuracy of the numerical procedure was tested both with various trial functions for which analytical methods for solution of the original integral equation are available, and with experimental data

taken from various measurements, with satisfactory results.

5. Use of integral geometry to calculate intersect distributions in small-angle X-ray scattering.† By H. WU,* *Department of Physics, Southeast Missouri State College, Cape Girardeau, Mo., U.S.A.* & P. W. SCHMIDT, *Physics Department, University of Missouri, Columbia, Mo., U.S.A.*

For an assembly of identical independent randomly-oriented particles with uniform electron density, suspended in a solvent with uniform electron density, all information obtainable from small-angle X-ray scattering can be shown to be contained in a function $G(M)$, called the intersect distribution function. An intersect, or chord, is defined to be a line which has both ends on the boundary of the particle. The intersect distribution $G(M)$ has the property that $G(M)dM$ is the probability that an intersect has a length between M and $M+dM$. By use of results from integral geometry [W. Blaschke, *Vorlesungen über Integralgeometrie*. Berlin: VEB Deutsche Verlag der Wissenschaften (1955)], equations have been obtained which permit $G(M)$ to be calculated much more easily than by methods developed previously [P. W. Schmidt, *J. Math. Phys.* (1967), 8, 475; H. Wu & P. W. Schmidt, *J. Math. Phys.* (1968), 9, 2237]. An approximate expression for $G(M)$ for small M has been obtained for a three-dimensional particle with an arbitrary smooth convex boundary surface. This expression can be written $G(M) = g_1 M + g_3 M^3 \dots$. The value of the coefficient g_1 reproduces the equivalent result obtained by R. Kirste & G. Porod [*Kolloid.-Z.* (1962), 184, 3] for the form of the characteristic function for small M . The approximation for $G(M)$ provides a general expression for the limiting form of the scattered intensity in the outer part of the small-angle scattering curve. Approximate expressions for $G(M)$ for a three dimensional particle have also been obtained for M in the neighborhood of values of M at which the first derivative of $G(M)$ is discontinuous.

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† Work supported by the National Science Foundation and Department of Defense Project Themis.

6. Principles of the correlation method for neutron small-angle scattering research. By F. HOSSFELD,* & R. AMADORI, *Institut für Festkörperforschung, Kernforschungsanlage Jülich, Jülich, Germany (BRD)*

In future neutron small-angle scattering research it might be necessary, in order to completely characterize the physical behaviour of special scattering systems, to study the dynamical, in addition to the static properties, by extending the experiments to inelastic scattering measurements. Because of the resolution required, with respect to momentum and energy transfer in small-angle scattering, the information available will be restricted by the neutron economics, which can be reasonably improved by the application of the correlation time-of-flight method. The principles of the correlation method using primary beams modulated according to (pseudo)-random sequences are outlined on the basis of a generalized theory. By comparison of the conventional time-of-flight experiment in inelastic scattering with the correlation method a gain factor is obtained which can be used to optimize the inelastic small-angle scattering experiments by selecting adequate sequences with optimal duty cycle. A survey on all pseudo-random binary sequences recently calculated and thus available to the experimentalists is presented. Computer simulations of typical experiments are used to demonstrate the power and the limitations of the correlation method.

This work is reported fully by F. Hossfeld, R. Amador & R. Scherm. (*On the Theory and Optimization of Correlation Time-of-Flight Experiments, Proceedings of the IAEA Panel Conference on Instrumentation in Inelastic Slow Neutron Scattering Research, Vienna 1969*) and F. Hossfeld & R. Amador. [*On Pseudo-random and Markov Sequences Optimizing Correlation Time-of-Flight Spectrometry, Report JÜL-684-FF (1970)*].

Experimental method

7. A neutron small-angle scattering apparatus with multidetector at the FRJ-2. By W. SCHMATZ & J. SCHELTEN,* *Institut für Festkörper- und Neutronenphysik, Kernforschungsanlage Jülich, Jülich, Germany (BRD)*

At the heavy-water moderated reactor in Jülich a high-resolution, high-intensity, small-angle scattering appa-

ratus has been constructed. Its basic features and the program of various studies in solid state physics, especially of magnetic problems will be discussed.

Neutrons are guided from a cold source inside the reactor hall into an external laboratory. The guidance is performed by total reflexion in a 27 m-long bent tube. The length of the small-angle scattering device is variable between 2 and 40 m. Corresponding to this, sizes of inhomogeneities between 20 and 2000 Å can be investigated using samples of 1 cm width. The multidetector consists of six position sensitive proportional counters of 5 cm diameter and 60 cm length. The resolution along the axis is 1 cm. A counting rate up to 20 kHz can be handled. The experiment will run on-line to a PDP8/I-4K computer. On-line operation includes data acquisition and reduction, change and registration of experimental parameters and output of all information on paper or tape. Experimental control is keyboard and/or reader oriented. First physical measurements will start with magnetic scattering on ferromagnetic Co precipitates in Cu. This investigation will check theoretical suggestions of transition from a single-domain to a multiple-domain structure with increasing precipitate size.

8. Messungen mit einer Totalreflexions-Kleinwinkelstreukammer. Von R. HOSEMANN, B. RÖDE, E. SCHNABEL,* & J. SPRINGER, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Deutschland (BRD)*

Es wird über eine Röntgenkleinwinkel-Streukammer berichtet, die einen Totalreflexions-Monochromator besitzt. Mit dieser Kammer, die verhältnismässig einfach zu justieren ist, lässt sich ein Auflösungsvermögen bei stark streuenden Präparaten von ca. 3000 Å und für schwach streuende von ca. 1000 Å erreichen. Entsprechende Messungen wurden an Latex (Dow) mit 880 und 2640 Å Durchmesser durchgeführt. Der Aufbau der Kammer wird beschrieben und Messresultate werden mitgeteilt.

9. Effect of the orientation of the specimen on small-angle X-ray scattering. By S. K. MENDIRATTA* & G. A. WALKER, *IBM Corporation, East Fishkill, N.Y., U.S.A.*

A simple specimen holder and attached rotating mechanism for a

Kratky camera are described. The axis of rotation of the specimen holder is the same as the turning axis of the vacuum tank in the Kratky camera. Thus it is possible to study the effect of the orientation of the sample on the small-angle scattering. This device can also be used to effectively increase the specimen thickness and therefore scattering from thin samples can be increased by simply rotating them. Orientation angle dependence of the scattering for some simple systems is discussed and compared with the experimental results.

10. Two modifications of the Kratky small-angle X-ray camera.† By R. W. HENDRICKS, *Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

A Kratky small-angle X-ray camera has been modified in two respects to provide increased sensitivity and performance. Flexible metal bellows seals have been mounted between the collimation system vacuum cover and the specimen chamber, and between the specimen chamber and the tank which provides a vacuum path to the detector. The elimination of four mylar windows in the X-ray path near the sample reduced the background by a factor of 15 at higher angles and by more than a factor of 50 at smaller scattering angles for a camera geometry having a 125 μ entrance slit. A flat piece of hot-pressed pyrolytic graphite has been mounted as a diffracted beam monochromator. Experimental results show the diffracting efficiency of the graphite to be about 25% – a value sufficiently high that for the same total counting time, the detector will record the same net number of X-ray photons as with balanced filters but with much improved statistics.

Published in *J. Appl. Cryst.* (1970), **3**, 348.

† Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

11. Comparison of the Kratky and Beeman collimation system for small-angle X-ray scattering.† By P. W. SCHMIDT* & I. S. PATEL, *Physics Department, University of Missouri, Columbia, Mo., U.S.A.*

Several scattering samples have been studied in the same laboratory with a

Kratky camera and also with a Bee-man four-slit collimation system. When the same sample is measured on both collimation systems, the scattering curves obtained from the two systems will differ appreciably because of the large difference in collimation conditions. However, when the measured curves are properly corrected for collimation effects, the corrected scattering curves from the two collimation systems should agree. This type of comparison thus provides a test of the collimation correction procedures used in small-angle scattering measurements. For most samples, we have found the results from the two collimation systems to be in good agreement. Explanations are offered for some of the small differences which are observed.

† Work supported by the National Science Foundation and Department of Defense Project Themis.

12. A comparison between the Bonse-Hart and the block collimation system. By O. KRATKY & H. LEOPOLD,* *Institut für physikalische Chemie der Universität Graz, Graz, Austria*

For samples of high scattering power we found a crossover point which could indicate the domains for the use of the Bonse-Hart diffractometer and the block camera of Kratky. At system resolutions $> 7000 \text{ \AA}$ the Bonse-Hart system gives more scattered intensity under the same conditions. At resolutions $< 7000 \text{ \AA}$ the block system gives the greater intensity. It should be pointed out that investigations demanding resolutions $> 7000 \text{ \AA}$ (0.7μ) could often be carried out more favourably by means of light scattering or with an ordinary microscope.

Samples of very low scattering power comprising practically all diluted solutions of macromolecules of biological or technical interest (proteins, virus, nucleic acids, chain molecules of natural or synthetic high polymers) cannot be investigated by the Bonse-Hart system for the following reasons:

- (a) the efficiency is by far too low;
- (b) the radiation background which often surpasses the level of sample scattering is higher, by more than one order, than for the block system.

For a sample of medium scattering power the Bonse-Hart system allows measurements down to somewhat

lower angles where the strongly increasing parasitic scattering terminates the angular range rather sharply. This advantage has its price in a lower scattered intensity by up to three orders and in a higher background level.

There is no essential difference between the systems concerning slit height correction; desmearing is necessary in both cases.

Published in *Makromol. Chem.* (1970). **133**, 181.

13. Bestimmung des K_{β} -Anteils der Primärstrahlung und Korrektur der Streukurven. Von P. ZIPPER, *Institut für Physikalische Chemie, Universität, Graz, Österreich*

Speziell für die Impulsregistrierung mittels eines Proportionalzählrohres in Verbindung mit einem Impulshöhenkriteriator wurde ein Verfahren entwickelt, welches es gestattet, bei der Aufnahme der Streukurven auf die Verwendung eines Filters zur Unterdrückung der K_{β} -Linie zu verzichten (P. Zipper, *Acta Phys. Austr.* (1969). **30**, 143).

Der K_{β} -Anteil der Primärstrahlung wird durch drei Messungen der Streuintensität eines Lupolenplättchens bei zwei verschiedenen Winkeln bestimmt und durch die Grösse γ , das Verhältnis der Intensitäten der K_{β} - und der K_{α} -Linie, ausgedrückt. Die Kenntnis des Intensitätsverhältnisses γ ermöglicht es, ohne β -Filter gemessene Streukurven mit Hilfe einfacher Rekursionsformeln zu korrigieren. Ausserdem besteht die Möglichkeit, auch bloss einzelne aus der Streukurve abgeleitete Parameter, wie etwa den Streumassenradius oder die Invariante, zu korrigieren, ohne dass eine Korrektur der gesamten Streukurve vorgenommen werden muss.

Das Verfahren zur Bestimmung der Absolutintensität mit Hilfe eines Eichlupolens (O. Kratky, I. Pliz & P. J. Schmitz, *J. Colloid Interface Sci.* (1966). **21**, 24) wurde geringfügig modifiziert und lässt sich nun auch ohne Kenntnis des K_{β} -Anteils der Primärstrahlung, allgemein anwenden.

14. Absolute intensity measurements in small-angle X-ray scattering. I. Theory. By R. W. HENDRICKS, *Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

Following a discussion of the defini-

tion of absolute intensity units, a general procedure for relating the absolute intensity scattered by a sample to the power detected in an X-ray counting system is developed. The effects of a nonuniform incident beam are treated rigorously. The theoretical basis of various methods for measurements of the intensity of the incident are discussed in detail. These include attenuation by multiple foils and measurement of the scattering from a calculable standard such as gases or quartz. The use of secondary standards, such as the standardization of polyethylene with a high-speed rotating disk, and the use of Ludox spheres are also considered.

Paper submitted to *J. Appl. Cryst.*

High polymers in the solid state

15. Small-angle X-ray and electron scattering study of crystalline polymers with special emphasis on the plastic deformational mechanism. By A. PETERLIN, *Research Triangle Institute, Durham, N.C., U.S.A.*

Small-angle X-ray and electron scattering is an excellent complementary technique to, but is not in competition with, electron microscopy. The latter method provides detailed information about morphology, the former is a Fourier transform and hence an average over the whole area covered by the X-ray beam. It is only by combination of both techniques that one can obtain a realistic model of a crystalline polymer and particularly of morphological changes occurring during plastic deformation which transforms the microspherulites of the starting material as crystallized from melt or solution into the highly oriented fiber structure.

Small-angle X-ray scattering first revealed the substantial change in long period during drawing. From its earliest appearance, the fiber structure exhibits a long period determined primarily by the temperature of drawing and to a minor extent by the rate of drawing but completely independent of the long period of the starting material. Such a change demands a far-reaching reorganization of the folded chain blocks during the destruction of the original lamellae. The process is discontinuous. There is no gradual transition from the long per-

iod of the starting material to that of the fiber structure.

By electron microscopy one was able to follow up the single stages of plastic deformation, particularly the appearance of micronecks at the properly oriented cracks of single lamellae. Every microneck transforms a section of the crystal into a microfibril. Blocks of folded chains are broken off and incorporated in the microfibril together with the unfolded sections of those macromolecules originally bridging the cracks between adjacent blocks. Such intrafibrillar tie molecules impart high tensile strength to the microfibril and hence to the whole fiber. The tendency to lateral coalescence of the microfibrils and to 'best matching' of adjacent crystal blocks produces densely packed crystal lamellae, nearly perpendicularly oriented to the fiber axis, which are so well documented by small-angle X-ray scattering and electron microscopy.

For further information on this subject see A. Peterlin & R. Corneliusen [*J. Polymer Sci. A2*, (1968), **6**, 1273]; A. Peterlin & F. J. Baltá Calleja [*J. Appl. Phys.* **40**, 4238]; A. Peterlin & K. Sakaoku [*Surface Morphology of Cold-Drawn Polyethylene. Clean Surfaces*, pp. 1-14. Edited by G. Goldfinger. New York: M. Decker Inc. (1970)]; and K. Sakaoku & A. Peterlin (*J. Polymer Sci. A2*. In the press).

16. Studies on glass transition phenomena in highly crystalline polymers by small-angle X-ray diffraction. By E. W. FISCHER & F. KLOSS,* *Institut für Physikalische Chemie, Universität Mainz, Germany (BRD)*

Measurements of the temperature dependence of the intensity of the small angle X-ray scattering at low temperatures are a very powerful method for detecting glass transitions in polymers of high crystallinity. Such measurements were performed on samples of solution-grown single crystals of isotactic polybutene-1, branched polyethylene (1.85 mol. % CH₃ branches) and linear polyethylene. The aim of these studies was to clear up the two problems: (a) the structure of the surface of single crystals, (b) the glass transition temperature of very thin polymer layers especially in the case of linear polyethylene.

In the case of polybutene-1 the glass transition temperature at -25°C measured by X-ray low-angle diffraction is in good agreement with reported values obtained by other measurements. The glass transition of branched polyethylene is found at -26°C whereas that of linear polyethylene at -125°C. A explanation for this shift of about 100°C is given. From the gradient of the intensity-temperature curve of linear polyethylene above T_g a value of the thermal expansion coefficient of the intercrystalline surface layer is obtained, that is in perfect agreement with the known expansion coefficient of the polyethylene melt. Conclusions are drawn from these results in regard to the so-called fold surface of polyethylene single crystals.

17. Interpretation of X-ray diffraction patterns of lamellar polyamide crystals.

By E. D. T. ATKINS, A. KELLER, D. M. SADLER* & F. M. WILLMOUTH, *H. H. Wills Physics Laboratory, University of Bristol, Bristol, England*

The diffraction patterns of the solution-crystallized polyamides referred to in the preceding paper reveal that the low- and wide-angle patterns are not independent, the relation between them depending to some extent on the sample preparation and treatment conditions. The higher orders of the basic lamellar period merge with the 00 l wide-angle reflexions. This unique situation arises because of the four repeats constituting the lamellae. In one extreme, in the case of perfect lamellar packing, we have the lattice which is sampled by the structure factor of the lamellar unit. In the other, when the lamellae are independent scatterers, the diffraction pattern is the transform of the lamella itself.

Several statements can then be made about the structure within the lamellae. Firstly, the width of the wide angle 002 reflexion gives a measure of the number of oxygen atoms in a periodic sequence across the lamellae. This number is eight, implying that the chains are extended through the lamellae. Another feature is the systematic weakness of the second order of the low angle pattern. This must arise from a discontinuity in electron density well within the layers. In view of the preceding conclusion, this discontinuity cannot arise from an alternation of ordered and randomly struc-

tured material. We associate it, therefore, with deeply buried folds. This picture also follows from several ideas about fold length fluctuations in chain-folded systems combined with the requirement that the fluctuations in polyamides must necessarily lead to large differences in fold length.

As, in 6-6 nylon, the oxygen atoms are unevenly spaced along the chain we can distinguish between the oxygen sequences associated with the cases when the amine or the acid is in the fold from the intensities in the 10 Å region. The results indicate a preference for acid folds.

Further potentialities of this kind of analysis are indicated.

Proposed for submission for publication in *J. Polymer Sci.*

18. Studies on chain folding in polyamides. By P. DREYFUSS, *Case Western Reserve University, Cleveland, Ohio, U.S.A.* & A. KELLER,* *University of Bristol H. H. Wills Physics Laboratory, Royal Fort, Bristol, England*

A series of polyamides of varying chemical composition were precipitated from solution to form sheaf-like objects consisting of single-crystal type lamellae. These can be collected in the form of orientated mats which display arced X-ray reflexions both in the wide- and low-angle regions. This enabled the fold surfaces to be indexed as 002. In a given polymer the long spacing has a characteristic value. In the series of 6-6, 6-10 and 6-12 nylons this long-spacing series is the ratio of the monomer length and corresponds closely to four monomer units. This number 4 features most prominently also in other, at the time of writing, less completely explored nylon series, although values of 3, 5 and 6 also occur. This trend, that is the number of monomer units rather than the number of carbon atoms determining the fold length, implies that the number of hydrogen bonds is the controlling factor. In view of this, and the fact that the chemical repeat period is only a small fraction of the fold length, the long period can only be apportioned between straight stems and folds in a limited number of ways. This enables some concrete suggestions to be made on the possible constitution of the fold itself.

Preliminary studies on this work are in the press for *J. Macromol. Sci. B*.

19. The determination and significance of isotropic and anisotropic density fluctuations. By R. PERRET & W. RULAND,* *Union Carbide European Research Associates, Brussels, Belgium*

In the usual theoretical treatment of the small-angle scattering from two-phase systems, the density within the two phases is considered strictly constant. This assumption holds for phases with a high degree of order or for voids; in many practical cases, however, the phases are non-crystalline or composed of imperfect crystals so that this assumption is no longer valid.

These density fluctuations produce systematic deviations from Porod's law which are detected by suitable intensity plots. The type of the plot applicable is determined by the type of fluctuation.

In polyethylene, the effect of an isotropic density fluctuation is superposed on the scattering due to the distribution of crystalline and non-crystalline domains. When measured with an 'infinite' slit, the transmission profile of the slit along the slit axis has to be taken into account for the determination of the absolute value of this fluctuation.

Non-graphitic carbons, in particular carbon fibres and vitreous carbons, show a one-dimensional density fluctuation the effect of which is superposed on the strong small-angle scattering produced by the micropore system present in these materials. This density fluctuation is produced by statistical variations of the interlayer spacing of the graphitic layers and of the layer size and shape in a given stack of layers. Owing to the anisotropy of this fluctuation the effect is orientation dependent in anisotropic carbons, e.g. carbon fibres.

20. The use of multiple small-angle scattering for the determination of structural parameters in the micron range. By R. PERRET* & W. RULAND, *Union Carbide European Research Associates, Brussels, Belgium*

Multiple scattering is often considered as an effect which is to be avoided or

reduced to a strict minimum when a quantitative interpretation of small-angle scattering is required. There are, however, cases where multiple scattering can be very useful since it permits an increase of the range of measurable sizes.

In recent studies on carbon fibres [R. Perret & W. Ruland, *J. Appl. Cryst.* (1969), 2, 209] the theory of multiple scattering given by V. Luzzati [*Acta Cryst.* (1957), 10, 643] was extended to systems with cylindrical symmetry and its application resulted in the determination of the average diameter of carbon filaments which is of the order of several microns.

This method of size determination has proved to be very useful for the determination of the swelling of carbon fibres which accompanies the formation of potassium intercalation compounds. Since the intercalation compounds are extremely sensitive to oxygen and the filament cross sections are very irregular, microscopic studies of this swelling are extremely complicated. With the multiple scattering technique the variation of the average diameter with the potassium intercalation can be measured without difficulty.

21. Absolute intensity of small-angle X-ray scattering and correlation function of crystalline polyethyleneterephthalate. By H. G. ZACHMANN* & G. KONRAD, *Institut für Physikalische Chemie, Universität, Mainz, Germany (BRD)*

The absolute intensity scattering of small-angle X-ray scattering of polyethyleneterephthalate samples crystallized under different conditions has been determined. The electron density difference calculated from the scattering power is not in agreement with that usually assumed. For samples cooled slowly from the crystallization temperature the calculated density difference is smaller than the expected value; for samples quenched from the crystallization temperature it is larger. Besides the scattering power the correlation function has also been calculated. The first maximum corresponds to the distance calculated from the position of the peak in the scattering diagram, and becomes smaller with increasing time of isothermal crystallization. The results are discussed.

22. Diagrammes de diffraction de rayons X aux petits angles par des échantillons de polyéthylène à texture d'orientation simple. Par J. J. POINT,* M. DOSIÈRE & A. GOFFIN, *Faculté Polytechnique de Mons, Mons, Belgique*

Par laminage et microtomie [J. J. Point, D. Gezovich, G. A. Homes & A. Keller, *J. Mater. Sci.* (1969), 4, 908] il est possible d'obtenir des échantillons de polyéthylène H. P. de dimensions macroscopiques et dans lesquels la presque totalité des cristaux ont la même orientation.

Le recuit thermique des échantillons n'altère pas les figures de pôle. On dispose donc d'échantillons, déformés à froid et ou déformés à froid et recuits à une température quelconque (jusqu'à quelques °C en dessous du point de fusion) qui sont uniformes en ce qui concerne l'orientation unique des cristaux.

Les diagrammes de diffraction de rayons X aux petits angles se composent essentiellement d'une paire de taches localisées dans le plan (010) du réseau réciproque (et aux plus hautes températures de recuit des ordres 2 et 3 correspondants).

Dans le cadre des modèles couramment utilisés, l'échantillon peut être décrit comme un empilement de lamelles de grandes dimensions transversales dont les faces de bases sont des plans (702) et ont une orientation remarquablement constante par rapport à la maille, bien qu'au cours du recuit, l'épaisseur des lamelles croît d'un facteur compris entre 1 et 2.

Les échantillons sont uniformes en ce qui concerne la transparence et la biréfringence. La déformation de l'échantillon lors du recuit thermique est décrite de la façon suivante. Un cube d'arêtes unitaires e_1, e_2, e_3 dirigées suivant les vecteurs unitaires $\bar{1}_a, \bar{1}_c, \bar{1}_b$ parallèles aux paramètres a, b, c de la maille, se déforme en un parallélépipède dont les arêtes $t(e_1), t(e_2), t(e_3)$ sont données par les relations suivantes:

$$\begin{aligned} t(e_1) &= a_{1a} \cdot \bar{1}_a + a_{1c} \cdot \bar{1}_c + 0 \cdot \bar{1}_b \\ t(e_2) &= a_{2a} \cdot \bar{1}_a + a_{2c} \cdot \bar{1}_c + 0 \cdot \bar{1}_b \\ t(e_3) &= 0 \cdot \bar{1}_a + 0 \cdot \bar{1}_c + 1 \cdot \bar{1}_b \end{aligned}$$

Les matrices de déformation

$$\begin{pmatrix} a_{1a} & a_{1c} & 0 \\ a_{2a} & a_{2c} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

sont données en fonction de la température de recuit.

Une observation importante est que cette matrice a une droite propre de valeur propre égale à 1 parallèle à *b* et que les deux autres droites sont dans le plan (010).

On observe en particulier que la dimension de l'échantillon parallèle à l'axe joignant les taches de diffraction aux petits angles décroît alors que l'épaisseur des lamelles croît.

On démontre de façon générale qu'un modèle où l'échantillon est supposé constitué d'empilements de cristaux lamellaires ne peut (même si on suppose un glissement interlamellaire, un glissement des colonnes de cristaux les unes par rapport aux autres et un échange de matière entre les cristaux lamellaires et une phase interstitielle éventuellement présente) rendre compte des déformations observées.

On rapporte l'anisotropie de gonflement et de dilatation thermique de ces échantillons. Le minimum du rapport de la dimension de l'échantillon après et avant le gonflement ou la dilatation thermique n'est pas dans la direction parallèle aux lamelles mais dans une direction sensiblement parallèle aux axes de chaînes. Ces observations conduisent à supposer l'existence de cristaux à chaînes étendues (ou au moins de chaînes connectant les lamelles) stabilisant une des dimensions de l'échantillon.

Le modèle proposé est analogue à celui de M. J. Hill & A. Keller [*J. Macromol. Sci.* (1969). B3, 153], et il est appuyé sur des observations faites par diffraction de rayons X aux grands angles et aux petits angles (sur les diagrammes de diffraction de rayons X aux petits angles, on observe une trainée radiale) et par l'analyse des résultats de A. Cowking, J. G. Rider, I. L. Hay & A. Keller [*J. Mater. Sci.* (1968). 3, 646].

A haute température, on observe en fonction de la température des variations réversibles de l'épaisseur des lamelles, de leur orientation, des dimensions et de la forme de l'échantillon. On ne peut rendre compte de ces observations à l'aide d'un modèle purement lamellaire.

En conclusion, il est définitivement établi qu'un modèle purement lamellaire est moins complexe que la structure réelle de l'échantillon qui doit comprendre en plus des lamelles, des cristaux à chaînes étendues. D'autre part, la constance et la valeur numérique de l'angle entre les faces des lamelles et les axes de chaînes n'ont pas d'explication simple.

Il convient de souligner que les échantillons à texture simple et à bas degré de symétrie réalisés et étudiés ici permettent de tester la validité des modèles proposés pour décrire la structure des hauts polymères.

23. Diagrammes de diffraction aux petits angles d'échantillons de polyamides doublement orientés et leur évolution lors de la déformation plastique.

Par J. J. POINT,* M. DOSIÈRE, A. GOFIN, *Faculté des Sciences, Mons, Belgique*

Les diagrammes de diffraction de rayons X aux petits angles d'échantillons de polyamides préparés par laminage sont comparés à ceux des monocristaux de polyamide préparés par cristallisation en solution.

Les distances de Bragg sont sensiblement les mêmes, mais les faces limites des lamelles ont des inclinaisons définies par rapport aux plans de liaison H (au contraire dans le cas des monocristaux ces plans limites sont parallèles aux plans de liaison H).

Dans le cas du nylon 6 α , le gonflement par une solution aqueuse de phénol, suivi de dégonflement rend les faces des lamelles parallèles à des plans de liaison H. Le même résultat est obtenu, sans changement de la dimension des lamelles parallèlement aux axes de chaîne, par un changement de phase α, γ . Un résultat analogue est obtenu par traitement thermique des échantillons de nylon 12 laminés.

Dans le cas des nylons 6, 11 et 12 les orientations anormales des diffractions de rayons X aux petits angles sont interprétées à l'aide d'un modèle de lamelles en gradins. Un désordre $\alpha\beta$ est une autre explication possible, mais seulement dans le cas du nylon 6. Les valeurs particulières des orientations des faces limites des lamelles, qui diffèrent d'une polyamide à l'autre, ne peuvent, être expliquées simplement.

La possibilité de déformer la maille des nylons 6 et 11 par un cisaillement parallèlement aux feuillettes de chaînes unies par des liaisons H est démontrée. L'amplitude des cisaillements de la maille, des lamelles et de l'échantillon sont les mêmes. Ce résultat met en évidence que l'échantillon ne comprend que la phase lamellaire et ouvre des voies nouvelles dans l'étude du polymorphisme des nylons.

24. Small- and wide-angle X-ray diffraction studies on isotactic polypropylene. By R. ZANNETTI, *Istituto Chimico, Università Bologna, Bologna, Italy*

Details are reported of the transition of the pseudo-hexagonal (smectic, paracrystalline, not crystalline-crystallizable) form of isotactic polypropylene (IPP) to the stable monoclinic form described by Natta. This solid-solid transition is carried out by annealing the pseudo-hexagonal form and it is interesting both for theoretical and practical considerations.

X-ray small-angle diffraction methods show that transition and joined crystallization phenomena are associated with a marked lamellar thickening, particularly evident in oriented specimens; the growing lamellar zones behave like those observed in many polymers as regards their dimensions and temperature-dependence phenomena.

The transformation mechanism of the pseudo-hexagonal form has been studied in unoriented specimens by radial atomic distribution analysis and it may be correlated with small-angle phenomena and data. Marked intramolecular rearrangements during the transition explain the gradual crystallization phenomena and lamellar thickening. This rearrangement is mainly a rewinding of the polymer helices, according to a statistical prevalence in the two senses of spiralization.

The transformation model explains: (a) the lower glass transition temperature of the IPP pseudo-hexagonal form in comparison with the determined value in monoclinic IPP; (b) the transparency and the easy stretching of the pseudo-hexagonal form; (c) the fibre and small-angle patterns of the same form.

Some theoretical considerations are in a good agreement with these experimental data.

25. Mosaikstruktur in Polyäthyleneinkristallen. Von H. ČACKOVIĆ,*† *Institut 'Ruđer Bosković', Zagreb, Jugoslavien* & R. HOSEMANN, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Deutschland (BRD)*

Isotherm bei 85°C hergestellte Polyäthyleneinkristalle wurden in parallel geordneten Bündeln röntgenographisch untersucht. Oberhalb 110°C

wächst beim Tempern die Langperiode in charakteristischer Weise. Aus der Äquator-Streuung und der integralen Breite einer Serie von $hk0$ -Reflexen wird eine ähnliche Zunahme der lateralen Ausdehnung der Gitterbereiche gefunden. Da es sich offensichtlich also um eine Gleichgewichtsform handelt, kann man nach der Wulffschen Gleichung aus der ziemlich genau bekannten Deckflächen-Energie der Einkristalle auf die Energie in den Korngrenzen zwischen den Mosaik-Blöcken schliessen und findet 68 erg.cm^{-2} . Aus der Breite der Reflexe konnte weiterhin geschlossen werden, dass zumindest in den untersuchten Fällen diese Korngrenzen durch 310 Netzebenen gebildet werden. In ihnen errechnet sich die zweidimensionale Kinken-Konzentration zu etwa 45%.

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26. Rekristallisation in heissverrecktem Polyäthylen mittels Röntgenkleinwinkelstreuung. Von J. LOBODA-ČAČKOVIĆ,*† *Institut 'Ruder Boskovic', Zagreb, Jugoslawe* & R. HOSEMANN, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Deutschland (BRD)*

Lineares Polyäthylen (Lupolen 6001 H) wurde etwa 10-fach bei 80°C verreckt und bei verschiedenen Temperaturen T getempert. Bei T oberhalb 110°C verraten die Röntgenkleinwinkel-Diagramme, dass zunächst die Langperiode mit der makroskopischen Dichte anwächst, um nach einigen Minuten bei konstanter Dichte zu wachsen, wobei offensichtlich die festen Grenzen zwischen amorphen und kristallinen Bereichen ausserordentlich aufgeraut werden, bis sich fast momentan Ultrafibrillen von doppelter und dreifacher Dicke bilden und dann schliesslich die festen Grenzen langsam wieder definierter werden und die Langperiode weiterhin mit der Dichte anwächst. Eine zweidimensionale Analyse der nullten, ersten und zweiten Schichtlinie und des Meridians eines Kleinwinkel-Diagrammes nach 10^4 Minuten Temperzeit und $T=120^\circ\text{C}$ gibt quantitativen Einblick in die Grösse und Form der kristallinen Bereiche und ihre Anordnung zueinander.

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27. The use of SAXS in a study of the bulk crystallisation of high polymers. By D. S. BROWN, K. U. FULCHER* & R. E. WETTON, *Department of Chemistry, University of Technology, Loughborough, Leics., England*

The bulk isothermal crystallization of high molecular weight poly(tetramethylene oxide) ($\varphi < 60\%$) has been studied over a range of temperatures using SAXS. The effects of primary and secondary crystallization on the structure have been investigated. The data obtained have been analysed using correlation functions based on a model of alternating layers of crystalline and amorphous material. This model was found to be applicable only after the early stages of primary crystallization. The sizes and widths of distribution of the crystalline and amorphous regions have been calculated as a function of time. Absolute intensity measurements have allowed the determination of the density difference between the amorphous and crystalline phases.

Chain molecules in solution

28. Determination of stiff chain parameters from scattering experiments. By W. BURCHARD* & K. KAJIWARA, *Institut für makromolekulare Chemie, Universität, Freiburg, Germany (BRD)*

Light scattering and X-ray small-angle scattering experiments have been performed from solutions of derivatives of cellulose and amylose. Both polysaccharides are built up of the same monomer unit and differ only in the way the units are linked together. This different binding has the consequence that cellulose can be approximated by a simple zig-zag chain model whilst amylose tends to form helices.

In spite of these different chain conformations the measured curves of the mean square radius of gyration versus the degree of polymerization and the curves of the X-ray small-angle scattering show a very similar feature. That is to say, these experiments can be well fitted by the freely rotating chain model, but with unreasonable values of the bond angles and the bond lengths, the latter being far too short.

When refining the model it turned out that the cellulose chain can be well fitted by a chain with symmetric potential of hindrance whereas the

amylose chain can be fitted by a simple model of a semiflexible fluctuating helix with a pitch height of 10.4Å and four residues per turn.

Up to now the X-ray small angle curves can be calculated only for the freely rotating chain. This has been done through the use of a theory of Daniels on the statistics of stiff chains. Reasons will be given for the good agreement between the experimental results and that simple model even for the case of a fluctuating helix.

29. X-ray small-angle and wide-angle investigations on marked polystyrenes in solution. By H. DURCHSCHLAG,* G. PUCHWEIN & O. KRATKY, *Institut für Physikalische Chemie, Universität, Graz, Austria* & J. W. BREITENBACH & O. F. OLAJ, *Institut für Physikalische Chemie, Universität, Wien, Austria*

Various fractions of *m*-bromopolystyrene and *o*-bromopolystyrene in benzene were studied by the X-ray small-angle and X-ray wide-angle methods. The combination of the two methods renders it possible to supply information on the short-range order and long-range order in the same molecule.

The concentration dependence of molecular weight and radius of gyration is discussed. Two possibilities of subtraction of a blank solution are compared.

With *m*-bromopolystyrene the determination of the persistence length is not directly possible but results after elimination of the crosssection factor ($a=17.3\text{Å}$). The *m*-polymer yields no wide-angle reflexions. The various parameters obtained can be explained with the existence of a coiled chain without regular conformation.

With *o*-bromopolystyrene the high mass covering per 1Å length, the large radius of gyration of the cross-section and a definite interbromine spacing ($l=4.6\text{Å}$) found in studies in the wide-angle field, afford indications for the appearance of helical ranges in solution. On the other hand the presence of large coil-ranges is shown by the direct determinability of the persistence length ($a=16.5\text{Å}$) as well as by the not too great deviation from the Gauss statistic of the coil. As the most plausible explanation of all findings with the *o*-polymer we suggest the co-existence of helical and coil ranges in solution. The

helical zones will however not extend over a large range, so that the general impression of a worm-like chain remains.

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30. The end-to-end distance of worm-like chains with curvature and torsion.
By R. G. KIRSTE, *Institut für Physikalische Chemie der Universität, Mainz, Germany (BRD)*

Like the persistent thread of Porod and Kratky [G. Porod, *Mh. Chem.* (1949). **80**, 251; G. Porod, *Z. Naturforsch.* (1949). **4a**, 401; O. Kratky & G. Porod, *Rec. Trav. Chim. Pays-Bas*, (1949). **68**, 1106] a wormlike chain is formed by the limiting process $l \rightarrow 0$, $\alpha \rightarrow 0$ starting from a valence angle chain with bond length l and valence angle $\pi - \alpha$. But the angle of rotation ϕ is hindered simultaneously and underlies a limiting process too. The calculation starts with the equation for the mean square end-to-end distance $\langle h^2 \rangle$ of a valence angle chain [M. V. Volkenstein & O. B. Ptitsyn, *Dokl. Akad. Nauk SSSR*, (1951). **78**, 657; *Zh. Fiz. Khim.* (1952). **26**, 1061].

$$\langle h^2 \rangle = Ll[1 + 2\{A(I-A)^{-1}\}_{33} - 2l^2\{A(I-A)^{-1} \times [I + A(I-A)^{-1}]\}_{33} + 2l^2\{A^{N+1}(I-A)^{-2}\}_{33}]. \quad (1)$$

L is the chain length, l is the bond length, N is the number of bonds in the chain, I is the unit matrix and A is the mean transformation matrix for the coordinate systems connected with two successive bond vectors. By calculation of the 33 elements of the matrix expressions a formula is obtained which has the form

$$\langle h^2 \rangle = Ll \frac{1 + \cos \alpha (1 + \eta)^2 + \varepsilon^2}{1 - \cos \alpha (1 - \eta)^2 - \varepsilon^2} + 2l^2[f_2(\eta, \varepsilon) + f_3(\eta, \varepsilon)]$$

with

$$\eta = \langle \cos \phi \rangle \text{ and } \varepsilon = \langle \sin \phi \rangle. \quad (2)$$

f_2 and f_3 are cumbersome functions which can be neglected for sufficiently long chains. In the limiting process the first term in equation (2) must yield $2La$ thus defining the persistence length a . The other items yield

$$2l^2(f_2 + f_3) \rightarrow -2a^2 \left[\frac{1 - 2\kappa + 2\tau(1 + \kappa + \tau/2)}{(1 + \tau)^2} \right]$$

$$+ \frac{A_{123} + A_{231} + A_{312}}{(1 + \tau)^2 (\lambda_1 - \lambda_2) (\lambda_2 - \lambda_3) (\lambda_3 - \lambda_1)}]$$

with

$$\kappa = \lim_{\alpha \rightarrow 0} \frac{1 - \cos \alpha}{(1 + \eta)^2},$$

$$\tau = \lim_{\varepsilon \rightarrow 0} \frac{\varepsilon^2}{(1 + \eta)^2},$$

$$A_{ijk} = 2 \exp \left(\frac{L}{a} \frac{1 + \tau}{\kappa} \lambda_i \right) \times \{ (\lambda_j - \lambda_k) (\lambda_i + \frac{1}{2}) [(1 + 2\tau + (\tau + 2\kappa)^2) \lambda_j \lambda_k + \kappa(1 + \tau + 2\kappa) (\lambda_j + \lambda_k) + \kappa^2] \},$$

$$\lambda_1 = u + v - \frac{1}{3},$$

$$\lambda_{2,3} = -\frac{1}{3} - (u + v)/2 \pm i\sqrt{3}(u - v)/2,$$

$$\left. \begin{array}{l} u \\ v \end{array} \right\} = \frac{1}{6} [1 - 9\kappa + 9\tau \pm 3\sqrt{3}(8\kappa^3 - \kappa^2 + \tau - 10\kappa\tau + 12\kappa^2\tau + 2\tau^2 + 6\kappa\tau^2 + \tau^3)^{1/3}]^{1/2}.$$

The expression is a real number in any case. Several special cases have to be considered partly leading to very simple formulae. $\kappa = \tau = 0$ leads to the formula of Porod & Kratky.

κ and τ appear as new parameters characterizing the type of the coil. They are connected with the curvature K and with the mean torsion T of the coil:

$$K = \frac{1 + \tau}{2a} \sqrt{\frac{2}{\kappa}} \text{ and } T = \frac{1 + \tau}{2a} \sqrt{\frac{\tau}{\kappa}}. \quad (4)$$

$\langle h^2 \rangle$ has been converted to the mean square radius of gyration $\langle r^2 \rangle$. Thus a comparison with the experimental function $\langle r^2 \rangle$ versus the molecular weight M is possible. Dilute solutions of polymethylmethacrylate and of cellulose trinitrate in acetone and of desoxyribonucleic acid in usual buffer exhibit a good agreement with the model calculation if the parameters κ and τ are taken as 0.5 and 0 respectively. The radii of gyration have been measured by small-angle X-ray scattering or by light scattering.

To be published in *Kolloid.-Z.*

31. Investigation of the structure of DNA in solution by small-angle X-ray scattering.
By R. G. KIRSTE & R. C. OBERTHÜR, **Institut für Physikalische Chemie, Universität, Mainz, Germany (BRD)*

Small-angle X-ray scattering and light scattering of trout sperm DNA in aqueous solution have been measured

[R. G. Kirste & R. C. Oberthür, *Makromol. Chem.* (1969). **127**, 301] in a wide range of momentum transfer $h = (4\pi/\lambda) \sin \vartheta$. Within a medium range of h the DNA molecules scatter like rigid rods with a cross section radius of gyration $r_c = 8.3 \text{ \AA}$. At $h < 0.015 \text{ \AA}^{-1}$ a deviation of this rod scattering function occurs which cannot be explained by the coiling of the thread alone, and may be due to a complex polyelectrolyte effect. For $h > 0.32 \text{ \AA}^{-1}$, on the other hand, the double helix structure affects the scattering function.

A maximum and a minimum are observed at $h = 0.38$ and $h = 0.50 \text{ \AA}^{-1}$, respectively. The measured intensity could be interpreted quantitatively as the scattering function of a double helical line (with pitch $H = 33.5 \text{ \AA}$, radius $R = 6.9 \text{ \AA}$ and phase difference between the two helices $\Delta\phi = 2.5 = 143^\circ$) which is multiplied with the Fourier transform of a Gaussian electron density distribution corresponding to an axial radius of gyration of $r_c = 3.75 \text{ \AA}$. This yields a total axial radius of gyration of the double helix of $r_c = 7.85 \text{ \AA}$.

A comparison of these parameters with the known conformations of DNA in fibres exhibits the best agreement with the *B* conformation. The agreement is still better if an additional scattering mass (counter ions) is assumed to be close to the phosphate groups of the solved DNA.

To be published in *Makromol. Chem.*

Proteins and viruses

32. A new analysis of experimental scattering functions of dilute monodisperse systems by using the mathematical apparatus of the theory of angular momentum. The determination of shape and inner structure of dissolved proteins.
By H. B. STUHRMANN, *Institut für Physikalische Chemie, Universität Mainz, Mainz, Germany (BRD)*

The electron density distribution of a molecule is expanded as a series of spherical harmonics Y_{lm} . From the rotational properties of the Y_{lm} it is deduced that the orientation of the partial structures, which are described by the sum of the multipole components with the same l , has no influence on small-angle scattering. There are no interference terms between these partial structures, i.e.

small-angle scattering functions of these partial structures superimpose independently. Therefore structures giving the same small-angle scattering can be generated by independent rotations of the partial structures. New partial structures are obtained by expanding the scatterer in a displaced coordinate system. This transformation does not affect SAXS and offers a new starting point for the construction of another family of solutions of SAXS.

The infinite number of solutions of SAXS of dilute monodisperse solutions is drastically reduced to few possible structures (shapes) in the case of two-phase scattering (or shape scattering) as described by G. Porod. Measuring the SAXS of particles in solvents with different electron density shape scattering $I_f(f=\text{form})$ can be separated from the SAXS I_s ($s=\text{Schwankung}$) arising from the deviation of the local electron density from the mean value and I_{fs} , a term containing the influence of both parts.

Correlating the coefficients of the power series of the shape SAXS with the coefficients of the expansion of the shape as a series of spherical harmonics, the shape of myoglobin has been determined. Up to now ten coefficients of the shape belonging to Y_{lm} with $l=0, 1, 2, 3$ have been calculated from the coefficients of the measured shape SAXS. The determination of the shape seems to be unique. The results are very similar to those found by crystallographic investigations. The shape is being refined by including more coefficients in the calculation.

The investigation of the inner structure, together with the interpretation of I_s and I_{fs} , is in progress.

The calculations are greatly facilitated by the properties of the $3j$ and $6j$ coefficients widely used in nuclear physics. The Hankel transformations of the multipole components are reduced to an algebraic problem by the introduction of Laguerre polynomials.

33. A small-angle X-ray investigation of ribonuclease.† By J. W. ANDEREGG,* *Biophysics Laboratory, University of Wisconsin, Madison, Wisconsin, U.S.A.* & R. W. HENDRICKS, *Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

Bovine pancreas ribonuclease, in 0.1 M NaH_2PO_4 and 0.15 M KCl solu-

tions, has been studied at 20°C in several concentrations by SAXS. The radius of gyration, extrapolated to zero concentration, is determined to be 14.4 Å and is, within our experimental error, independent of buffer. Using two-component solution theory the molecular weight in the phosphate solution is determined as 14300 daltons, in good agreement with the known weight. The shape of our scattering curve does not fit exactly any of the curves for constant electron density ellipsoids of revolution. However, it is best fit by a prolate ellipsoid with an axial ratio of approximately 2.5:1. These data will be compared with the calculations (based on single crystal data) by Kartha (this conference). A value for the molecular weight in the KCl solution is currently being determined using multicomponent solution theory.

† Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

34. Small-angle X-ray scattering calculations on ribonuclease. By G. KARTHA, *Center for Crystallographic Research, Buffalo, New York, U.S.A.*

The group of enzymes having ribonuclease activity has been studied in very great detail by various techniques. Many of the studies on the structure function relationship of this enzyme have been carried out on bovine pancreatic ribonuclease. The X-ray diffraction studies of ribonuclease crystals at 2 Å resolution have yielded a three-dimensional model for the folding of the polypeptide chains in the molecule as they occur in these crystals.

It is of interest to know how much this structure resembles the structure of molecules in solution. One possibility that is considered here is that of calculating the small-angle scattering properties of the ribonuclease model obtained from crystallographic studies for comparison with results from solution studies. Both the radius of gyration and the radial intensity distribution function have been calculated on the basis of the model and the results will be discussed.

35. X-ray small-angle studies on the allosteric glyceraldehyde-3-phosphate dehydrogenase from yeast. By H.

DURCHSCHLAG,* G. PUCHWEIN & O. KRATKY, *Institut für Physikalische Chemie, Universität, Graz, Austria* & I. SCHUSTER & K. KIRSCHNER, *Max-Planck-Institut für Physikalische Chemie, Göttingen, Germany (BRD)*

Strong evidence in favour of the allosteric mechanism of NAD binding to yeast GAPDH has been obtained with the X-ray small-angle scattering technique [H. Durchschlag, G. Puchwein, O. Kratky, I. Schuster & K. Kirschner, *FEBS Letters*, (1969), **4**, 75; *Eur. J. Biochem.* Submitted for publication].

Samples of yeast GAPDH were investigated at pH 8.5 and 40°C and five different degrees of saturation with the coenzyme NAD. Because of the temperature sensitivity of the sample the use of a special flow device became necessary.

Apo-enzyme revealed a contraction in volume depending upon the degree of saturation. Fully saturated, the contraction amounts to 7%. As the observed degree of contraction is not linearly proportional to the degree of saturation, the simple sequential mechanism is ruled out. Furthermore the predictions of the allosteric mechanism are quantitatively fulfilled.

Hollow circular cylinders with $h:2r_1=0.6:1$ (apo-enzyme) or $h:2r_1=0.58:1$ (holo-enzyme) may be regarded as sufficiently equivalent in scattering. Even if the molecule consists of four subunits they consequently must be arranged in such a way that the entire particle is very similar to a hollow cylinder. The experimental determination of the radius of gyration (apo-enzyme: $R=32.1$ Å; holo-enzyme: $R=31.7$ Å) leads to the calculation of the absolute particle dimensions.

The results show that the enzyme molecule contracts upon binding NAD. Moreover, the kind of structural changes occurring in the allosteric transition can be described in terms of an increase in the inherent anisotropy and a considerable reduction of the solvent included in the tetrameric assembly.

36. Small-angle X-ray scattering of liquids and lipoproteins. By G. G. SHIPLEY* & D. ATKINSON, *Unilever Research Laboratory, Welwyn, Herts., England*

X-ray diffraction and small-angle X-ray scattering methods have been

used to examine dilute aqueous dispersions of neutral and charged phospholipids.

Egg-yolk lecithin (EYL) in a dilute dispersion exists as a two phase system, a lamellar lipid-water structure ($d \approx 65 \text{ \AA}$) in excess water [F. Reiss-Huson, *J. Mol. Biol.* (1967), **25**, 363]. Sonication, or sonication followed by gel filtration [C. Huang, *Biochemistry*, (1969), **8**, 344], has been used to produce more homogeneous dispersions of EYL, the latter method supposedly producing single lipid-bilayer vesicles. X-ray scattering from (a) shaken (b) sonicated and (c) sonicated and filtered, EYL dispersions shows the presence of the multilamellar structure in the shaken dispersion, a gradual removal of the sharp diffraction lines characteristic of this structure on increasing the sonication time, and finally the presence of a broad scattering peak in the region $0.5 \leq h \leq 1.5 \text{ \AA}^{-1}$.

In contrast to EYL, ox-brain phosphatidylserine (PS), a lipid possessing a net negative charge, is able to incorporate large amounts of water between the lipid bilayers [G. G. Shipley, R. B. Leslie & D. Chapman, *Nature, Lond.* (1969), **222**, 561]. The X-ray scattering from dilute dispersions of PS obtained by shaking alone is almost identical to the scattering from the sonicated dispersions of EYL, thus indicating a close structural similarity between the two systems.

The relationship between the theoretical scattering from multilamellar and single lipid-bilayer vesicles has been examined for spherical particles as a function of the lamellar order. An important feature of the step electron density models used to describe the bilayer organization is that, in order to produce a theoretical curve consistent with the experimental scattering from sonicated EYL dispersions, a region of negative electron density corresponding to the hydrocarbon chain region is required. The evidence obtained so far suggests that no drastic structural change occurs in the lipid bilayer region on limited sonication.

Further small-angle X-ray scattering and ultracentrifugation studies of phospholipid-cytochrome *c* complexes in iso-octane [G. G. Shipley, R. B. Leslie & D. Chapman, *Biochim. Biophys. Acta*, (1969), **173**, 1] show that the aggregate size of the extracted complex is dependent upon the lipid

to protein ratio and in turn indicates that protein-protein interactions are an important feature of the aggregation process.

A preliminary X-ray scattering study of natural and reconstituted human serum lipoproteins [A. Scanu, E. Cump, J. Toth, S. Koga, E. Stiller & L. Albers, *Biochemistry*, (1970), **9** 1327], particularly fraction HDL₂ (a) gives dimensions for the natural HDL₂ consistent with existing electron microscope and centrifugation data and (b) indicates that the reconstituted HDL₂ is similar but not identical to natural HDL₂.

37. Small-angle X-ray scattering of dilute solutions of bovine fibrinogen. By K. LEDERER,* *Department of Biological Sciences, State University of New York at Albany, Albany, N.Y., U.S.A.* & H. CHESSIN, *Department of Physics, State University of New York at Albany, Albany, N.Y., U.S.A.*

SAXS measurements were performed on bovine fibrinogen solutions, $c = 3$ to 22 mg.ml^{-1} , at 6°C . Armour bovine fibrinogen was purified by the method of Laki and dissolved in phosphate buffer, $\text{pH} = 6.40$, $\Gamma = 0.42 \text{ M}$ (0.40 M NaCl , $0.01 \text{ M NaH}_2\text{PO}_4$, 0.0055 M NaOH , $0.01 \text{ M } \epsilon\text{-amino-}n\text{-caproic acid}$, $0.0033 \text{ M cysteine}$). The clottability of the samples was consistently 93 to 96%. The SAXS measurements were carried out using a special X-ray copper tube (Kratky), a Kratky camera and a proportional counter with pulse height discriminator. The scattering intensity was recorded in an angular range from 0.0014 to 0.070 radians. At angles greater than 0.045 radians, the intensity appeared to obey Porod's $1/\theta^3$ law. Collimation errors (infinite slit length) were corrected using the computer program of Heine. The absolute intensity was measured by a polyethylene standard supplied by Kratky and coworkers. The following molecular parameters could be determined: The radius of gyration ($R = 142 \pm 5 \text{ \AA}$), the molecular weight ($M = 406000$ to 478000 ; depending on an assumed partial specific volume $\bar{v} = 0.70$ to $0.72 \text{ cm}^3.\text{g}^{-1}$), the molecular volume [$V = (1.02 \pm 0.10) \times 10^6 \text{ \AA}^3$; from Porod's invariant integral], internal hydration 0.56 – $0.81 \text{ g water/g protein}$; also depending on $\bar{v} = 0.72$

to 0.70), and the surface to volume ratio ($S/V = 0.44 \pm 0.10 \text{ \AA}^2/\text{ \AA}^3$).

The angular dependence of the scattering intensity was compared with theoretical scattering curves of various fibrinogen models based on electron microscopy. The theoretical scattering curve of the cage-like, isotropic model of Köppel turned out to be the one closest to the experimental curve. The agreement between this model and the SAXS data is however not complete. Expected side maxima are completely smeared out. The widely accepted notion of an elongated fibrinogen molecule does appear to be incompatible with the data.

This work was supported by Research Grants GM 14891-02 and -03 from the National Institute of General Medical Science, NIH, administered by Professor R. D. Allen.

To be submitted to *J. Mol. Biol.*

38. X-ray small-angle scattering of phosphorylase *b* in solution. By G. PUCHWEIN* & O. KRATKY, *Institut für physikalische Chemie, Universität Graz, Austria* & C. F. GÖLKER & E. HELMREICH, *Physiologisch-Chemisches Institut, Universität, Würzburg, Germany (BRD)*

Muscle glycogen phosphorylase *b* in glycerophosphate buffer, $\text{pH} = 7.5$, $\Gamma/2 = 0.13$, was studied under a variety of conditions (concentration range of protein 2.56 to 13.65 mg/ml , temperatures 21 and 30°C ; content of the allosteric effector $5'$ -AMP: 0 to $5 \times 10^{-3} \text{ M}$) in order to derive a structural model of the molecule and to determine the influence of $5'$ -AMP on its structure.

At 30°C phosphorylase *b* was present in solution as a quite homogenous dimer as shown by the sedimentation behaviour in the ultracentrifuge. The presence or absence of $5'$ -AMP did not result in any significant change of the scattering behaviour. At 21°C on the other hand the majority of the molecules were present as tetramers in a solution containing $1 \times 10^{-3} \text{ M } 5'$ -AMP and $2 \times 10^{-1} \text{ M NaF}$ though the presence of a substantial amount of dimeric molecules was indicated by a molecular weight in between that of a dimer and a tetramer.

On the assumption – corroborated by ultracentrifugal analysis – that only

two species of phosphorylase *b* molecules, dimers and tetramers, were present, it was possible to derive prismatic models for both dimer *b* and tetramer *b* with the axes of 55·3, 61·6, 109·4 and 55·3, 109·4, 123·2 Å respectively. Deviations at large angles of the theoretical scattering curves of the prismatic models from the experimentally determined curves and the difference in volume between the models and the real molecules are taken to suggest a substructure in the molecules. This is also indicated by the electromicroscopic data of D. A. Chignell, W. B. Gratzer & R. C. Valentine [*Biochemistry*, (1968), 7, 1082] and R. C. Valentine & D. A. Chignell [*Nature, Lond.* (1968), 218, 950]. For a discussion of a substructure, theoretical scattering curves for models made up of ellipsoidal subunits are presented and compared with the experimental curves.

To be published in *Biochemistry*.

39. Investigations of helix pomatia haemocyanin. By I. PILZ* & O. KRATKY, *Institut für physikalische Chemie der Universität Graz, Austria* & I. MORING-CLAESSON, *Fysikalisk-Kemiska Institutionen, Uppsala Universitet, Sweden*

Haemocyanin, the blue blood pigment of the snail *helix pomatia*, was studied with the help of the small-angle X-ray scattering in pure water and in 0·05 *M* borate buffer at pH 8·2.

In water we found a homodisperse solution of the entire molecules, the molecular weight of which was $8\cdot95 \times 10^6$. The scattering curve agreed very well with the shape of a hollow cylinder of the following dimensions: cylinder height 360 Å, inner diameter 150 Å and outer diameter 330 Å. The great number of subsidiary maxima, which appear in the scattering curve, and also the high degree of swelling indicate that the molecule is composed of subunits.

At pH 8·2 we found fragments of haemocyanin, which had a molecular weight of about 9×10^5 , that is to say, these fragments are tenths of the whole molecule.

40. Röntgen-Kleinwinkel-Untersuchungen an α -Keratin-Fasern. Von H. HALBOTH,* *ENKA-Glanzstoff AG, Wuppertal-Elberfeld, Deutschland (BRD)*,

G. HEIDEMANN, *Textilforschungsanstalt, Krefeld, Deutschland (BRD)* & H. ZAHN, *Deutsches Wollforschungsinstitut an der Rheinisch-Westfälischen Technischen Hochschule, Aachen, Deutschland (BRD)*

Mit einer evakuierbaren Lochblendenkamera, einer modifizierten Kiessig-Kamera, wurden auf Film die Textur-Diagramme verschiedener α -Keratin-Fasern aufgenommen. Hierzu standen verschiedene Sorten Wolle, Tier- und Menschenhaar zur Verfügung. Neben dem qualitativen Vergleich wurde versucht, aus der Intensitätsmessung der äquatorialen Kleinwinkel-Streuung dieser Fasern mit einer Kratky-Kamera quantitative Aussagen zu gewinnen.

Am Beispiel von Alpaca-Proben, die von den gleichen Tieren aus unterschiedlichen Lebensbedingungen stammen, wurde ein Zusammenhang zwischen mechanischen Festigkeitseigenschaften und der Intensität diskreter Röntgen-Kleinwinkel-Reflexe gefunden. Die Fasern mit der größeren Festigkeit lieferten das Röntgen-diagramm mit den schärferen Reflexen.

In verschiedenen Medien gequollene Mohair-Proben zeigten Röntgen-diagramme, die auf unterschiedliche Gitteraufweitungen schliessen lassen. In Abhängigkeit der Konzentration von Propanol in Wasser wurden ebenfalls Gitteränderungen des gequollenen Faser-Materials beobachtet.

Spezifische Markierungen der Aminosäure-Reste dieser Fasern durch Reagenzien, die Schweratome enthalten, führten zu Intensitätsänderungen bestimmter Meridianreflexe. Durch diese röntgenographischen Ergebnisse von spezifisch markierten Aminosäure-Resten wird die Theorie gestützt, dass die Aminosäure-Reste der α -Keratin-Fasern in bestimmten Sequenzen vorliegen.

Literatur

- G. Heidemann & H. Halboth, *Nature, Lond.* (1967), 213, 71.
 M. Spei, G. Heidemann & H. Halboth, *Nature, Lond.* (1968), 217, 247.
 M. Spei, G. Heidemann & H. Zahn, *Naturwissenschaften*, (1968), 55, 346.
 G. Heidemann & H. Halboth, *The Fibrillar Swelling of α -Keratin*. Im Druck.

H. Halboth & G. Heidemann, *Alpaca as an Example for the Comparison of Low-Angle X-ray Diffraction Diagrams and Mechanical Properties of α -Keratin Fibres*. In Vorbereitung.

H. Halboth & G. Heidemann, *Röntgenographische Strukturuntersuchungen an α -Keratinfasern*. In Vorbereitung.

41. Röntgenkleinwinkelmessungen an den Bakteriophagen *fr* und R17. Von P. ZIPPER* & O. KRATKY, *Institut für Physikalische Chemie, Universität, Graz, Austria* & R. HERRMANN & TH. HOHN, *Max-Planck-Institut für Virusforschung, Tübingen, Deutschland (BRD)*

An den *E. Coli*-Phagen *fr* und R17 wurden umfangreiche Röntgenkleinwinkelmessungen vorgenommen. Die Streukurven beider Phagen erweisen sich als nahezu identisch. Das aus der Streuintensität beim Winkel null bestimmte Molekulargewicht steht in bestem Einklang mit der bekannten chemischen Zusammensetzung der Phagen. Der Streumassenradius der Phagen beträgt $105,2 \pm 2,1$ Å.

Wie aus Messungen in einem 0,02 *M* Tris-Puffer abgeleitete radiale Elektronendichteverteilung erkennen lässt, bestehen die Phagen aus einem Kern und einer dichteren Hülle. Messungen in Rohrzuckerlösungen zeigen, dass der Kern die RNS enthält. Allerdings ist nicht die gesamte RNS im Kern lokalisiert. Wir können daher annehmen, dass ein Teil der RNS (rund 20%) in die Proteinhülle eingebaut ist.

Ein auf dieser Basis berechnetes Modell, welches im besonderen die Überlappung von RNS und Protein im Innenteil der Hülle berücksichtigt, stimmt mit der experimentell bestimmten Elektronendichteverteilung bestens überein. Der mittlere Radius der Phagen beträgt demnach 131,7 Å, die integrale Dicke der Proteinhülle 26,8 Å. Der mittlere Aussenradius der RNS ist in diesem Modell 107,8 Å, aus Messungen in einer konzentrierten Rohrzuckerlösung (800 g.l⁻¹) ergibt sich ein Radius von mindestens 105 Å.

Die mit der Röntgenkleinwinkel-methode bestimmten Dimensionen stehen in bestem Einklang mit elektronenmikroskopischen Befunden.

Submitted for publication in *Eur. J. Biochem.*

Nucleic acids and complex biological particles

42. Small-angle X-ray scattering studies of nucleic acids in solution. By V. LUZZATI, *Centre de Génétique Moléculaire, CNRS, Gif-sur-Yvette, France*

The results of the SAXS studies of two-stranded DNA are discussed, with special reference to the problems specific of polyelectrolytes.

A review is given of previous studies on the one-stranded rod-like conformation of DNA and poly A.

A recent analysis is described of the conformation of poly C in water and in water-alcohol solutions, at neutral pH, and as a function of temperature based upon SAXS and spectroscopic (OD, CD, ORD) experiments. The results indicate that the short-range conformation of poly C remains rod-like under conditions in which the spectroscopic properties undergo large changes, commonly associated with a helix \rightarrow coil transition.

These results lead to general considerations about the conformation of the nucleic acids in solution.

43. Small-angle X-ray scattering from E. Coli ribosomes. By J. W. ANDEREGG,* W. S. SMITH & W. R. TOLBERT, *Biophysics Laboratory, University of Wisconsin, Madison, Wisconsin, U.S.A.* & W. E. HILL, *Chemistry Department, University of Montana, Missoula, Montana, U.S.A.*

Small-angle X-ray scattering measurements have been made on the 70S, 50S, and 30S ribosomes from the MRE600 strain of E. Coli. The 70S ribosome scattering curve best matches that of an ellipsoid of dimensions $135 \times 200 \times 400$ Å. The 50S ribosome appears as an oblate ellipsoid of dimensions $115 \times 230 \times 230$ Å, the 30S ribosome as an oblate ellipsoid of dimensions $55 \times 220 \times 220$ Å. It is not obvious how the 30S and 50S subunits could be joined together to match the 70S scattering curve.

Our measurements also show that both the 50S and 30S particle expand rather isotropically as the Mg^{3+} level is lowered. The 30S core particle, produced by removing some protein from the 30S ribosome by means of 5M CsCl, is also shown to be an expanded structure with a radius of gyration of 87 Å, compared with 59 Å for the intact 30S particle. We have

also disassembled the 30S particle into its constituent protein and RNA and then reconstructed the whole particle following the methods of Nomura. Except for an effect apparently due to aggregation, the scattering curve for the reconstructed particle was very similar to that of the original 30S ribosome.

44. Low-angle X-ray scattering by bacterial flagella from S. Typhimurium. By R. E. BURGE, *Physics Department, Queen Elizabeth College, London, England*

Low-angle X-ray diffraction patterns of detached flagella in the form of cast solid films have been examined at various conditions of specimen relative humidity from 100 to 0% both without staining and following staining with uranyl acetate and phosphotungstic acid. The packing of the very short flagellar fragments in the preparations (mean length 4 to 10 times the diameter) was found to be a function of the mean flagellum length. The resulting low-angle equatorial reflexions (first order spacing varying from 420 to 190 Å) are explained on the basis of a lattice showing Boltzmann separation statistics.

Under certain conditions, the uranyl acetate stain is found to deposit on the flagellum surface as an annular deposit of radius close to 70 Å. The phosphotungstate stain produces considerable swelling indicating the presence of a flagellum core that can be penetrated following mechanical disruption.

Preliminary experiments are described of the scattering in solution of both flagella and flagellin, the latter corresponding to the dissociated subunits of the flagella. The radius of gyration of the flagellum is about 60 Å and the radius of gyration of the subunit about 20 Å. The mode of association is considered of the flagellin subunits within the intact flagellum.

Likely to be published in *J. Mol. Biol.*

45. Structure determination of the myelin membrane. Phase information based on heavy-metal labeling. By C. K. AKERS* & D. F. PARSONS, *Department of Biophysics, Roswell Park Memorial Institute, Buffalo, N.Y., U.S.A.*

Even though the myelin membrane is an atypical membrane with its unusual

chemical and physical properties, the membrane lends itself to X-ray diffraction investigation due to its stacking arrangement. In order to calculate the electron density distribution from the X-ray diffraction spectra, the phase sign of each reflection must be known. Phase sequences for the myelin membrane have been reported previously based on various techniques such as sweeping the Fourier transform by swelling the nerve, electron microscopy and step-function model building. Owing to questionable assumptions, which each technique contains, an independent phase determination is necessary. Heavy-metal labeling coupled with a computer analog is such a technique and is a variation of the heavy-atom phasing technique used in single-crystal protein structure determination.† Various parameters of the metal-label computer analog will be discussed. It should be emphasized that the metal-label computer analog is a general technique and promises to provide more structural information about other biological materials.

† This technique has been applied to the myelin membrane of the frog sciatic nerve.

46. Die Wechselwirkung der DNS mit Actinomin. Von H. WAWRA,* *Institut für Molekularbiologie, Österreichische Akademie der Wissenschaften, Graz, Österreich.* W. MÜLLER, *Gesellschaft für Molekularbiologische Forschung, Stöckheim über Braunschweig, Deutschland (BRD)* & O. KRATKY, *Institut für physikalische Chemie, Universität, Graz, Österreich*

Es wird die Wechselwirkung von Na-DNS und Actinomin in verdünnten, wässrigen NaCl-Lösungen mit den Methoden der Röntgenkleinwinkelstreuung untersucht. Dafür mussten aus hochmolekularer DNS durch Ultraschallabbau Teilchen geeigneter Länge hergestellt werden, so dass neben dem Querschnitt auch die Teilchenlänge mit der Röntgenkleinwinkelstreuung noch zu erfassen war. Die Messungen erfolgten an mit Actinomin gesättigten DNS-Lösungen bis herab zu einer DNS-Konzentration von 0,045 g/100 ml. Es konnte dabei eine Streckung der abgebauten DNS-Partikel bei Anlagerung von Actinomin um 18% festgestellt und die Menge des an die DNS gebundenen

Actinamins bestimmt werden: im Mittel wird auf 7,1 Basenpaare ein Actinomin-Molekül angelagert. Gleichzeitig wurde eine die DNS-Partikel umgebende Hülle aus Gegen- und Bei-Ionen beugungsmässig festgestellt und deren räumliche Dimension ermittelt. Im Verlauf der Auswertung ist es auch gelungen, aus den vorliegenden Pseudo-Querschnittstreckkurven die für unendlich lange Teilchen gültigen Querschnittstreckkurven-Intenteile zu rekonstruieren.

47. Studies of the conformation of phenylalanin specific t-RNA at higher temperatures and of the influences of counter ions on the radius of gyration. By I. PILZ* & O. KRATKY, *Institut für physikalische Chemie, Universität Graz, Austria* & F. CRAMER, F. VAN DER HAAR & E. SCHLIMME, *Max-Planck-Institut für experimentelle Medizin, Göttingen, Germany (BRD)*.

At room temperature up to 40°C the phenylalanin specific t-RNA is a rather compact molecule, the shape of which could be best described by an elongated body (length 89 Å), which has two different cross sections with mean diameters of 22 Å and 36 Å. If we raise the temperature of the solution up to 58°C the t-RNA molecule begins to unfold and at 70°C it shows a scattering curve typical of a chain molecule.

Besides the change in conformation of the t-RNA molecule at higher temperatures, the influence of the counter ions present in the solution on the experimentally found radius of gyration was studied. For this purpose the t-RNA solution was dialysed several times against distilled water and then against a buffer containing only one certain kind of counter ions. As univalent ions Li^+ and Cs^+ were used and as divalent ions Ba^{2+} and spermidin $^{2+}$. With each kind of ion a series of concentrations was studied whereby the concentration of the t-RNA was varied from 2 mg.ml $^{-1}$ to 20 mg.ml $^{-1}$. These investigations showed that the value of the radius of gyration is strongly influenced by the counter ions. The radius of gyration found for t-RNA with caesium as counter ion was, for instance, more than 10% higher than the value found with lithium as counter ion. These results show clearly that the counter ions must be taken into account if the

experimental radius of gyration is compared with that calculated from the atomic coordinates of a suggested model.

Inorganic systems

48. Small-angle X-ray scattering study of CdS-MnS systems obtained by precipitation. By K. KRANJC* & M. PAIC, *Institute of Physics, University of Zagreb, Zagreb, Yugoslavia*

In order to establish the degree of dispersity required in investigations of the optical properties of mixed crystals of cadmium and manganese sulphides in powder form, ten specimens with various amounts of manganese sulphide (from 0 up to 2.42 mole%) were investigated by the SAXS technique. The specimens were obtained by introducing, under the same conditions, an aqueous solution of ammonium sulphide into the mixtures of aqueous solutions of cadmium and manganese sulphates of various concentrations. The precipitates were washed by centrifugation and dried over silica gel at room temperature.

A Kratky camera, photographic film and Ni-filtered copper radiation at 35 kV were used. All scattering curves showed a similar general trend. The experimental scattering curves were interpreted by Porod's theory, and the slit-corrected scattering curves were analysed on the basis of the statistical distribution of particles. No correspondence between the Maxwellian distribution of particle sizes and the scattering curves was observed. By resolving the scattering curves into four Gaussian curves, the mass and number fractions and the radii of gyration of four groups of particles were established.

The parameters describing the systems, as obtained by both methods of analysis, appeared to be in fairly good agreement. The systems were composed of globular particles. In nine out of ten specimens the sizes of most particles varied from 10 to 12 nm, their specific surfaces being between 5.0×10^4 and 7.6×10^4 m 2 kg $^{-1}$. The specimen containing the greatest amount of manganese sulphide appeared more finely dispersed than the others. However, no definite correspondence between the grain size and the content of manganese could be

found. The electron micrographs did not show a clear picture of the individual particles, but the shape and size of the particles seemed in agreement with the X-ray results.

49. The mechanism and kinetics of the ω transformation in a Ti-25 at. % Nb alloy. By R. W. HENDRICKS,* C. C. KOCH & G. R. LOVE, *Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

The early stages of the ω -phase formation in a Ti-25 at. % Nb alloy have been investigated using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). Thin foils, formed by pack-rolling, were solution annealed at 1000°C in a vacuum of 10^{-9} torr and quenched in helium. After correction for double Bragg scattering and all other non-segregation effects, analysis of the SAXS intensity on an absolute basis shows that almost all of the single-phase disorder is retained on quenching. Aging at temperatures between 325 and 400°C for times from 1 to 90 min allows the formation of clusters with radii of gyration from 15 to 40 Å. These clusters have been identified by TEM and electron diffraction to have the ω -phase structure. The SAXS patterns indicate a very high volume fraction of precipitate with strong interparticle interference effects. The experimental results may be interpreted in terms of a variation of Cahn's theory of spinodal decomposition.

50. A computer program for desmearing of SAXS data applied to $(\text{KPO}_3)_n$ scattering curves. By P. KORNERUP, *Regnecentret, Aarhus Universitet, Aarhus, Denmark* & B. T. JENSEN* & S. E. RASMUSSEN, *Kemisk Institut, Aarhus Universitet, Aarhus, Denmark*

SAXS scattering is measured with a Kratky camera and the intensities are recorded with a proportional counter. The basic assumption is that the diffuse primary beam can be likened to a parallel beam bundle with dimensions and intensity distribution as measured in the detector plane. Looking at the conditions in the detector plane the measured intensity [L. A. Feigin, *Kristallografiya*, (1967). 12, 274] is described at a distance m between the horizontal symmetry lines

of the trace of the primary beam and the detector slit as

$$I(m) = K \int_{-a/2}^{+a/2} \int_{-b/2}^{+b/2} \int_{-a_r/2}^{+a_r/2} \int_{-b_r/2}^{+b_r/2} L(z, t) \times I_0[(m-z+z_r)^2 + (t-t_r)^2]^{1/2} dt dz dt_r dz_r \quad (1)$$

z and t are the coordinates of the area $dzdt$ in the primary beam. $L(z, t)$ is a weighting function for the intensity. This function is obtained by measuring the intensity along the vertical $L(z)$ and the horizontal $L(t)$ trace of the primary beam. The computer program calculates $L(z)$ and $L(t)$ as polynomials of even degrees in correspondence with the observed values using the method of least squares. z_r, t_r are the coordinates of the area $dz_r dt_r$ in the detector slit. $[(m-z+z_r)^2 + (t-t_r)^2]^{1/2}$ is the distance between the areas $dzdt$ and $dz_r dt_r$ under consideration. The expression is integrated over the dimensions $2a \times 2b$ of the primary beam and the dimensions $2a_r \times 2b_r$ of the detector slit.

$I_0(m)$ is the scattering function corresponding to point collimation measured with an infinitely small detector slit. The I_0 function is approximated with rational functions finding their coefficients in correspondence with equation (1) using the method of least-squares.

The computer program written in Algol is applied to the correction of scattering curves of $(\text{KPO}_3)_n$ K14 [H. Malgren, *Acta Chem. Scand.* (1948) 2, 147] in 0.4 M aqueous NaCl solutions.

The corrected scattering curves show an evidence for a polydispersion of the $(\text{KPO}_3)_n$, the mean molecular weight is estimated to be 1.2×10^6 and the plot of $I\theta^2$ as a function of θ indicates a random coil structure.

51. Diffusion-controlled decomposition and crystallization in lithium-barium-silicate glasses. By R. BRÜCKNER* & D. NAU, *Max-Planck-Institut für Silikatforschung, Würzburg, Germany (BRD)*

Numerous investigations were made in the field of microheterogeneity of the glass structure by means of electron microscopy. These investigations, together with thermodynamic considerations, have lead to the realization, that in most simple glass-forming

silicate melts a decomposition or a phase separation takes place in the thermodynamically metastable temperature range. The present state of knowledge and the new field of glass ceramics requires the investigation of the kinetics of decomposition and crystallization. The small angle X-ray scattering (SAXS) seems to be a powerful tool in that way.

The present paper deals with the problem of to what extent the SAXS method is useful for investigations of this kind. The calculations are based not on the usual method of desmearing the measured SAXS curves, but on an optimization process using a least-squares fitting to reduce the errors caused by collimation effects. The results show that it is possible to get from SAXS curves the distribution of droplets in the decomposed glass matrix, at least that part of the distribution with the larger droplets, the growth rate of the particles and from the decomposition curve, the composition of the separated phases. This information is sufficient for the calculation of the diffusion coefficient and its activation energy. Also the influence of crystallization is available. The crystalline phases are lithium and barium disilicate, if the crystallization temperature is low enough and activated from the surface, whereas tridymite is obtained at higher temperatures within the range of composition (silica-rich part of the system). The decomposed droplet-phase consists of nearly pure vitreous silica.

References to this work are:

D. Nau & R. Brückner, *Röntgen-Kleinwinkelstreuung und Teilchengrößenverteilung in entmischten Silikatgläsern. Kolloid.-Z. & Z. Polymere*, (1970). In the press.

D. Nau & R. Brückner, *Diffusionskinetische Entmischung und Kristallisation im System Li₂O-BaO-SiO₂*. *Glastech. Ber.* (1970), 43, 369.

The first publication refers to the method and the second to its application.

Metals, crystals

52. SAXS study of the kinetics of coherent phase separation in a quenched Al-15 at. % Zn alloy. By R. ACUÑA & A. BONFIGLIOLI,* *Technology Division, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina*

The kinetics laws determined by absolute SAXS measurements at low

temperatures, do not agree with the predictions of the spinodal theory in the case of a quenched Al-15 at. % Zn alloy. The influence of the composition fluctuations on the experimental results is analysed on the basis of the Cook's theory (H. Cook, *Brownian Motion in Spinodal Decomposition*, Ford Motor Laboratory Report, 1969) and it is shown that they play an important role in the studied alloy. In particular, fluctuations allow one to account for some of the discrepancies between the spinodal theory and the present results. Difficulties in the application of Cook's theory are pointed out.

53. Quantitative investigation on the metastable miscibility gap of Al-Zn-Mg Alloys. By K.-H. DÜNKELOH* & V. GEROLD, *Max-Planck-Institut für Metallforschung, Institut für Metallkunde, Stuttgart, Germany (BRD)*

Small-angle X-ray scattering from aluminum alloys containing 1 to 2 mole % MgZn_2 (i.e., 2 to 4 at. % Zn) has been investigated by measuring quantitatively the integrated intensity. As the scattering is relatively weak, background diffraction has to be taken into account. With the aid of a computer program reliable results have been obtained.

Thin foils of the alloys were homogenized at 450°C, rapidly quenched into water and aged at room temperature. A metastable coherent precipitate with particle sizes of the order of 20 Å produces small-angle scattering. With prolonged ageing time the integrated intensity reaches a final value which depends linearly on the zinc content of the alloy. From this dependence the metastable solubility limit of zinc was found to be 1.1 at. % at room temperature, which is considerably less than the value for the binary alloy Al-Zn (1.7 at. %). The zinc content in the metastable alloy can be estimated to be about 60 at. %. Its exact value depends on the mean atomic volume of the precipitate which is not well-known at present.

54. Röntgenkleinwinkeluntersuchungen an schmelzflüssigen Metallegierungen bei Temperaturen bis zu 1000°C. Von J. C. HÖHLER* & S. STEEB, *Institut für Sondermetalle, Max-Planck-Institut für Metallforschung, Stuttgart, Deutschland (BRD)*

Zunächst wird eine kombinierte Klein- und Weitwinkelapparatur be-

schrieben, welche die vollautomatische Registrierung von Röntgeninterferenzen im Vakuum oder in einer Schutzgasatmosphäre gestattet. Die Einsatzmöglichkeiten dieser Apparatur für Hochtemperatur-Untersuchungen an Legierungsschmelzen werden umrissen. Es folgen die Beschreibungen von Messungen an zweikomponentigen Legierungen mit Aluminium-Matrix und Hinweise für die quantitative Auswertung mit dem daraus abzuleitenden physikalischen Größen bzw. Strukturmodellen.

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55. Small-angle scattering of X-rays on γ -irradiated LiF. By O. WOHOFKY* & W. WADELICH, *I. Physikalisches Institut der Technischen Hochschule, Darmstadt, Germany (BRD)*

A thin LiF single crystal is irradiated at room temperature with different doses of ^{60}Co γ -rays and the small-angle X-ray scattering intensity is determined. During irradiation defects of Frenkel type are created. Only after a dose of 2×10^8 rad a weak scattered intensity is to be observed.

The analysis of the scattering curves leads to the assumption that the regions of changed electron density are flat discs with diameter of several lattice spacings.

It is known from optical absorption measurements that vacancies persist as isolated defects. The regions of changed electron density, which are the scattering centres, must be agglomerated interstitial atoms.

56. X-ray small-angle scattering near Bragg peaks of γ -irradiated LiF single crystals. By H. SPALT* & H. PEISL, *I. Physikalisches Institut der Technischen Hochschule, Darmstadt, Germany (BRD)*

X-ray small-angle scattering near Bragg peaks caused by the distortion fields of lattice defects in γ -irradiated LiF single crystals is determined. The distribution of X-ray intensity in the reciprocal space may be understood assuming the defects to form clusters. Also the dependence of the scattered intensity on the concentration of defects is in good agreement with this assumption. From optical absorption experiments it is well known that va-

cancies are present as isolated defects (F centres). Therefore the formation of clusters can be attributed to interstitial defects only. The sizes of the clusters and the number of interstitial atoms per cluster are determined. A report on the occurrence of intensity oscillations at some distance from the Bragg peaks, and on their interpretation, is given.

References to this work are:

H. Spalt, *Z. angew. Phys.* (1970). 29, 269.

H. Trinkaus, H. Spalt & H. Peisl, *Phys. stat. sol. (a)* (1970). 2, K97.

Critical phenomena

57. X-ray studies of critical opalescence in argon.† By H. D. BALE,* B. C. DOBBS & P. W. SCHMIDT, *Physics Department, University of Missouri, Columbia, Missouri, U.S.A.*

The small-angle X-ray scattering from argon has been studied near the critical point at constant density for several values of temperature and density in the one-phase region. The measurements extend an earlier study of critical opalescence in argon at constant pressure (J. E. Thomas & P. W. Schmidt, *J. Chem. Phys.* (1963). 39, 2506). The angular distribution of the scattering at constant density was determined. The relative isothermal compressibility, which is proportional to the reciprocal of the zero-angle scattered intensity, was evaluated for several densities in the neighborhood of the critical density. At the critical density in the one-phase region near the critical temperature, the compressibility was found to be proportional to $[(T - T_c)/T_c]^{-\nu}$, where T is the absolute temperature of the sample, and T_c is the critical temperature. By means of special slits which allowed the sample transmission to be measured at different heights in the sample, the densities of the two coexisting phases in the two-phase region were determined. The coexistence curve could then be obtained. The shape of the coexistence curve was found to agree with the predictions of scaling-law theories of the critical point [M. Vicentini-Missoni, J. M. H. Levelt-Sengers & M. S. Green, *Phys. Rev. Letters*, (1969). 22, 389].

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58. Small-angle X-ray scattering of carbon dioxide in the neighborhood of its critical point.† By B. CHU* & J. S. LIN, *Department of Chemistry, State University of New York, Stony Brook, N.Y., U.S.A.*

Small-angle X-ray scattering of carbon dioxide in the vicinity of its critical point was used to investigate the static critical behaviors of systems undergoing second order phase transitions, in particular, the divergences of the isothermal compressibility (K_T) and of the long-range coherence length (ξ) along the critical isochore and on the liquid side of the coexistence curve as the critical point was approached. Using isothermal compressibilities computed by means of numerical differentiation of Michels' PVT data as our reference points, we obtained $\nu = 1.24 \pm 0.09$ at $\rho = \rho_c$ where $K_T \propto \epsilon^{-\nu}$ with $\epsilon = (T - T_c)/T_c$. The reciprocal scattered intensity was proportional to K^2 over the entire range of our investigation in the $\rho - T$ diagram, although we neglected measurements in the immediate neighborhood of the critical point because of gravitational effects. With $I(0)/I(K) = 1 + \zeta^2 K^2$ and $\zeta \propto \epsilon^{-\nu}$, we found that $\nu = 0.6$ (7) at $\rho = \rho_c$ and $\nu \approx 0.6$ when $\rho =$ (coexisting liquid). $K = 4\pi\lambda^{-1} \sin(\theta/2)$. The magnitude of ξ agreed with line-width studies of Cummins & Swinney if we introduced a temperature-independent constant $b = \frac{2}{3}$ as proposed by Kawasaki.

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59. Some critical scattering observations on the liquid Na-Li system. By H. BRUMBERGER* & N. A. ALEXANDROPOULOS,† *Department of Chemistry, Syracuse University, Syracuse, N.Y., U.S.A.*

The scattering of radiation has been used to study critical phenomena in various systems. Critical demixing of binary liquid systems has been investigated most often with mixtures of organic liquids (for instance, nitrobenzene-*n*-heptane) with the exception of Bi-Zn, Pb-Ga and Bi-Ga, which were subjected to neutron scattering

experiments and appeared to display Ornstein-Zernike behavior [G. D. Wignall & P. A. Egelstaff, *J. Phys. C* (1968), **1**, 1]. It is of interest to examine, by X-ray scattering, additional metallic systems, in which the interactions are of a different nature from those in organic mixtures, and which may therefore show qualitative differences in critical behavior.

We report here some preliminary X-ray opalescence measurements on the sodium-lithium system near its critical composition (58 wt.% Na) and temperature ($\sim 301^\circ\text{C}$), using Mo $K\alpha$ radiation and a high-resolution Kratky camera. Experimental details and difficulties will be discussed briefly. The salient features of the slit-corrected scattering data are (a) that the opalescence effect appears to extend over a relatively large temperature range ($\sim 10^\circ\text{C}$) [H. Brumberger, N. G. Alexandropoulos & W. Claffey, *Phys. Rev. Letters*, (1967), **19**, 555], (b) that essentially Ornstein-Zernike (OZ) behavior is found in a part of the small-angle range (i.e. I^{-1} is linear in h^2 , where $h=4\pi\lambda^{-1}\sin\theta$) but that the OZ curves at different temperatures are not parallel and, finally (c) that the OZ curves appear to curve upward and merge at the smallest angles. While the last observation is internally consistent, it must be recalled that it appears in the smallest angular range accessible to our instrumentation, where the background is relatively high and slit corrections are most significant. More extensive measurements in this angular region therefore appear necessary.

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Miscellaneous applications of small-angle scattering

60. Small-angle X-ray scattering studies of liquid crystal phase transition. By G. W. BRADY, *Bell Telephone Laboratories, Murray Hill, N.J., U.S.A.* & C. C. GRAVATT, *Institute for Materials Research, National Bureau of Standards, Washington, D.C., U.S.A.*

Phase transitions in nematic and cholesteric liquid forming materials have been investigated by small-angle X-ray scattering. Measurements were performed on *p*-azoxyanisole in the isotropic and nematic liquid regions and on cholesteryl bromide in the isotropic and cholesteric liquid regions. For

p-azoxyanisole pretransitional phenomena have been observed in the isotropic liquid at temperatures as great as 15° above the isotropic-nematic transition. These phenomena, which are indicative of long-range ordering in the isotropic region, are strongly influenced by sample purity, and are not evident in the purest samples. D. C. electric fields have been found to induce ordering in the isotropic region which is observable by small-angle X-ray scattering, but the effect is very weak and is complicated by conductive flow in the samples. Container surfaces have not been found to contribute in a measurable way to the ordering phenomena. It was not possible to observe any ordering effects, or to detect the isotropic-cholesteric transition, in cholesteryl bromide by small-angle X-ray scattering.

Details of this work are given by C. C. Gravatt & G. W. Brady [*Molecular Crystals and Liquid Crystals*, (1969), **7**, 355 and *Liquid Crystals and Ordered Fluids*, p. 455. Edited by J. F. Johnson & R. S. Porter. New York: Plenum Press, (1970)].

61. Small-angle X-ray scattering studies of the random packing behavior of hard spheres in the high-density limit. By C. C. GRAVATT, *Institute for Materials Research, National Bureau of Standards, Washington, D.C., U.S.A.* & G. W. BRADY, *Bell Telephone Laboratories, Murray Hill, N.J., U.S.A.*

The high-density-limit radial distribution function of a hard sphere fluid has been determined by small-angle X-ray scattering studies of polystyrene latex sphere samples. Measurements were made on air-dried samples of latex sphere suspensions in a Bonse-Hart small-angle diffractometer, and all intensity data were corrected for the effect of slit height by an infinite slit height desmearing procedure. The influence of the sample attenuation factor on the scattering curves was analyzed. It was found that the scattering curves were modified to a large extent by the distribution of sphere diameters present in the sample, with typical samples having of the order of a 3% variation of diameters. The nature of the diameter distribution could be determined in two ways, either by direct curve fitting or by deconvolution of the experimental curves. Fourier transformation of the slit-corrected

intensity data was performed to study the packing behavior of the hard sphere fluid system. In addition, since the scattering equations for hard spheres are well-known the effects of termination error and other computational complications in the Fourier transformation could be analyzed for this system.

Details of this work are given by C. C. Gravatt & G. W. Brady [*J. Appl. Cryst.* (1969), **2**, 289 and *J. Chem. Phys.* (in preparation)].

62. The role of small-angle scattering in the theory of liquids. By S. N. BAGCHI, *Department of Physics, Loyola College, Montreal, Canada*

From the standpoint of the diffraction theory, the differences between crystals, liquids and gases depend primarily on the relative distances between the scattering centres and their fluctuations. Consequently, it is useful to formulate a general kinematic theory of diffraction by matter in any state of aggregation. In order to develop such a theory it is necessary to extend the usual concept of the 'lattice'. It is found that a necessary and sufficient condition for this is to define the generalized lattice as a statistically homogeneous entity. Consequently, it is important to distinguish clearly between a cluster, a macrolattice and a simple lattice occurring in a substance. Based on this concept of a generalized lattice, (i.e., a statistical distribution of arbitrarily distorted lattice cells), a general expression for the scattered intensity function, which degenerates to the well-known formulae of the conventional theories under well-defined conditions, has been deduced previously.

Since the probability of occurrence of the p th neighbour in a generalized lattice can be calculated from a few fundamental coordination statistics (for the case of simple liquids only one, namely, the first neighbour statistics, is needed), the partition functions (p.f.) of matter in any state of aggregation and, in particular, those of simple liquids have been calculated. For this, a careful and proper analysis of Radial Distribution Functions (RDF) of liquids is needed. Further, it is shown that the conventional method of analysis of RDF of liquids is in principle wrong. A new method is suggested.

Assuming the superposition principle of interacting potentials a new theory of liquids involving this RDF is proposed [S. N. Bagchi, *Kinematic theory of diffraction by matter of any kind and the theory of liquids*. In *Advanc. Phys.* (1970). 19, June issue]. For a satisfactory evaluation of the p.f. and consequent testing of the theory, even for simple substances like argon, one needs the average size of the clusters as well as RDF curves at various temperatures and pressures. It is hoped that such detailed studies would throw considerable light on the mechanism of phase transitions, in particular, that of crystal-liquid transition.

Detailed analyses of RDF of many simple liquids near their melting points suggest that liquids are essentially distorted micro-crystallites, the degree of distortion of individual lattices being practically the same as in the crystalline state at the melting point. Consequently, phase transitions are primarily governed by conditions which lead to singularities associated with the transformation of a statistically homogeneous entity into a (statistically) inhomogeneous system.

63. Echelle absolue de l'intensité diffuse. Application au problème de la concentration. Par D. TCHOUBAR* & J. MÉRING, *Centre de Recherche sur les Solides à Organisation Cristalline imparfaite, Orléans, France*

On évalue le plus souvent l'intensité absolue diffusée (rapport de l'intensité diffusée à l'intensité du faisceau transmis) en la rapportant à l'unité d'épais-

seur de l'échantillon. Nous croyons préférable de rapporter cette intensité à l'unité de masse. Cette façon de procéder présente des avantages pratiques: la mesure de la masse diffusante par unité de surface de l'échantillon plat se fait avec une précision plus grande que la mesure de l'épaisseur. En outre se trouve éliminée l'indétermination de Babinet. Avec l'échelle absolue rapportée à la masse:

- (a) La limite de Porod fournit directement \bar{l} (moyenne numérique des longueurs des cordes des particules). Elle est invariante par rapport à la concentration.
- (b) Le contenu intégral de la diffusion centrale fournit directement la mesure de porosité $p_x = 1 - c$ (c = concentration en volume)

Il est presque toujours possible de mesurer la porosité directement (sans intervention des rayons X). Soit p_0 le résultat de cette mesure. Il est utile de la confronter à p_x . Il peut arriver et il arrive souvent que $p_0 > p_x$. Cela signifie que le système poreux contient des éléments diffusants de dimension excessive, ce qui entraîne l'existence d'un corps central de diffusion intense aux très petits angles, inaccessible à la mesure et échappant à l'intégration. Dans ce cas seule la limite de Porod est produite par la totalité de la matière.

On doit envisager deux cas:

- (a) Le cas très fréquent (fibres textiles, carbones) est celui où la substance diffusante est formée d'agrégats de

grande dimension, mais possédant une porosité interne. Dans ce cas, p_x mesure cette porosité interne. La limite de Porod ne pose pas de problème.

- (b) Le cas plus difficile est celui de particules sans porosité interne, mais présentant des échelles de dimensions très différentes. La diffusion par les particules les plus grosses échappe au calcul du contenu intégral. Dans ce cas la mesure de p_x n'a pas de signification. La confrontation de p_x à p_0 permet d'éviter des interprétations totalement erronées.

64. Röntgenkleinwinkelstreuung von Farbstoffassoziaten in Lösung, ein Bericht über Untersuchungen aus dem Grazer Laboratorium. Von H. OELSCHLAEGER, *Institut für Physikalische Chemie, Universität, Graz, Österreich*

Gelöste Farbstoffe bilden häufig Assoziat aus mehreren Molekülen. Die Grösse der Assoziat variiert mit Konzentration, Temperatur und Elektrolytgehalt der Lösung. Am Beispiel des Cu-Phthalocyanintetrasulfonsauren Natrium wurde ein solches System mit Hilfe der RKWS näher untersucht. Dabei tritt eine Reihe prinzipieller Schwierigkeiten auf. Dennoch lassen sich ungefähre Aussagen über Grösse, Form und Grössenverteilung der Assoziat machen. Danach haben diese die Form von schiefen Stapeln und bestehen aus 2 bis über 20 Molekülen. Assoziationskonstanten und Assoziationswärmen konnten abgeschätzt werden.