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Surface Order and the Sectorization of Polymethylene Lamellae

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ABSTRACT: Two *n*-paraffins, *n*-$C_{50}H_{102}$ and *n*-$C_{60}H_{122}$, each form sectorized lamellae when crystallized from a poor solvent. They also form continuous solid solutions with one another, and this cosolubility in the solid state creates a disordered surface of the chain-end packing. When solid solutions of the two components are crystallized, the sectorization is found to persist to at least 25% (by weight) concentration of the smaller chain in lamellae of the longer chain component. It is apparent, therefore, that a well-ordered crystal surface is not a necessary precondition for the appearance of lamellar sectors. Since the co-mixing of chain lengths will affect the average symmetry of the layer, it is clear that, as for polyethylene, this criterion will have no influence on the growth of the three-dimensional lamellae from solution which are, in fact, 4-fold twins. It also follows that observed sectorization behavior in polymer crystals cannot, *by itself*, be taken as evidence for regular chain folding, as has been continuously advocated.

Introduction

n-Paraffins packing in the orthorhombic perpendicular methylene subcell[1] and in rectangular layers[2] have often been used as a model for polyethylene, which shares the layer packing with the same methylene subcell[3] and, therefore, crystallizes in lozenge crystals with the same shape. Obviously, the difference between the infinite polymer chain and the monodisperse oligomeric *n*-paraffin chain (however, below a given length[4,5]) is that the former is required to fold at the lamellar surfaces to allow stems to re-enter the lamellar interior. The nature of this fold geometry has been strongly debated in the literature.[6] Its structure has often been associated with the appearance of 4-fold twins as the lamellae are crystallized by self-seeding from a poor solvent. Bright field electron microscopy and other light microscopic techniques have been used to characterize these sectorized crystals.[7–14] Based on these observations, a tight, adjacent re-entry model is often used for the fold patterns in crystals grown from solution, and in the bulk, and several possible fold patterns have been suggested.[8,10,15] However, it has been pointed out on several occasions[16,17] that, although sectorization and its related internal structure can be interpreted most simply in terms of a regularly folded, regularly structured interphase, it was not necessarily a unique interpretation of the observed crystal morphology.

Although it is not surprising, perhaps, that *n*-paraffins beyond a certain chain length are required to fold under certain crystallization conditions[4,5] and thus form sectorized lamellar crystals similar to those of polyethylene,[18] it must also be stated quite clearly and unequivocally that chain-folding of any type, in itself, is not a necessary requirement for crystal sectorization. As might be expected, polymethylene molecules with an internal fold structure and with a large enough perimeter, e.g. the larger cycloalkanes, will also crystallize in lamellae that mimic polyethylene.[19] On the other hand, in 1986, a paper describing a sectorization phenomenon for *unfolded* *n*-paraffins was published,[20] and many features of bright-field electron microscope images were found to be quite similar to the chain-folded polymer crystals. These included the crystallographic orientation of diffraction-contrast bands in individual sector domains. Subsequent high-resolution images[21] demonstrated that the molecular packing of successive bands was again similar to that found for polyethylene.[22] Similar results have since been obtained[23] from the *n*-alkane, *n*-$C_{94}H_{190}$.

A working hypothesis that can be derived from these results is that a certain chain length in the "stem-packing" region of a monolamellar crystal favors an oblique layer packing, perhaps the one described by Kitaigorodskii[2] where the oblique layer axis corresponds to a diagonal of the orthorhombic methylene subcell. This would lead to a 4-fold twin nucleus, which, common to the polymer and oligomer crystals, results in three-dimensional habits for either case. Since well-defined, atomically-flat surface layers are associated with oblique layer chain packings, e.g. as visualized in localized corrugations in heated alkane crystals,[24] it is therefore important to ask whether an ordered surface is required in order for the sectorization phenomenon to appear. For the nonfolded *n*-paraffin chains, one way to test this requirement is to look at the crystallization behavior of solid solutions where disordered surfaces are developed. Such a study is described below.

Materials and Methods

The two *n*-paraffins used in this investigation, *n*-pentacontane, *n*-$C_{50}H_{102}$, and *n*-hexacontane, *n*-$C_{60}H_{122}$, were purchased from Fluka AG (Buchs, Switzerland) and both were stated by the manufacturer to be 99% pure. Thermodynamic and crystallographic data for these alkanes and their binary combinations were published earlier.[25,26] For this study, binary combinations of these two paraffins were made in either of two ways. In one preparation, the paraffins were combined by weighing into a glass vessel and the mechanical mixture was then dissolved in an adequate volume of toluene (8 g/L) at 100 °C. The solution was allowed to crystallize in ice water and the crystals were filtered, washed with methanol, and dried in vacuo overnight. Finally 0.01% solutions of the precipitates were made in warmed toluene. For the second preparative series, the combined alkanes were weighed into an aluminum DSC pan and the temperature of the vessel was then raised above the melting point of the longest chain ingredient to fuse the two components. After cooling to room temperature, the fused contents were scraped out of the vessel to be solubilized in light petroleum by warming, taking care that the resulting solution would be dilute enough to encourage growth of monolamellar crystals.[20,21] (For the toluene solutions described below, a further dilution could be carried out

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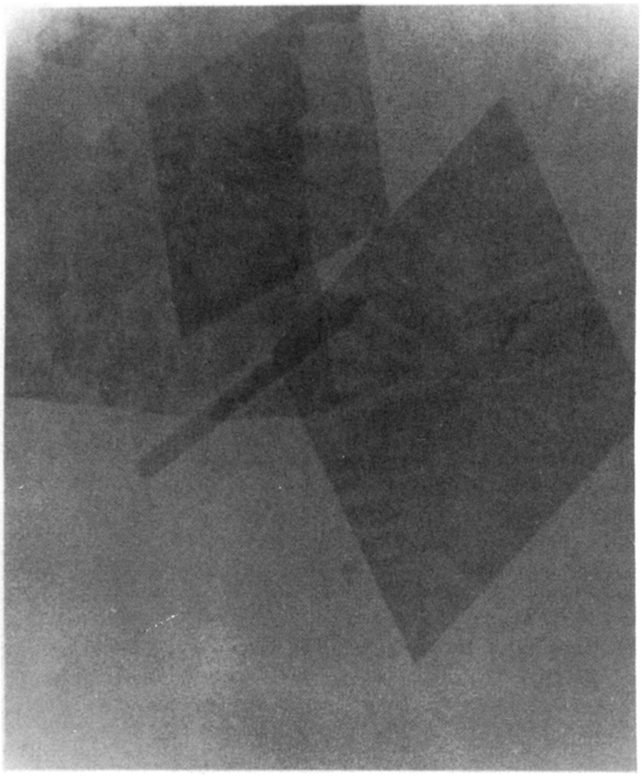

Figure 1. Bright field electron micrograph of a monolamellar paraffin solid solution crystal (x) n-$C_{50}H_{102}$/(1 − x) n-$C_{60}H_{122}$, $x \leq 25$ wt %.

before recrystallization from a solution which had been cooled from higher temperature (e.g. initially heated to 80–90 °C), again to favor formation of monolamellar crystals.) As a control, lamellar crystals of n-$C_{168}H_{338}$ were also grown to visualize the bright-field contrast expected for folded chains. These crystals also were grown isothermally from toluene using a technique quite similar to the growth of polyethylene monolamellar single crystals.

Samples for bright-field electron microscopy were prepared in the following way. A dilute solution of the paraffin binary solid (or a pure paraffin) in either of the two solvents is warmed to allow a cloudy suspension to clear. A drop of this warmed solution is then placed onto a carbon-film-covered 300 mesh copper electron microscope grid and allowed to cool for ca. 30 s before the drop is blotted at the grid edge with filter paper. This allows crystallization to occur (in a way quite analogous to the "self-seeding" procedure used for polyethylene or the longer n-$C_{168}H_{338}$ paraffin) and the large lamellae to settle on the grid surface before the excess solvent is removed.

Bright field electron microscopy was done at 100 kV with a JEOL JEM-100CX II electron microscope under usual low-dose conditions (i.e. control of illumination with the microscope condenser lenses and use of a sensitive photographic film, Kodak DEF-5 X-ray film, to record the images). Direct magnification used in these experiments is 10000×. In a typical experiment, one searches in electron diffraction mode to find a pattern from a single microcrystal. The center beam of the pattern is then defocused to allow visualization of the crystal habit in the shadow image. If this appears to be a suitable crystal (judged by habit only), then a bright field image is recorded. After many years of work with such samples, it can be stated unequivocally that no appreciable radiation damage occurs while these images are being photographed because of the very low beam doses that the sample receives.[27]

Results

The typical bright field image from a solution-crystallized solid solution monolamellar lozenge is shown in Figure 1. The crystals are shown to have four sectors and, in each, dark diffraction-contrast bands are found to run along a direction corresponding to ⟨130⟩ in the orthorhombic methylene subcell.[20,21] Although the sectorization of sharp diffraction contrast bands is identical to that of chain-extended pure n-paraffins,[20,21,23] n-C_nH_{2n+2} with chain length $n \geq 40$, the visualization of such details in (x) n-$C_{50}H_{102}$/(1−x) n-$C_{60}H_{122}$ persists to $x = 25$ wt %. Beyond this concentration limit, the lamellae exhibit no directional bright-field contrast but rather have a flat, continuous contrast. There appears to be no solvent dependence for this phenomenon, as long as the components are quite soluble in either solvent only when they are warmed. (That is to say, the conditions for crystal growth require that the lamellae should be formed in suspension as the solution is cooled rather than by evaporation of the solvent.)

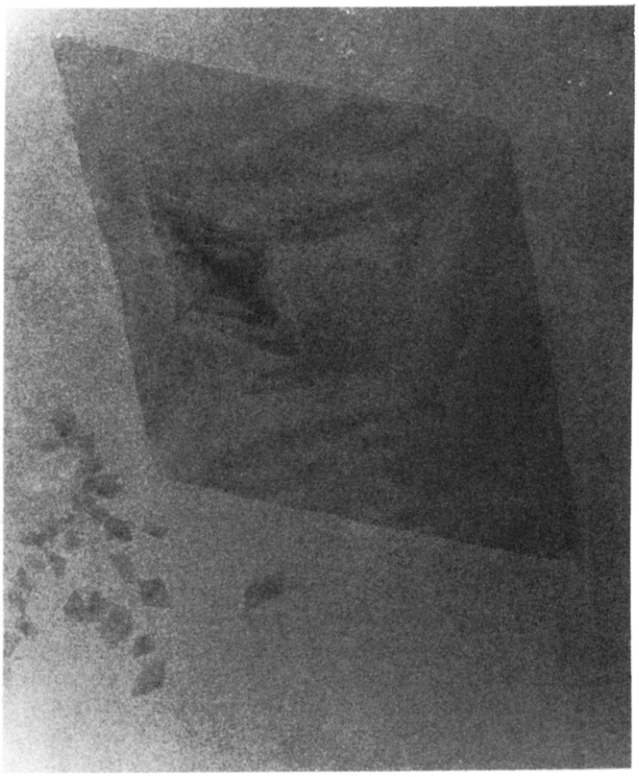

Figure 2. Bright field electron micrograph of a chain-folded monolamellar crystal of n-$C_{168}H_{338}$.

When chain-folds are present in the component molecules, e.g. as in n-$C_{168}H_{338}$, the dark field bands in individual sectors run along ⟨1,−3,0⟩,[12] shown in Figure 2, which is a crystallographically equivalent direction in the orthorhombic cell. Note that the sectorization is similar to that observed in polyethylene lamellae.[7–14] As shown in earlier high-resolution electron microscopy of sectorized lamellae, molecular packing in both paraffin[21] and polyethylene[22] directs an oblique layer tilt axis along the methylene subcell diagonal, corresponding to one of Kitaigorodskii's $R[\pm1,\pm1]$ layers.[2] The direction of this tilt axis, moreover, changes for each lamellar sector. Hence, the growth of a three-dimensional lamellar habit from solution must be nucleated by a 4-fold twin where the lamellar sectors meet at the projected diagonals. Decoration experiments on the sectorized paraffin lamellae with polymethylene segments from the vapor phase[28] reveal that the crystal surface is reasonably flat enough to serve as an epitaxial substrate.[21]

Discussion

Since low molecular weight molecules, i.e. the n-paraffins, are used here as analogs of an infinite chain polymer, it is possible to use the rules of organic chemical crystallography, developed by Kitaigorodskii,[2] to predict what two-dimensional layers are possible for such compounds. First, it must be emphasized that, while such two-dimensional layers are not, themselves, crystals, in the conventional sense of the term, they are energetically important components of crystals. Indeed, crystals are obviously generated when such layers as these are stacked on top of one another to generate a three-dimensional array. These layers, moreover, often represent a major fraction of the nonbonded interactions in the ensuing three-dimensional space lattice. While this statement may be obvious for the linear chain molecules, Scaringe[29] has shown that it also applies to many other molecular organic materials.

Given a two-dimensional layer of molecules, there are two major factors which control the packing arrays permitted within the layer. The first is that of greatest packing density. While its importance to the methylene "subcell" region of a paraffin (or polyethylene) layer may be apparent, such close packing also affects the nature of the chain end surface. That is, the chain ends themselves must be constrained to a smooth plane in the lowest energy structure, even for a single lamellar layer. This result is true not only for the *n*-paraffins but also for their monofunctional derivatives such as the fatty acids, wax esters, etc., as verified by examination of their crystal structures.[30]

The second factor which affects an *n*-paraffin layer packing is molecular symmetry.[2] For example, an odd-numbered *n*-alkane with chain length greater than nine carbons will pack preferentially in a *rectangular* layer of untilted chain axes. This is because these molecules have *mm* symmetry and will retain one of the mirror elements within the two-dimensional layer. Even-chain *n*-paraffins with chain lengths greater than 24 carbons have molecular symmetry $2/m$ and are only required to preserve a center of inversion in the layer packing.[2] Thus *oblique* layers (with tilted chain axes) are energetically favored although a rectangular layer is also possible. For the even chain *n*-paraffins with chain length near C_{36}, the preferred layer packing involves a chain tilt around the subcell $a = 7.42$ Å axis, termed $R[0,\pm1]$ (where the bracketed numbers m,n represent longitudinal translations along the chain subcell repeat, $c_0 = 2.54$ Å, corresponding to the $a = 7.42$, $b = 4.96$ Å directions). Longer, even-chain paraffins are observed[23,31] to crystallize from the melt into the alternative $R[\pm2,0]$ oblique layer. Similar tilted chain structures exist[30] for the fatty acids, etc., where the chain tilt is a mechanism whereby the cross-sectional area of the projected subcell array can compensate for the cross section of a functional group.[1] The molecular tilt axes are the same as those identified for the *n*-paraffins. Kitaigorodskii[2] also proposed oblique layers tilted around the subcell diagonal, hence $R[\pm1,\pm1]$, but no crystal structures have been identified yet for any polymethylene compounds where this can be found as a uniform layer packing in the orthorhombic perpendicular subcell.[1]

From the relatively simple experiment described above, it is, first of all, possible to conclude that sectorization in polymethylene lamellae is not dependent upon the presence of a well-ordered surface. The two *n*-paraffins used to form binary solids in these crystallization studies are known to form nearly ideally melting solid solutions, given evidence from a previous construction of the phase diagram,[25] as well as electron diffraction studies of lamellar spacing in epitaxially oriented samples.[26] In their vibrational spectroscopy study of the n-$C_{46}H_{94}$/n-$C_{50}H_{102}$ binary combinations, Kim et al.[32] found that the lamellar surfaces of these solids contain chains that are conformationally-disordered at the chain ends, in addition to the longitudinal disorder within the bounds of the lamellar thickness expected for any *n*-paraffin solid solution.[33,34] For the mole fractions of n-$C_{60}H_{122}$ which permit formation of sectorized crystal habits (as low as 0.71), several average lamellar structures can exist,[26] mimicking, e.g., the layer packing symmetry and thickness of n-$C_{57}H_{116}$, n-$C_{58}H_{118}$, n-$C_{59}H_{120}$, or n-$C_{60}H_{122}$, i.e. either odd- or even-chain structures. This means that considerable surface disorder, i.e. an atomically-rough arrangement of the chain ends, exists and yet sectorized crystals can grow. Thus, in contrast to Kitaigorodskii's symmetry criteria stated above, an average layer symmetry in this case does not define the original oblique layer crystallized from solution, especially since an average *mm* molecular symmetry (of an average odd-chain layer, for example) should not lead to any tilted chain packing. The paraffin binary solid solutions investigated by Kim et al.,[32] moreover, are completely analogous to the ones considered here, since the chain length n-$C_{46}H_{94}$ will also lead to a sectorized lozenge.[20] Similar principles may also be relevant for solid solutions composed of shorter chain alkanes. While it was not so identified by the authors of a recent paper,[35] it is clear that the scanning micrograph of a diesel wax crystal (Figure 7b of ref 35) also strongly resembles the sectorized morphology expected for polyethylene.

What significance do these results have for polyethylene? It is clear that an interplay of fold geometry and stem packing is involved in the crystallization of the polymer. For example, the collapse of three-dimensional lozenges of the polymer and paraffin crystals lead to respectively different distributions of bright field bands in the sectors (compare Figures 1 and 2), even if their directions are crystallographically equivalent. It is also apparent from a study of melt- and solution-crystallized cycloalkanes[36] that crystallization conditions that favor either more ordered or disordered folds can affect the type of crystal packing when a limited chain perimeter is investigated. This seems to be less important for the larger cycloalkanes however, i.e. after the "stem" regions are long enough to establish energetically what layer packing should occur.[19] It is also known from decoration experiments[28,37] that, in certain cases, chain folds can have a common average direction. However, nothing conclusive has been shown whether these folds represent tight, adjacent reentries of the chain or extend further in a particular lattice direction on the lamellar surface.

From the present studies, which establish that surface ordering is not critically related to the phenomenon of sectorized crystallization, we would propose generally that it is the stem packing itself that determines the initial nucleus that leads to the 4-fold twinned lamellae and hence the existence of the sectorization phenomenon. This appears to be a function of the length of the chain "stem" which runs through the lamella and/or the solubility limits in the solvent used for crystallization. In other words, the van der Waals interactions in the layer are energetically more important than the fold constraints as a primary consideration for crystal growth. On the other hand, observed behavior of mixed-chain paraffin layers as well as polyethylene indicates that the average symmetry of the stem segments does not, by itself, dictate what kind of layer (oblique or rectangular) will grow from dilute solution. For folded-chain crystals, the folds themselves may play a secondary role in determining how the three-dimensional habit collapses, especially if they are oriented, more or less, in a common direction over a crystal sector.[28,37]

This secondary role would correspond to their relatively smaller energetic contribution to the lamellar packing.

Irrespective of the details of the mechanism(s) of sectorized crystallization, these new results make clear that regular chain folding is not required (since no chain folding is present in the materials studied in this work). Consequently, the conclusion that sectorization in polyethylene or other polymers crystallized from dilute solution[7-13] or from the melt[14] is infallible evidence for regular chain folding is not correct, since it is shown here that such relatively low resolution morphological details in an electron micrograph, by themselves, are insufficient and even dangerous criteria for assigning a particular surface structure at atomic resolution. The present results have shown that the importance of the surface chain packing geometry to crystallization is probably less relevent than the question of why 4-fold twinned lamellae of polymethylene compounds should grow *preferentially* as the stem regions exceed a certain length.

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References and Notes

(1) Abrahamsson, S.; Dahlén, B.; Löfgren, H.; Pascher, I. *Prog. Chem. Fats Other Lipids* **1978**, *16*, 125.
(2) Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultants Bureau: New York, 1961.
(3) Bunn, C. W. *Trans. Faraday Soc.* **1939**, *35*, 482. Charlesby, A. *Proc. Phys. Soc., London* **1945**, *57*, 496.
(4) Ungar, G.; Stejny, J.; Keller, A.; Bidd, I.; Whiting, M. C. *Science* **1985**, *229*, 386.
(5) Stack, G. M.; Mandelkern, L.; Kröhnke, C.; Wegner, G. *Macromolecules* **1989**, *22*, 4351.
(6) Mandelkern, L. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon: Oxford, 1989; Vol. 2, p 363.
(7) Niegisch, W. D.; Swan, P. R. *J. Appl. Phys.* **1960**, *31*, 1906.
(8) Reneker, D. H.; Geil, P. H. *J. Appl. Phys.* **1960**, *31*, 1916.
(9) Bassett, D. C.; Frank, F. C.; Keller, A. *Nature* **1959**, *184*, 810.
(10) Bassett, D. C.; Frank, F. C.; Keller, A. *Philos. Mag.* **1963**, *8*, 1739, 1753.
(11) Bassett, D. C.; Keller, A. *Philos. Mag.* **1961**, *6*, 345.
(12) Bassett, D. C.; Keller, A. *Philos. Mag.* **1962**, *7*, 1553.
(13) Boudet, A. *J. Mater. Sci.* **1984**, *19*, 2989.
(14) Bassett, D. C.; Olley, R. H.; Al Raheil, A. M. *Polymer* **1988**, *29*, 1539.
(15) Geil, P. H. *Polymer Single Crystals*; Wiley: New York, 1963; p 129.
(16) Mandelkern, L. In *Characterization of Materials in Research, Ceramics Ceramics and Polymers*; Burke, J. J., Weiss, V., Eds.; Syracuse University Press: Syracuse, NY, 1975; p 369.
(17) Mandelkern, L. *Annu. Rev. Mater. Sci.* **1976**, *6*, 119.
(18) Organ, S. J.; Keller, A. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 2409.
(19) Ihn, K. J.; Tsuji, M.; Isoda, S.; Kawaguchi, A.; Katayama, K.; Tanaka, Y.; Sato, H. *Macromolecules* **1990**, *23*, 1781.
(20) Dorset, D. L. *J. Macromol. Sci., Phys.* **1986**, *B25*, 1.
(21) Dorset, D. L.; Hanlon, J.; McConnell, C. H.; Fryer, J. R.; Lotz, B.; Wittmann, J. C.; Beckmann, E.; Zemlin, F. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 1696.
(22) Revol, J. F.; Manley, R. St. J. *J. Mater. Sci. Lett.* **1986**, *5*, 249.
(23) Dorset, D. L.; Alamo, R. G.; Mandelkern, L. *Macromolecules* **1992**, *25*, 6284.
(24) Keller, A. *Philos. Mag.* **1961**, *6*, 329.
(25) Dorset, D. L. *Macromolecules* **1990**, *23*, 623.
(26) Zhang, W. P.; Dorset, D. L. *J. Polym. Sci., B: Polym. Phys.* **1990**, *28*, 1223.
(27) Dorset, D. L. *J. Electron Microsc. Tech.* **1985**, *2*, 89.
(28) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 205.
(29) Scaringe, R. P. In *Electron Crystallography of Organic Molecules*; Fryer, J. R., Dorset, D. L., Eds.; Kluwer: Dordrecht, 1991; p 85.
(30) Shipley, G. G. In *Handbook of Lipid Research*; Small, D. M., Ed.; Plenum: New York, 1986; Vol. 4, p 97.
(31) Takamizawa, K.; Ogawa, Y.; Oyama, T. *Polym. J.* **1982**, *14*, 441.
(32) Kim, Y.; Strauss, H. L.; Snyder, R. G. *J. Phys. Chem.* **1989**, *93*, 485.
(33) Lüth, H.; Nyburg, S. C.; Robinson, P. M.; Scott, H. G. *Mol. Cryst. Liq. Cryst.* **1974**, *27*, 337.
(34) Dorset, D. L. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 8541.
(35) Bennema, P.; Liu, X. Y.; Lewtas, K.; Tack, R. D.; Rijpkema, J. J. M.; Roberts, K. J. *J. Cryst. Growth* **1992**, *121*, 679.
(36) Dorset, D. L.; Hsu, S. L. *Polymer* **1989**, *30*, 1596.
(37) Lotz, B.; Wittmann, J.-C. In *Electron Crystallography of Organic Molecules*; Fryer, J. R., Dorset, D. L., Eds.; Kluwer: Dordrecht, 1991; p 217.