

and diffusion under applied stress, and special phenomena such as the growth of Dauphiné twins in quartz crystals, are all of interest in particular to petrologists, and there has been much disagreement about the magnitude and even the sign of some of these effects. One of the leaders of this community, the Australian rock-mechanics expert *Mervyn Paterson*, some years ago wrote a masterly overview<sup>[13]</sup> of the whole field (he calls it non-hydrostatic thermodynamics) in which he sought to inject rigor into what had sometimes been a hand-waving discussion. *Paterson* does discuss coherent transitions, e.g., the  $\alpha/\beta$  transition in quartz, but not from the viewpoint later developed by *Cahn*, *Larché*, *Johnson* and *Voorhees*. He is concerned here by such matters as the change in transition temperature occasioned by a uniaxial stress and how that change depends upon the crystallographic direction of that stress in a highly anisotropic crystal. It may be

that the time is now ripe for a convergence of the metallurgists' and geologists' approaches.

- [1] A. Kochendörfer, H.-G. Müller, *Arch. Eisenhüttenwes.* 26 (1955) 291.
- [2] K. Shimizu, *Trans. Jpn. Inst. Metals* 27 (1986) 907.
- [3] V. S. Arunachalam, R. W. Cahn, *Proc. 3rd. AIME Bolton Landing Conf.*, (Claitor's Publishing Div., Baton Rouge) 1970.
- [4] L. A. Bendersky, P. W. Voorhees, W. J. Boettinger, W. C. Johnson, *Scripta Metall.* 22 (1988) 1029.
- [5] W. C. Johnson, M. B. Berkenpas, D. E. Laughlin, *Acta Metall.* 36 (1988) 3149.
- [6] W. C. Johnson, P. W. Voorhees, D. E. Zupon, *Acta Metall.* 37 (1989) in press.
- [7] J. W. Cahn, F. C. Larché, *Acta Metall.* 32 (1984) 1915.
- [8] A. L. Roitburd, *Sov. Phys. Solid State Engl. Transl.* 26 (1984) 1229.
- [9] W. C. Johnson, *Metall. Trans.* 18A (1987) 1093.
- [10] W. C. Johnson, P. W. Voorhees, *Metall. Trans.* 18A (1987) 1213.
- [11] W. C. Johnson, C. S. Chiang, *J. Appl. Phys.* 64 (1988) 1155.
- [12] C. S. Chiang, W. C. Johnson, *J. Mater. Res.* 4 (1989) 678.
- [13] M. S. Paterson, *Rev. Geophys. & Space Phys.* 11 (1973) 355.

## Networks Composed of Rigid Rod Polymers

By Matthias Ballauff\*

The physics and chemistry of networks of rubbers is a subject of long-standing interest in polymer science. To illustrate the tremendous technical importance of this field it suffices to mention the tire industry. Considerable profit is made from the advantageous properties of materials exhibiting rubber elasticity. All network polymers used for techni-

cal purposes are composed of flexible macromolecules, and the physics of rubber elasticity has been developed based on the fact that flexible chains are crosslinked.<sup>[1,2]</sup> In two recent publications<sup>[3,4]</sup> *Vilgis*, *Boué* and *Edwards* for the first time

set up a theory of rubber elasticity for networks composed of rigid rod polymers. Figure 1 schematically depicts a rubber consisting of rods connected by flexible hinges. The first question to be asked when looking at Figure 1 is what is the degree of freedom of such a structure? More than one hundred years ago *Maxwell*<sup>[5]</sup> showed that there is a limiting functionality  $m_c$  (or an upper critical dimension) given by  $m_c = 2d$  with  $d$  being the space dimension. This can be exemplified by considering two-dimensional networks in a simple square lattice configuration (see Fig. 2).

The functionality is four in this case which exactly corresponds to the limiting functionality in two dimensions

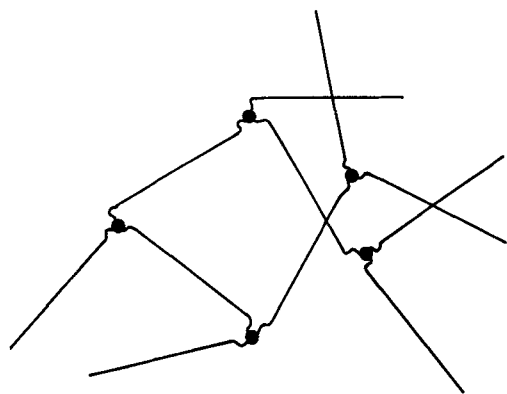


Fig. 1. Schematic representation of a network of rods connected by flexible hinges.

cal purposes are composed of flexible macromolecules, and the physics of rubber elasticity has been developed based on the fact that flexible chains are crosslinked.<sup>[1,2]</sup> In two recent publications<sup>[3,4]</sup> *Vilgis*, *Boué* and *Edwards* for the first time

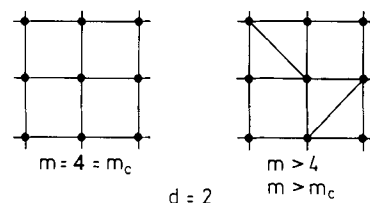


Fig. 2. Critical functionality for two dimensional networks:  $m = 4 = m_c$ : network can be deformed by shearing (left hand side);  $m > 4$ , i.e.,  $m > m_c$ : rigid network (right hand side).

( $d = 2$ ). This network can be deformed by shearing. If one increases the functionality beyond four by putting down rods on some diagonals (see Fig. 2) the lattice becomes entirely rigid and the elasticity is no longer of entropic nature but of a purely energetic nature, i.e., deformation of this network requires the bending and elongation of bonds. The same

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argument applies in three dimensions in the case of simple cubic topology. Here the limiting functionality is  $m_c = 6$ .

The above named authors succeeded in elaborating a theory of rubber elasticity for rigid rod networks with  $m < m_c$ . The method applied is rather involved and will not be discussed here. The principal result of the calculation is shown in Figure 3.

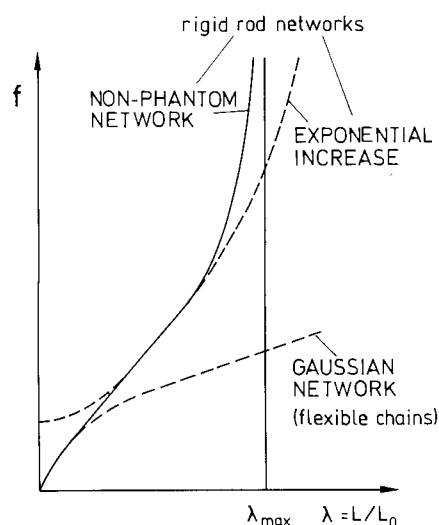


Fig. 3. Theoretical stress-strain relation of a rod network.

Here the stress per unit area  $f$  is plotted as a function of strain  $\lambda$ , where  $\lambda$  denotes the linear extension divided by the length at rest ( $\lambda = L/L_0$ ). At low extensions the behavior resembles the results found for conventional networks.<sup>[1,2]</sup> At larger deformations the stress-strain relation crosses over to an exponential increase. Here obviously the rod-like nature of the chains within the network comes into play. It has

to be noted that these results were derived for phantom networks, i.e., for systems without entanglement constraints. The authors also succeeded in including the latter effect into the model. Here theory predicts a maximum deformation at which the stress, as a function of strain, will diverge. This maximum deformation is a function of the concentration at the formation of the rod network. The physical argument leading to this divergence is again quite obvious: Due to the entanglement constraint the rods cannot move through each other but exert a mutual steric hindrance. With increasing extension of the network more and more rods will intersect and decrease the number of degrees of freedom of the system until the critical strain is reached.

This theory is the first attempt to tackle the problem of rigid rod networks. It is a mean-field approach and treats only isotropic systems. Such networks can be synthesized by simultaneous polymerization and cross-linking reaction. A totally different situation arises if cross-linking is effected in ordered liquid crystalline solutions or melts of rod-like polymers. Here the cross links would fix the liquid crystalline order even when the solvent is removed or the temperature is raised beyond the point of phase stability. This obviously provides numerous opportunities to design a whole class of new polymeric materials. The present work by Vilgis, Boué and Edwards thus could become an example for an interesting technical development preceded by theoretical ideas.

[1] P. J. Flory, *Polym. J. (Tokyo)* 17 (1985) 1.

[2] T. A. Vilgis in G. Allen, J. C. Bevington, (Eds.): *Comprehensive Polymer Science*, Vol. 6, Pergamon, Oxford 1989, p. 227.

[3] F. Boué, S. F. Edwards, T. A. Vilgis, *J. Phys.* 49 (1988), 1635.

[4] T. A. Vilgis, F. Boué, S. F. Edwards in C. Picot (Ed.): *The Molecular Basis of Networks*, Springer, Heidelberg 1989, in press.

[5] J. C. Maxwell, *Trans. R. Soc. Edinburgh* 26 (1870), 1.

## Books received:

**Topics in Applied Physics, Vol. 62. – Photorefractive Materials and Their Applications II.** Ed. by P. Günter and J.-P. Huignard Springer, Berlin 1989. xviii, 367 pp., bound, DM 124.— ISBN 3-540-19202-6. **Applied Superconductivity.** By A. M. Wolsky et al. Noyes, Park Ridge, USA 1989. Clothbound, USD 59.— ISBN 0-11-8155-1191-4. **Analysis of Polymers, An Introduction.** By T. R. Crompton. Pergamon, Oxford 1989. viii, 362 pp., bound, DM 165.— ISBN 0-08-033942-5. **High Temperature Corrosion of Ceramics.** By J. R. Blachere and F. S. Pettit. Noyes, Park Ridge 1989. ix, 188 pp., bound, USD 39.— ISBN 0-8155-1188-4. **The Effects of Radiation on High-Technology Polymers.** Ed. by J. H. O'Donnell and E. Reichmanis. A.C.S., Washington 1988. xi, 293 pp., bound, USD 65.95.— ISBN 0-8412-1558-8. **Epoxy Resin Chemistry II.** Ed. by R. S. Bauer. ACS, Washington 1983. x, 310 pp., bound, USD 44.95.— ISBN 0-8412-0077-1. **Ultra-Fast Silicon Bipolar Technology.** Ed. by L. Treintinger and M. Miura-Mattausch. Springer, Heidelberg 1989. ix, 167 pp., bound, DM 59.— ISBN 3-540-50638-1.

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The closing date for nominations is 2 October 1990. Further details from Dr. J. F. Gibson, RSC, Burlington House, London W1V 0BN (UK).

**Neuchatel Switzerland:** The Third International Conference on Surface Modification Technologies will be held at CSEM (Centre Suisse d'Electronique et de Microtechnique) Neuchatel, Switzerland from August 28 to September 1, 1989. The Conference is jointly sponsored and organized by the Minerals, Metals, Material Society (TMS), USA, the Metallurgical Society of AIME, and the CSEM. General Meeting Information is available from M. Karl; TMS, 420 Commonwealth Drive, Warrendale, PA 15086, USA, Tel. 412-776-9050.