class of liquid crystalline materials on graphite.[4, 5] Evidently, the molecules are imaged as they are adsorbed flat on graphite, quite like the phthalocyanine rings on copper. However, in this case no isolated molecules, but rather an ordered array is imaged. The intermolecular interaction within the monolayer may stabilize the position of any particular molecule, thereby reducing molecular motion sufficiently for STM imaging. The contrast is attributed in this case to the modulation of the local work function of the substrate by the polarizable molecular adsorbates. Indeed, functional groups which are electronically as dissimilar as benzene and cyclohexane can have similar contrast when imaged by the STM. This is explained by their comparable polarizability. However, it should be noted that alkane residues also have similar polarizabilities but give a different contrast in the STM. Obviously, the issue of contrast generation still remains a matter of debate.

A quite general way to reduce molecular motion is to increase the number of segments per molecule interacting with the substrate, a feature typical in polymer adsorption. Interestingly, high resolution STM images of DNA and double stranded RNA have recently been obtained by *T. P. Beebe* et al.[6] and *G. Lee* et al.[7] Both groups could resolve, minor and major grooves of the double helices adsorbed on graphite. However, the pitch periodicity was found to vary considerably. This can be attributed to the combined forces of the surface, partial dehydration and possibly intercalation with ionic species. To draw conclusions about the contrast mechanism is very difficult in these cases, since the samples were prepared by allowing buffer solutions of DNA and RNA to evaporate on graphite and the STM investigation was performed in air immediately after the last amounts of water were observed to evaporate. It cannot be excluded, therefore, that traces of electrolyte may contribute to the conductivity. Furthermore, it should be mentioned that due to the thickness of the molecule it is more complicated to interpret high resolution images of this material, than it was in the examples given before.

Our understanding of the processes involved in imaging organic adsorbates is considerably improving. This is both stimulating and encouraging for those working in this research area.

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[1] J. P. Rabe, *Adv. Mater. (1989)* 13; *Angew. Chem. Int. Ed. Engl. Adv. Mater. 28* (1989) 117; *Angew. Chem. Adv. Mater. 101* (1989) 117.
[2] P. H. Lippel, R. J. Wilson, M. D. Miller, C. Wöll, S. Chiang, *Phys. Rev. Lett. 62* (1989) 171.
[3] H. Ohtani, R. J. Wilson, S. Chiang C. M. Mate, *Phys. Rev. Lett. 60* (1988) 2398.
[4] J. K. Spong, H. A. Mizes, L. J. LaComb Jr., M. M. Dovek, J. E. Frommer, J. S. Foster, *Nature 338* (1989) 137.
[5] J. S. Foster, J. E. Frommer, *Nature 333* (1988) 542.
[6] T. P. Beebe Jr., T. E. Wilson, D. F. Ogletree, J. E. Katz, R. Balhorn, M. Salmeron, W. J. Siekhaus, *Science 243* (1989) 370.
[7] G. Lee, P. G. Arscott, V. A. Bloomfield, D. F. Evans, *Science 244* (1989) 475.

Phase Equilibria under Stress

By Robert W. Cahn*

Ever since the Phase Rule was first formulated more than a century ago, it has been recognized that hydrostatic pressure is a variable that must affect phase equilibria; the normal neglect of this variable in the construction of ordinary metallurgical equilibrium diagrams is merely a recognition that atmospheric pressure is minimal, and a flourishing research field is centered upon the investigation of new polymorphs and new transition temperatures under large pressures. Nevertheless, in the last few years the whole field has been given a quite new impetus by a small group of thermodynamics theorists who have examined the whole issue afresh.

Before we look at these new developments, let us dispose of some of the other ways in which an applied stress can affect phase dispositions. Here the major interest attaches, not to hydrostatic pressure but to uniaxial stress – a simple tension or compression. One important category is that of martensitic transformations, as in ordinary carbon steel. Here, a phase transforms by combining a macroscopic shear with more complex localized strains. When a cubic crystal transforms, it can typically form 24 crystallographically equivalent orientations or variants. An applied stress in the elastic range will favor a few of these orientations, or even a single one, over all the others. This has often been experimentally confirmed (e.g. by *Kochendörfer* and *Müller*,[1] who in this way created virtually a single crystal of a martensitic phase). This same phenomenon is crucially involved in the much studied family of shape-memory alloys, which return to an 'imprinted' shape on gentle heating.[2]

Again, when a single crystal of a cubic disordered phase is cooled so as to create a non-cubic superlattice, then a very small applied compression can pick out one of the, e.g., three

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possible variants to the complete exclusion of the others: this was demonstrated for the ordering transition of CuAu (cubic → tetragonal) by *Arunachalam* and *Cahn*.[3] More recently, those who study superalloys, the family of materials used in the construction of jet engines, have found that internal stresses within a two-phase alloy, resulting from a slight mismatch between the lattice parameters of the two epitactically intergrown 'coherent' phases, can modify the shapes of the dispersed phase particles. This effect can be substantial enough to cause dangerous deterioration of creep resistance. A very recent example of such an observation[4] refers to a dispersion of a phase with B2 order in a matrix with a Heusler ($L2_1$) type of order. The disperse particles form an array of tiny parallel cuboids, but on prolonged annealing a structural change takes place, a population of dislocations arises which winds down the internal stresses and the microstructure changes radically. The topic has been more generally treated by *Johnson* et al.[5]

The most recent work of this kind is also in some ways the most surprising. The long established and practically very important theory of Ostwald ripening – the coarsening of large precipitates at the expense of small ones in a nonuniform dispersion – has proved to be vulnerable. *Johnson* et al.[6] have shown that coherent misfit stresses can drastically alter the kinetics of Ostwald ripening, and can even lead to an inversion of the process, in the sense that smaller particles will grow at the expense of larger ones. One impatiently awaits experimental verification!

All of these diverse phenomena seem peripheral: in all of them, the orientation or morphology of a phase is affected by stress, but the volume fractions and compositions of the constituent phases should not at first sight be affected. A phase equilibrium is altered only when these two linked variables are changed. This is the issue addressed by the seminal work of my American namesake, *John Cahn*, and his French collaborator *Larché*.[7] They consider in quantitative detail the situation of a coherent two-phase solid in which the kind of elastic mismatch referred to above arises. In fact, as they show, both the magnitude of the lattice parameter mismatch and the detailed geometry of the two phases affect the Gibbs free energy of each phase. What this implies is that the Gibbs free energy of each phase is affected by the amount and morphology of the other phase. However, the classical tangent construction (see Figure) in which the composition and volume fraction of each phase is determined by drawing the common tangent in an isothermal plot of the Gibbs free energies of the two phases, depends on the absolute nature of these free energy plots. If the free energy of phase *A* of a certain composition depends on the volume fraction and disposition of phase *B*, then the tangent construction loses its validity. This has a striking consequence: in a binary alloy, a two-phase field is not what we are used to. Conventionally, all alloys within a two-phase field at a given temperature consist of differing proportions of two phases which always have the same compositions. Where the new theory of coherent stress-sensitive equilibria is valid, the compositions of the two constituent phases change as the two-phase field is traversed, and the ordinary lever rule can no longer be employed to compute the volume fractions of the two phases. Somewhat similar ideas were put forward the same year[8] by the Russian theorist *Roitburd* (who is now settled in America).

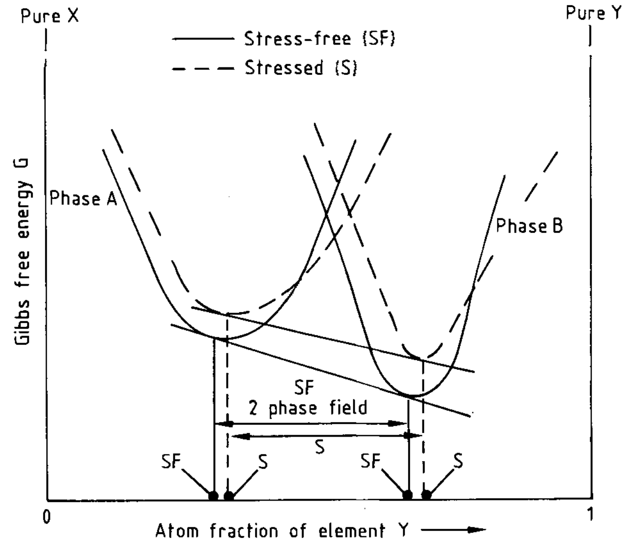

Fig. 1. Schematic diagram of the possible effect of non-hydrostatic stress (internal and external) on the free energies of two coexisting phases in the absence or presence of stress. Stress modifies the two-phase field. Only under very special conditions can the common tangent construction of free energy curves be used to depict phase equilibria in non-hydrostatically stressed solids [11].

These radical ideas due to *Cahn* and *Larché* have been further developed recently by two Americans, *Johnson* and *Voorhees*,[9, 10] who are making the running in this field at present. One of their conclusions is that a sort of catastrophic instability may arise so that more than one stable state is possible for the same two-phase alloy when it is subject to self-generated internal stress. The theory has also been applied to the practically important case of elastically stressed heteroepitaxial thin films,[11, 12] where the crucial rôle of coherency stresses in affecting electronic properties has been recognized for some time. The theoretical treatments have focused on elastic self-stresses (i.e., those due to lattice mismatch); the possible rôle of externally applied stresses has still to be addressed. It is clear that theory has run a long way ahead of experimental verification; it is possible that systematic experiments involving intentionally applied external stresses might go some way towards testing the theorists' predictions. Such experiments may also reveal parallels between the older work outlined at the beginning of this article and the more recent theories.

In parallel with the metallurgical literature, indeed somewhat ahead of it in point of time, has been a vigorous debate within the geological/mineralogical community concerning the rôle of non-hydrostatic stresses in phase equilibria in rocks. Phenomena such as pressure solution phenomena, crystallization under stress (the geologists call this recrystallization), shear transformations in rocks such as quartzite, 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[13] 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 α/β 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.

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[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. 18 A* (1987) 1093.
[10] W. C. Johnson, P. W. Voorhees, *Metall. Trans. 18 A* (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 technical purposes are composed of flexible macromolecules, and the physics of rubber elasticity has been developed based on the fact that flexible chains are crosslinked.[1, 2] In two recent publications[3, 4] *Vilgis, Boué* and *Edwards* for the first time set up a theory of rubber elasticity for networks composed of rigid rod polymers.

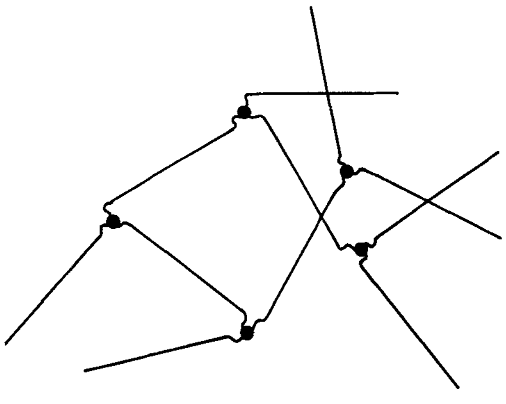

Fig. 1. Schematic representation of a network of rods connected by flexible hinges.

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*[5] showed that there is a limiting functionality m_c (or an upper critical dimension) given by $m_c = 2\,d$ with d being the space dimension. This can be exemplified by considering two-dimensional networks in a simple square lattice configuration (see Fig. 2).

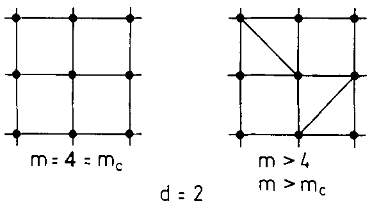

Fig. 2. Critical functionality for two dimensional networks: $m = 4 = m_c$: network can be deformed by shearing (left hand side); $m > 4$, i.e., $m > m_c$: rigid network (right hand side).

The functionality is four in this case which exactly corresponds to the limiting functionality in two dimensions ($d = 2$). 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 energic nature, i.e., deformation of this network requires the bending and elongation of bonds. The same

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