Computer simulation of network formation processes, structure and mechanical properties of polymer networks

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The possibilities offered by computer simulation for the investigation of polymer networks are discussed. Instantaneous crosslinking can be simulated by fixing the conformation of a set of linear macromolecules. Equilibrium crosslinking requires a complete rearrangement of the conformation after formation of each crosslink. The conformations of the lattice models of polymer networks with certain topologies can be constructed using a Monte Carlo procedure for obtaining the equilibrium configurations of the junction points, and the methods of generating conformations of polymer chains with fixed end-to-end distances. The deformational properties of polymer networks, taking into account the finite length of chains, can be investigated by the use of a model of interacting junction points, quasi-particles. The way of investigating the entanglement effects and the interchain interactions are proposed. Polymer chain mobility may be simulated by the molecular dynamics of the 'pearl necklace' model. Destruction processes in polymer networks can be simulated by a Monte Carlo method if the breakage of a strand connecting two junction points is regarded as an elementary event.

INTRODUCTION

The main purpose of this paper is to discuss computer methods used in solving some of the problems arising in the process of fabrication, testing and utilization of polymer networks. The paper will not discuss the *results* of the investigation of polymer networks by methods of computer simulation. Only a few experiments have been carried out using these methods, and their influence on the development of the theory of polymer networks is insignificant.

The goal of a 'perfect' theory of polymer networks can be formulated quite simply and divided into two parts: (1) prediction of the structure of the polymer network formed by macromolecules of a given chemical nature under given conditions; (2) determination of the properties of networks of given topology formed from chains having given characteristics.

There are two classical analytical approaches to these problems. The first one is the Stockmayer–Flory theory of gel formation[1] created more than thirty years ago and developed extensively by many authors with the application of more mathematical methods. The second is the classical theory of rubber elasticity with a history of almost fifty years[2,3].

There is no doubt that these theories are basically sound, but there is also no doubt that they do not satisfy the requirements postulated for a 'perfect' theory. There are many experimental facts which find ambiguous interpretation by means of these theories, even if we take into consideration their most recent development.

Moreover, some assumptions used in these theories cannot be regarded as proven. As an example we can mention the assumption made in all theories of rubber elasticity that the entropy change due to the extension of polymer chains does not depend on the concentration of a polymer solution.

It would be very useful for the development of the theory to perform a set of experiments in which the conditions of network formation were strictly defined and in which the network structure would be investigated in detail. It is practically impossible to perform such experiments on a real polymer, but the methods of computer simulation may be used.

We can simulate the process of network formation to determine the structure of the network in detail and to calculate network properties. The difficulties we encounter are associated with the limited speed and memory of modern computers, which are very important. We cannot simulate the process of network formation as exactly as we might desire. Simplified models must be used, assumptions made, and the problem divided into separate steps. The peculiarity of these assumptions and simplifications when compared with those made in analytical theories is that they can be checked on more complex or sometimes simpler models also by the methods of computer simulation.

The general scheme of simulation of a network formation process will be outlined and an ideal desirable scheme will be compared with one which can be practically realized.

SIMULATION OF NETWORK FORMATION

Consider a set of linear macromolecules having a number of reactive groups which can form chemical bonds between macromolecules, leading to the formation of a network. An assumption will be made that a bond can be formed only between groups which have approached each other so that they are in contact. The crosslinking itself will be considered as a random process.

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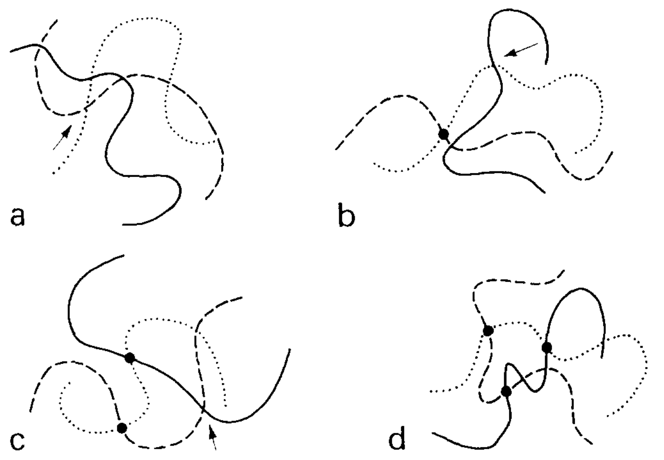

Figure 1 Successive steps of network formation (a → d); places where new crosslinks are to be formed are shown by arrows

Assuming that the formation of each new bond is instantaneous, the process of network formation can be presented as a sequence of discrete crosslinking events occurring at the moments t_1, t_2, etc. (*Figure 1*). There are two extreme cases which can be simulated simply.

(1) *Instantaneous crosslinking.* This takes place in such conditions that chain conformations have no time to rearrange themselves during the time interval between two successive crosslinking events, i.e an absolute 'conformation memory' exists. To simulate such a process, the conformations of all macromolecules in the system must be generated, the positions of contacts between the reactive groups determined, and the groups which ought to form crosslinks chosen. It is reasonable to assume that all crosslinks are formed simultaneously. In such a way we shall obtain a network having a determined topology. To determine the average characteristics of a polymer network we must repeat the simulation of the crosslinking process several times using different macromolecular conformations with the probability proportional to their statistical weights.

(2) *Equilibrium crosslinking.* This takes place so that the complete rearrangement of macromolecular conformations occurs during the time interval between two successive crosslinking events, i.e. conformation memory does not exist. Such a process can be simulated by generation of the conformation of a partly formed network after formation of each crosslink. This conformation must be statistically independent of the conformation in which the previous crosslink was formed. In this case the kinetics of the network formation process can be followed in detail.

The intermediate situation (network formation with limited conformation memory) can also be simulated with the use of molecular dynamics or lattice methods to be discussed later. In this case some difficulties of an algorithmic nature appear.

The crosslinking occurring during polymerization can also be simulated. In this case, the competition between crosslinking, chain growth, initiation and termination must be considered.

A possible scheme for such a simulation is shown in *Figure 2*. The simulation may elucidate the role of the competition between the reactions of intramolecular and intermolecular crosslinking. The former leads to the reduction of polymer coil dimensions and, consequently, to the reduction of the intermolecular crosslinking probability.

The possibility of simulating a network formation in a given polymer system depends on the models chosen for the polymer chains in the system considered. Different models of polymer chains will be discussed in the following section.

SIMULATION OF THE CONFORMATION OF A POLYMER NETWORK

We shall first consider the structural models of linear macromolecules used in the computer simulation studies (*Figure 3*). Three different models may be postulated.

(a) Atomic models which represent a macromolecule as a system of atoms connected by rigid bonds forming definite valence angles and interacting with each other with classical atomic potentials.

(b) 'Pearl-necklace' models represent a macromolecule as a chain of rigid spheres connected by bonds with a constant length. In these models each sphere represents not an atom but a segment of a macromolecule.

(c) Lattice models represent a macromolecule as a chain consisting of units occupying sites in a certain three-dimensional lattice. In comparison with atomic models, the lattice units omit some of the detailed characteristics of macromolecular structure but allow us to study the conformations of larger chains. Using lattice models we can simulate macromolecules of different flexibilities by varying the statistical weight of the forward step on a lattice (the step with a valence angle 180° on a simple cubic lattice, and the step leading to the *trans* isomer on a tetrahedral lattice). The quality of solvent can also be taken into account if two units are forbidden to occupy one lattice site and if an attractive energy is assigned to units occupying adjacent sites.

Different models can now be considered. The junction point can be represented as a constant bond between two units occupying adjacent lattice sites, or as a point of intersection of two chains. The latter case is illustrated by the network formed by three chains arranged on a two-dimensional square lattice (*Figure 4*). In this case the excluded volume of the chain units can be taken into account

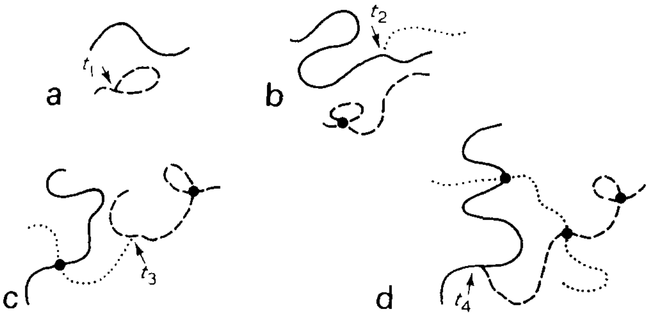

Figure 2 Scheme of the crosslinking process occurring during polymerization

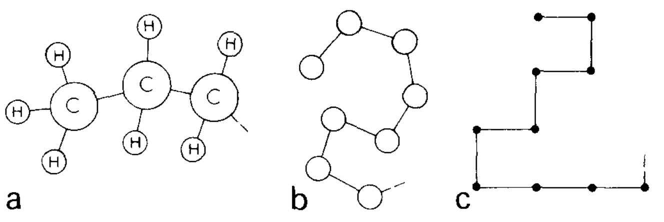

Figure 3 Models of linear macromolecules: (a) atomic model; (b) 'pearl-necklace' model; (c) lattice model

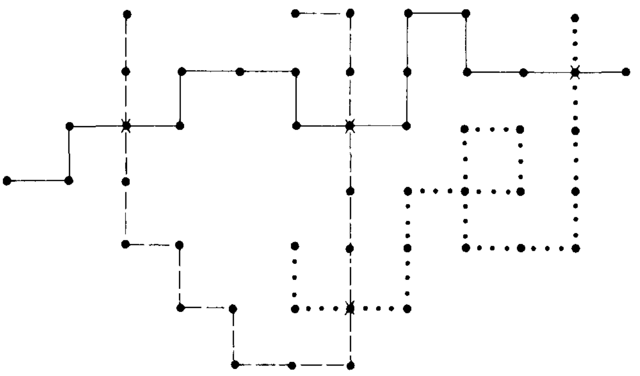

Figure 4 Two dimensional lattice model of a polymer network

by forbidding the superposition of bonds connecting the units.

To investigate the conformational properties of linear macromolecules, averaging must be performed over the ensemble of possible conformations of a model chain. If a model is used in which the attraction between units is not taken into account, all possible conformations have equal statistical weights. Thus conformations can be generated starting from one chain end and adding one unit after another in the positions determined by the probabilities dictated by the flexibility of the chain. All possible conformations of the model network with a given topology, formed by chains interacting without attraction, also have equal statistic weights. To construct a conformation for such a network we must first place junction-points in some lattice sites and then connect them by strands. Since each strand consists of a definite number of chain units, only some configuration points are admitted. Moreover, different admissible configurations of junction-points have different statistical weights because the number of ways in which two points occupying fixed positions can be connected by a strand depends on the number of units in the strand and on the distance between the end-points. The approximate analytical form of this dependence is an inverse Langevin function which approaches a Gaussian distribution at small end-to-end distances. For chains on a body-centred lattice an expression is obtained which is valid and exact for all distances[4]:

$$W(n, \vec{\Delta x}) = \prod_{i=1}^{3} \frac{n}{\left(\frac{n + \Delta x_i}{2}\right)! \left(\frac{n - \Delta x_i}{2}\right)!} \tag{1}$$

Here, n is the number of chain bonds, and $\vec{\Delta x}$ is the difference between the coordinates of the strand ends. If, for some value of i, $|\Delta x_i| > n$, this expression is equal to zero.

The algorithm for sampling different possible configurations of junction-points has been proposed[5]. It is based on the method proposed by Metropolis *et al.* for Monte Carlo simulation of the statistical properties of simple fluids[6]. In this algorithm junction-points are regarded as quasi-particles interacting only if connected by one or several strands. One possible configuration of the junction-points is chosen and then one of the junction-points occupying some lattice site is displaced to some other lattice site. Using equation (1) we can find the ratio of the number of strand conformations corresponding to the initial configuration of junction-points, W/W', to one obtained after the displacement of one junction. If $W'/W \geqslant 1$ the transition to the new configuration takes place; otherwise it can occur only with some probability, equal to W'/W. This procedure is repeated several times until a configuration statistically independent of the initial configuration is obtained. As the result the ensemble of different configurations of junction-points, appearing with a frequency proportional to their appropriate statistical weights is obtained.

The algorithm proposed by Vologodskii *et al.*[4] is used to construct the conformations of all the chains forming a network of a given topology and corresponding to some definite configuration of junction-points. If it is necessary to connect the points with coordinates $\vec{x}$ and $\vec{x} + \vec{\Delta x}$ by n steps on a body-centered lattice, a step must be chosen with the vector $\vec{\delta}^l (1 \leqslant l \leqslant 8; \vec{\delta}^l = \pm 1)$ having the probability:

$$P(n, \vec{\Delta x}, \delta^l) = \prod_{i=1}^{3} \frac{n - \Delta x_i \delta_i^l}{2n} \tag{2}$$

Using the algorithm, all conformations of the chains connecting two lattice sites with equal probabilities are obtained.

The network formed by chains arranged on a body-centred lattice is not the best model of a real polymer network, but the algorithm can be modified for other lattices including a tetrahedral lattice[5].

The procedure for the simulation of the network formation using the structural model with chain conformations constructed on a body-centred lattice was applied by us to the investigation of the process of intramolecular crosslinking[7]. Simulating the kinetics of crosslinking it was found that the process is self-accelerating. The conformational characteristics of crosslinked polymer coils at different degrees of crosslinking were obtained.

The results of calculations performed for the crosslinked chains having no more than 150 units have shown that the simulation performed, even for the simplest structural model, requires considerable computer time. Using better computers and determining more efficient algorithms it may be possible to construct model networks consisting of chains including no more than several thousands of units (segments). However, even a network consisting of twenty chains, each including fifty units, is quite small. Almost half of its units are situated on the surface. At the same time it is important to obtain results valid for macroscopic networks consisting of a large number of chains. The same problem occurs during computer simulation of the structure of simple fluids[6] and concentrated polymer solutions[8]. In such cases periodical boundary conditions must be used. The same method can be applied to polymer networks.

A two-dimensional network with periodical boundary conditions is shown in *Figure 5*. Chain conformations in the cells surrounding the central cell reproduce exactly the conformations in the central cell. By analysing the topology of the part of the network occupying the central cell it can be determined whether a gel is formed in such a network.

There is another approach permitting simulation of the structure of polymer networks consisting of a great number of chains. This approach was used by Topolkaraev *et al.*[9] for the simulation of oligomeric networks formed by crosslinking of tetrafunctional aromatic diamines with bifunctional diepoxides. The diamine was represented by a point on a two or three-dimensional lattice, and the diepoxide by a bond between two adjacent lattice sites (*Figure 6*). Different topological structures formed at different ratios of the

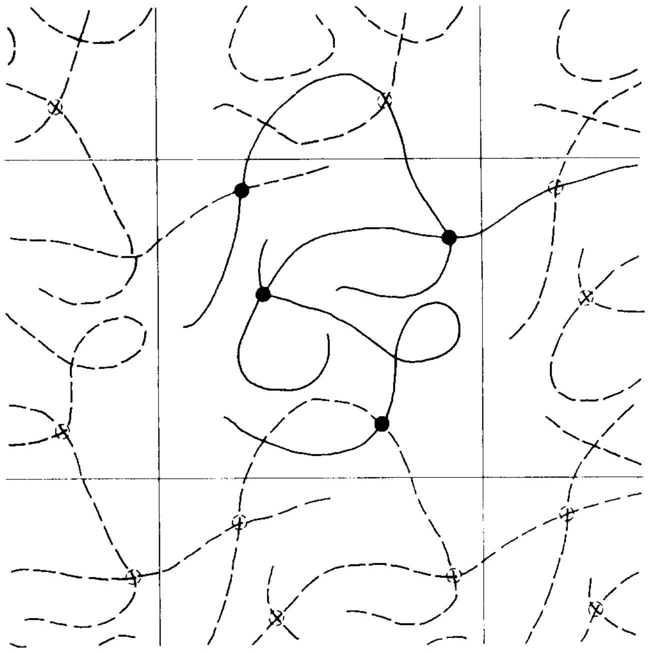

Figure 5 Model of a polymer network with periodical boundaries

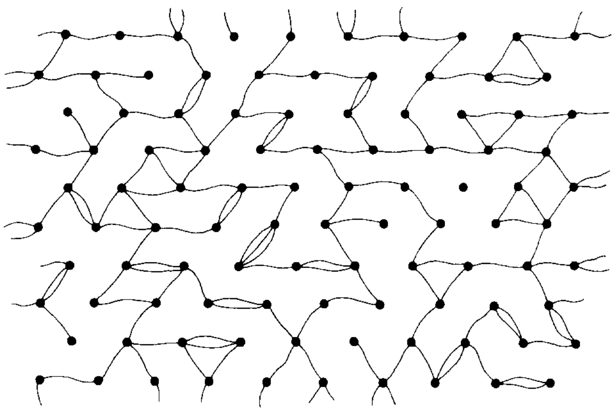

Figure 6 Model of an oligomeric network formed from diamines crosslinked with diepoxides

reacting components and their mechanical properties were studied^{10}.

This approach can be used to simulate the process of network formation. In this case the centre of inertia of each macromolecule is represented by a point. These points must be distributed in space at random and bonding of non-adjacent points must be possible. The dependence of the probability of crosslink formation on the distance between the points to be connected can be determined rather easily. The use of such an approach permits the simulation of polymer networks consisting of thousands of chains.

SIMULATION OF THE DEFORMATIONAL PROPERTIES OF POLYMER NETWORKS

Investigation of the mechanical properties of different networks simulated by a computer can provide a more exact determination of the number of elastically active chains, and elucidate the cause (or causes) of the discrepancy between the experimentally obtained stress–strain curves and those predicted by a classical theory of rubber elasticity.

It is rather unreasonable to simulate polymer networks with detailed conformations of all chains. A network can be represented as a system of junction points interacting as quasi-particles. Such a system can be studied by molecular dynamics or Monte Carlo methods. The stress–strain curve for a network with a certain topology can be obtained, as well as the equation of state for a system of particles representing the atoms in a simple fluid. If only two-particle interactions between the junction points directly connected by a chain are taken into account it should be possible to investigate the effects of network topology and the finite length of strands connecting junction points, but not the effects of entanglements between strands or intermolecular interactions of chain units. The latter effects must be treated separately.

A direct approach to the investigation of the effect of entanglements is to consider a network with a given topology and given conformations of strands connecting junction points, and to determine the pairs of loops which are entangled (see *Figure 7*). Then the deformation (extension) of the network of the same topology should be simulated and the fraction of conformations having the same set of entanglements calculated for different configurations of junction points. This procedure is very difficult to realize on a computer and requires a large amount of computer time. It is more reasonable first to calculate the probability of an entanglement between two strands separated by a given distance, then to determine the probabilities of different sets of entanglements for a given topology and, finally, to consider the influence of entanglements on the mechanical properties of polymer networks using the phenomenological approach used by Graessley and Pearson^{11} or a similar study.

To accomplish the first part of this program, two chains were considered^{12} having average end-to-end distances H and separated by the distance ξH (*Figure 8*). The chains were extended to the form of loops by phantom chains which did not interest the two chains under consideration. To exclude the possibility of intersection, the chains were arranged on two interpenetrating tetrahedral lattices having no common lattice points, and forming together a body-centered lattice. The ensemble of chain pairs was generated and the topological relation between the loop pairs was determined by means of Alexander polynomials. It was found that for a given arrangement of chain ends, the entanglement probability is a function of ξ only if the number of units in every chain is not less than twenty. This probability is different when the lines connecting chain ends are parallel, non-coplanar, or perpendicular to each other. In the first two cases the entanglement probability can be approximated by an exponentional function of the relative distances $0.1 < \xi < 1$. At $\xi = 1$ this probability was less than 0.05 and only when $\xi < 0.2$ did it exceed 0.2.

For two non-intersecting chains with excluded volume, arranged on a tetrahedral lattice, the entanglement probability at given 000 increased with an increase of chain length.

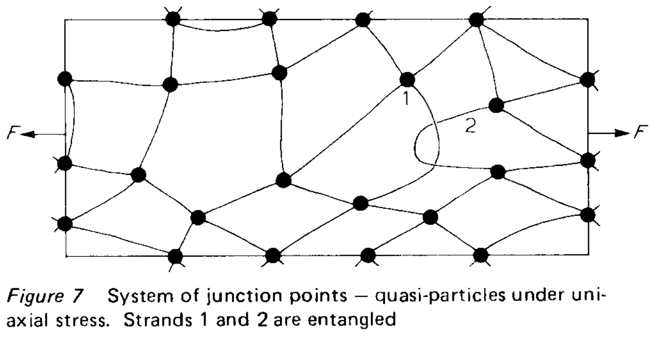

Figure 7 System of junction points – quasi-particles under uniaxial stress. Strands 1 and 2 are entangled

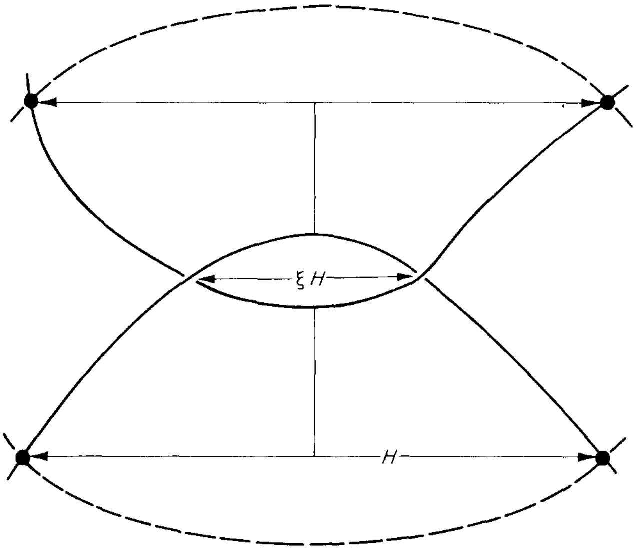

Figure 8 Entanglement between two strands. $\bar{h}^2$ mean square end-to-end distance

At $n = 81$ and $\xi = 0.2$ it was less than 0.1. From these preliminary results it can be derived that the entanglement effects may be significant only when the network strands consist of more than 50–100 segments. The effects of entanglements on the mechanical properties of polymer networks may be studied with the use of the model of junction points (quasiparticles) if we take into account not only two-particle interactions of junction points connected by strands, but also the four-particle potential between the pairs of junction points connected by entangled strands*.

To elucidate the role of the intermolecular interactions of polymer chains we must calculate the entropy of the model polymer network. For large networks it is a very difficult task. However, using small models of regular polymer networks with periodical boundary conditions, and performing calculations for various degrees of network deformation (extension) we can see how an increase in concentration of the polymer chains affects the number of possible conformations of these chains. It is clear that the results should depend on the flexibility of the chains. Only after such calculations are made can the computer simulation of mechanical properties of a polymer network (taking into account intermolecular interactions) be performed.

For network models containing chains with units which can occupy not only lattice sites, calculations requiring averaging over the ensemble of network conformations will probably not be performed in the near future, since the construction of such chains with fixed ends would require too much computer time. Such models can be useful in the simulation of the local relaxation processes in polymer networks.

SIMULATION OF CHAIN MOBILITY IN POLYMER NETWORKS

There are many reports of the relaxation properties of linear macromolecules which are simulated with the use of lattice models. The change of conformation takes place due to elementary jumps of units by a 'Γ' or a 'Π' mechanism (*Figure 9*)[14]. For lattice models of polymer networks, these types of jumps are not sufficient since the junction points in this case do not move. It is rather difficult to suggest any adequate mechanism providing for the movement of junction points in the lattice models of polymer networks[15]. Therefore the simulation of polymer chain mobility in polymer networks has to be done by the method of molecular dynamics using a 'pearl necklace' model.

The molecular dynamics method[16] requires a numerical solution of the Newtonian dynamic equations for a system of interacting particles. This method has been used by many authors for the study of relaxation in simple fluids. In recent years this method has also been applied to polymer systems[17–20].

The dynamic equations for a system of particles whose motion is limited by rigid bonds must be solved in order to apply the molecular dynamics method to a polymer system. For such a system the dynamic equations for each particle cannot be written in Cartesian coordinates. It seems natural to reduce the number of equations to be solved by using generalized coordinates, i.e. to solve them in the form of Lagrangian equations of the second kind. This was found to be impractical for the system with a great number of rigid bonds because the equations were too complicated. In 1972 Balabaev *et al.*[17] proposed the use of Lagrangian equations of the first kind. The paradox of this method is that the number of equations to be solved increases with the number of rigid bonds, but these equations can be solved using a rather simple computer algorithm. Recently, Darinsky *et al.*[20] have applied the method to the investigation of a polymer system having a density approaching that of a polymer melt. The pearl necklace model was used and the interaction potential between the units not directly connected by a rigid bond was chosen in the Lennard-Jones form. The valence angle was not fixed but the parameters of the potential were chosen so that the mean value of the angle was close to the value of the tetrahedral angle.

The above method can also be applied to polymer networks. The conformation of a polymer network can be generated by arranging the strands connecting junction points on a tetrahedral lattice, and thus relaxation of the network allowing the units to leave the lattice sites can be simulated. Simulation of the relaxation of a single chain having one junction (*Figure 10*) was performed[21]. This allowed the authors to evaluate the hindering effect of the junction on the mobility of polymer segments situated near the junction point. It was shown that rotational mobility was reduced significantly only for the segments adjacent to the junction. The reduction of the translational mobility was also trans-

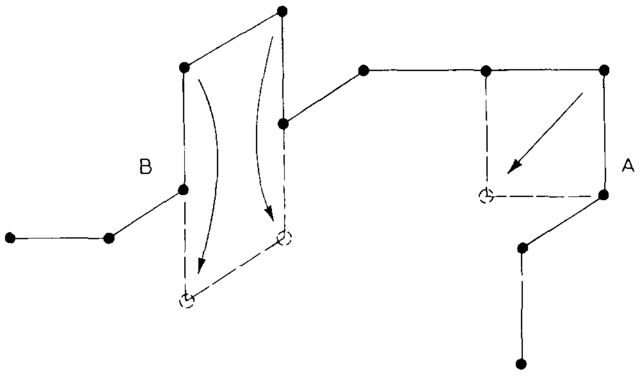

Figure 9 Elementary jumps in a chain constructed on a simple cubic lattice. A, Γ jumps; B, π jumps

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* The dependence of the probability of formation of two unentangled loops on the distance between their centres has been calculated by Frank-Kamenetskii *et al.*[13]

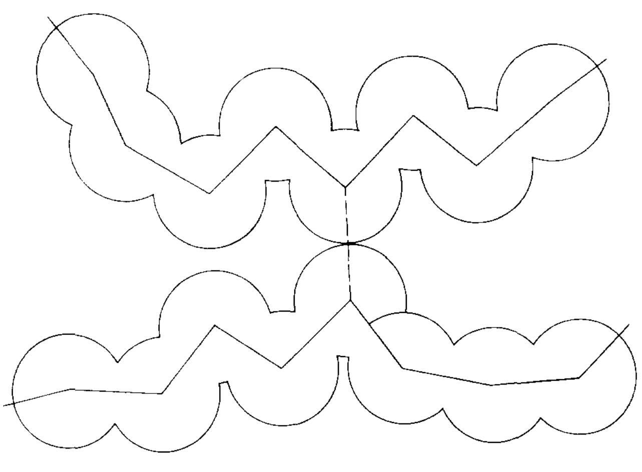

Figure 10 Model of two crosslinked chains studied by molecular dynamics method

mitted to segments more remote from the junction. The transition to the systems with many junctions does not present any difficulties. Using such a method, atomic models of specific polymer networks can be investigated.

The molecular dynamics method has limited possibilities because it allows the investigation of the relaxation of the system during time intervals not longer than 10^{-8} sec. Investigation of slower relaxation processes can be performed by the method of Brownian dynamics of polymer chains with rigid bonds based on the solution of the Langevin dynamic equations[22]. For model polymer networks this method has not yet been used.

SIMULATION OF THE DESTRUCTION PROCESS IN POLYMER NETWORKS

To simulate destruction in a model polymer network we must define which can be broken, and a law governing an elementary breakage event. A fracture process was simulated for a network consisting of junction points located in the undeformed state on a simple cubic lattice, connected by elastic bonds[23] (*Figure 11*). A stretching force applied along the Z-axis causes displacement of junction points along this axis.

The breakage of one of the bonds intersecting the $X-Y$ symmetry plane is regarded as an elementary destruction event. The breakage of a bond was assumed to be a random thermal fluctuation process characterized by an average expectation time, τ_i, dependent on the stress applied to this bond according to the Zhurkov formula[24]:

$$\tau_i = \tau_0 \exp \frac{U_0 - \gamma\sigma_i}{KT} \qquad (3)$$

where τ_0, U_0 and γ are constants.

The destruction process was simulated starting from the state in which all bonds were unbroken. The Monte Carlo method is used to determine which bond breaks first and at which moment. As a break of one bond results in a redistribution of the tensions in the remaining bonds, the distribution taking place after each break was calculated by solving a system of linear equations by the iteration method. *Figure 12* shows the successive stages for two realizations of the fracture under different loads. Time was expressed as a fraction of the period τ required for the fracture of all bonds intersecting the fracture plane.

The model used in this study gives an adequate description of brittle fracture of highly oriented amorphous crystalline polymers but cannot be regarded as a good model of a polymer network exhibiting rubber elasticity.

The same method can be used for the simulation of destruction in more realistic models of polymer networks. Extension of a polymer network at a constant rate can be simulated using a method junction points – quasi-particles, and the effect of breaking the strained strands on the stress–strain curves can be studied.

CONCLUSIONS

Computer simulation methods offer a good opportunity to study network formation processes, structure, and different properties of polymer networks. It is important to note that these methods allow simulation of strictly defined processes, determination of network structure in all its details, and the study of properties of systems with known topology. At the same time it should be emphasized that the calculations for model polymer networks are difficult to realize in practice and require a large amount of computer time. Thus the choice of the models must be made carefully.

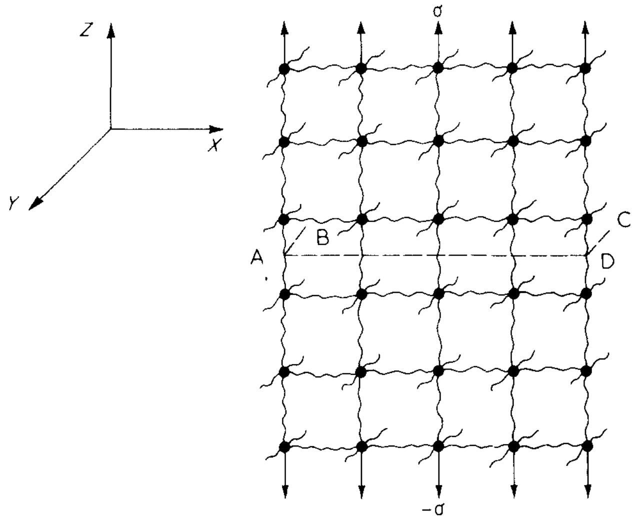

Figure 11 Newell–Rosenstock network on a simple cubic lattice. ABCD = the fracture plane

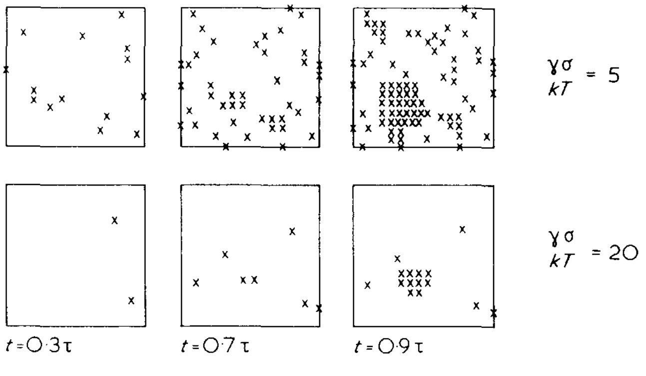

Figure 12 Successive configurations of broken bonds in the fracture plane

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