Computer Simulation of Coil Deformation

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The deformation behavior of statistical coils in the condensed state were studied by computer simulations. The simulated systems consisted of single and double chains, each with $(N-1)$ segments, which could rotate about their junctions. Van der Waals interactions were considered between all junctions. Equilibrium conformations were obtained by potential energy minimization using a modified Newton algorithm. During the simulated deformation, all initial coils transformed into a highly oriented fibril and a residual coil. Combining the behaviour of several coils, the energy increased nearly linearly with the extension ratio and due to this the retractive force was independent of the extension rate. © 1994 Academic Press, Inc.

INTRODUCTION

The general scheme of the process of cold drawing of polymers is that after a region of elastic behaviour many glassy or semi-cristalline polymers begin to neck and yield depending on the conditions of temperature and draw ratio. The tensile stress tends to be independent of the draw ratio until strain hardening appears. The material is oriented from a quasi isotropic state to its natural draw ratio within the necking region. Numerous attempts have been made to describe the mechanism for the plasticity of polymers based on the concepts of adiabatic heating, production of free volume under stress, and the theory of Newtonian viscous flow of Eyring. For a summary, see Ward [1] and Argon [2]. Morphological studies by electron microscopy showed that the neck consists of deformation zones, shear bands, and similar states [3]. Another morphology which is closely related to shear bands are crazes. Michler [4] and Hopfenmüller [5] found that shear bands can be regarded as collapsed crazes.

Altogether it is obvious that necking is a non-homogeneous problem, so that the well established theories of affine deformation of polymers (Kuhn, Grün, Flory) are not very suitable. They, too, afford that during the deformation process the neck is in a quasi liquid phase which should result from the production of heat during deformation [6]. But Zachmann [7] has shown that the arising heat is much too low to melt the material into a kind of elastic phase. The model of Robertson [8] depends on a shear field which increases the free volume and thereby allows increased site-change processes.

As a first step to describe the inhomogeneous deformation of solid polymers we constructed statistical chains on the computer. The segments of the chains were allowed to rotate freely about their junctions. Additionally we considered van der Waals interactions between all junctions. After achieving equilibrium conditions by minimizing the potential energy the chains were deformed by applying stepwise forces or extensions to them. After each step the chains could relax by minimizing the energy. The conformations obtained are similar to the analysis of the deformation behavior of a collapsed linear coil in a poor solvent by Halperin *et al.* [18], but the origin of the deformation mechanism is different. Whereas in the case of Halperin's analysis the created surface energy is the only reason for the shape of the deformed coil, we generalized the problem. The potential energy due to van der Waals interactions as well as nonsaturated van der Waals bonds at the surface of the coil determine the deformation behavior.

COMPUTER SIMULATION

The following assumptions have been made to carry out the simulations.

Assumptions

For our simulations we used systems with Z chains. Each chain consisted of $(N-1)$ segments, which could freely rotate around their junctions. Nevertheless one can say, one segment is one monomer; it is better to think of something like Kuhn's statistical segment. The conformation of such a coil is therefore described by N junctions under the influence of several intra- and intermolecular interactions. We have considered:

- the elasticity within one segment (molecule bond)

- van der Waals interactions between all junctions of one chain

- van der Waals interactions between all junctions of different chains

- external forces.

The conformations were obtained by energy minimization using a modified Newton algorithm. This algorithm computes the nearest relative minimum to the starting conformation in the direction of decreasing energy. This means that our simulations take place at $T = 0$ K. The time for finding a minimum in energy was not restricted. In other words the deformation velocity is nearly zero. Because of these two reasons we also neglected entropical effects (by the way, the coil-strand transition model (Kreitmeier [10], Göritz [11]) showed that entropy is also negligible at reasonable finite temperatures). In this paper we do not focus on rotation potentials and on fixed angle bondings. We have made simulations with fixed bond angles. The results are, apart from zig-zag chains, the same as without them. Furthermore, we believe that rotation or torsion can be neglected in a first attempt, because the possible changes can be ruled out by a larger statistical segment. Nevertheless we will check these assumptions in further investigations.

The Energy of the Coil

Figure 1 shows the model chains. The following notations are used:

- $^{a}\mathbf{r}_i$: vector to junction i of chain a

- $^{a}\mathbf{R}_i$: vector to junction i of chain a in the initial state.

To describe the van der Waals interaction mathematically we have chosen Morse-potentials (Fig. 2); the elasticity within one segment is specified by a Hookean spring. The total potential energy U of our system is

$$U = \sum_{a=1}^{Z} \left\{ \frac{E}{2} \sum_{i=1}^{N-1} (|^{a}\mathbf{r}_{i+1} - {}^{a}\mathbf{r}_i| - S_0)^2 \right.$$
$$+ D \sum_{i=1}^{N} \sum_{j=i+2}^{N} \left[\left(1 - \exp\left(k - k \frac{|^{a}\mathbf{r}_i - {}^{a}\mathbf{r}_j|}{R_0} \right) \right)^2 - 1 \right]$$
$$+ D \sum_{b=a+1}^{Z} \sum_{i=1}^{N} \sum_{j=1}^{N} \left[\left(1 - \exp\left(k - k \frac{|^{a}\mathbf{r}_i - {}^{b}\mathbf{r}_j|}{R_0} \right) \right)^2 - 1 \right]$$
$$\left. + \sum_{i=1}^{N} {}^{a}\mathbf{F}_{(\text{ext}),i} \cdot ({}^{a}\mathbf{R}_i - {}^{a}\mathbf{r}_i) \right\}$$

with

E: Young's modulus of a spring

$S_0 =$ equilibrium segment length

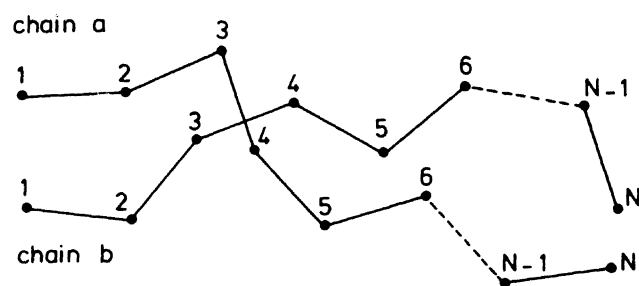$D =$ bonding energy of the van der Waals interaction

FIG. 1. Model chains for the computer simulations.

$R_0 =$ equilibrium distance of the van der Waals interaction

$k =$ determines the range of the van der Waals interaction

$^{a}\mathbf{F}_{\text{ext},i} =$ external force on junction i of chain a.

Since a covalent bond is much stronger than the van der Waals interaction, we neglect van der Waals interactions between successive junctions along a chain ($j = i + 2$ in the second sum of the second term).

We choose in our simulations one segment to consist of three monomers. Using average values of bond energy and bond length the resulting parameters are,

$$E = 60 \frac{\text{eV}}{\text{Å}^2}, \quad S_0 = 4 \text{ Å}, \quad D = 0.1 \text{ eV}, \quad R_0 = 3 \text{ Å}, \quad k = 5.$$

With this choice of k the Morse potential is similar to the Lennard–Jones potential. Modifications of these parameters in a reasonable range have no influence on the qualitative results of the simulations.

Concept of the Simulations

To evaluate the conformations we used energy minimization according to a modified Newton algorithm [13]. To
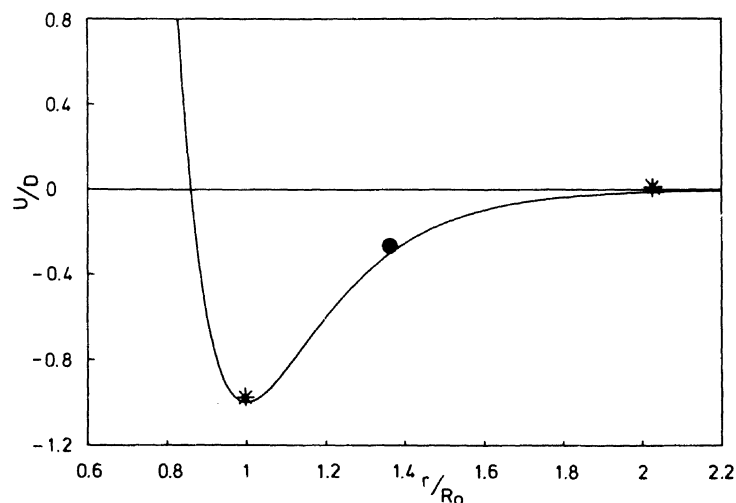

FIG. 2. Morse potential $u = D(1 - \exp(5 - 5(r/R_0)))^2 - D$. Total energy for two bonds at position (●) is greater than for bonds at positions (∗).
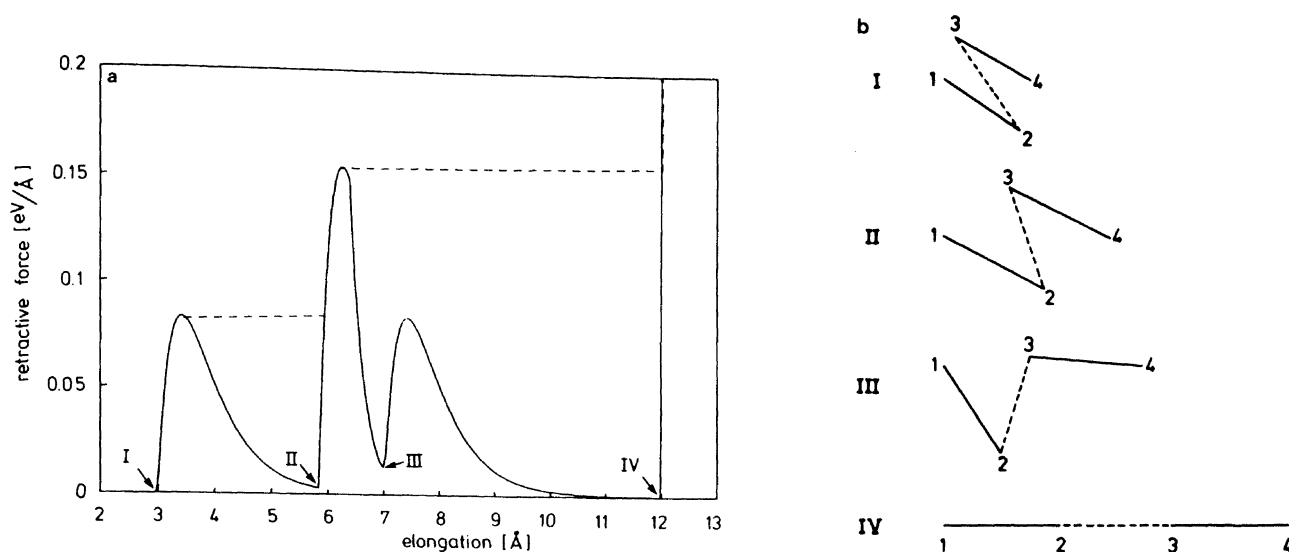
FIG. 3. (a) Retractive force versus elongation for method (a) ——— and method (b) ---- for a three-segment chain. See text for explanation. (b) Conformations for a three-segment chain for positions I, II, III, IV of Fig. 3a.

obtain better and faster results we calculated the derivatives and used the routine E40LBF of the NAG Fortran Library Mark 13. The simulations were performed on a COMPAREX and on several SUN (Sparc Station 1) computers. To obtain an initial coil we arranged the segments in statistical manner, determining the direction of one segment by random numbers. After placing a segment we minimized the energy. This procedure supplies statistically arranged chains with interactions in equilibrium. In some way the coils are collapsed because of the energetic interactions.

Two computer experiments were made:

(a) Increasing the elongation in every iteration step and energy minimization afterwards. Computing the retractive force of the system in every iteration step.

(b) Increasing the external force on one junction in every iteration step and energy minimization afterwards.

Computing the elongation of the system in every iteration step.

In both experiments the coils were held tight in space by fixing one or several junctions.

RESULTS

For a better understanding of simulations with many segments (large N) we describe the general behaviour with one chain consisting of three segments (four junctions).

Figure 3a shows the result of both methods, experiment (a) and (b), for this chain. The draw direction in case (a) respectively the direction of the external force on junction 4 in case (b) is identical with the x-direction. In both methods junction 1 was fixed. In case (a) the simulated curve describes the behaviour of the retractive force of the
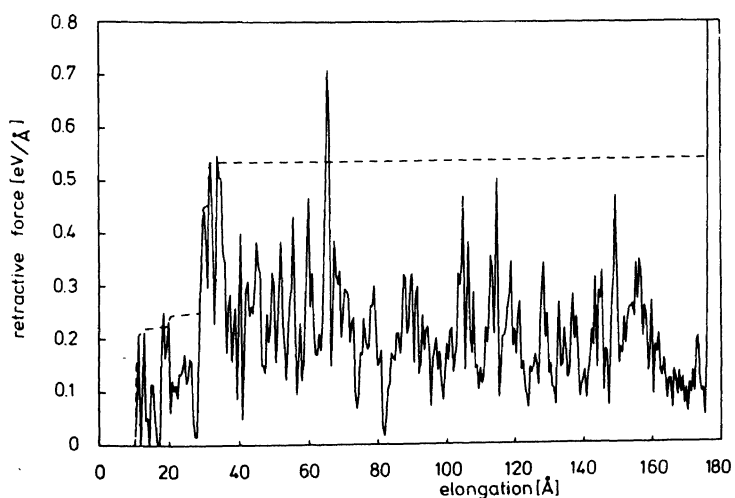

FIG. 4. Retractive force versus elongation for method (a) ——— and method (b) ––– for a 50-segment chain (cf. text).
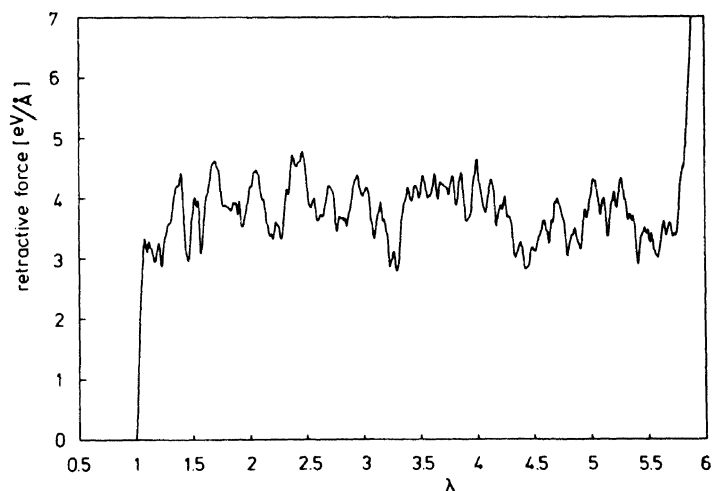

FIG. 5. Retractive force versus elongation for a superposition of 20 simulated chains (method (a)).

system during the stepwise elongation. The force increases and decreases. In case (b) the curve is calculated by gradually increasing the external force. If the retractive force on the coil begins to decrease while increasing the external force (cf. case (a)) the elongation of the coil jumps. When the retractive force reaches the external force level again the rapid elongation stops.

Although the approach differs, there is a good correlation between both simulations. The second curve jumps when the first curve shows a peak.

Let us discuss curve (a) in more detail: In the initial state (point I in Fig. 3a) all considered van der Waals interactions (between the junctions $1 \leftrightarrow 3$, $2 \leftrightarrow 4$, $1 \leftrightarrow 4$) are at their equilibrium distance R_0. The segments are arranged like a helix (see also Fig. 3b, I).

Between points I and II only the interaction $1 \leftrightarrow 4$ becomes stretched. The chain twists. If the point of inflection of the Morse-potential (Fig. 2) of this interaction is reached, the retractive force as the derivative of the Morse potential decreases with increasing elongation. At point II the chain is nearly planar (Fig. 3b, II) and the retractive force of interaction $1 \leftrightarrow 4$ is nearly zero.

After point II the interactions $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$ are stressed. Instead of changing both interactions simultaneously, after a certain elongation it is energetically more favourable for the system to stress only one interaction and relax the other. Thus, at point III the interaction $1 \leftrightarrow 3$ is nearly in equilibrium, whereas $2 \leftrightarrow 4$ is highly elongated (see also Fig. 3b, III). The reason for this is due to the Morse potential. The energy for two bonds being around position ● of Fig. 2 is greater than for one bond being at the minimum and one bond having left the potential (points ∗).

Between points III and IV also $1 \leftrightarrow 3$ is stressed. Finally at point IV the chain is fully elongated and the segments themselves are loaded. Due to this the retractive force of the system increases very rapidly.

The conformations at the points I, II, III, and IV are shown in Fig. 3b.

Let us consider the other case. In curve (b) the external force on juncion 4 is increased. Starting at the initial state (point I) the interaction $1 \leftrightarrow 4$ becomes stressed first. For every iteration step at the equilibrium elongation of the chain the external force is equal to the retractive force in absolute terms. Since after the point of inflection of the Morse-potential the retractive force decreases with increasing elongation the elongation must now jump to a higher level at which the external force is again equal to the retractive force. This jumping process repeats itself if the retractive force decreases between points II and III.

Now we describe a more complex simulation. Figure 4 shows the results of both methods for one chain with 50 segments. Again in case (a) the curve describes the behaviour of the retractive force of the coil-strand system formed during deformation, whereas in case (b) the force is given and thus the elongation only jumps to higher levels. The shape of the curves results from a permanent relaxation
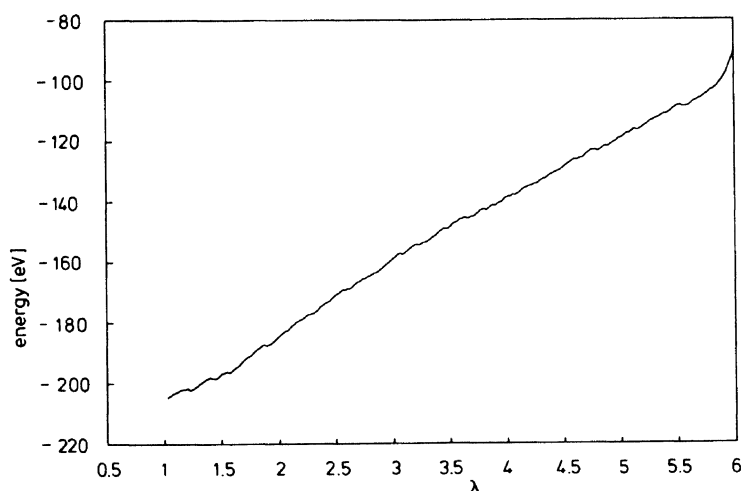

FIG. 6. Energy versus draw ratio derived from the superposition of 20-chain simulations.
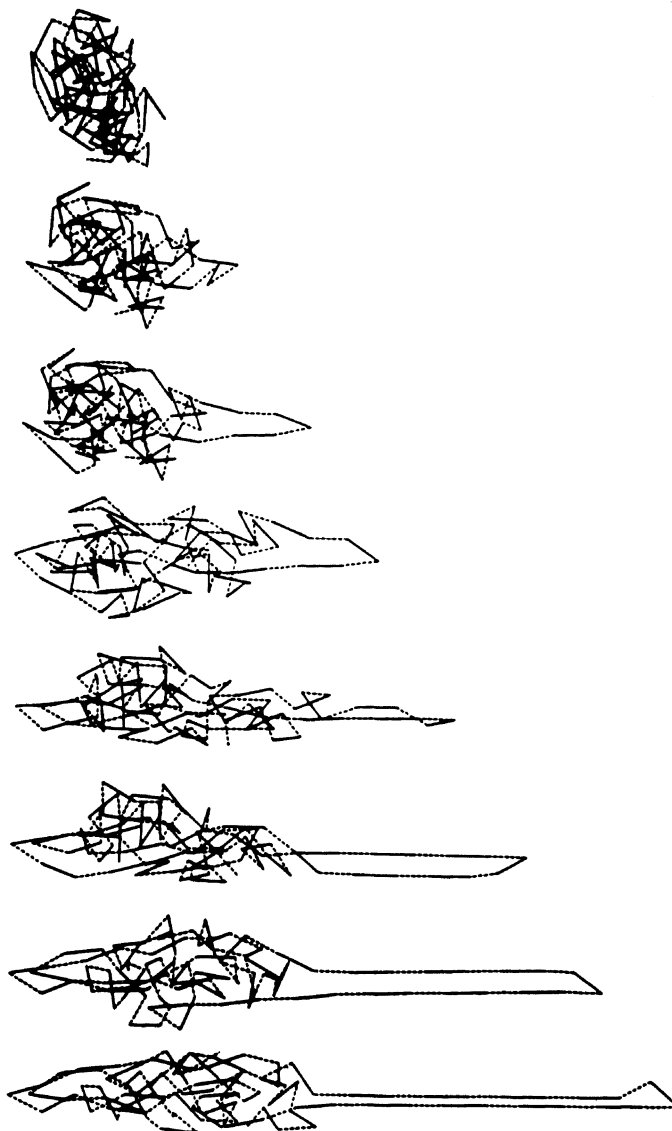

FIG. 7. Conformational pictures of the simulation of two chains, each with 50 segments. Between each diagram there are 40 iteration steps.
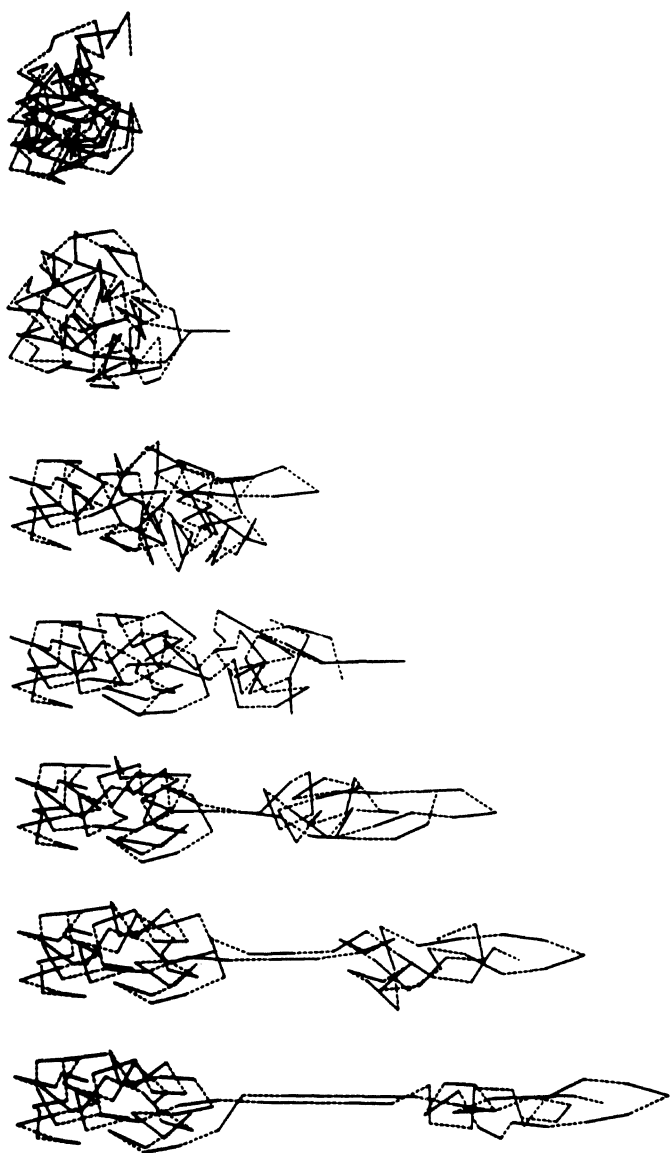
of the extension ratio. The energy is nearly proportional to the extension ratio. It seems likely that the remaining fluctuations disappear if more chains are combined.

During deformation all simulated coils formed a highly oriented fibril and a rest coil.[1] Figure 7 shows the deformation of a coil of two chains, each chain with 50 segments. Figure 8 shows another coil of two chains with 50 segments. Between each conformation shown in the pictures are 40 iteration steps (one step = 0.2 Å elongation). In both figures each chain was fixed, but only one chain was drawn. In Fig. 7 the elongated chain forms the fibril, whereas in Fig. 8 both chains of the coil are stretched and thus the fibril consists of segments of both chains. The different behaviour results from the structure of the coils (entanglements). Both in Fig. 7 and Fig. 8 the residual coils are homogeneously deformed.

CONCLUSION

The present paper shows that within our simulation restrictions an isotropic coil is not transformed to an ellipsoid. We obtain a highly oriented fibril and a more or less isotropic residual coil. Thus the deformation is inhomogeneous. The simulations provide a linear energy law and constant retractive force after a phase of homogeneous stretching. These results are interesting with respect to crazes or hard elastics. Measurements on crazes [3] and on hard elastics [12] have shown a constant retractive force at the interface of the crazes or the lamellae. In the coil strand transition a first hint for the suggestion of the craze formation can be seen. For crazes a flow of material from the relatively unstretched bulk into a highly oriented fibril is proposed. This seems to be equivalent to our coil–strand formation.

Our future work will be focused on larger systems. In addition, the restrictions of zero temperature and slow strain rates are to be overcome.

FIG. 8. Conformal pictures of the simulation of two chains, each with 50 segments. Between every picture there are 40 iteration steps.

and formation of van der Waals bonds during deformation. The retractice force increases very quickly, provided that the part of the chain between the fixed junctions is completely oriented and the segments themselves are stressed. Although the difference between the two approaches is significantly greater than in the case of three segments (because of the great number of changing van der Waals bonds the changing bonds are not the same in the two simulation methods) a good correlation exists. Curve (b) is nearly an envelope to curve (a).

Since method (a) shows more detail, we used this in the following investigations.

To obtain an approach to the real behaviour of polymer chains and to obtain better statistical results, we added the curves of 20 simulated chain deformations with numbers of segments between 30 and 50. Figure 5 shows the resulting force versus the extension ration curve and Fig. 6 shows the energy versus the extension ratio. After a phase of elastic (Hookean) deformation the force is on average independent

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[1] Coil-strand formation is not quite unknown in the wide field of polymer physics. In extensional flows in dilute solutions of polymers there exists a similar transition to a stretched coil (cf. Frenkel [14], DeGennes [15], Ryskin [16]) which also have been studied by computer simulations (Larson [17]). Nevertheless the two approaches are not the same. In the case of the dilute solution the reason for the transition is given by the balance of the nonlinear stretching force (due to the high gradients in flow: $f_F \sim \lambda^2$) and the entropic retractive force ($f_S \sim (\lambda - 1/\lambda^2)$) ($\lambda$ being the extension ratio.) In contrast to that the simulations in the presented form do not consider entropic retractive forces at all. The retraction is due to energetic contributions which result from the "non-bonded, quasi long-range" interaction of the segments of a coil in the collapsed state.

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