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Constrained equilibrium in network-like polymer systems: a concept of irreversible thermodynamics

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Abstract

Network-like polymer systems are considered to be composed of thermodynamically equivalent subsystems. On deformation up to large strains, the shape of these subsystems is believed to be transformed according to the law of affinity. The thermodynamics of such systems is presented. This description is then extended so as to be able to describe relaxation processes. Special attention is directed to a discussion of constrained equilibrium states because of their being representative of many polymer systems. The methods of classical thermodynamics of irreversible processes are shown to be appropriate for describing large deformations of many different network-like systems such as polymer glasses and semicrystalline polymers.

For the deformation experiments discussed here, the whole energy balance during deformation is known from stretching calorimetric measurements. This is a significant presumption for obtaining clear, fundamental conclusions; they would be difficult to achieve otherwise.

Keywords: LDPE; Network, Polymer; Polymer glass; Relaxation; Thermodynamics

1. Introduction

Polymers are "network-like systems" [1–6]. In a melt this network is made up of entanglements. In semicrystalline systems, crystals operate as multifunctional junctions. All kinds of junctions might be considered as constraints restricting the conformation of chains and essentially determining their configuration during deformation. If junctions are released during deformation, irreversible processes begin. To describe such time-dependent processes in polymer network-like systems, we utilize the existence of equivalent subsystems of deformation. They are the smallest units that can be transformed according to the law of affinity [1,3]. The

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ensemble of densely packed subsystems defines the global level of constraints. This "structural level" guarantees intrinsic homogeneity during deformation and makes network-like systems a natural candidate for the application of the thermodynamics of irreversible processes [7–12].

We present relations that allow time-dependent phenomena to be described in a generalized Onsager approach [13–15]. We are essentially interested in studying quasi-permanently constrained equilibrium states. General principles are deduced leading to a unique characterization of constrained equilibrium states in very different network-like systems.

A most interesting example is the description of thermo-elasticity in cold-drawn polymer glasses [16]. As an example of a non-homogeneous network-like system, we have studied the stress–strain behaviour of semicrystalline low-density polyethylene (LDPE) [1,3]. This is a representative candidate for many reasons. First of all we know the relevant parameters of the colloid structure. By describing the stress-strain behaviour, one then has, for example, the possibility of recognizing the mechanism and principles according to which this colloid structure is transformed during deformation. We can identify rules which control how the rubbery and crystalline regions cooperate.

From stretching calorimetric measurements [17–21], the total energy balance is obtained. If irreversible processes come into play, special formulations are necessary. The description of these results alone demonstrates the power of the thermodynamics of irreversible processes.

2. Thermodynamically equivalent subsystems

The system is considered to be comprised of $N^{(s)}$ homogeneous subsystems which are densely packed together. If there are no boundary effects and if each subsystem is in equilibrium we have the fundamental relationship

$$dG^{(s)} = -S^{(s)}\,dT + V^{(s)}\,dp + f\,dL^{(s)} \tag{1}$$

where the intensive variables temperature T, pressure p, and force f, should be equal over the whole assembly. The subsystem s shows the entropy $S^{(s)}$, volume $V^{(s)}$ and length $L^{(s)}$ in the direction of the force.

Allowing for local exchange of extensive quantities, such as internal energy or volume, theremodynamic equilibrium is achieved. The subsystems are then thermodynamically equivalent. These subsystems should also represent smallest volume elements that are transformed according to the law of affinity. Hence, we arrive at the conditions

$$\langle S^{(s)}\rangle = S \qquad \langle V^{(s)}\rangle = V \qquad L^{(s)} = L \tag{2}$$

If the number of subsystems is fixed during deformation

$$\begin{aligned} dG &= N^{(s)}[-S^{(s)}\,dT + V^{(s)}\,dp + f\,dL^{(s)}] \\ &= -S\,dT + V\,dp + f\,dL \end{aligned} \tag{3}$$

$$S = N^{(s)}S^{(s)} \qquad V = N^{(s)}V^{(s)} \qquad L = N^{(s)}L^{(s)}$$

Hence, the macroscopic behaviour is a copy of processes synchronized over the whole subsystem assembly so as to guarantee that each is transformed according to the law of affinity.

One may account for boundary effects if the mean size of the subsystems is known so as to formulate

$$\begin{aligned} \mathrm{d}G &= \mathrm{d}G^{\infty} - \mathrm{d}G^{0(\mathrm{s})} = \mathrm{d}G^{\infty}\left(1 - \frac{\sigma^{(\mathrm{s})}}{R^{(\mathrm{s})}}\right) \\ \mathrm{d}G^{0(\mathrm{s})} &= \frac{\sigma^{(\mathrm{s})}\,\mathrm{d}G^{\infty}}{R^{(\mathrm{s})}} \end{aligned} \tag{4}$$

where $\sigma^{(\mathrm{s})}$ is the interfacial free enthalpy related to the free enthalpy of equivalent subsystems. In the unstrained state they are assumed to be spheres of radius $R^{(\mathrm{s})}$. The relative interfacial situation may in general depend on the strain itself as well as on the type of strain.

In an equilibrium system, the size of the subsystems, characteized by $R^{(\mathrm{s})}$, should be determined thermodynamically. Yet the interfacial effects are in general extremely small ($\sigma^{(\mathrm{s})}/R^{(\mathrm{s})} \ll -1$). In most polymers, it is unlikely that the size of the subsystems is thermodynamically determined. We have to develop at least a treatment of constrained equilibrium states. Subsystems should then be characterized. It might be that $R^{(\mathrm{s})}$ as the "global hidden variable" can be used for defining these subsystems. The "hidden variable" $R^{(\mathrm{s})}$ would then determine the constraint-density in the subsystems network.

3. Non-equilibrium states

We assume that homogeneity is also guaranteed in non-equilibrium states. Moreover, the distance to equilibrium should be so small that we are allowed to use irreversible thermodynamics [7–12]. The Gibbs relationship may be written as [13–15]

$$\mathrm{d}G[T,p,(\xi_k^{(\mathrm{s})})] = \sum_{\mathrm{s}}\left(\mathrm{d}g^{(\mathrm{s})}[T,p,(\xi_k^{(\mathrm{s})})] - \sum_{k=1}^{M} A_k^{(\mathrm{s})}\,\mathrm{d}\xi_k^{(\mathrm{s})}\right) \tag{5}$$

where $A_k^{(\mathrm{s})}$ is the affinity of the kth relaxation mode in the subsystem (s) conjugated with the hidden variable $\xi_k^{(\mathrm{s})}$. To allow deviation from equilibrium between subsystems leads to sophisticated and complicated situations [22]. If, however, local equilibrium is guaranteed by rapid processes, the subsystems should be equivalent even under non-equilibrium conditions. We are then led to the symmetry conditions

$$\langle A_k^{(\mathrm{s})}\rangle = A_k \qquad \langle \xi_k^{(\mathrm{s})}\rangle = \xi_k \tag{6}$$

So we arrive at

$$\mathrm{d}G[T,p,(\xi_k)] = N^{(\mathrm{s})}\left(\mathrm{d}g[t,p,(\xi_k)] - \sum_{k=1}^{M} A_k\,\mathrm{d}\xi_k\right) \tag{7}$$

Relaxation modes are strictly synchronized within the whole assembly of subsystems. Modes of the same identity operate simultaneously within each of them. This model explains, for example, why relaxation in networks is synchronized up to the largest strains [15]. Here, the relaxation modes seem to be coupled in a scalar and isotropic manner to the network, i.e. to the global level of the ensemble of equivalent subsystems.

4. Constrained equilibrium

Constrained equilibrium states are now clearly defined by fixing the whole set of hidden variables ($\mathrm{d}\xi_k = 0$, $\xi_k = \mathrm{const}_k$). There might therefore exist a very large number of different constrained equilibrium states. The existence of the Gibbs potential in Eq. (5) requires that the extremum principles be fulfilled

$$\begin{aligned} (S)_{U,V,(\xi_k)} &= \max\big|_{(\xi_k)} \\ (U)_{S,V,(\xi_k)} &= \min\big|_{(\xi_k)} \\ (G)_{T,p,(\xi_k)} &= \min\big|_{(\xi_k)} \end{aligned} \tag{8}$$

Provided the hidden variables (ξ_k) are constant, the extremum values of the thermodynamic potentials are well defined. Any set of hidden variables (ξ_k) describes a different constrained equilibrium state. Integrability conditions have to be satisfied. One of them reads

$$\left(\frac{\partial Q}{\partial L}\right)_{T,p,(\xi_k)} = -T\left(\frac{\partial S}{\partial L}\right)_{T,p,(\xi_k)} = T\left(\frac{\partial f}{\partial T}\right)_{p,L,(\xi_k)} \tag{9}$$

The differential heat of deformation is uniquely related to the temperature coefficient of the force. We learn from the next relationship

$$\left(\frac{\partial f}{\partial \xi_k}\right)_{T,p,L,\xi_r \neq \xi_k} = -\left(\frac{\partial A_k}{\partial L}\right)_{T,p,(\xi_r)} \qquad r = 1, \ldots, M \tag{10}$$

that the distance from equilibrium determines how the force depends on the hidden variable ξ_k.

5. An interesting example

The deformation potential of an incompressible elastic continuum can be written as [23–25]

$$\begin{aligned} W &= G_0\phi \\ \phi &= 1/2(\lambda^2 + 2/\lambda - 3) \end{aligned} \tag{11}$$

where G is the modulus, and λ is the strain defined by

$$\lambda = L/L_0 \tag{12}$$

with L as the macroscopical length in the direction of the force applied and L_0 the fiducial length.

Let us discuss a Gaussian network comprised of phantom chains [24–26]. The shear modulus is determined by the density of the permanent junctions. The modulus is proportional to the temperature

$$G_0 = \rho RT/M_c \tag{13}$$

where ρ is the mass density and M_c is the molecular weight of the chains.

To consider the junctions as permanent constraints is equivalent to defining the hidden variable ξ_N by

$$\xi_N = 1/M_c \equiv N^{(s)} \tag{14}$$

where each Gaussian chain is assumed to operate as a permanent subsystem of deformation. We then arrive at

$$f = \frac{\partial W}{\partial \lambda} = G_0 D = \xi_N \rho RTD \tag{15}$$

$$D = \lambda - \lambda^{-2}$$

so that Eq. (10) reads

$$\frac{\partial f}{\partial \xi_N} = \rho RTD = -\frac{\partial A}{\partial L} \tag{16}$$

The "distance to equilibrium" as given by the affinity A is equal to

$$A = -\rho RT\phi \tag{17}$$

Strain energy disappears in the unstrained network. This defines the equilibrium state of reference. In a strained network the entropy is reduced according to

$$\Delta S = -\frac{W}{T} = -\xi_N \rho R\phi = \xi_N \frac{A}{T} \tag{18}$$

The distance to equilibrium is continuously increased with strain. In this model the phenomenological "hidden variable" ξ_N defines a network. This example shows that it should be possible to characterize network-like systems even under more complicated conditions by describing quasi-static stress–strain experiments.

6. Strain-induced release of junctions

If the strengths of the junctions are low enough, strain-induced release of contacts ($\Delta\xi < 0$) may be enforced during the stretch. The system has to go into new equilibrium states with a reduced density of junctions. At temperatures far above the glass transition these processes are different from the ones in the glass transition range or in polymer melts with entanglements as non-permanent junctions [27]. Relaxation runs very fast. At each strain the entropy is maximized nearly immediately. If the junctions are released in unique dependence on strain, we are led to the entropy production

$$\Delta\dot{S} = -\rho R\phi \frac{\Delta\xi_N}{\Delta\lambda}\dot{\lambda} > 0 \qquad \frac{\Delta\xi_N}{\Delta\lambda} < 0 \tag{19}$$

It holds true that strained networks with a strain-reduced density of junctions of the type under discussion here cannot recover their original density.

This is one of the reasons why the junction density is mostly found to be constant when the system is unloaded. To discuss some interesting consequences, let us define as isotropic incompressible visco-elastic body, the modulus of which decreases, for example, proportionally to the strain. The mechanical equation of state is written as

$$\begin{aligned} f &= \frac{G_0}{\lambda}(\lambda - \lambda^{-2}) = \xi_N(\lambda)\frac{\rho RT}{M_{c0}}(\lambda - \lambda^{-2}) = G_0(1 - \lambda^{-3}) \\ \xi_N(\lambda) &= \frac{1}{\lambda} \qquad g_0 = \frac{\rho RT}{M_{c0}} \end{aligned} \tag{20}$$

We arrive at the strain-energy function

$$\begin{aligned} W &= \frac{G_0}{2}(2\lambda + \lambda^{-2} - 3) = \frac{G_0}{2}(I_2 - 3) = \frac{G_0}{\lambda}\left(2\lambda^2 + \frac{1}{\lambda} - 3\lambda\right) \\ &= \xi_N(\lambda)\frac{\rho RT}{M_{c0}}\left(2\lambda^2 + \frac{1}{\lambda} - 3\lambda\right) \end{aligned} \tag{21}$$

This system is mechanically stable

$$\frac{\partial f}{\partial \lambda} = \frac{3G}{\lambda^4} > 0 \tag{22}$$

If the modulus decreases inversely proportionally to λ^α

$$\begin{aligned} f &= \frac{G_0}{\lambda^\alpha}(\lambda - 1) = G_0(\lambda^{(1-\alpha)} - \lambda^{-\alpha}) \\ \frac{\partial f}{\partial \lambda} &= G_0((1-\alpha)\lambda^{-\alpha} + \lambda^{-(1+\alpha)} - \lambda^{-\alpha}) \end{aligned} \tag{23}$$

we recognize that for $\alpha > 1$ the system is no longer stable. Under homogeneous deformation conditions, systems with $\alpha = 1$ show the maximum release of junctions.

7. Relaxation under strain-induced network transformation

The above model is appropriate for discussing relaxation into the "softest state of reference" that might be represented by a network with decreasing density of junctions. To describe relaxation let us introduce the constitutive equation [1,13–15]

$$(g)_{T,p} = \frac{f_{20}}{2} w(\lambda) + \sqrt{w(\lambda)} \sum_i f_{11}^{(i)} \xi_i + \frac{1}{2} \sum_i f_{02}^{(i)} \xi_i^2 \tag{24}$$

A set of hidden variables (ξ_i) is coupled to the global level defined by the network itself. This network has the strain-energy density $w(\xi)$. The f_{ik} terms are constants for describing the elastic properties and the relaxation times. It was shown elsewhere [13–15] that the time-dependent nominal force of the network-like "Onsager-type system" is equal to

$$f(t) = \left(\frac{\partial W}{\partial \lambda(t)}\right)\left\{1 + \frac{\Gamma}{G_0}\left[1 - \frac{1}{\Gamma}\int_0^t m(t-t')\sqrt{\frac{W(t')}{W(t)}}\,\mathrm{d}t'\right]\right\} \tag{25}$$

where W is the strain energy function. For a Gaussian network, W is, for example, equal to Eq. (11). For a discrete relaxation time distribution $h_i(\tau_i)$, the memory function is written as

$$m(t-t') = \sum_i \frac{h_i}{\tau_i}\,\mathrm{e}^{-(t-t')/\tau_i} \tag{26}$$

where τ_i is the relaxation time of the a priori Onsager mode, and h_i is its relative fraction. Γ is the relaxation strength defined by the difference between the glass modulus G_g and that of the network G_0

$$\Gamma = G_g - G_0 \tag{27}$$

It is now crucial that we assume that the density of junctions decreases with strain. We have at least to account for the additional hidden variable ξ_N (see Eq. (20)). If relaxation is sufficiently rapid, the global level runs through constrained equilibrium states, making ξ_N a unique function of strain. We restrict ourselves to these conditions.

With the use of the strain energy function as defined in Eq. (21), we calculated stress–strain cycles as shown in Fig. 1. The shape depends on the strain energy function, on the strain rate and on the relaxation–time distribution. Hence, strain-induced modifications of the hidden variable ξ_N should become identifiable by interpreting quasi-static stress–strain experiments.

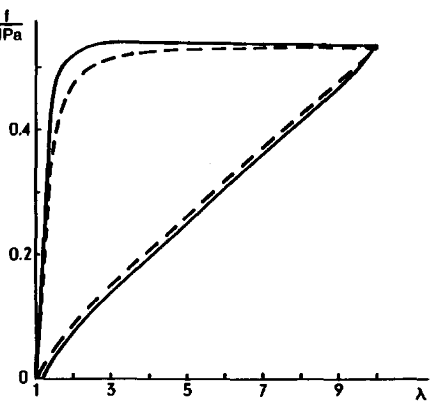

Fig. 1. Stress–strain cycles computed with the aid of Eqs. (51), (25), (48) and (26); quasi-static; ——, finite constant strain rate.

8. Conclusions

If the times determining the experimental window are very much larger than the relevant relaxation times we should observe the constrained equilibrium stress–strain pattern as represented by the broken curve in Fig. 1. The modulus is continuously and irreversibly reduced. This determines the shape of the quasi-static stress-strain pattern.

It is important that the density of constraints is assumed to be constant during unloading ($G_0/\lambda_{ma} = G_0\xi_{ma} = \text{const}$; where λ_{ma} is the maximum strain in the first stretch). This is behind the typical hysteresis observed in the first stress–strain cycle. The restoring forces during unloading are too weak to release any junctions. Thus, the quasi-static unloading stress–strain curve provides information about the actual density of junctions in the network. With the aid of an appropriate theory, it should be possible to give the number of junctions released during the stretch.

Under the given circumstances, the strain energy which is recovered is smaller than that stored during the first stretch. The entropy produced and transferred to the heat bath (which is the sample itself) is uniquely defined by the difference between the work put into the sample during the stretch and that fraction retained during unloading (at constant λ_{ma})

$$\begin{aligned}
W_{\text{stretch}} &= \frac{G_0}{2}(I_2(\lambda_{ma}) - 3) \qquad I_2 = 2\lambda_{ma} + \lambda_{ma}^2 \\
W_{\text{unload}} &= \frac{G_0}{2\lambda_{ma}}(I_1(\lambda_{ma}) - 3)^2 \qquad I_1 = \lambda_{ma}^2 + 2\lambda_{ma}^{-1} \\
\eta &= \frac{W_{\text{stretch}} - W_{\text{unload}}}{W_{\text{stretch}}} = \frac{Q_{\text{dis}}}{W_{\text{stretch}}}
\end{aligned} \tag{28}$$

One recognizes that in the model used here the strain-dependent strain energy dissipation does not depend on the density of junctions. The dissipation of strain energy always displays the same relative features. Moreover, it can be seen from the plot in Fig. 2 that network-like systems show asymptotically the dissipation ratio

$$\eta(\lambda_{ma} \gg 1) \approx \frac{\lambda_{ma} - \lambda_{ma}/2}{\lambda_{ma}} = 0.5 \tag{29}$$

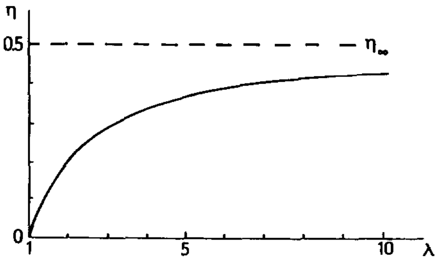

Fig. 2. The dissipated fraction of strain energy in a elastically stable, homogeneously extended and incompressible network-like system with maximum softening allowed for stability reasons.

This fraction gives the maximum dissipation of strain energy of network-like systems, the modulus of which is uniquely reduced under "quasi-static" deformation conditions. For any other softening behaviour of stable network-like systems, the dissipation must be smaller. The dissipated strain energy increases, of course, if visco-elastic effects come into play (see Fig. 1).

Far above the glass transition, the entropy production is spontaneous and approximately unique in strain rate. We arrive straightforwardly at the dissipation function Ψ

$$T\Delta\dot{s} = \Psi = \frac{\mathrm{d}}{\mathrm{d}t}(\Delta W(\lambda)) \tag{30}$$

With Eq. (28) we come directly to the formulation of the strain energy of our model system

$$W = \frac{G_0}{2\lambda}\{2\lambda^2 + \lambda^{-1} - 3\lambda\} \tag{31}$$

The function $\Delta W(\lambda)$ in Eq. (30) is the difference between the strain energy increment of the softening network and the network of the reference with "quasi-permanent" junctions ($G/\lambda = \mathrm{const}$). We have then

$$\Delta W = G_0(2\lambda^2 + \lambda^{-1} - 3\lambda)\left(\frac{1}{\lambda} - \frac{1}{\lambda + \Delta\lambda}\right) \tag{32}$$

So we arrive at the relation

$$\Psi = \frac{\mathrm{d}\Delta W}{\mathrm{d}\lambda}\dot{\lambda} = G_0\left(1 + \frac{1}{2\lambda^3} - \frac{3}{2\lambda}\right)\dot{\lambda} \tag{33}$$

The minimum entropy production of this type of network-like system with decreasing density of junctions, even under the condition $\mathrm{d}\lambda/\mathrm{d}t = \mathrm{const}$, depends on strain. At sufficiently large strains, the entropy production is predicted to become stationary. This also holds qualitatively in real networks with finite chain length and global interactions.

9. Cold-drawn polymer glasses: stress–strain behaviour

Extending a polymer glass to large-strain plastic deformation can occur. The description of the stress-strain pattern of glassy polycarbonate [16] reveals, nevertheless, the existence of a network composed of a set of strain-invariant constraints. Polymer glasses, when greatly strained, pass through activated states so as to satisfy the conditions of constrained internal equilibrium.

The mechanical equation of state was defined by [16]

$$\begin{aligned} f &= \frac{A}{A_0} f_{\mathrm{eg}} + G_{\mathrm{g}}(\lambda - \lambda^{-2}) \\ f_{\mathrm{eg}} &= (\lambda - 1)E_{0\mathrm{g}}\,\mathrm{e}^{-(\lambda - 1)/\varepsilon_{\mathrm{yield}}} \end{aligned} \tag{34}$$

where E_{0g} is the elastic modulus, G_g is the shear modulus of the network composed of strain-invariant constraints, $\varepsilon_{\text{yield}}$ defines the yield strain, and A is the actual and A_0 the original cross-section of the sample.

With the aid of the above equation, the stress–strain pattern of the heterogeneously extended polycarbonate is fairly well reproduced by the calculation (Fig. 3(a)). The system is not stable everywhere. It undergoes a "jump-like" transformation into a thermodynamically non-neighboured state with greatly increased strain ($\lambda'' > \lambda'$). A neck is formed. This "strain-induced" transformation satisfies all the criteria of a phase transition characterized by the coexistence of phases that are in a state of constrained equilibrium. The occurrence of the transition is strongly related to an existing network composed of quasi-permanent constraints ($G_g(\xi_{N\text{glass}})$).

One has to be aware that the energy-elastic force (first term on the right-hand-side of Eq. (34)) drops rapidly to zero at strains $\lambda > \lambda_{\text{yield}} = 1 + \varepsilon_{\text{yield}}$. In the new phase ($\lambda'' > \lambda'$), the strain energy changes as in a network. The strain energy is determined by a large "elastic" component stored in the short-chain network (B in Fig. 3(a)) and by the energy A (Fig. 1). The entropy in the network is clearly related to the segmental orientation [16]. Deformation runs by mechanically activated motions within the very short network composed of fixed constraints. The stress–strain pattern of a glass represents a well-defined sequence of constrained equlibrium states. Because the polymer glass is defect-saturated (related to equilibrium in the undercooled melt just above the glass transition), molecular configurations are changed without producing or annihilating defects. If friction is negligible, one might call this an ideal plastic deformation.

10. Cold-drawn polymer glasses: segmental orientation distribution

In the sense of the above models, a polymer glass is a network-like system [3,16,28,29]. During the freezing process, a high density of constraints come into existence so that the liquid-like dynamics is frozen in. At temperatures far below the glass transition range, the set of constraints ($\xi_{N\text{glass}}$) = const. cannot be changed even during large deformations. Having extremely short chains (their lengths in the range of a monomer unit), strain-invariant segments are forced into high orientation. Even if we do not know very much about the details of cooperations when a polymer glass is cold-drawn, our concept demands that: if the glass runs strain-activated through constrained equilibrium states (frozen-in when the force is released), the orientation distribution should satisfy the extremum condition [3,30] as given in Eq. (8)

$$(S_{\text{orient}})_{T,p,\lambda,(\xi_{N\,\text{glass}})} = \text{maximum} \tag{35}$$

Because the strain-invariant segments behave like anisometric rigid rods with a defined aspect ratio, the orientation distribution should be identical with the Oka–Kratky–Kuhn function [31,32]. We have calculated [3] how the second and fourth moments of the segmental orientation distribution of polycarbonate [3,34]

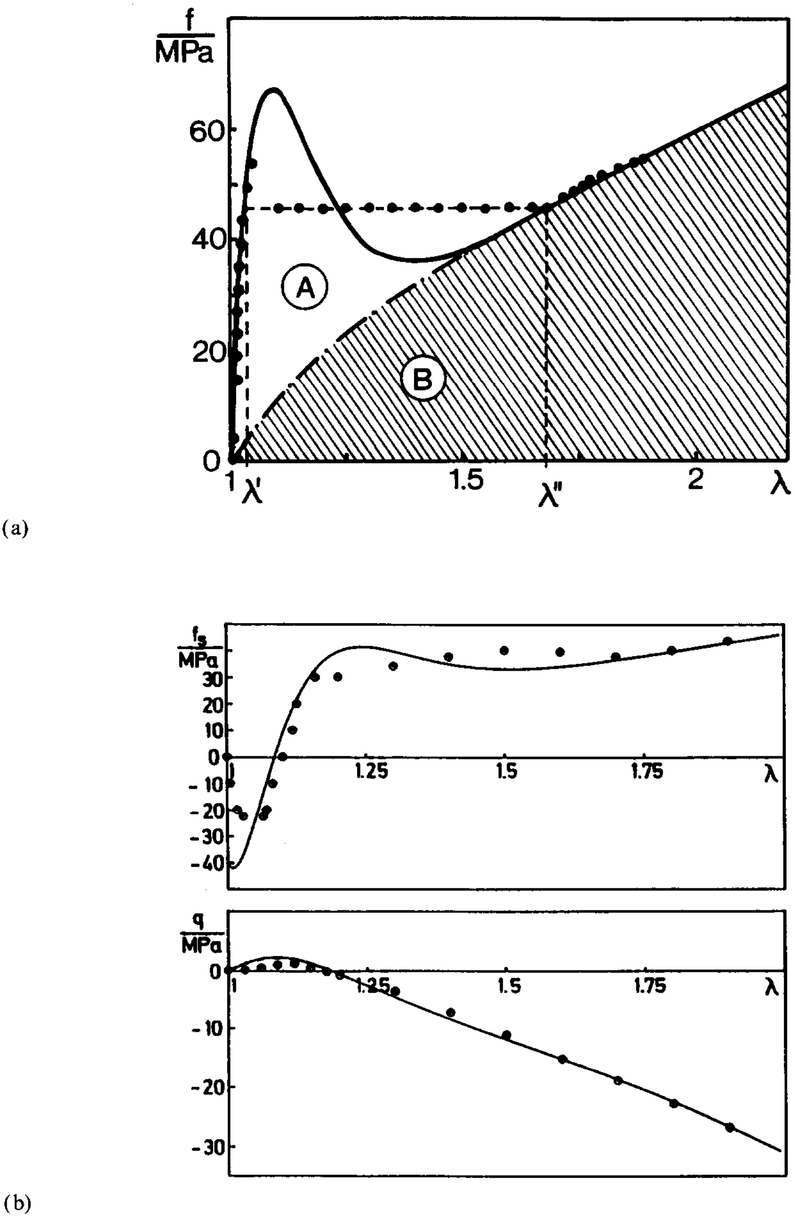

Fig. 3. (a) Nominal stress pattern of polycarbonate (●) at 295 K stretched with a strain rate of $d\lambda/dt = 0.015\%\ \mathrm{min}^{-1}$. The solid line is computed with the aid of Eq. (35) (parameters: $E_{0g} = 2000$ MPa; $\varepsilon_{\mathrm{yield}} = 0.085$; $G_g = 34$ MPa. (A) is the maximum strain energy needed for deforming the solid component; (B) is the work stored by the network during deformation. (b) Differential and total heat exchange during quasi-isothermal expansion of polycarbonate at $T = 295$ K: ⊙, experimental results; ——, computed with the aid of Eq. (37). The parameters used were: $G_{gh} = 6$ MPa; $TG_{gs} = 28$ MPa; $d \ln \varepsilon_y/dT = 0.002$ K; $d \ln E_{0g}/dT = -0.0025$ T K; $\beta_g = 6.5 \times 10^{-5}$ K.

are interrelated under the above supposition (Fig. 4(a)). Moreover, segmental orientation is enforced in a glass to occupy one of the configurations through which the system should run under constrained equilibrium conditions ($\xi_k = \text{const}$). The orientational entropy is then maximum [3,30] (see Fig. 4(b)).

It is crucial that we prove this hypothesis in another way.

11. Thermo-elasticity under constrained equilibrium conditions

Whether or not the glass occupies a sequence of constrained equilibrium states during the stretch can be determined by discussing thermo-elastic properties under constrained equilibrium conditions. The appropriate equations were derived [16]

$$\begin{aligned}
\left(\frac{\partial Q}{\partial \lambda}\right)_{T,p,\xi_k} &= T\left(\frac{\partial f}{\partial \lambda}\right)_{T,L,(\xi_k)} \\
&= \frac{E_{0\mathrm{g}}}{\lambda}\,\mathrm{e}^{(\lambda-1)/\varepsilon_{\mathrm{yield}}}\Gamma - \beta_{\mathrm{g}} G_{\mathrm{g}} D + \frac{\partial G_{\mathrm{g}}}{\partial T} D - \beta_{\mathrm{g}} G_{\mathrm{g}}\left(\lambda + \frac{2}{\lambda^3}\right) \\
\Gamma &= 3\beta_{\mathrm{g}}(\lambda - 1) + (\lambda - 1)\frac{\partial \ln E_{0\mathrm{g}}}{\partial T} - \beta_{\mathrm{g}}\lambda \\
&\quad + \frac{\lambda - 1}{\varepsilon_{\mathrm{yield}}}\left(\beta_{\mathrm{g}}\lambda + (\lambda - 1)\frac{\partial \ln \delta_{\mathrm{yield}}}{\partial T}\right)
\end{aligned} \tag{36}$$

where β_{g} is the linear expansion coefficient in the glassy state defined by

$$\beta_{\mathrm{g}} = \frac{\partial \ln L_0}{\partial T} \tag{37}$$

The heats exchanged are measured in a Müller-type stretching micro-calorimeter. From the data shown in Fig. 3(b) it can be seen that the calculation is relatively accurate. Internal equilibrium should therefore be very rapidly established. Below the level as determined by a set of strain-invariant hidden variables ($\xi_k = \text{const}_k$), strain-activated platzwechsel can only occupy "equilibrium configurations constrained by a set of hidden variables".

Glasses may in fact be considered as network-like systems. The subsystems of deformation are the smallest possible segment aggregations that operate in mechanically activated states as subsystems of deformation. Segmental configurations below the network defined by ($\xi_k = \text{const}_k$) satisfy the condition of local equilibrium. When the stretch is stopped one of the large number of possible equilibrium configurations is frozen in.

12. Large extensions of semicrystalline polymers (LDPE)

As another example we now discuss largely strained semi-crystalline systems. It is widely accepted that small crystals in semicrystalline polymers operate as active

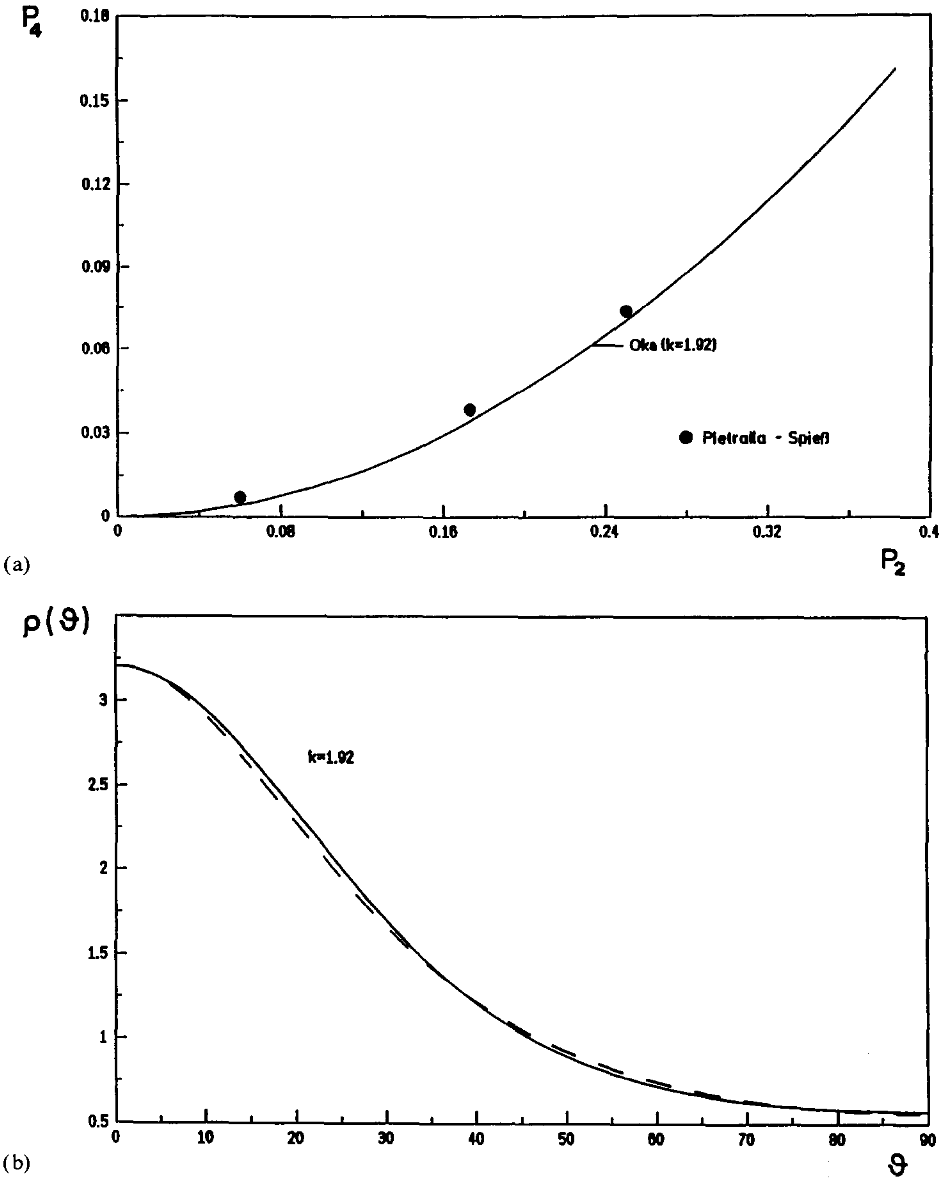

Fig. 4. (a) The second (P_2) and (P_4) moments of cold-drawn polycarbonate according to Pietralla and Spiess [34]. The solid line is computed by using the principle that the segments should be oriented so as to maximize the orientational entropy. (b) – – –, the maximum entropy segmental orientation distribution $\rho(\varphi)$; and ——, the Kratky–Oka equation [3].

multi-functional fillers [1–3,6,35]. They constitute a well-defined set of constraints. An important feature is that these crystals suffer plastic deformation, including melting and recrystallization processes. The density of the effective constraints is therewith continuously diminished with strain. An interpretation of large deformations of semicrystalline polymers should therefore clearly prove the utility of our model.

13. Fundamental assumptions

Equivalent subsystems of deformation should be represented by crystal clusters large enough to guarantee an affine transformation [1,3] (see Fig. 5). This demands a logical cooperation between rubbery layers and crystals. The forces exerted on both components should on average be equal to

$$\langle f^{\mathrm{amorph}}(\lambda_i)\rangle = \langle f^{\mathrm{crystals}}(\lambda_{\mathrm{ce}})\rangle = f^{\mathrm{macroscopic}}(\lambda) \equiv f(\lambda) \quad (38)$$

where λ_i, λ_{ce}, λ are the strains within the rubbery regions, the crystals and the macroscopic sample respectively. To describe the stress–strain behaviour in semicrystalline samples we apparently need only the mechanic equation of state of the rubbery regions, provided that the intrinsic strain within these regions is known. This quantity depends, of course, on the configuration of the crystals, and, therefore, also on how the colloid structure changes on strain. For eutectoid copolymers one succeeds in giving explicit formulations.

14. The colloid-structure parameters

The relations given here were deduced elsewhere [36,37]. The structure of the copolymer chains is characterized by the distribution of non-crystallization c-units (nc-units). The molar fraction x_{c} of crystallizable units (c-units) is then defined by

$$x_{\mathrm{c}} = \frac{n_{\mathrm{c}}}{n_{\mathrm{c}} + n_{\mathrm{nc}}} \qquad x_{\mathrm{c}} + x_{\mathrm{nc}} = 1 \quad (39)$$

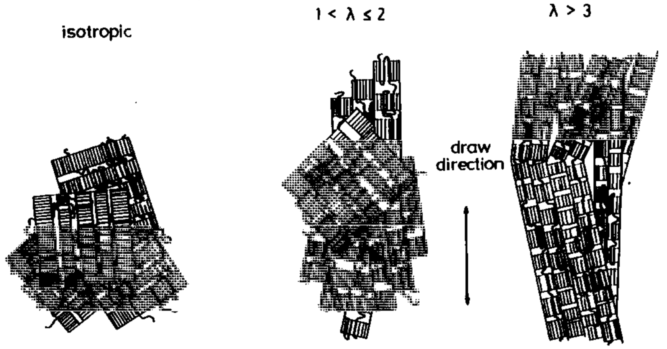

Fig. 5. Sketch of the cluster structure in a semicrystalline polymer and its transformation with strain.

where n_c and n_{nc} are the mole numbers of c- and nc-units. A length distribution of c-sequences, each comprised of c-units only, is built up. For thermodynamic reasons, extended c-sequence crystals as mixed micro-phases are formed (EMCs). Their thickness distribution is uniquely determined by the c-sequence length distribution. We confine ourselves to the example of a random eutectoid copolymer with the distribution function given by

$$x_y = x_{\mathrm{nc}}^2 x_{\mathrm{c}}^{y(T)-1} \tag{40}$$

where $y(T)$ is the smallest stable EMC. According to the conditions of coexistence in the eutecoid multi-component system, melting of EMCs runs selectively and consecutively starting at lowest temperature with EMCs of smallest thickness $y(T)$. The relative molar fraction of EMCs therefore depends uniquely on temperature and is equal to

$$w_{\mathrm{p}} = x_{\mathrm{c}}^{y(T)-1}[y(T)x_{\mathrm{nc}} + x_{\mathrm{c}}] \tag{41}$$

The mean thickness of EMCs is deduced to be given by

$$y_{\mathrm{p}} = \frac{x_{\mathrm{c}}}{x_{\mathrm{nc}}} + y(T) \tag{42}$$

The total volume of the EMCs including the defect layers is assumed to operate as a "solid filler" [1,3].

15. The cluster network

In the sketch of a cluster structure in a semicrystalline system and its transformation during extension as drawn in Fig. 5, it is illustrated that a larger set of clusters should only be able to operate as a subsystem of deformation [1–3,38–41]. In the unstrained system, they should be isotropically linked in their environments. The effective mean chain-length within a subsystem of deformation may then be defined by

$$y_{\mathrm{m}} = \alpha y_{\mathrm{p}} \frac{1 - w_{\mathrm{p}}^{1/3}}{w_{\mathrm{p}}^{1/3}} \tag{43}$$

where α relates the length of the elastically effective chains to the mean distance between neighbouring crystals. Constraints in the sense of our approach are developed by ECMs which operate as multi-functional junctions whereby they themselves "fill" a well-defined volume.

The crystals ensemble itself has to suffer plastic deformation by shear-sliding processes within the lamellae or by twinning, melting and recrystallization as other mechanism of plastic deformation [42,43]. It may happen, in addition, that chains are pulled out of ECMs and segmental slip occurs, so that the effective network chain length is steadily increased with strain. All these processes are found to be defined and logically interrelated.

The dependence of the chain length on strain was formulated elsewhere [1–3]

$$\cdot\, y_{\mathrm{m}} = \alpha y_{\mathrm{p}}(T)\frac{1-u}{u} \qquad u = \left(\frac{w_{\mathrm{p}}}{\lambda}\right)^{1/3} = (w_{\mathrm{p}}\xi_N)^{1/3} \tag{44}$$

The hidden variable ξ_N is here defined to be written as

$$\xi_N = \frac{1}{\lambda} \tag{45}$$

where ξ_N gives just the "rigid and active fraction of crystals" [1,3]. Due to softening, the distance to equilibrium is continuously and systematically reduced. Entropy is produced accordingly. We learn from the relation

$$\operatorname*{limit}_{\lambda\to\infty} u = w_{\mathrm{p}}^{1/3} \operatorname*{limit}_{\lambda\to\infty} \xi^{1/3} = w_{\mathrm{p}}^{1/3} \operatorname*{limit}_{\lambda\to\infty} \lambda^{-1/3} = 0 \tag{46}$$

that at infinitely large strain, no junctions exist any more.

In our model, heterogeneous deformation occurs. In comparison to the macroscopic deformation, the rubbery regions may be extended to very high degrees. There "overdrawing" depends on the fraction of rigid and active crystals. This fraction is reduced due to plastic deformation. The mean field ansatz [1,3]

$$\lambda_i = \frac{\lambda - u}{1 - u} = \frac{\lambda - (w_{\mathrm{p}}\xi_N)^{1/3}}{1 - (w_{\mathrm{p}}\xi_N)^{1/3}} \tag{47}$$

turned out to be reasonable. The hidden variable ξ_N gives just the fraction of active ECMs.

The stress–strain pattern can then be described with the aid of the van der Waals model

$$f = \frac{\rho RT}{M_{\mathrm{c}}}(\lambda_i - \lambda^{-2})\left\{\frac{1}{1 - \sqrt{\phi/\phi_{\max}}} - a\sqrt{\phi}\right\} \tag{48}$$

$$\phi(\lambda_i^2 + 2/\lambda - 3)/2 \qquad \phi_{\max} = \phi(\lambda_{\max})$$

whereby the maximum strain $\lambda_{\max}$ is related to the mean chain length y_{m} according to

$$\lambda_{\max} \approx \sqrt{y_{\mathrm{m}}} \tag{49}$$

so that the molecular weight of the chains M_{c} can be written as

$$M_{\mathrm{c}} = M_{\mathrm{u}}\lambda_{\max}^2 \tag{50}$$

where M_{u} is the molecular weight of the strain-invariant ("entropy-invariant") unit.

16. Branched polyethylene at large extensions

With the parameters as given in Table 1, quasi-static stress–strain patterns of low-density polyethylene (LDPE) were fairly well described (Fig. 6). In the small-strain regime, there are some discrepancies. The nominal force is otherwise correctly

Table 1
The primary structure parameters of LDPE [a]

T/K	y_m	$y(T)$	y_p	w_p
293	35.4	28	57	0.76
303	42.4	30	59	0.73
313	52.4	34	63	0.69
323	69.1	38	67	0.64
333	88.4	43	72	0.58
343	101.1	45	74	0.56
353	151.3	53	82	0.47
363	274.2	68	95	0.34

[a] $x_\mathrm{nc} = 0.33$; $M_\mathrm{u} = 14\ \mathrm{g\ mol^{-1}}$; $\alpha = 6.5$; thermodynamic parameters from Refs. [1,2,3,35,36].

reproduced. The cluster network is composed of primary structure elements. The number and shape of these elements (ECMs,w_p) depend on temperature as predicted by the thermodynamics of eutectoid copolymers.

Whether or not we can identify subsystems of deformation is now crucial. Their existence is indicated with the results shown in Fig. 7. Independent of a sophisticated cooling or heating program, one observes at each temperature the same stress–strain curve. This is understandable if a defined configuration of constraints exists, which changes irreversibly at each temperature, but in the same manner with strain. This conclusion was the reason for defining relationships (44) and (45). The constraints are, however, disposed by the ECMs themselves in unique dependence on the crystallinity. The hidden variable ξ_N seems to characterize the deformation of the subsystems. To guarantee their affine transformation an increasing fraction of the crystals has to be "plasticized".

In any case, Eq. (48) represents a generalized equation of state defined by

$$\frac{\partial g(T,p,L,(\xi_i))}{\partial L} = f[T,p,L,(\xi_i(T,p)] \tag{51}$$

It is possible to formulate the thermo-elastic equations of state. This has been done recently [3]. Here, we only give a comparison between experiment and calculation, see Fig. 8. Surprisingly, the strain energy is in fact totally transformed into heat in the large strain regime ($\lambda > 1.5$)($\Delta Q/\Delta W = 1$). The system behaves in a network-like manner with a decreasing density of junctions that is accompanied by a nearly instantaneous entropy production. Hence, the stress–strain behaviour of LDPE can be treated at each temperature as a sequence of equilibrium states, the constraints of which vary uniquely with strain.

In the small-strain regime, effects come into play which are very much larger than the classical Thomson-effect. This discrepancy has not yet been interpreted.

First principles seem to regulate cooperation between the crystals and non-crystallized regions. The mechanisms are coupled so as to minimize strain energy. This statement is equivalent to assuming the existence of subsystems of minimum size. In each constrained equilibrium state, the entropy is maximum (being, of

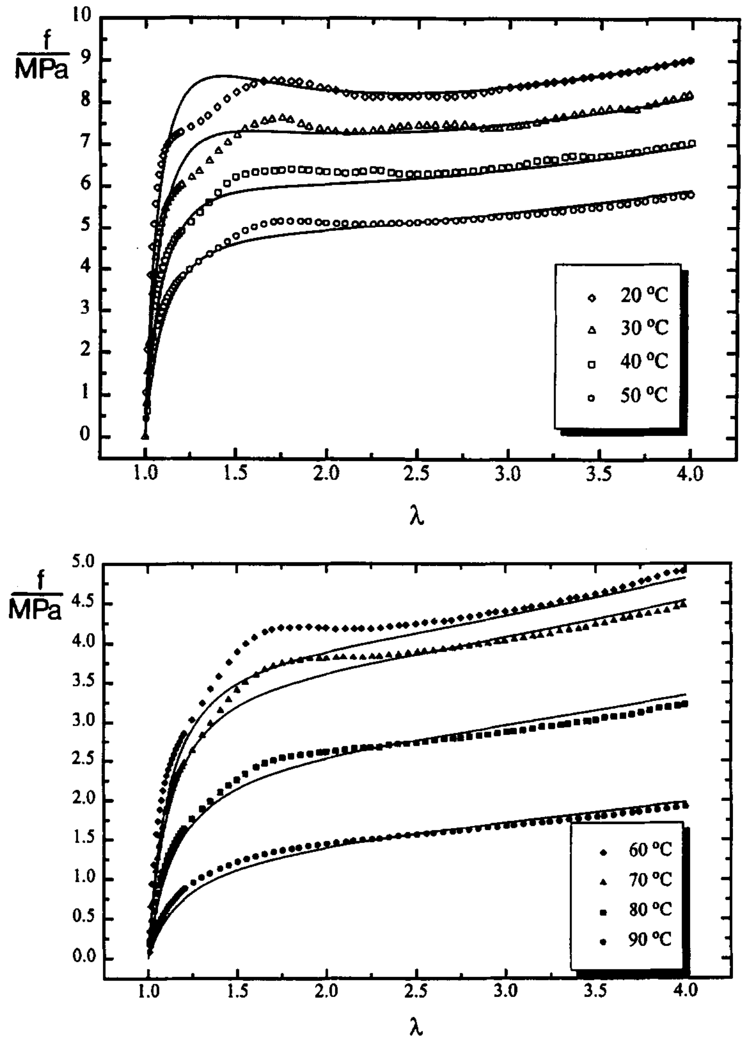

Fig. 6. Stress–strain pattern of LDPE measured at the temperatures indicated. Solid lines are computed with Eqs. (25) and (48) using the parameters listed in Table 1.

course, smaller than in the limits of absolute equilibrium), while the internal energy is minimum. This is in good agreement with the discovery that in the large-strain regime, semicrystalline systems behave in a network-like manner. The total heat exchanged during deformation is identical with that of a permanent, purely entropy-elastic network. We have, however, shown above that a defined fraction of strain energy of the networks with a decreasing density of junctions should be dissipated. This must also be true for semicrystalline LDPE. The above results are understandable only if the entropy production is always minimum. According to

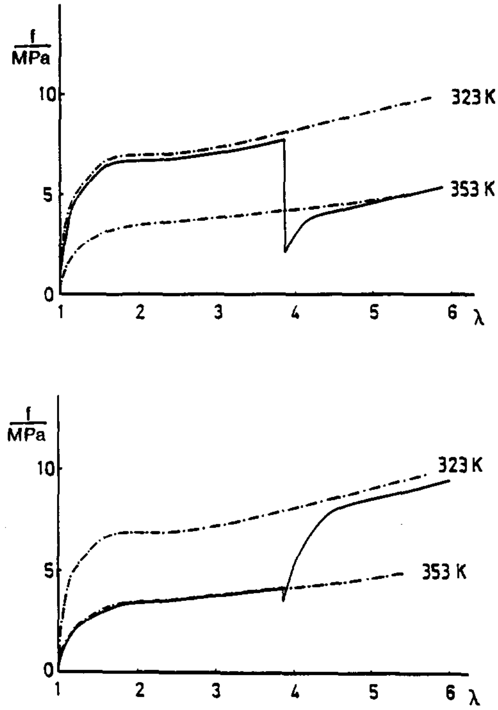

Fig. 7. Stress–strain measurements (solid line) of LDPE [1]. Elongation was stopped on changing the temperature. Different traces are indicated with extra symbols.

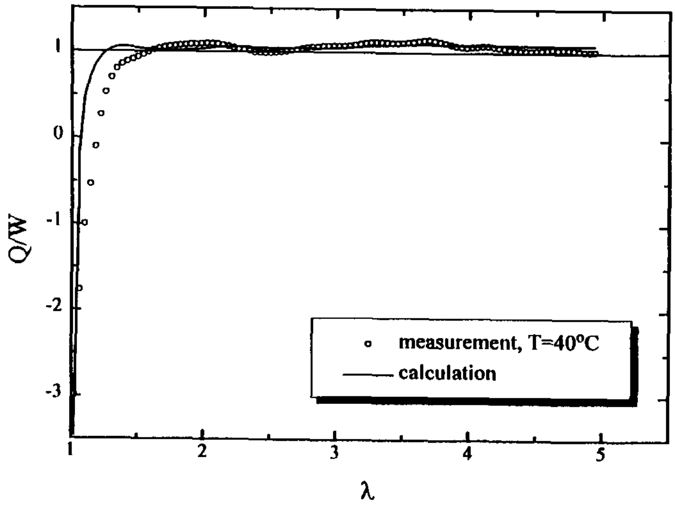

Fig. 8. Quotient of heat and work of deformation $Q/W \approx f_s/f$ of LDPE measured at 313 K by increasing strain stepwise [3].

the thermodynamics of irreversible processes, the underlying processes should then run under stationary conditions.

In agreement with these conclusions, the orientational entropy of crystals is maximum so as to satisfy Eq. (8) [3]. In addition, shear sliding within the crystal core seems only to run across minimum energy planes. Hence, during deformation, semicrystalline systems pass through a sequence of constrained equilibrium states. The density of constraints is diminished with strain.

17. Some speculative suggestions

The results discussed indicate a method as to how constrained non-equilibrium states in network-like polymer systems may be described. The situation seems to be controlled by the operation of equivalent subsystems of deformation. Their level is constituted by a set of constraints which form a global network. The size of the subsystems reaches a minimum value in polymer glasses because of being nearly identical with the dimensions at which a liquid-like short-range order is observed. This is equivalent to having the highest density of quasi-permanent constraints. In semicrystalline systems the subsystems are substantially larger, being comprised of a defined number of clusters. The topological features of these equivalent subsystems are substantially different from those of a polymer glass. Yet, many different systems behave in a network-like manner. The systems discussed display similarities in the large-strain regime. Here, entropy changes are dominant, proving in both cases the existence of a network of equivalent subsystems.

The energies dissipated are strictly controlled by the network properties, including softening effects and plastic deformation. The behaviour is also modified by the temperature-induced changes of an extra set of hidden variables. In glassy polycarbonate, this explains the temperature dependence of yielding [16]. In semicrystalline systems this leads to a softening in the stress–strain behaviour at elevated temperatures [1,3].

Network-like polymer systems seem to display "functional self-similarity". The mechanisms are coordinated so as to guarantee an affine transformation, at least of the subsystems of deformation. Any larger volume is then per definition transformed according to the law of affinity. But it is noteworthy that below this level defined by constraints ξ_N, the thermodynamic extremum principles are also satisfied. Hence, network-like systems do "optimize" themselves.

It was important that we had knowledge of the total energies. The strain energy and the heats exchanged were measured during deformation in a stretching microcalorimeter. The power of such a device is impressively demonstrated with the discovery that semicrystalline polymers like LDPE are fully entropy-controlled in the regime of $\lambda > 1.5$. Nobody would a priori suggest this striking behaviour. Hence, knowledge of the total energy balance allows the nature of the deformation, including irreversible processes, to be identified. It is more gratifying that Müller and Engelter had the idea of measuring the total energy balance and designed an appropriate apparatus [17].

Finally we have to confess that despite knowing general rules, we can still not explain how or why the special mechanism in these very different systems is activated.

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