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The Müller-Calorimeter and Applications

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Abstract

Stretching calorimetry by measuring both heat and work exchange makes it possible to get insight in the thermodynamic behavior of the system in question. It is possible to decide whether the mechanical equation of state describes the system completely, or other mechanisms influencing the heat exchange only have to be considered. A stretching-calorimeter performing this requirements is described. The efficiency is exemplarily shown in case of a Hookian solid and elastic and viscoelastic rubber deformation.

Introduction

"Classic" calorimetric measurements are based on measuring heat exchange under defined boundary condition forms not transfering other energy than heat /1/. Their attraction is that systemtypical knowledge can then be drawn from the data by the use of adequate thermodynamic relations. The effects are directed to transformation of internal freedoms or energy transitions due to reactions.

Yet, according to the fundamental relation of Gibbs

$$TdS = dU - \sum_i dW_i$$

S : entropy

T : absolute temperature

W_i: i^{th} energy form

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a more completed description should take advantage of simultaneous exchange of different energy forms. A step in that direction has been done by A.Engelter and F.H.Müller who first derived a high-sensity stretching calorimeter /2,3,4/ With this device it is possible to measure under isoperibolic conditions both of the energy forms involved, heat- as well as work of deformation /2 - 7/.
We want to demonstrate by measurements on typical systems that interesting new insights can be gained by the discussion of data obtained with the aid of the "Müller-Calorimeter". Some of the results can only be found with the aid of this method.

Thermodynamics

Up to now deformation processes as isobaric isothermal simple extension are only realized,which will first be discussed in the limits of reversible processes. The proper potential function is the Gibbs free energy g the differential form of which reads

$$dg = -SdT - Vdp + dW \tag{1}$$

V : volume, p : pressure
S : entropy, T : temperature

where we have explicitely to define W as strain energy function. With l as the length of the sample, f as force we have for originally isotropic systems

$$(2) \qquad dW = f \cdot dl$$

such that the coordinate frame is taken to be equal to (T, p, l).

Hence, rewriting equation (1) for isothermal-isobaric processes we arrive at

$$(3) \qquad dg\ (T,p,l)\Big|_{T,p} = f \cdot dl\Big|_{T,p}$$

We are then led to the "thermoelastic equations of state" /8,9,10,11/

$$(4) \qquad f = \left(\frac{dg}{dl}\right)_{T,p} = \left(\frac{\partial h}{\partial l}\right)_{T,p} - T\left(\frac{\partial S}{\partial l}\right)_{T,p}$$

$$= f_h + f_S$$

where the enthalpy and the entropy are defined as h(T,p,l) and S(T,p,l).
The force can therefore be considered to be comprised of two terms, f_h as enthalpic-component and f_s as entropic component.

It is possible to relate these two components to the mechanical equation of state f(T,p,l) and its temperature coefficient $(\partial f(T,p,l)/\partial T)_{l,p}$ /8-12/ :

$$(5) \qquad f_h \equiv \left(\frac{\partial h}{\partial l}\right)_{T,p} = f - T\left(\frac{\partial f}{\partial T}\right)_{l,p}$$

$$f_S \equiv -T\left(\frac{\partial S}{\partial l}\right)_{T,p} = T\left(\frac{\partial f}{\partial T}\right)_{l,p}$$

We have to notice that

$$(6) \qquad f_S = -T\left(\frac{\partial S}{\partial l}\right)_{T,p} = -\left(\frac{\partial Q}{\partial l}\right)_{T,p}$$

what is indeed the differential amount of heat exchanged during isobaric isothermal simple elongation.

Hence, measuring dQ, dl and f we are in the position of giving a thermo-elastic characterization of systems in the mode of simple elongation.

The Calorimeter

A. Engelter and F.H. Müller constructed the first high-sensitive stretching calorimeter to study the thermodynamic behavior of polymers /2,3/ using a differential manometer as sensor to compensate the deformation heat electrically in the reference cell. The stretching-calorimeter ("Müller-calorimeter") used in our group was built with a Tian-Calvet-Calorimeter modified by Barberi /21/ in a version with two-sides open heat flux cells.

This gives allowance for constructing a stable stress-strain mechanics outside the calorimeter. Thus forces do not affect the sensitive calorimeter cell. The whole calorimeter device /22,23/ is surrounded with a copper jacket thermostatized, allowing isoperibol (and quasi isothermal) conditions in the region 10°C to 150°C. The most sensitive region of the calorimeter cell has a diameter of 9 mm and 40 mm length, it covers the total sample and its traction rod clamps. The thermopile

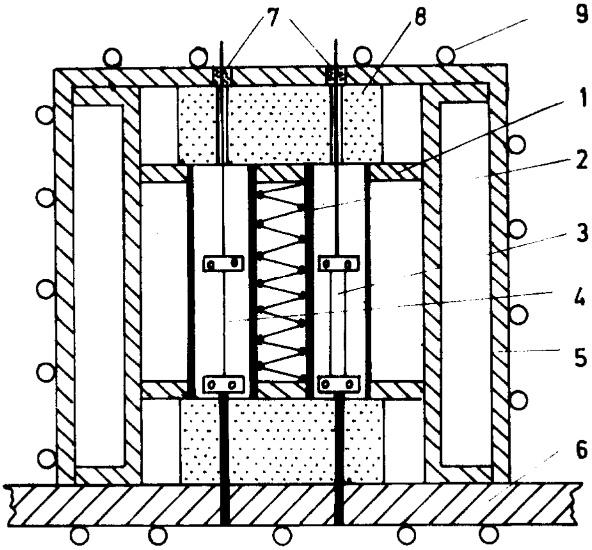

Fig. 1: Stretching calorimeter. 1 = Heat flux calorimeter, 2 = Thermopile, 3 = Sample, 4 = Stretching dummy, 5 = Copper jacket, 6 = Stable botten plate, 7 = Copper brush, 8 = Teflon lid, 9 = Copper tube.

has a thermal sensitivity of 120 μV/mW with very low noise, thus allowing a resolution (thermal noise) of the calorimeter of 0.2 μW at room temperature with a stability of the baseline of ± 0.4 μW per hour. At 100°C the resolution is 0.4 μW and the stability about ± 0.6 μW per hour. The calorimeter allows measurements of stretching heats down to 50 μJ with a resolution of ± 30 μJ. The time constant of thermal relaxation is 60 seconds.

Calibration of the calorimeter was done both electrically with a resistor instead of the sample and by the "Thomson heat" accepted from a solid body with known linear expansion coefficient during force change according to the equation

$$(6a) \qquad dQ / df = l_0 \cdot \beta \cdot T$$

(Q = heat, f = force, l_0 = length without force, β = linear expansion coefficient, T = temperature (in K)). The "Thomson heat" of the traction rod has always to be taken into account, depending on force changes and length within the range of the calorimeter cell sensitive for heat exchange. This correction term is usually about 0.25 mJ/N.

Polycrystalline Hookian Solid

The well-known phenomenological Hookian equation of state for quasi-isotropic as well as for isotropic solids is given by

$$(7) \qquad f = K_{T,P} (l - l_0)$$

where $K(T,P)_{T,P}$ is the phenomenological "spring-constant" at invariant (T,P). The fiducial length in the isotropic unstrained state is defined as $l_0 (T,P)$, l is the macroscopic length of the sample in the elongated state.

The thermo-elastic equations of state are then derived to be equal to

$$(8)\qquad f_h = K_{T,p}\cdot(1 + (T\cdot\beta - 1)\cdot l_o) - T\left(\frac{\partial K_{T,p}}{\partial T}\right)_{l,p}\cdot(1 - l_o)$$

$$f_S = -K_{T,p}\cdot\beta\cdot T\cdot l_o + T\cdot\left(\frac{\partial K_{T,p}}{\partial T}\right)_{l,p}\cdot(1-l_o)$$

$\beta = \ln l_o/\partial T$ is the linear coefficient of thermal expansion in the unstrained state.

For $(\partial K_{T,P}/\partial T)_{L,P}\cdot(1 - l_o) \ll K_{T,P}\cdot\beta\cdot T\cdot l_o$ with $K_{T,P} \cong K$ we get the approximative relations:

$$(9)\qquad f_h = K\cdot\left(1 + (\beta\cdot T - 1)\cdot l_o\right)$$

$$f_s = -K\cdot\beta\cdot T\cdot l_o$$

Having determined K from the stress-strain data, there is no further adjustable paramter in equations (9) provided that β is known. It is therefore very satisfactory that measurements of Göritz /7/ who has stretched a steel-wire (Chronifer 1808) at T = 294 K, can fairly well be computed with the aid of η = Q/W. Calculated by integration of the equations (9), η has the very simple form /11/

$$\eta = \frac{Q}{W} = \frac{2\beta \cdot T}{\varepsilon} \quad \text{with} \quad \varepsilon = \frac{\Delta l}{l_o} \tag{10}$$

We note from the equations (9) that the thermo-elastic contributions of the "internal freedoms" as represented by phonons are submitted to the general condition:

$$\left(\frac{\partial h^{(i)}}{\partial l}\right)_{T,p} = T \cdot \left(\frac{\partial s^{(i)}}{\partial l}\right)_{T,p} = K \cdot \beta \cdot T \cdot l_o \tag{11}$$

which means that the anharmonicity of the lattice potential is changed on deformation in unique dependence of β and $K \cdot l_o$. This fundamental thermoelastic correlation must be seen as consequence of having the phonons in states of internal equilibrium. Equation (11) expresses symmetry related directly to the principle of equipartion of energy: On deformation the anisotropy of the potential is increased. The number of phonon states with energies below kT is enlarged. Having under adiabatic conditions the total energy distributed over this increased number of states, the average kinetical energy per freedom is decreased: The sample cools down. To keep the temperature constant heat must therefore be transfered into the system the amount of which must exactly comply with relation (11) (see sketch in figure 2).

It is interesting but not well known that this transformation of the lattice dynamics is dominant at smallest extensions when compared with the change of

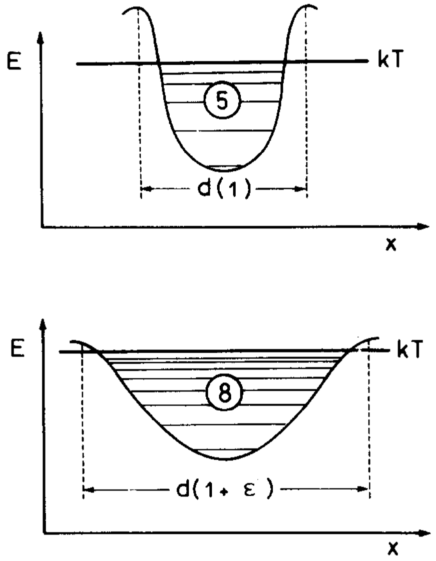

Fig. 2: Schemata of the potential functions in the unstrained (d(1)) and the elongated state (d(1 + ε)). Due to increased "anharmonicity" in the deformed lattice, the number of oscillatoric levels occupied at the temperature T is rised (⑤ → ⑧). Under isothermal isobaric process conditions heat must be transfered into the sample the amount of which is dependent of detailed properties of the phonon system.

the potential energy due to the affine static lattice expansion (dW). This is indicated with the very salient up-turn in the η (ε)-plot drawn out in figure (3). Theoretically we find that η (ε) has a pole at $\varepsilon = 0$.

It is on principle possible to characterize this thermoelastic properties also by measuring f and $(\partial f/ \partial T)_{l,P}$. Yet, in accordance with the equations (8) only that

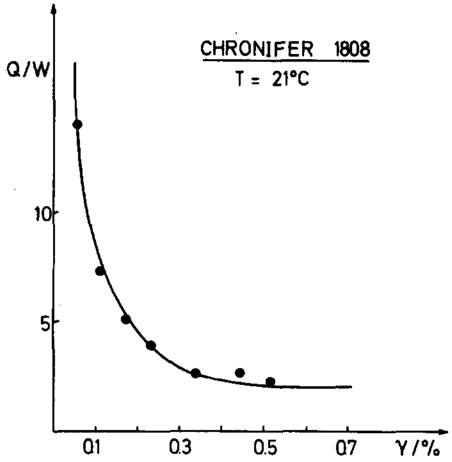

Fig. 3: Plot of $\eta = Q/_W$ versus ε for a steel wire (Chronifer 1808) deformed in simple extension at room temperature according to D.Göritz /7/. The solid line is computed with the aid of equation (10) β assigned to $4.05 \cdot 10^{-5} K^{-1}$.

processes which contribute to thermal expansion can be analysed by this method. Here we have to stress the important advantage of stretching-calorimetry: Strain dependent reactions or even so "rotatoric freedoms" will clearly be indicated by appropriate contributions to f_s.

Hence, reflecting the data and their interpretation shown in figure (3) we arrive at the conclusion that in the steel sample investigated in the Hookian range there are no rotatoric freedoms or no defects developed on extension.

Molecular Networks

Macromolecular networks comprised of chemically crosslinked chains reveal the typical feature that very large extension can be achieved with relatively small forces. The network undergoes a global transformation by a cooperative orientation of the "network" vectors between neighbored crosslinks and a belonging dilatation. This is illustrated in the sketch shown in figure (4). The question arises how the short range properties which are liquid-like are correlated to this network transformation. According to the thermodynamics given in the introductory section we only have to know the equation of state to answer this question.

Surprisingly, a full description is indeed possible with the aid of a van der Waals model /10,11/. We consider the network on the global level to be represented as a conformational van der Waals gas with weak interactions. The essential model parameters are the maximum elongation $\lambda_m = l_{MAX}/l_o$ uniquely determined by the average finite length of the chains and the global interaction parameter a. The equation of state reads

$$(12) \quad f = \frac{\varrho \cdot R \cdot T}{\lambda_m^2 \cdot M_{St}} \cdot \frac{\langle r^2 \rangle}{\langle r_o^2 \rangle} \cdot D \cdot \left(\frac{D_m}{D_m - D} - a \cdot D \right)$$

ϱ is the density, R the gas constant, T the absolute temperature. M_{St} defines the molecular weight of the stretching invariant segment in the chain the definition of which

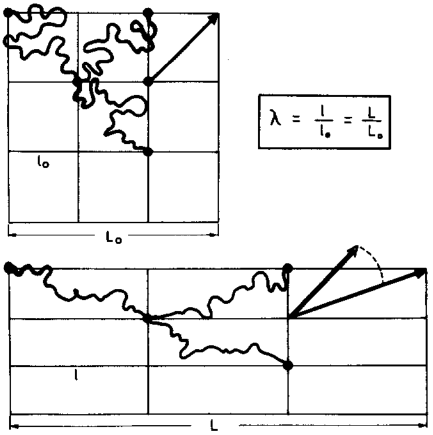

Fig. 4: Illustration of the affine transformation of an isotropic network. An idealized representation of the fiducial state is given in the upper part. The chain-end-to-end vectors are submitted on simple elongation to an collective orientation as well as a defined dilatation as indicated with the lower part of this figure.

allows to formulate λ_m in terms of the number of segments per chain n_{St}($\lambda_m = n_{St}^{1/2}$) /8,9,14,15/. By the memory term $\langle r^2 \rangle / \langle r_o^2 \rangle$ the change of the squared average of the network vectors related to the appropriate change of the chain-end-to-end vector of the equivalent freely jointed chain is taken into consideration for rubbers with non-isoenergetical rotational isomers /8,9,14/.

The symbol D stands for

$$D = \lambda - \lambda^{-2} \tag{13}$$

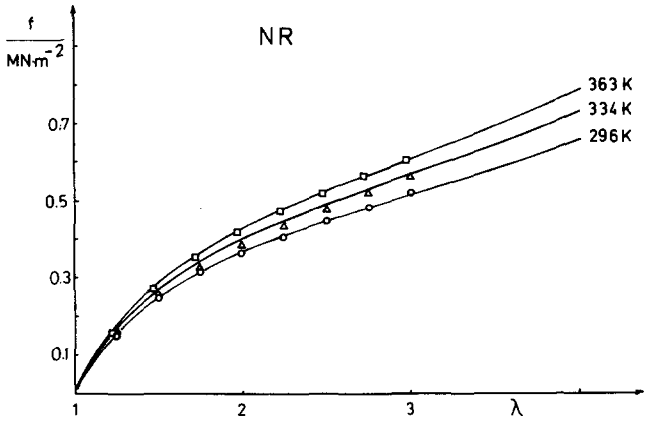

Fig. 5: The thermo-elastic data of rubber for simple extension at temperatures as indicated with each curve.

A The stress-strain data.
The solid lines are computed with the aid of the van der Waals equation of state (12)
(parameters: $\lambda_m = 10.5$; $a = 0.253$

$$\frac{\varrho RT}{\lambda_m^2} \cdot \frac{<r^2>}{<r_o^2>} = 124 \text{ mol} \cdot m^{-3}$$

$$\beta = 2.4 \cdot 10^{-4}\ K^{-1};$$

$$d \ln <r_o^2>/_{dT} = 11.8 \cdot 10^{-4}\ K^{-1}).$$

having D_m accordingly defined as

$$D_m = \lambda_m - \lambda_m^{-2} \tag{14}$$

The belonging thermoelastic equations of state can be derived straight forward applying the general relations (5) Measurements on natural rubber and calculations are drawn out in figure (5). The full characterization at different temperatures as shown by evidence is only possible in this case if

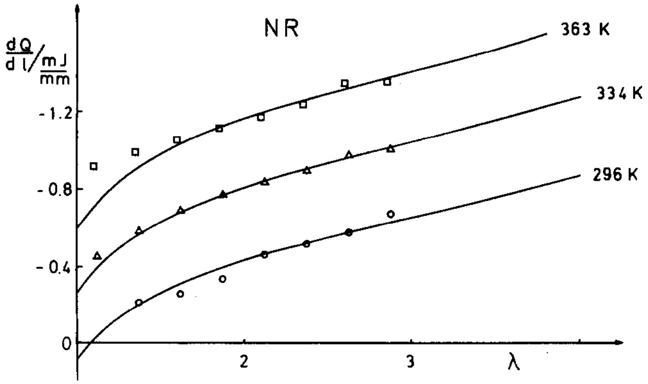

Fig. 5: B Differential heat of deformation. Solid Lines computed with thermo-elastic equation of the van der Waals equation of state. It is necessary to consider in addition strain-dependent rotatoric motions. Solid line is computed, for details see reference / 11,13,14/.

strain dependent rotatoric freedoms are also considered. This striking phenomenon could only be found on the use of a stretching calorimeter. It is very satisfactory that this result in the corresponding parts is also fully consistent with data derived from a thermodynamic analysis of mechanical measurements.

It is furthermore interesting to recognize that internal equilibrium is found to be always adjusted up to largest strain. The necessary increase of volume on stretching /8,9,11/ produces the so-called thermoelastic inversion (i.e. change of sign in dQ/dl at small λ's, see figures (5,6). This effect is caused by production of holes /10,11/. One may consider these processes as quasi-chemical reactions strain-regulated by conditions of internal equilibrium.

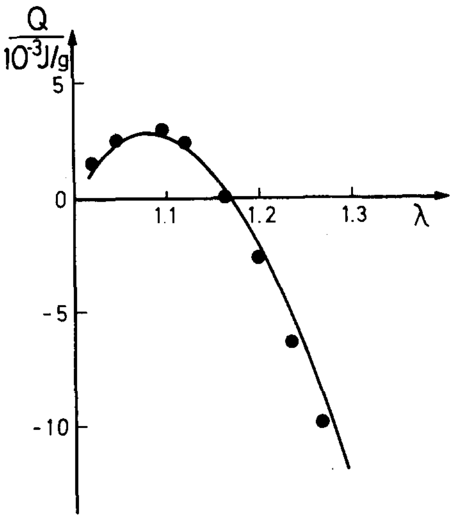

Fig. 6: The integral deformation of heat for isothermal-isobaric extension of rubber at room temperature. The solid line is computed with the aid of the thermo-elastic equations of state of van der Waals networks. The "thermo-elastic inversion" /5,8,9,10,11/ is caused by production of "holes" on elongation which is at least outdone by heat related to the orientational entropy changes in the network ($T \cdot \Delta S_{or} = Q_{or} < 0$) /11/.

Viscoelastic Deformation

On hand of this last example we want to demonstrate an interesting application of stretching calorimetry to an irreversible process. Recalling the fact that entropy production should be accompanied by a defined production of heat, it is evident that those contributions must be indicated by $dQ_{irr}/dl < 0$. In simple visco-elastic systems dQ/dL can be written as /16,17/

$$(15) \quad dQ/_{dl} = (dQ/_{dl})_{rev} + (dQ/_{dl})_{irr}$$

We consider a semicrystalline block copolymer (PU-elastomer) comprised of so-called hard-segments which are chemically different from the "weak-segments". The hard-segments constitute rod-like crystals representing crosslinking elements in a "crystal network". This is illustrated in figure (7). The weak segments are operative as tie-molecules linking neighbored rods. Rods and amorphous layers are staggered within clusters which are the appropriate subsystems of deformation multifunctionally connected with their neighbors.

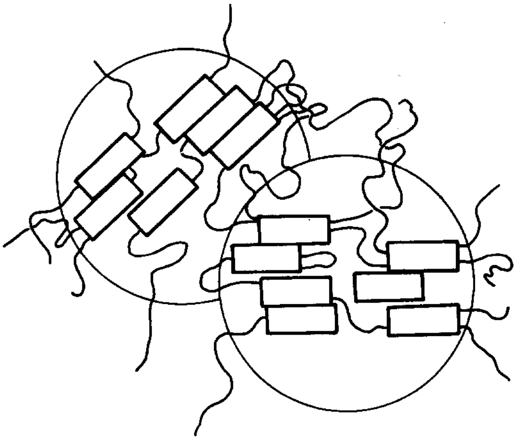

Fig. 7: Two-dimensional sketch of a cluster-network with the clusters multifunctionally linked to their neighbors. The rectangulars represent the solid rods comprised of hard segments. The basic deformation mechanism is the affine transformation of the clusters.

We now focuss our interests to a discussion of the deformation mechanism without going into details. On deformation we expect two characteristic processes, (a) the network deformation which should be reversible and (b) a plastic transformation in the assembly of solid rods. Indeed, this simple model can be shown to be correct. The total of the

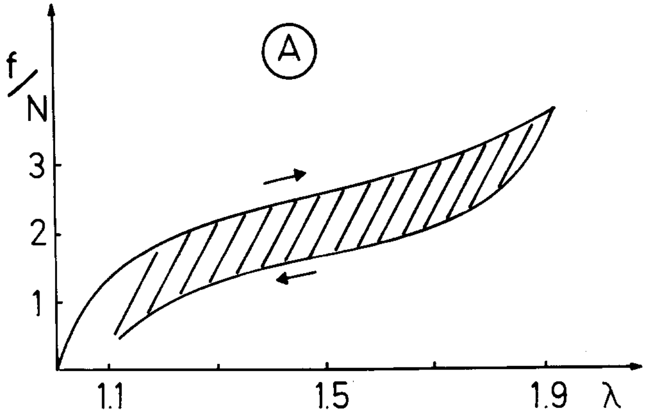

Fig. 8: A The quasi-static stress-strain behavior of PU-Elastomers / 6, 24 / for the first cycle .

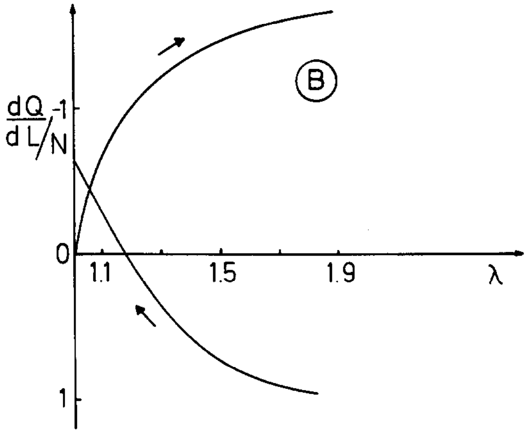

Fig. 8: B Differential heats of deformation.

measured dQ/dl is drawn out in figure (8) together with the quasi-static stress-strain curve. It is now easily verified that we can indeed achieve a concize interpretation by the use of relation (15).

If we assume that the work represented by the hysteris area of the stress-strain curve, is fully dissipated, the dQ/dl data can be separated into the two parts as depicted in figure (9). With $(dQ/dl)_{irr} = f^{①} - f^{②}$ approximately fullfilled the area of the hysteris in the stress-strain curve must be identical with $\int (dQ/dl)_{irr}\, dl$. If we do not consider smallest extensions, this turned out to be true.

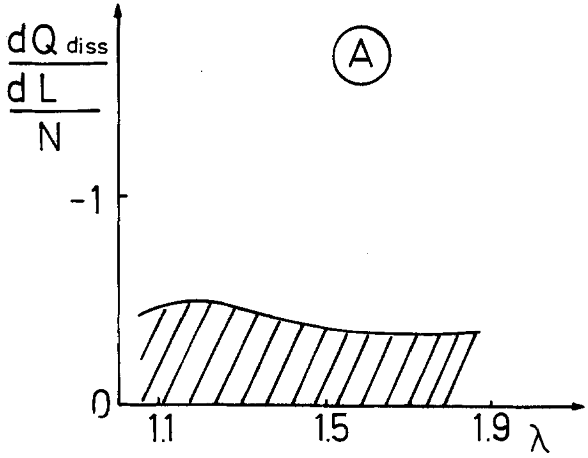

Fig. 9: A The differential heat dissipated in the first cycle of simple elongation. The hatched area is in full accord with "hysteris-area" as indicated in figure 8 A

In conclusion, the heterogeneous system is found behave very simple: The solid rods undergo a strain-regulated plastic deformation as fillers bound to a network constituted by the rods themselves. The "amorphous" weak segments are rubberlike. It is very satisfactory that the thermoelastic properties of these components correlate with the actual average length of these chain-segments /18/.

Hence, a very defined interpretation is possible in this case thus providing a basis for a theoretical discussion of large irreversible deformations in semicrystalline polymers.

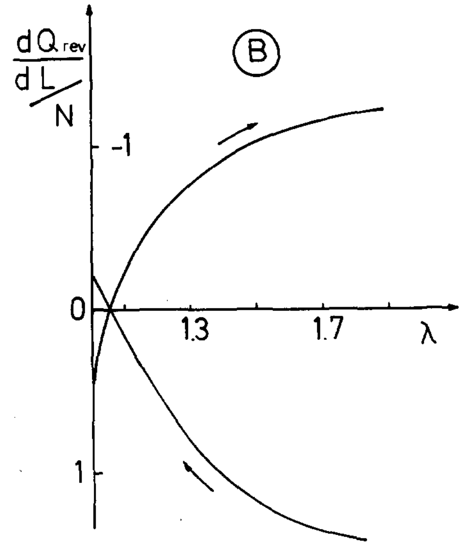

Fig. 9: B The differential reversible heat of extension of PU-elastomer by the course of which the deformation in the non-crystallized regions can clearly be identified as rubber-like.

Conclusive Remarks

We want to point out that interesting investigations have for example been done on muscles /19/. Moreover, experiments on relaxation phenomena in rubbers are successfully under investigation, thus, taking up an idea given by Debye in early times.

Yet, we hope to have demonstrated by three typical experiments the possibility of getting new insights into deformation mechanism with the aid of a "Müller-calorimeter". Its principe is methodically a consequent extension of classical calorimetry.

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