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Fluctuation dynamics and relaxation in glass-forming liquids polymer networks and low molecular weight systems

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Abstract The dynamics in glass forming liquids is described by defining *conformons* as a new type of bosons. Activation or deactivation can be induced. Most significant is that conformons may spontaneously decay. This allows to redistribute all the modes so as to maximize the entropy. Stationary equilibrium then is characterized by broad conformon distribution. This universal spectrum has topologically analogous origins as the black body radiation. It is possible to describe the temperature dependence of fluctuations i.e. of their contribution to the heat capacity accounting empirically also for the glass transition. It appears to be reasonable to define relaxation mode spectra. To this end, the number complexions of a conformon and its mean relaxation time are related to each other by a power law. Its key parameter α describes empirically how fluctuations and relaxation modes are connected with each other. Under thermo-rheological simple conditions actual relaxation time spectra are then obtained by a congruent shift of the whole spectrum (WLF-procedure). The

shape of a relaxation time spectrum does not depend on temperature or pressure (pressure-temperature-frequency relationship). Moreover, it is also strain-, strain-type and strain-rate invariant. The new approach is successful in deducing the master curve of the real and the imaginary parts of the complex shear modulus or of the complex compliance. Dielectric susceptibility data of polymers and low molecular glass formers are satisfactorily reproduced. In contrast to the dielectric experiments mechanical relaxation behave more complex. In networks junctions fluctuations take influence which is increased in filler loaded rubber of poly-vinyl-chloride. Interpretations are discussed on a set of representative experiments. The description of all these experiments proves the utility of the conformon model the physical ideas of which are discussed in this paper.

Key words Thermodynamics and dynamics – relaxation-modes – relaxation-time spectra – glass-forming polymers and low molecular weight compounds – α-process

Introduction

Liquids show a continually fluctuating disordered structure. If *Stationary fluctuation modes* come in existence one has for many reasons to expect a spectrum [1, 2, 3, 4].

To show this we like to recall first the phenomenological description of large deformations in permanent polymer networks [5, 6]. With the use of the van der Waals network model [7] the strain energy (i.e. the thermodynamic limit) is formulated. Thermodynamics of irrevers-

ible processes [13–25] allows then a full description of relaxation. It turns out that one needs a *broad relaxation time spectrum the shape of which does usually not depend on temperature, pressure, strain type and strain rate*. The fluctuation dynamics in liquids is therefore expected to behave analogous and to show the same symmetries.

It is then the object of this paper to describe the fluctuations in glass forming liquids, to formulate the stationary equilibrium conditions and to relate fluctuation dynamics and relaxation. If one starts with the equations of motion one is encountered with the handicap that a "system of normal coordinates" cannot be defined [3,4, 8]. For liquids it is therefore not possible to *directly prove the existence of stationary fluctuation modes. For this reason, we simply postulate the existence of such fluctuation modes whereby each of them should undergo incessant transitions among its micro-states. The free energy of each mode is minimized this way. "Mode-entropy" and the mode energy are strictly related to each other (primary saturation).* We call these stationary modes *conformons* [9,10,11].

Conformons are assumed to suffer induced activation or *annihilation* and *spontaneous decay*. Conformons with different energies can, of course, be produced. At equilibrium the free energy of the whole conformon ensemble is minimum (*second saturation*). The resulting spectrum is just the Planck-distribution. The reduced energy-density distribution of conformons is universal. *Conformons should behave like Bosons* [12].

To describe relaxation we now should know how relaxation processes are related to the fluctuations. We should be aware that conformons themselves can also occupy non-equilibrium states. The momentary configurations deviate then from the stationary equilibrium pattern. Due to the intrinsic dynamics conformons automatically relax toward equilibrium. At small enough distortions the equalization might be considered as Onsager process. If the whole system behaves linear conformon spectrum and relaxation time-distribution must uniquely be related to each other. To satisfy this condition each relaxation time is defined as product of a thermodynamically determined factor (*relaxation mode*) and a kinetic factor. The relaxation modes are directly connected with the conformon spectrum and kinetically equivalent. If the planck distribution of conformons cannot be disturbed to measurable extents *relaxation phenomena are altogether "intra conformon processes"*.

A last point it should be considered that disordered systems freeze in at the dynamic glass temperature T_g at and below of which fluctuations cannot be activated any more. We propose here shortly a new interpretation of the Vogel–Fulcher temperature [1,2,27] within the framework of the conformon model.

In what follows we formulate the above ideas and prove their utility by describing equilibrium properties, relaxation and retardation experiments carried out on polymer- and low-molecular weight glass-formers.

Strain-energy of networks

In terms of the van der Waals network model it is possible to explicitly formulate the strain energy function [12,22,23]

$$W(\lambda) = -G[2\phi_m(\ln(1-\eta)+\eta)+2/3\,a\phi^{3/2}] = Gw$$

$$\eta = \sqrt{\phi/\phi_m}; \quad \phi = 1/2(\lambda^2 + 2/\lambda - 3); \quad \phi_m = \phi(\lambda_m)$$

$$\lambda_m = \sqrt{y}; \quad y = M_c/M_u; \quad G = \rho RT/M_c = \rho RT/M_u\lambda_m^2$$

$$(1)$$

ρ is the mass density, R is the gas constant. M_c is the mean molecular weight of the chains, M_u the entropy invariant unit. T is the absolute temperature. λ_i is the strain in direction i defined by the ratio L_i/L_{io}. L_i is the actual length while L_{io} is the original length. The first van der Waals parameter, λ_m, gives the maximum strain the network can be stretched to. The second van der Waals parameter a accounts for global interactions between network chains. The mechanic equation of state reads
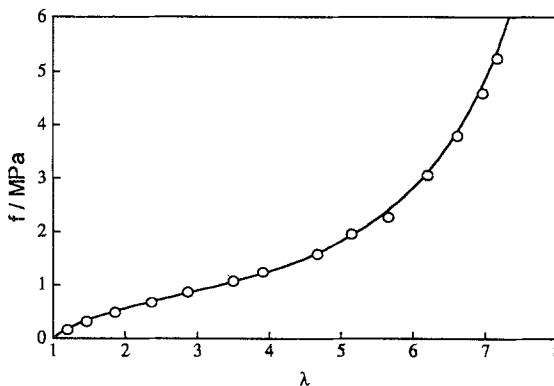
$$f(\lambda) = G(\lambda - \lambda^{-2})\left(\frac{1}{1-\eta} - a\phi^{1/2}\right) \tag{2}$$

The stress-strain pattern of a poly-methyl-methacrylate network is indeed fairly well described (Fig. 1).

Irreversible thermodynamics

At "small enough distances from equilibrium" we are allowed to apply thermodynamics of irreversible processes

Fig. 1 Quasi-static stress-strain pattern of natural rubber at $T = 353$ K ($\lambda_m = 10$, $a = 0.27$, $M_u = 68\ \text{gmol}^{-1}$)

[13,14,15,16,17–25]. The system of coordinates is then extended by defining a discrete spectrum of hidden variables $\{\xi_i(t)\}$. The differential of the Gibbs-function is written as

$$dg = -sdT + Vdp + fd\lambda - \sum_i A_i d\xi_i \qquad (3)$$

V is the volume. A_i is the affinity of the i-th independent process. The conjugated extensive variable $\xi_i(t)$ depends on time. As material equations we introduce the linear Onsager relations [18,19,20,21,22]

$$\left(\frac{\partial \xi_i}{\partial t}\right)_{T,p} = \alpha_i A_i(T, p) . \qquad (4)$$

The rate of each process is directly proportional to its "distance from equilibrium" characterized by the affinity A_i. The complete set of hidden variables defines a phenomenological relaxation time spectrum as a unique function of temperature and pressure. Equalization runs under the necessary condition of $ds/dt > 0$.

In permanent networks the relaxation modes $\{\xi_i(t)\}$ should be linked in the network in an isotropic and scalar manner [23, 24, 25]

$$g_{T,p}(\lambda) = (1/2)z_{10}w(\lambda) + w(\lambda)^{1/2}\sum_i z_{12}^{(i)}\xi_i$$

$$+ 1/2\sum_i z_{20}^{(i)}\xi_i^2 \qquad (5)$$

The coefficients z_{ik} can be expressed by measurable quantities like the glass-modulus G_{glass} and the plateau modulus in the rubbery state G. In the mode of simple extension the solution was shown to be given by

$$f(t) = G\frac{\partial w}{\partial \lambda}\left[1 + \frac{\Gamma}{G}\left(1 - \frac{2}{\Gamma}\Psi\right)\right]$$

$$\Psi = \int_0^t m(t - t')\left[\frac{w(t')}{w(t)}\right]^{1/2}dt'$$

$$\Gamma = G_{glass} - G; \qquad \partial w/\partial\lambda = \lambda - \lambda^{-2} \qquad (6)$$

For a constant strain rate the strain parameter is written as

$$\lambda(t) = 1 + \dot{\varepsilon}t; \quad \dot{\varepsilon} = const . \qquad (7)$$

The memory function $m(t - t')$ is equal to

$$m(t - t') = \sum_i \frac{h_i}{\tau_i}e^{-\frac{t-t'}{\tau_i}} \qquad (8)$$

h_i is here j-th component of the normalized discrete relaxation time spectrum. Each mode is typified by its relaxation time τ_k. According to Eqn. (7) the relaxation time spectrum should be strain-, strain rate- and strain type-invariant. By the way, the use of the discrete relaxation time spectrum is equivalent to a non-exponential ap-

proach which might be described with the aid of the KWW-function [45].

Examples

Under thermo-rheological simple conditions a "master curve" [2, 10, 11] of the shear modulus can be constructed. The relaxation time spectrum in then deduced by means of a known mathematical procedure [2, 24]. Stress strain cycles under constant strain rates can be fitted without any parameter adjustments if the network parameters (λ_m, a, M_u), the spectrum $h(\tau)$ and the WLF-parameters [2] are known.

As representative example we show measurements on PMMA-networks. Real part G' and imaginary component G'' of the complex shear modulus are depicted in Fig. 2. The belonging spectrum $h(\tau)$ is shown in Fig. 3.
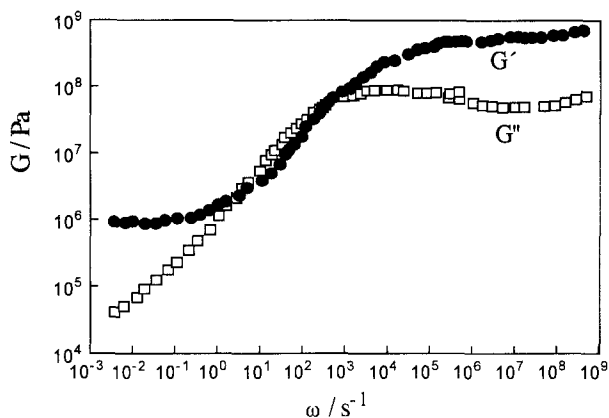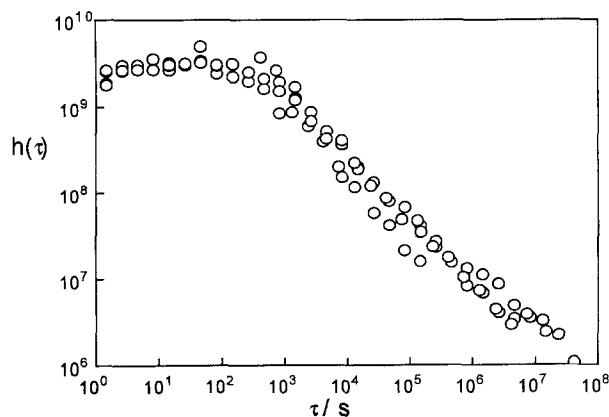

Fig. 2 Master-curves of PMMA according to [11]

Fig. 3 $h(\tau)$ of PMMA-networks (see capture in Fig. 4) at 417 K (WLF-parameter $B = 6.2$, $C = 65$ K according to [11, 28, 56]

According to the results plotted in Fig. 4 the set of stress-strain cycles of PMMA-networks is fairly well reproduced (by also using the WLF-relation [25]).

We are led to conclude: relaxation during deformation of polymer networks is described as linear response by a set of Onsager-processes which are altogether linked in the same way to the network. Unloading curves have to cross over the equilibrium curve at the same macroscopic strain λ provided that the samples were stretched up to the same maximum strain λ_{max} (see Fig. 4). The temperature-frequency relationship [1,2] and the superposition principle [1, 2, 3, 10, 17, 18, 19, 20] hold true.

The relaxation spectrum is phenomenologically defined. In the following *sections we prefer to use discrete distributions*.

The conformon

We define an isotropic set of conformational (or configurational) modes in a homogeneous liquid. We call them *conformons* [5, 7, 8]. They should act like weakly interacting quasi-particles.

At equilibrium each conformon runs through many equivalent iso-energetic conformations which should be realizable with the same à priori probability. The conformon is in equilibrium if its free energy is minimized. The situation may be illustrated by using the "void"-model. A conformon should then comprise a definite number of cooperatively fluctuating voids of equal size (y). With u_y as the mean energy and s_y the conjugated entropy the mean Helmholtz energy f_y of a conformon may be written as

$$f_y = u_y - Ts_y \tag{9}$$

u_y and s_y may be considered as the partial molar quantities

Fig. 4 Stress-strain cycles of a PMMA-network ($\lambda_m = 5.6$, $a = 0.44$, $M_u = 118 \, \mathrm{gmol^{-1}}$) according to [?, 28, 56]

which describe the change of the system's energy by activating a single "y-conformon". The mode index should also characterize the "size" of the energy. At internal equilibrium the number of isoenergetic configurations per mode should be adjusted so that the *condition of saturation* is satisfied

$$u_y = Ts_y \tag{10}$$

With Boltzman's statistical definition of the entropy we arrive then at

$$u_y = k_B T \ln \Omega_y \tag{11}$$

k_B is Boltzmann's constant. $\Omega_y(T, V)$ is the number of accessible configurations of the "y-conformon", V the volume. An explicit formulation of Ω_y cannot easily directly be deduced. It may be useful to know that its value is uniquely related to the energy u_y.

The number of complexions of a conformon $\Omega_y(T, V)$ i.e. its fluctuations should increase with u_y or at constant u_y decrease when the temperature is raised. The "correlation length" of the fluctuation modes changes with temperature. At very high temperatures this length should be squeezed down to lowest values and approach a "gas-like" behaviour.

The Vogel–Fulcher Limit

We account for the occurrence of the glass-transition by postulating

$$u_y = y_{min} u_0 = RT_0 \ln \Omega_{oy} \tag{12}$$

T_0 should be the Vogel–Fulcher temperature [1, 2, 26]. u_0 is the energy of activation related to a reference unit (PE: CH_2-unit). y_{min} characterizes as the minimum of the energy of conformons. Rewriting Eqn. (12) we are led to the interesting relation

$$T_0 = \left(\frac{u_0}{k_B}\right)\left(\frac{y_{min}}{\ln \Omega_{oy}}\right) \tag{13}$$

If the energy u_0 is always positive we should observe that fluctuations cannot any more be activated at temperatures below T_0. For n-alkanes one then finds at $T_0 = 277 \, \mathrm{K}$ from the second factor with $y_{min} \approx 0.1$ CH_2-units ($u_0 = 5400 \, \mathrm{J/mol}$) that the number of accessible complexions Ω_{oy} approaches one ($\Omega_{oy} = 1.26$). The existence of the glass transition relies therefore on the hypothesis that disordered systems should show on the atomistic level a smallest "void" with a finite activation energy $y_{min} u_0$. The smaller the mean size parameter, the lower the configurational freedoms. At T_0 the system behaves then not as a liquid because the necessary set of equivalent configurations ($\Omega_y > 1$) is not available any more.
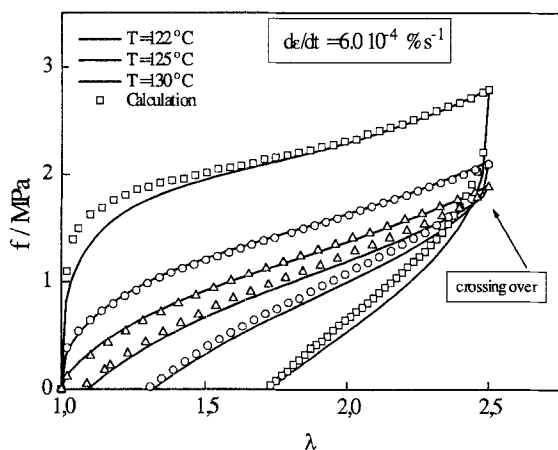
The universal conformon distribution

It is now the key assumption that conformons can suffer induced activation or annihilation. But they should also spontaneously decay. At equilibrium the concentration of conformons is determined by Boltzmann's law and the condition that the entropy of the whole ensemble is maximized. With u_y as average energy of the y-th mode we have therefore

$$N_y/N_0 = e^{-\frac{u_y}{k_B T}} = e^{-\ln \Omega_y} = (\Omega_y^{-1}) \qquad (14)$$

where we introduced Eqn. (13). The relative number of "high energy modes" is exponentially reduced.

The stationary conformon spectrum is deduced analogously as it is known for the radiation law [15,32]. We do not want to go through the steps of deriving the conformon spectrum. *Significant is that the dispersion relation for isotropically and homogeneously distributed modes is used (like the electro-magnetic modes in an enclosure). The density of the modes should then be proportional to* $(\ln \Omega_y)^2$. If the mean energy of the conformons is related the average energy $k_B T$

$$\frac{u_y}{k_B T} = \frac{\ln \Omega_y}{e^{\ln \Omega_y} - 1} = \frac{\ln \Omega_y}{\Omega_y - 1} \qquad (15)$$

we arrive at the equilibrium distribution of conformons

$$H(\Omega_y) = H_0(\ln \Omega_y)^2 \frac{\ln \Omega_y}{e^{\ln \Omega_y} - 1} = H_0(\ln \Omega_y)^3 \frac{1}{\Omega_y - 1}. \qquad (16)$$

We do not want to give here the explicit formulation of the front factor H_0. Eqn. (16) can be cast into the reduced form

$$H_{red}(u_y, T) = \frac{H(\Omega_y)}{H_0} = (\ln \Omega_y)^2 \frac{\ln \Omega_y}{e^{\ln \Omega_y} - 1} = \frac{(\ln \Omega_y)^3}{\Omega_y - 1}. \qquad (17)$$

Eqn. (17) is obtained as a universal equation that should characterize the fluctuation dynamics in glass-forming liquids (or liquids in general) . There are typical features might help to prove the reliability of this result.

Temperature dependence of the heat-capacities

As we have shown elsewhere [26] one arrives by integration of the energy density to an analogue of Stefan–Boltzmann's law. The total energy density of conformons is found to be proportional to $K_{tot}(T^4 - T_0^4)$. The ratio of c_p/c_v is then deduced to be given by

$$\frac{c_p}{c_v} = 1 + \frac{\beta_{glass}^2}{\kappa \rho c_v} T + \frac{4 K_{tot}}{c_v} T^3 \qquad (18)$$

β_{glass} is the linear coefficient of thermal expansion. κ is the

isothermal compressibility, K_{tot} the more complicated front factor of the total energy. Hence, the temperature dependence of the heat capacities of liquids should show two terms: The first term is the "inharmonic oscillator term" while the second one accounts for the contribution of the fluctuations.

It is to be seen from the plot in Fig. 5 that the "c_p/c_v-master curve" of n-alkane melts are fairly well reproduced including the jump of $c_p(T)$ at the idealized glass transition. According to Fig. 6 the same holds for mercury melts covering a temperature range of about 600 degrees [27]. Recently we succeeded, in addition, in calculating the excess Debye–Waller factor as deduced from incoherent neutron-scattering pattern.
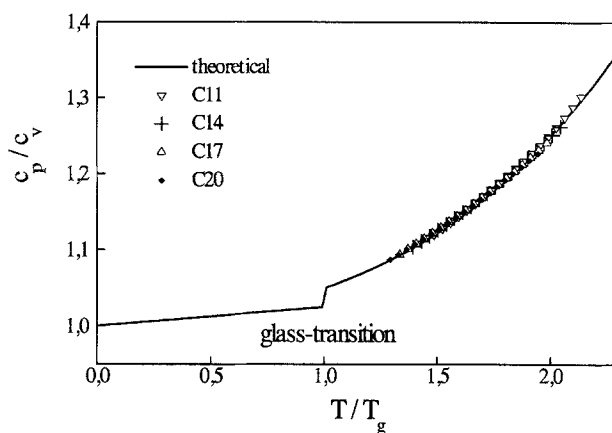

Fig. 5 c_p/c_v of n alkane oligomer melts also according to [26] ($\beta_{glass}^2/\kappa\rho c_v = 9 \ 10^{-5} \ K^{-1}$, $K_{tot}/c_v = 1.18 \ 10^{-9} \ K^{-3}$

Fig. 6 $c_p(T)$ of mercury (data from the Chemical Handbook): (A) the original data, the solid line computed with the aid of Eqn. (18) ($c_v = 0.035$ cal/g, $\beta_{glass}^2/\kappa\rho = -6.55 \ 10^{-6}$ cal/g K (negative because the large temperature coefficient of the compressibility governs the temperature dependence), $4 \ K_{tot} = 6 \ 10^{-12}$ cal/gK^3); (B) the contribution of the fluctuations
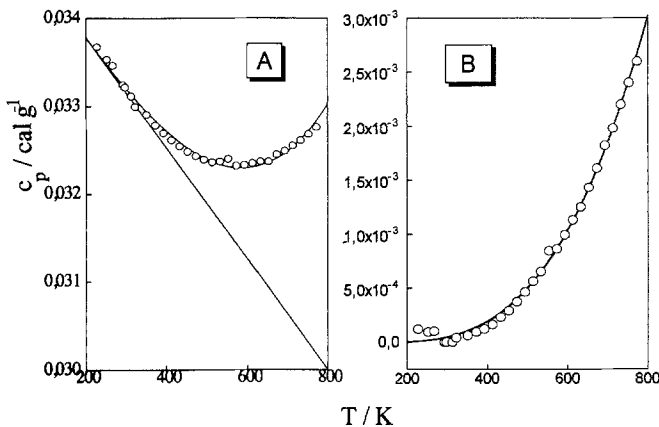
These results prove impressively that significant equilibrium properties of fluctuations seem correctly to be described with the aid of the conformon model.

Relaxation Time and the Conformon's Complexion

The question arises as to how relaxation and fluctuation dynamics are related. We now assume that each relaxation time spectrum should be characterized by a *relaxation mode distribution* $h(\tau_{oy})$ where each of the relaxation modes τ_{oy} is directly connected with its conjugated Ω_y. This implies that the relaxation time should increase with the number of accessible isoenergetic conformations. Under these assumptions one is led to define the empirical power law

$$\Omega_y = \zeta \tau_{oy}^\alpha . \qquad (19)$$

According to Eqn. (19) each relaxation mode τ_{oy} should be coupled in the same manner to the number of complexions Ω_y. Different physical relaxation processes may behave different what should be indicated with different values of the coupling parameter α. The relaxation mode distributions in liquids thus are coupled to the thermodynamically determined fluctuations the reduced energy density distribution of which is universal.

The number of complexions should be absolutely scaled. The conformational entropy must be positive everywhere. Since its minimum value is zero the necessary condition has to be satisfied

$$s_{10} = 0: \quad \zeta \tau_{o1}^\alpha = 1: \quad \zeta = 1: \quad \tau_{o1}^\alpha \equiv \Omega_1 = 1 \qquad (20)$$

The parameter ζ must be equal to one. With the aid of the Eqns. (16), (19) and (20) the *relaxation-mode spectrum* is obtained to be written as

$$h(\tau_{oy}) = h_0 (\alpha \ln \tau_{oy})^2 \frac{\alpha \ln \tau_{oy}}{e^{\alpha \ln \tau_{oy}} - 1}$$

$$= h_0 (\alpha \ln \tau_{oy})^3 \frac{1}{\tau_{oy}^\alpha - 1} . \qquad (21)$$

The resemblance of the Eqns. (16) and (21) manifests how strict equilibrium dynamics and relaxation are interrelated. Individual processes are characterized by the values the relaxation power h_0 and the coupling parameter α must be assigned to such as to fit experimental data. A broad distribution of relaxation modes is predicted.

The relaxation time distribution

We now define the relaxation times τ_y by multiplying each relaxation mode τ_{oy} with the same kinetic factor τ_{kin}

$$\tau = \tau_{oy} \tau_{kin}$$

$$\log\left(\frac{\tau_y}{\tau_{oy}}\right) = \log(\tau_{kin}) \equiv \log(a_T) . \qquad (22)$$

This relation yields thermo-rheological simplicity [1,2]. The shape of each relaxation time spectrum should be invariant. This shift factor $\tau_{kin} \equiv a_T$ depends on the temperature and the pressure at which the experiment is carried out. The shift factor a_T relates the experimental relaxation time spectrum to the fundamental relaxation mode distribution. To discuss relaxation of different systems it is suggested to compare the relaxation mode spectra.

Comparison with experiments

To deduce the *shear relaxation mode spectrum*, the shear relaxation time spectrum must be shifted until the maximum of the theoretical conformon spectrum is fitted. Yet, applying this procedure to different networks we were not successful. We therefore define the "two-term" extension of Eqn. (16)

$$H(\Omega_y) = H_0 (\ln \Omega_y)^3 \left[\frac{1}{\Omega_{y1} - 1} + \frac{\Gamma}{\Omega_{y2} - 1} \right] . \qquad (23)$$

In view of Eqns. (20) and (22) it is consequent to write here

$$\Omega_{y1} = \tau_{oy}^{\alpha_1}; \qquad \Omega_{y2} = \tau_{oy}^{\alpha_2} . \qquad (24)$$

Both mode spectra should be individually coupled to the conformon spectrum but showing the same kinetics. We deduce the extended version of the shear relaxation mode spectrum

$$h(\tau_{oy}) = h_0^* (\ln \tau_{oy})^3 \left[\frac{\alpha_1^3}{\tau_{oy}^{\alpha_1} - 1} + \Gamma^{co} \frac{\alpha_2^3}{\tau_{oy}^{\alpha_2} - 1} \right]$$

$$= h_0 (\ln \tau_{oy})^3 \left[\frac{1}{\tau_{oy}^{\alpha_1} - 1} + \frac{\Gamma}{\tau_{oy}^{\alpha_2} - 1} \right]$$

$$\Gamma = \Gamma^{co} \left(\frac{\alpha^2}{\alpha_1}\right)^3; \quad h_0 = h_0^* \alpha_1^3 . \qquad (25)$$

Two different parameters α_1 and α_2 are introduced. The density of the second fraction of conformons related to h_0 is described by the parameter Γ. The quality of the fits of relaxation mode spectra of polymer networks to the conformon spectrum can be seen from the plots depicted in Fig. 7. The calculations were carried with identical parameters (with exception of negligible differences in the relaxation power parameter h_0). Different degrees of crosslinking seem not to matter much. The conformon spectra of the networks shown here are identical indicating that they are crosslinked to about the same degrees. This
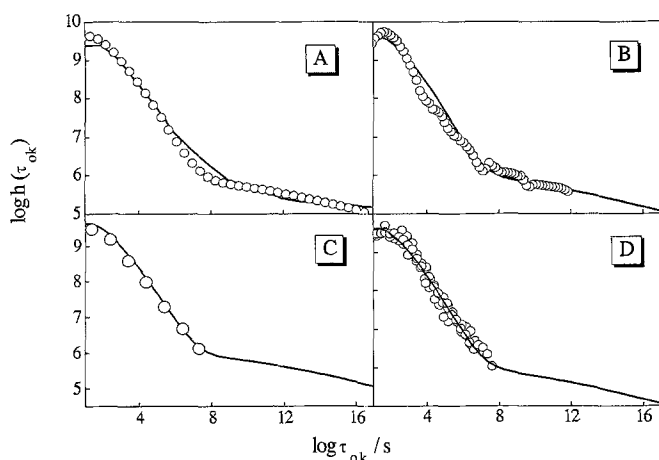
Fig. 7 The relaxation mode spectra $h(\tau_{co'})$ of (A) natural rubber [?], (B) hevea [2], (C) n-butyl-acrylate [2] and (D) PMMA [11], Solid lines theoretical: $h_0 = 3\ 10^9$, $\Gamma = 1.3 - 610^{-6}$, $\alpha_1 = 1, \alpha_2 = 0.2$
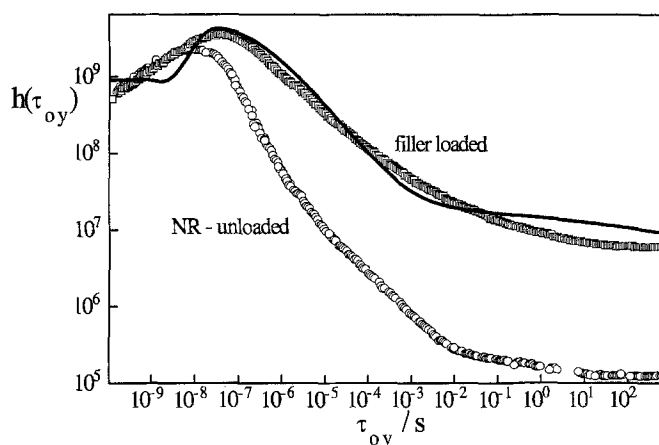

Fig. 8 The relaxation mode spectrum $h(\tau_{oy'})$ of natural rubber (o) and a sample loaded with carbon black (N110) (□) (filler volume fraction = 0.18) according to [50] : solid line computed with $h_0 = 3\ 10^9$, $\Gamma = 3.4\ 10^{-5}$, $\alpha_1 = 1, \alpha_2 = 0.2$

Table 1 Conformon parameters

$\alpha_1 = 1$; $\alpha_2 = 0.2$; $\Gamma = 1.36\ 10^{-6}$
h_0 characterizes the relation power

impressively proves universal features in the fluctuation dynamics of polymer networks. The similarities of relaxation spectra of polymers was first observed and discussed by Ferry [2].

The spectrum is mainly controlled by the first term in Eqn. (26). The parameter α_1 is equal to one. These relaxation processes should be linearly coupled to the equilibrium fluctuations. α_2 is found to be smaller showing a value of about 0.2. The small fraction of the modes 2 ($\Gamma = 1.37\ 10^{-6}$) turns out to be invariant too. This spectrum is much broader than the first component.

An interesting example

To identify origins of the second term in Eqn. (25) let us look at the shear-relaxation mode spectra of a natural rubber network loaded with carbon black (volume fraction = 0.18). Filler loaded rubbers built up a non-homogeneous fractal cluster structure [28, 29]. Each primary particle is quasi-permanently linked in the soft rubbery matrix by many adsorption sites (more than 1000 each). The mechanic properties are strongly modified. According to figure 8 we, nevertheless, arrive at a satisfactory representation of the experimental data. The parameter Γ is only different being more than 23 times larger than the one in the unloaded network.

In poly-vinyl-chloride (PVC) the situation is similar. PVC shows small, but very defective crystals [30]. These small crystals should operate like rigid colloid particles multi-functionally linked in the network. We come here to a satisfying reproduction of the data by increasing increase the parameter Γ by a factor of about five.

In both systems the complex pattern of solid colloid particles fluctuates showing the same type of slow modes as observed in amorphous networks. Solid inclusions of colloid particles increases the fraction of the highly correlated and slower fluctuations. The coupling parameter α_2 is in all examples assigned to the value of 0.2. The relative relaxation power increases, but remains nevertheless comparably small (smaller than about $\Gamma = 4\ 10^{-5}$). The extremely small fraction of slow processes obtained for permanent networks ($\Gamma = 1.36\ 10^{-6}$) may therefore be thought to be attributed to cooperative fluctuations of junctions or aggregates of junctions (entanglements or permanent crosslinks). Permanent junctions, entanglements or "tube effects" [31] induce "own" relaxation modes. These slower modes should also isotropically and homogeneously be distributed.

The "freezing point"

At smallest relaxation times one mostly observes a tail of the spectrum which should not be attributed to fluctuations as discussed until now. These "high frequency processes" might run within aggregates the shape of which is "frozen in" [22, 32, 33, 34]. Consequences are illustrated in Fig. 9. We use here a simple approach by defining below
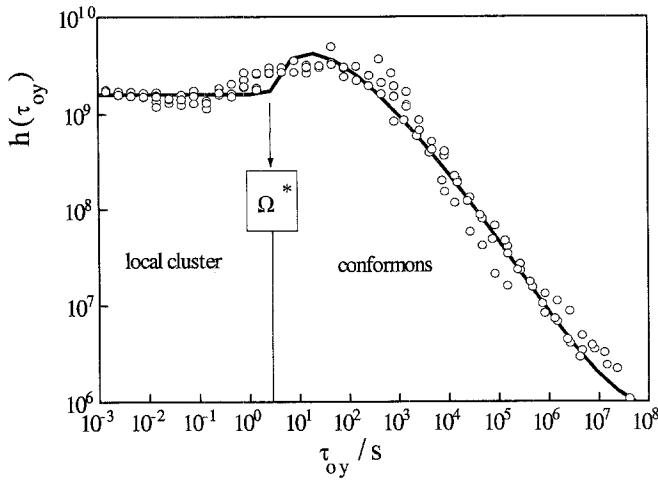
Fig. 9 The "extended" relaxation mode spectrum $h(\tau_{oy'})$, of a PMMA-network [11]: solid line theoretical: $h_h = 3\ 10^9$, $\Gamma = 1.36\ 10^{-6}$, $\alpha_1 = 1$, $\alpha_2 = 0.2$, $H^{loc} = 1.6\ 10^9$, $\Omega^* = 0.1 - 0.4$

$\Omega < \Omega^*$ constant elements, calling them H^{loc}.

$$H = H^{loc}(\Omega < \Omega^*) + H(\Omega \geq \Omega^*) \tag{26}$$

In disordered systems the density in packing of atoms or molecules is limited. The free excess volume should show a minimum value [33–41]. Small and non-fluctuating aggregates are built up. The conformon spectrum should therefore be truncated, cut off at a critical value of about $\log \Omega^* \approx 0.2$–0.5. Below this limit aggregate fluctuations cannot be activated any more. Relaxation might here run via cooperatively coupled local processes which should strongly depend on details in the molecular structure (β-processes).

Ω^* is observed to have about the same value for those systems we have looked at until now. This may be taken to support the iso-excess free enthalpy hypothesis (a generalization of the iso-free volume hypothesis). According to this hypothesis the relative thermodynamic excess properties should be the same [35, 36, 37, 38, 46] at the quasi-static glass transition temperature.

Shear modulus

It is a crucial question whether we can evaluate the components of the complex relaxation shear modulus. At small enough amplitudes the components of the complex shear relaxation modulus are given by the relations [1, 2]

$$G'(\omega) = G_e + \sum_y h(\tau_y) \frac{\omega^2 \tau_y^2}{1 + \omega^2 \tau_y^2}$$

$$G''(\omega) = \sum_y h(\tau_y) \frac{\omega \tau_y}{1 + \omega^2 \tau_y^2} \tag{27}$$

G_e is the static modulus of the permanent network.

With the aid of the Eqn. (25) and Eqn. (27) the components of the complex shear modulus, $G'(\omega)$ and $G''(\omega)$, of natural rubber, PMMA and poly-butadiene networks are fairly well reproduced see figures 10 and 11. In each case the plateau modulus of the network G_e was known from quasi-static deformation experiments.

The shape of the relaxation time spectrum is the same for the networks discussed here (see parameters listed in the legends). The experimental time window determines the WLF-shift of the relaxation mode spectrum. This result manifests universal features of the dynamics in polymer networks. The existence of permanent and quasi-permanent junctions modifies this dynamics. The fraction of slower modes shows topologically the same behaviour as the rapid fraction. Spontaneous decay of slow modes for example has to occur. Cooperative fluctuations of the junctions ensemble maximize the entropy yielding a broadened distribution of the relaxation mode spectrum.

Compliances

Another test of our model is whether the frequency dependence of the complex compliance is understood. For a linear response – assumed to exist even in largely strained networks – the retardation time spectrum $l(\tau)$

Fig. 10 The real part G' and the imaginary component G'' of the complex shear modulus of (A) a NR-network according to [51]. The solid lines are computed with the aid of the equation (27) by using the same parameters as given in the capture of figure 6 ($h_0 = 6.5\ 10^7$ Pa, $\log a_T = 9.5\ 10^8$, $H^{loc} = 1.6\ 10^9$, $\log \Omega^* = -0.4$, $G_e = 0.36\ 10^6$ Pa); (B) PMMA-network according to [11]. Solid lines computed ($h_0 = 7.5\ 10^7$ Pa, $\log a_T = 3.9\ 10^5$, $H^{loc} = 1.6\ 10^9$, $\log \Omega^* = 0.4$, $G_e = 0.9\ 10^6$ Pa)
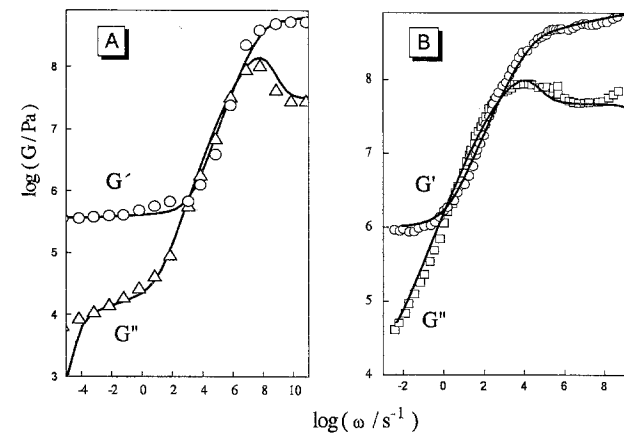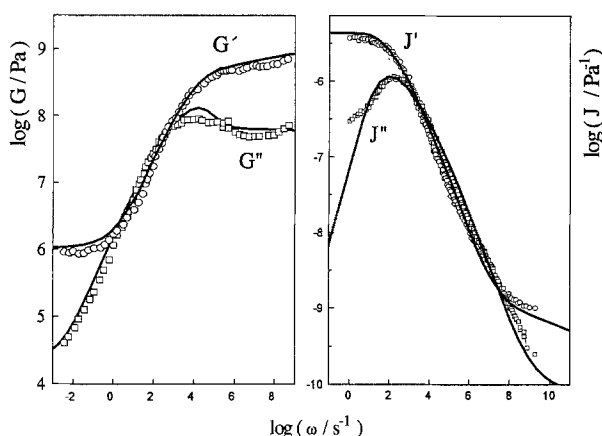
Fig. 11 (A) The real part G' and the imaginary component G'' of the complex shear modulus of poly-butadiene network according to [52]: Solid lines are computed with the aid of the equation (27) by using the set parameters: $h_0 = 1.05\ 10^8$ Pa, $\log a_T = 1.89\ 10^9$, $\Gamma = 2.7\ 10^{-5}$, $\alpha_1 = 1$, $\alpha_2 = 0.2$, $H^{loc} = 1.6\ 10^9$ Pa, $\log \Omega^* = 0.4$, $G_e = 9\ 10^4$ Pa; (B) The real part J' and the imaginary component J'' of the complex compliance of poly-butadiene network according to [53]. The solid lines are computed with the aid of the equation (29) by using the same set of parameters as given above

and the relaxation time spectrum $h(\tau)$ should uniquely be interrelated according to [2]

$$l(\tau) = \frac{h(\tau)}{(G'(1/\tau) - G''(1/\tau) + 1.37\ h(\tau))^2 + \pi^2 h(\tau)^2} \qquad (28)$$

$G'(1/\tau)$ and $G''(1/\tau)$ can be computed with the aid of the Eqns. (25) and (27). $l(\tau)$ is a unique function of $h(\tau)$. The components of the complex compliance are then written as

$$J'(\omega) = J_e + \sum_y l(\tau_y) \frac{1}{1 + \omega^2 \tau_y^2}$$

$$J''(\omega) = \sum_y l(\tau_y) \frac{\omega \tau_y}{1 + \omega^2 \tau_y^2}. \qquad (29)$$

The quality of the calculations is to be seen by the results depicted in the Fig. 12

Dielectric susceptibilities

It is now interesting whether α-process of the dielectric susceptibility can be described. Here we use the "classical" relations [2]

$$\varepsilon'(\omega) = \varepsilon_e + l_\varepsilon \sum_y l(\tau_y) \frac{1}{1 + \omega^2 \tau_y^2}$$

$$\varepsilon''(\omega) = l_\varepsilon \sum_y l(\tau_y) \frac{\omega \tau_y}{1 + \omega^2 \tau_y^2}$$

$$l(\tau_y) \approx \frac{1}{h(\tau_y)} \qquad (30)$$

ε_e is the static susceptibility. The retardation spectrum turned out to be well represented by the approximative relation depicted as the last equation [2].

Non-equilibrium polarization is induced by an electrical field. Depolarization then is expected to run similar as in mechanical experiments. Yet, the response depends on how "depolarization" is coupled on the conformon dynamics. The "retardation power" is fitted by adjusting of the parameter l_ε. The quality of the description is to be seen from the results depicted in the figures 12–13. The model system of poly-methyl-phenyl-siloxane (PDMS) [56] is also very well described (Fig. 13B). From the results shown in Fig. 13A we see that polymer systems behave "*pressure-rheologically simple*". Within the pressure regime of these experiments the shape of the relaxation time distribution is invariant.

This proves the existence of a unique *pressure-temperature-frequency relationship* in accord with the general formulation in Eqn. (4) where the affinity is written as a unique function of temperature and pressure.

Significant now is that the computations were done by only using the first term in Eqn. (25) ($\Gamma = 0$, $\alpha_1 \equiv \alpha$). l_ε gives the relaxation power and is, of course, adjusted. The fraction of the slower conformons seem not to be "dielectrically active" ($\Gamma = 0$). Fluctuations of the junctions ensemble are not "visible". Relaxation processes within small aggregates do also not modify in the dielectric α-process (see table 2) ($H^{loc} = 0$). This leads to the striking "symmetry condition" $\Gamma = 0$.

Fig. 12 $\varepsilon''(\omega)$ of polystyrene (fraction of the mean molecular weight $M = 11000$) at the temperatures as indicated [54]. The solid lines are computed with the aid of the Eqn. (30) by using the parameters $l_e(373.7) = 234$; $l_e = 219$; $\log a_{373.7} = 2.6\ 10^{-5}$; $\log a_{394} = 0.023$; $\Gamma = 0$, $\alpha = 0.35$. H^{loc} is at least more than three orders of magnitude below the value used in describing mechanical experiments: $H^{loc} \approx 0$
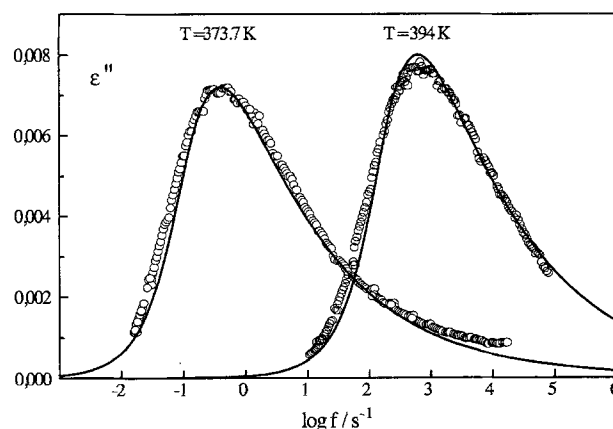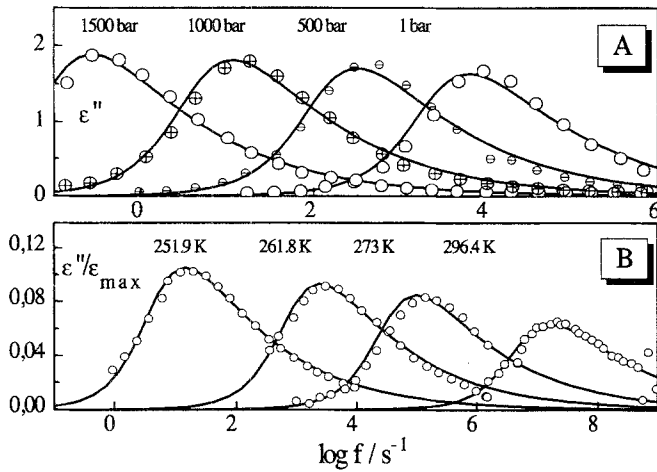
Fig. 13 (A) $\varepsilon''(\omega)$ of PVAC at 353 K and the pressures as indicated [55]. Solid lines computed with $l_e(1500) = 0.86$, $h_0(1000) = 0.91$, $h_0(500) = 1$, $h_0(1) = 1$, $\log a_{1-500} = 1.65\ 10^5$, $\log a_{1000} = 1.44\ 10^{-3}$, $\log a_{500} = 1.65\ 10^{-2}$, $\alpha = 0.45$, $\Gamma = 0$; (B) $\varepsilon''/\varepsilon''_{max}$ of poly(methyl-phenyl-siloxane) $(M_n = 28500$, $T_g = 247$ K) according to [56]. Solid line computed with $l_e(251.9) = 135$, $l_e(261.8) = 246$, $l_e(273) = 285$, $l_e(196.4) = 370$, $\log a_{251.9} = 0.96\ 10^{-3}$, $\log a_{261.3} = 0.13$, $\log a_{273} = 2.82$, $\log a_{296.4} = 9.4\ 10^2$, $\alpha = 0.4$; $H^{loc} = 0$; $\Gamma = 0$
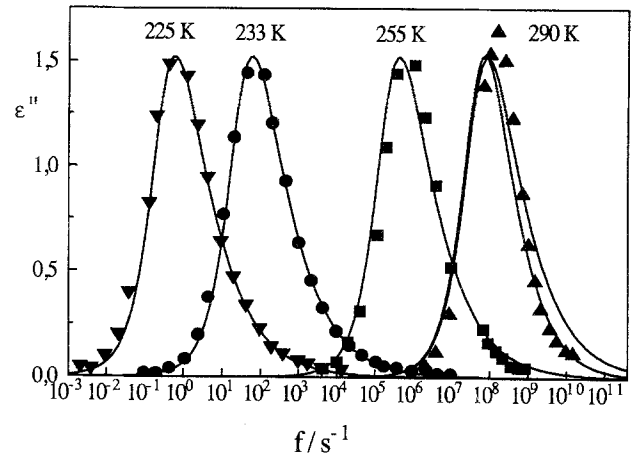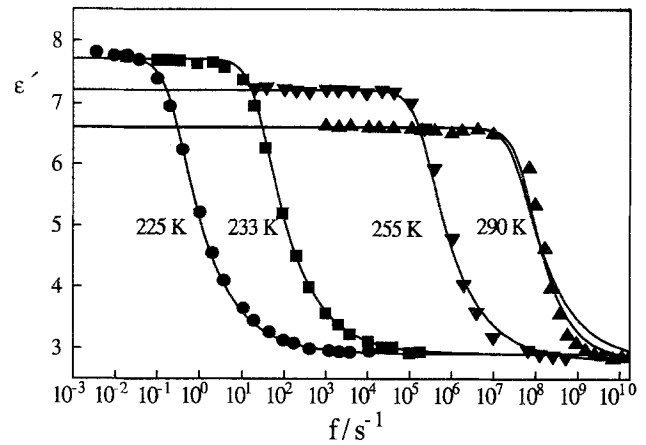
Table 2 Dielectric susceptibilities

$\alpha = 0$, 35–0.8; $\Gamma = 0$
l_e adjusted

α-relaxation in low-molecular weight glasses

Up to now we considered polymer systems. Yet, a glass-transition is also observed in many low molecular weight "glass-forming" systems [3, 39]. It is a crucial question whether we succeed in describing these α-processes. They were extensively discussed in literature [1, 2, 3, 4, 39, 40, 40]. We select representative examples.

We present in figure 14 the dielectric susceptibilities in super-cooled salol measured over a larger temperature regime according to [57]. The solid lines are computed with $\Gamma = 0$ and the parameters as listed in table 3. l_e freely adjusted shows different values for both ε' and ε''. At high frequencies ε'_e falls systematically to slightly lowered values when the temperature is raised. The dashed curve at 290 K is computed with $\alpha = 0.6$. At elevated temperatures relaxation is enhanced $(\alpha = 0.8)$. The "width" of the relaxation mode spectrum is reduced.

Glass-forming low molecular weight systems show analogous fluctuations as polymer networks. The system studied here behaves not thermo-rheologically simple everywhere. This is in accord with the conclusions drawn in the literature [3, 12, 47].

Fig. 14 The real (a) and imaginary parts (b), ε' and ε'', of the dielectric susceptibility of salol as functions of frequency at the labelled temperatures according to Dixon et al. [57]. Solid lines computed, parameters in Table 3
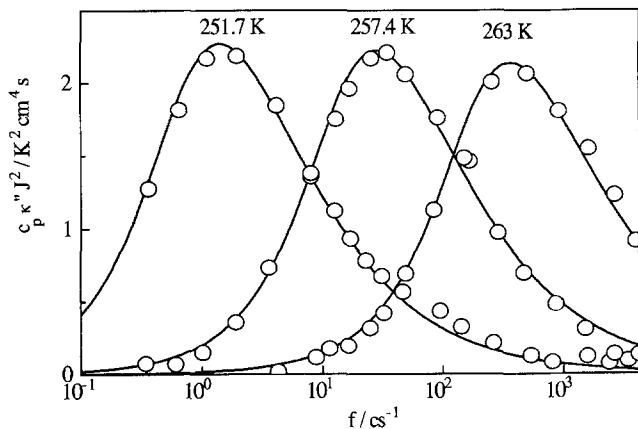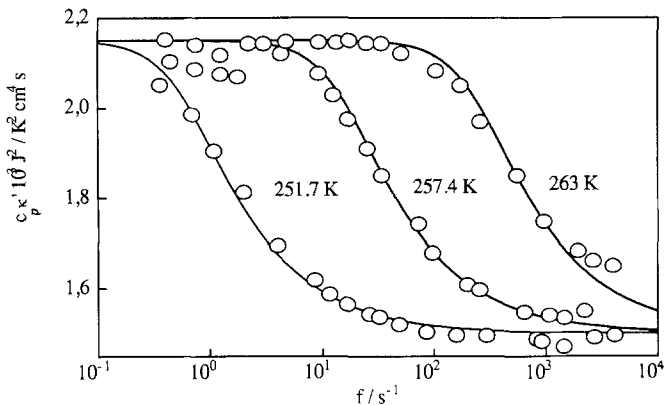
Table 3 Salol

$\Gamma = 0$				
T/K	225	233	255	290
α	0.6	0.6	0.6	0.6/0.8
$\log a_T$	$6.6\ 10^{-5}$	$7.8\ 10^{-3}$	78	$6.5\ 10^{34}$
ε'				
l_e	0.36	0.36	0.37	0.39
ε_e	3	2.95	2.9	2.8
ε''				
l_e	0.37	0.37	0.37	0.33

Next, we show the reactive and absorptive components of a susceptibility, essentially the dynamic specific heat c_p, measured by Dixon and Nagel [65]. Fitting the value in the glass $(c_p\kappa)'_{glass}$ the data are nicely reproduced. The parameter α must be put to the value of 0.62 (see Fig. 15). A problem is that the factor l_0 of $(c_p\kappa)''$ is obtained to be 2.8 times larger that the one of $(c_p\kappa)'$. These experiments are

not isothermal [16–20]. Without discussing the problems we rest content that our description reproduces the data with a fixed set of fundamental parameters (see Fig. 15). Within the small temperature range of these experiments, these systems behave thermo-rheological simple. Interesting is that the imaginary part of the complex dielectric susceptibility, ε'', can be reproduced by using about the same parameter as for polymer systems ($\Gamma = 0$; $\alpha = 0.5$, l_0 adjusted) (see Fig. 15).
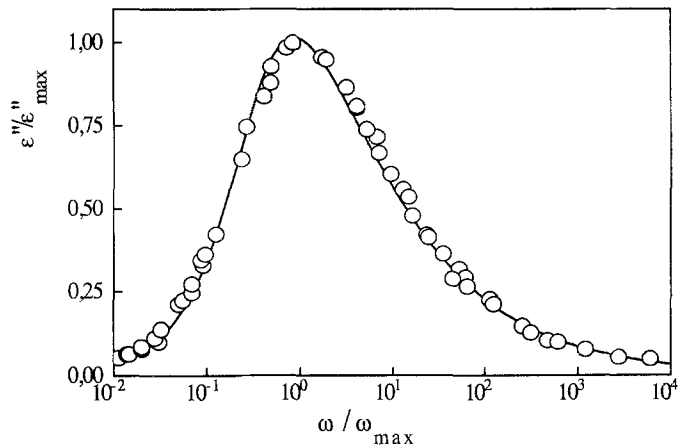
We recognize that different physical processes might be individually coupled on the dynamics. This yields to special features essentially in low molecular weight glass formers. Differences are indicated with slightly enlarged values of the coupling coefficient α. It is a challenge to develop an interpretation of the power law as defined in the Eqn. (20).

Another well known glass forming system is the mixed salt 0.4 Ca(NO$_3$)$_2$ 0.6 KNO$_3$ (to be referred as CKN [3, 4]. Here, the quality of the description is to be seen by evidence from the plot in Fig. 16. The original data have been rescaled and normalized by Fuchs et al. [4]. We now succeed in describing these data with the parameters $\alpha = 0.6$; $\Gamma = 0$; $l_0 = 7.26$. Ultrasonic longitudinal waves produces density fluctuations. We therefore have to conclude–and there are other results not given here–that *the volume relaxation mode spectrum should have same shape as the shear relaxation mode spectrum.*

Interesting are dielectric studies of dilute solutions of small polar molecules in the supercooled liquid state [41]. Solutes of different size and shape in (essentially) non-polar solvent ortho-terphenyl were investigated. The experimental data in Fig. (17) are fairly well described *not*

Fig. 15 Reactive (a) and absorptive part (b) of the frequency dependent product $c_p\kappa$ of the specific heat c_p and the heat conductivity κ form ortho-terphenyl (OT) plus 9% ortho-phenyl phenol [58]. The solid lines are computed with equation 26: $\alpha = 0.8$; $\Gamma = 0$, $(c_p\kappa)_{glass} = 1480$ J^2/K^{2}cm^{4}s, $l_e(\varepsilon') = 0.289$J^2/K^{2}cm^{4}s, $h_0(\varepsilon'') = -0.357 = l_e(\varepsilon')$, $\log a_{251.7} = 2.95\ 10^{-4}$, $\log a_{257.4} = 5.6\ 10^{-3}$, $\log a_{263} = 0.078$. (C) normalized dielectric permittivity, solid lines computed with $\Gamma = 0$ and $\alpha = 0.8$
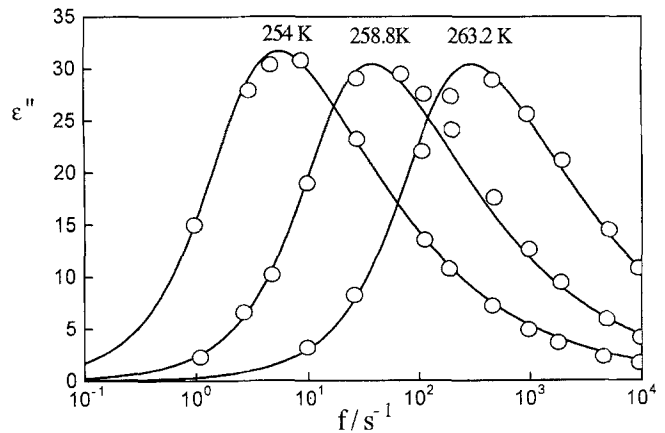

Fig. 16 Dielectric loss data measured for OT with 4.2% anthrone by Williams and Hains [59] plotted as normalized spectrum. The data represent a master curve for different temperatures. The solid line is theoretical with $\Gamma = 0$; $\alpha = 0.5$; $l_e = 1.63$, $\log a_T = 5.4\ 10^{-5}$

Fig. 17 See text for explanation

showing any effect originated with the low concentrations of the polar solute. Similar effects were observed in polymer solutions [2].

Hence, the fluctuation dynamics in super-cooled liquids involved here and detected by dielectric measurements is characterized by the universal reduced spectrum independent of the constituents, polymers, networks or low molecular weight molecules.

Final remarks

In many papers [1, 2, 3, 4, 47, 48, 42, 43, 44, 45, 46, 47] the α-process was studied and interpreted. The mode coupling theories [3, 4, 12] offer interesting and new descriptions. Here, we propose now the *conformon model as alternative.* It is based on the intuitive definition of stationary modes in disordered dynamic systems like liquids where the elements are not localized.

In (super-cooled) liquids which are in equilibrium it is assumed that a broad set of cooperative modes (conformons) comes in existence. A conformon represents an stationary mode in a dissipative system with an "internal stationary dynamics". Each conformon always changes its configuration so as to occupy in time a well defined number of iso-energetic conformations. At each moment conformons represent one of their many equivalent realizations of the activated mode. The mean conformational entropy is then adjusted so as to fulfil the condition of "saturation" as formulated in the equation (13) (first condition of saturation).

Conformons can be created or annihilated. But they suffer also spontaneous decay. All conformons linked in the same "heat bath" (scalar, isotropically and homogeneously) the energies put into may then be used for newly activating conformons. In stationary equilibrium Boltzmann's law fixes the equilibrium density of conformons of different energy. Gas like mixing of the whole set of conformons maximizes the entropy and the energy density distribution of conformons results analogously as for electro-magnetic modes in an enclosure. The ratio of the total energy and entropy is fixed to a well defined value (second saturation condition). *The reduced conformon spectrum itself is universal.*

Most important is, of course, that the conformon model describes also the thermodynamic limit. This leads straight forwardly to analogues of Boltzmann's law and Wien's displacements law [32]. The latter one demands for example that the volume of liquids should grow linearly with temperature. That the temperature dependence of the specific heat capacities in *n*-alkane melts and mercury melts show the typical T^3-dependence strongly supports the reliability of our model. It proves that conformons

should obey a photon statistics. This statement is also in accord with the finding that "excess Debye–Waller factor" as deduced from incoherent neutron scattering experiments [48] above the Vogel–Fulcher temperature can as well be described within the framework of the conformon model.

Within the framework of out model it seems to suggest itself that freezing of fluctuations is coming about if there the changes of place are more and more reduced und therewith the dynamics which allows to minimize the free energy by maximizing the entropy per each mode.

According to the principles of thermodynamics of irreversible processes fluctuations and relaxation should strictly be interrelated. In our model relaxation is treated as "intra-conformon" process the rate of which decreases with number of equivalent complexions, Ω_y. This is the reason why a broad relaxation mode spectrum comes about. The coupling parameter α defines empirically how the relaxation mode τ_{oy} and the number of complexions, Ω_y are linked together. The simple kinetic scaling by factorizing each mode in the same manner should be understood as to define a mean "mobility" of the elementary units in the liquid.

A unique behaviour is also indicated with the finding that dielectric relaxation in the α-regime of the systems involved here does not vary so much with the molecular conditions (with exception of the relaxation power). Different polymers, low molecular compounds and anorganic salt mixtures can in any case be described by using about the same coupling coefficient α ranging from 0.35 up to 0.6–0.8. Recently, we proved that the molecular weight dependence of the kinetic factor agrees with what is known from viscosity measurements [2]. According to this result the relaxation mode spectra in low molecular weight glass former melts should exhibit larger coupling parameters. Relaxation should then on average run more rapidly as in polymers ($\alpha_{low} > \alpha_{poly}$) and the width of the relaxation mode spectrum should be smaller for low molecular weight glass formers.

The α-process in mechanic experiments on polymer networks is more complex because fluctuations on the "global level" can be measured. To identify dissipation with a relative relaxation power of about $\Gamma \sim 10^{-6}$ elucidates the outstanding accuracy of the mechanical measurements. The whole shear relaxation mode spectrum turns out to be strain-, strain rate- and strain-type-invariant. Moreover, there are evidences that the shape of the volume relaxation mode spectrum is the same as the shear retardation spectrum.

For high frequency processes the eigen-volume of the molecular elements come into play. Below the critical complexion number $\log \Omega^* \approx 0.2$–0.6 one observes many rapid, but also cooperative relaxation mechanisms. They

cannot be related to conformational fluctuations. These cooperative relaxation processes run probably within somehow fixed aggregates. We discuss these matters in subsequent paper where we shall treat "β-relaxation processes" [1, 2, 3].

With the knowledge of the conformon spectrum and the way how relaxation is coupled on the dynamics many interesting and new interpretations of experiments are possible. This holds essentially true when the spectrum is composed of components which are not only differently coupled to the fluctuations but show also a different kinetics (different dependencies of the shift-factors).

The imperative influence of the fluctuation dynamics in (glass-forming) liquids turns out to be overwhelming [1–12, 38, 47]. We shall show in another paper that the dynamic structure factor as deduced from incoherent neutron scattering and the photon-photon correlation of polymers and low molecular weight glass formers can be described by using the conformon model [49].

The conformon model is an intuitive treatment of fluctuations in liquids. These systems behave complex because of showing dynamic properties in between the ones of crystals (phonons as quasi-particles) and gases. The deduction of the central and empirical equations employed here (the stationary modes, the power law and the Vogel–Fulcher relation) has not been the aim of the present paper.

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