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   CONDENSED MATTER AND POLYMER PHYSICS

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11. **ABSTRACT**
    The Electronics Technology Division requires understanding of their mission and related problems of novel phenomena and materials with unusual properties for possible device applications. Theoretical and numerical modeling was conducted to obtain a fundamental understanding of low frequency dynamic responses of condensed matter with emphasis on polymers, photoelectronic materials, semiconductor interfaces, amorphous metals and amorphous semiconductors.
1.0 INTRODUCTION

The work consisted of writing, modifying, and running computer programs in BASIC and Fortran and using these computer codes for theoretical modelling of the NRL theory of low frequency relaxation phenomenon. Data analysis performed included work on dynamics of entangled polymer melts, physical aging of glasses, dielectric relaxation near the glass transition, and transient luminescence, transport and photoconductivity in chalcogenide glasses. Specifically, the following physical problems were theoretically modelled and compared with experimental data.

2.0 POLYMER MELTS

Application of the NRL model to polymer melts provides a quantitative explanation for the viscoelastic properties of entangled polymer chains including \( G(t), G''(\omega), G^*_{\omega} J^* \) and \( \eta \) as well as their molecular weight dependences. The model predicts simultaneously the temperature dependence of \( \eta \) as given approximately by the Vogel form and the shift factor \( a_T \) in the WLF form. Modelling is quantitatively successful for entangled linear as well as branched polymers.

3.0 PHYSICAL AGING

Aging effects are found to be contained in an increase in the NRL model parameter \( \eta \) as aging proceeds, resulting in a shift of the entire spectrum of relaxation times. The class of creep compliance functions corresponding to the NRL model relaxation modules turns out to naturally describe Andrade creep behaviour and at long times produces flow like behaviour. The modelling allows quantitative comparisons with creep measurements on glasses, amorphous metals, and polymers.

4.0 Na\( \delta \)-ALUMINA

Frequency and temperature dependences of the dielectric response of the fast ionic conductor Na\( \delta \)-alumina is found to be described by the NRL model. In particular unusual properties in the region from 50 to 300K, in which a transition from a glass-like to a liquid-like phase takes place now be understood by means of this modelling of Na\( \delta \)-alumina data.

5.0 TRANSPORT IN CHALCOGENIDE GLASSES

The chalcogenide glasses are the most thoroughly studied amorphous semiconductor systems. The transient transport data, transient optical data, dynamical dielectric relaxation data, and the volume and enthalpy recovery data of chalcogenide glasses are found to conform to the NRL model predictions. All the available data
has been analyzed, in particular the recent transient optical and transport data, allowing for the first time a clear distinction between predictions of various models. NRL model behavior is found in all cases and transport by small polaron hopping is confirmed.

6.0 PUBLICATIONS

The attached paper resulted from work done on the contract.
STRESS RELAXATION AND LOSS MODULI MEASUREMENTS IN LINEAR AND BRANCHED POLYMER SYSTEMS CORRELATED WITH STEADY STATE VISCOSITY: MOLECULAR WEIGHT DEPENDENCIES

by

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Nearly a decade ago, de Gennes\textsuperscript{1} introduced the concept that entangled polymer chains relax by reptation. Doi and Edwards (DE)\textsuperscript{2} have developed a model relating the dynamics of reptating chains to viscoelastic properties. They assumed that in polymer melts and solutions with chain entanglements, reptation would be the dominant motion. The stress relaxation modulus $G(t)$ in the terminal region has been given and from it the plateau modulus, the viscosity $\eta$ and the recoverable compliance $J^e$ can be obtained together with their dependences on $M$, in particular for $M$, in close agreement with the $M^\alpha$ law of large mol. wt. linear polymers.

Acceptance of the de Gennes-DE model will follow confirmation by microscopic probes such as neutron scattering. Unfortunately, the results of a recent experiment\textsuperscript{3} designed for such a test fail to support the existence of reptation. Until reptation is confirmed we must be aware of it being at the present time an assumption. The purpose of this work is to show that the fundamental mechanism (FM) behind a unified model (UM) of dynamical processes in condensed matter\textsuperscript{4} readily provides an explanation for the $M^\alpha$ dependence, as well as viscoelastic properties including $G(t)$, $G''(t)$, $G_\Phi$, and $J^e$. The reptation assumption is not required.

Besides, the same FM predicts simultaneously the temperature dependence of $\eta$ as given approximately by the Vogel form, and the shift factor $a_0$ in the WLF form.\textsuperscript{5} The reptation model, however, does not address the temperature dependence problem at all. Moreover, the UM is applicable to both entangled linear and branched polymers, while the reptation model in its present form is inapplicable to branched polymers.

No coherent description of the FM and the UM will be attempted here. For details the reader is referred to Refs. 4-9. It has been shown that the relaxation rate $\gamma_i$ of a mode $i$ is modified by the FM to be time dependent according to $\gamma_i \sim (\omega_0 - \omega)^{-\alpha}$ where $\alpha = 0.577$, $\omega_0$ is a cut-off frequency and $\alpha$ is the infrared divergence exponential with $0 < \gamma < 1$. The rate equation for mode relaxation is modified from $dQ_i/dt = -(1/\tau_i)Q_i + dQ_i/dt$ as $\omega(t) = (\omega_0 - \omega)^{-\alpha}$. The solution of which is $Q_i(t) = Q_i(0) \exp[-(\omega_0 - \omega)t/(1-n\eta)]$ where $Q_i(0)$ is modified by the PH to be time dependent. According to $Q_i(t) = Q_i(0) \exp[-(\omega_0 - \omega)t/(1-n\eta)]$.

When $n=0$ reduces to $Q_i(t) = Q_i(0) \exp[-(\omega_0 - \omega)t/(1-n\eta)]$.

This specific fractional exponential relaxation function being a consequence of a FM has led us to work out its unifying predictions in many fields and materials. We point out here the aforementioned shift from $\omega_i$ to $\omega_i$, which we shall in this work use to derive the $M^\alpha$ relation, etc., has been repeatedly tested and verified in other areas including electron transport\textsuperscript{10,11} in amorphous SiO, and chalcogenide glasses, ion transport in conductors,\textsuperscript{11} dielectric and structural relaxations near $T_c$ for polymers and small molecule glasses,\textsuperscript{12} relaxation of bulk polycarbonate,\textsuperscript{13} volume recovery\textsuperscript{14} of PVA, etc.

To start with consider the Rouse model. The Rouse modes have periodic functions of bond positions along the chain. The $i$-th mode has characteristic period equal to $N/\omega$ and relaxation time $\tau_i = \omega_i^2 \tau_c$ where $\omega_i$ is the monomer mol. wt. and $\tau_c$ is the friction coefficient.

The lower modes govern the large scale motions and have the longest relaxation times. The Rouse model gives a good description of data on linear chain polymers of low mol. wt., with $M^\alpha$ for $N \ll \gamma$. For longer chains, $\eta$ is a much stronger function of $N$. For $N \ll \gamma$, the $M^\alpha$ power dependence holds.
In some linear systems $\mu$ appears to be larger than 3.4. In branched systems, $\mu$ can be considerably larger especially at high mol. wts. The change in $N$ dependence occurs smoothly as $N$ varies. When $N$ exceeds $N_{\mu}$, a plateau region appears in $G(t)$, $G'(t)$, and $G''(t)$ where $G''(t)$ decreases and $G'(t)$ increases. These $N$-dependence are a direct indication of chain entanglement which sets in when $N > N_{\mu}$, and gives rise to a temporary network structure due to interlocking of the chains. Thus the onset of entanglement introduces a coupling between chains. If $N$, the average mol. wt. between entanglements is commonly defined through the plateau modulus by $N = \mu \rho T / G^*$, the number of entanglements per molecule is $N/N_{\mu}$.

Internal Rouse modes with $1 > N/4M = 1$ involve cooperative motions over distances smaller than the entanglement spacing. They are of sufficiently short range and are unaffected by entanglement coupling. In our model this implies the coupling of the $i\bar{i}$ Rouse modes to the correlated states in the polymer melt so solution cannot occur through the entanglement junctions and it is so weak that effectively $n_{\mu} = 0$ for all $i\bar{i}$, and these are unshifted. On the other hand, lower modes motions with $i < i\bar{i}$, which impose cooperations that extend beyond the entanglement spacing, are coupled via the entanglement junctions to the correlated states of the polymer system and have nonzero $n_i$ values. These modes are slowed down and accounted for Eq. (1) their $\tau_i$'s are shifted to the large $\tau_i$ values. This is because $w_i > \tau_i$ which follows from the expected size $N_{\mu}$ of $w_i$ and the typical relaxation times in the plateau region and the terminal zone. The degree of cooperation is largest in the motion of the terminal relaxation mode $\tau_{i\bar{i}}$ and decreases as $i$ increases. Hence $n_i$ is maximum for $i\bar{i}$ modes and decreases as $i$ increases towards $i$. The "gap" in the relaxation time spectrum between the other $i\bar{i}$ modes and the $i\bar{i}$ node creates a plateau region. The gap is not a true gap, having some contributions from the higher $i$ modes in the group $i < i_1 < \cdots < i_n$ that have smaller $n_i$ and thus smaller shifts from $\tau_i$ to $\tau_i$ in other words, since $n_{i_1} > n_{i_2} > \cdots > n_{i_n}$ the shift $\log \tau_{i_1} - \log \tau_i$ is not uniform with respect to $i$. The transition region comprises an unshifted Rouse spectrum of $i\bar{i}$ modes. Each of the $i < i_1$ modes is individually shifted and adjusted to have the fractional exponential form of $\exp(-t/\tau_i)$. The $\tau_i$ now characterizes the time scale of the $i$-th non-exponential relaxation mode. The spacings between the $\tau_i$'s are different, much more nonuniform and wider than the rigidly shifted Rouse spectrum. This can be seen from Eq. (1) as due to the $(1-n_{i_1})$ power and that $n_{i_1} > \cdots > n_{i_n}$. The resulting spectrum, even though individual components are nonexponential, is much narrower than the rigidly shifted Rouse spectrum as we shall see later. Recall that $\tau_{i_{\mu}}$ for all $i$. However, $\tau_i$ for $i < i_1$ is shifted to $\tau_i$ which now varies as $N^{-1}$. Since $27(1-n_{i_1})22$ we see the pseudo-gap or the plateau region widens as $N$ increases. The separation between $\tau_i$ and $\tau_i$ is much larger than that between $\tau_i$ and $\tau_{i_{\mu}}$. Hence the terminal region is limited entirely due to $\tau_i$. $\tau_i$ is proportional to $N^{-1}$. Its contribution to the viscosity $\eta$ according to the Rouse model is $(\pi N^2/\mu T) \omega_0 \mu^{-1}$. That the terminal relaxation time $\tau_{i_{\mu}}$ and $\eta$ have different $N$-dependences is not in agreement with experiment. This last failure is not surprising because the Rouse model should not be applicable in its original form at high mol. wts. Entanglement means the chain cannot execute all Rouse-like motions. Some special confinement such as the fixed tube used by DE is appropriate though the total suppression of sustained transverse motions in the tube model is unrealistic. Nevertheless we consider next the chain in the tube and consider all the results with our FH. The reader should realize that the tube model referred to here means only chain confinement by a tube and no reptation is involved. In fact the thrust of this work is to show that, without the reptation hypothesis, the FH which has already explained many properties in other related and unrelated fields, once more satisfactorily accounts for the polymer melt properties when the chain is confined in a tube.

The development initially follows closely the works of DE and of Grassley except we replace the reptation modes by our FH shifted fractional exponential relaxing Rouse modes with shifted $\tau_i$ for $i < i_{\mu}$. Configuration rearrangements in
within the tube model. The plateau region has some contribution from the unevenly shifted (i.e., \( n=0 \)) Rouse modes for \( i=1 \).

The plateau region has some contribution from the unevenly shifted (i.e., \( n>0 \)) Rouse modes for \( i=2, 3, \ldots \), -1 in a tube. The derivation of a rheological constitutive equation within the tube model by Doi, and the predictions of stress-strain experiments which follow from this, is largely unaffected by our replacement of reptation dynamics by Fl dynamics. This is due to the approximate factorizability of the time dependence and the strain dependence. Thus many of the successful rheological predictions of DE are carried over into our model while we also retain the advantages of the Fl dynamics. We present finally the predictions of our model for both linear and branched polymers. The results are displayed in Figs. 1-6. The \( G'(\omega) \) data and the predictions are both for the terminal zone. Note that for concentrated solutions of linear polymeric melt (Fig. 1), the \( G'(\omega) \) dispersion is well fitted by model prediction with \( n=0.925 \) which at the same time predicts both \( \eta \) and \( \eta' \) should be on with \( \mu = 2/(1-0.475) = 3.8 \). On the other hand branched polymers (Fig. 4) of lower mol. wt. than that in Fig. 2 requires \( n = 0.56 \) to 0.61 which predicts \( \mu \approx 4.5 \) to 5.1. Our model predicts that dispersion of the viscoelastic functions (determined by \( n \)) at the terminal region is correlated with the Fl behavior via the relation \( \eta^p_a = 2/(1-n) \) and the size of \( JG_0^N \) via the relation \( JG_0^N = (1-n)/(2/(1-n_i)/I^2) \). For linear polymers, typically we find from dispersion that \( n \) ranges between 0.4 to 0.5 for HDPE. These \( n \) values give 3.26 for 2 and 25.0 for 20, all in agreement with data. For branched polymers, \( n \) typically has larger values which implies larger \( \mu \) and \( JG_0^N \). When \( n \) is a function of \( N \), the model further predicts that both \( \eta \) and \( JG_0^N \) become \( N \) dependent. All these features are in remarkable agreement with data. Details and further implications of the model will be presented elsewhere.

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Fig. 1
Loss Modulus for Polystyrene Halt
\(G' = 215,000\) for Polystyrene
Solid Curve:
\(n = 0.425\)

Fig. 2
Loss Modulus for 4-arm Polystyrene
S181A, \(\bar{M}_n = 18.27 \times 10^5\)
- 105 °C
- 170
- 208
Solid Curve:
\(n = 0.7\)

Fig. 3
Relaxation Modulus Data (+)
32.6% Solution of Polyethylene in Aromatic
Solid Curve:
\(n = 0.475\)
\(k = 4\)
\(\omega = 3.8 \times 10^8\) radian/sec

Fig. 4
Relaxation Modulus Data for 4-armed Star-shaped Polystyrenes
- CS-81
- CS-99
- CS-25

CURVES:
1 - \(n = 0.61, L^* = 4, \omega = 0.8 \times 10^8\) sec
2 - \(n = 0.68, L^* = 4, \omega = 3.8 \times 10^8\) sec
3 - \(n = 0.50, L^* = 4, \omega = 1.5 \times 10^8\) sec