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A simple model for relaxation phenomena in linear polymer chains

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Abstract. A quasi one-dimensional kinetic Ising-like model is developed to study relaxation phenomena in linear polymer chains. In the case where the number N of bonds in the chain is very large, the model Hamiltonian reduces to the one giving the intramolecular energy of the Gibbs–di Marzio lattice model. The equations governing the dynamics of the different correlation functions are derived for this model and used to study relaxation phenomena in the system in the long-chain limit. First, the dielectric response where two cases are considered, namely, a single dipole placed in the middle of the chain and N non-interacting dipoles. In both cases a Debye behaviour is obtained. The effect of the temperature is introduced by considering a temperature-dependent relaxation time and surprisingly good agreement between the temperature dependence of the frequency of the maximum of the loss curve as computed with the model and experimental data of PMA and PVAC is obtained. Second, the relaxational heat capacity is analogously calculated; in this case, however, although the parameters used in the actual computations correspond to PMA and PVAC, respectively, no comparison with actual experimental results was feasible. One finds that here the behaviour is not Debye and no simple universality arises from the theoretical predictions.

1. Introduction

The glass transition in supercooled liquids has been the subject of numerous studies in the past few decades. Experimentally, the techniques that have been most widely employed to probe the response of the system to an external perturbation include ultrasonic absorption, thermal spectroscopy, dielectric relaxation, photon-correlation spectroscopy and light and neutron scattering. This response may be described either as a function of time $\phi(t)$ or as a function of frequency $\psi(\omega)$ (generalized susceptibility) which are of course simply related to each other. The theoretical calculation of $\phi(t)$ or $\psi(\omega)$ in terms of molecular parameters rests on the possibility of devising a microscopic model in which the main characteristics of glass-forming systems are embodied. This is clearly an unresolved problem in general and hence for convenience of the analysis many empirical expressions involving adjustable parameters have been widely used: Two common forms for $\psi(\omega)$ and $\Phi(t)$ are the so-called Cole–Davidson formula

$$\psi(\omega) = (1 + i\omega\tau)^{-B}$$

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and the Kohlrausch–Williams–Watts (kww) expression

$$\Phi(t) = \exp(-t/\tau)^b$$

where τ is the relaxation time, and B and b are two parameters whose value lies between zero and one. In the case that $B = b = 1$ these two relations reduce to those of the ideal linear Debye relaxation process.

On the other hand, there is ample evidence that some kind of ‘universality’ is present both in the anomalous kinetic properties and in the abrupt changes in thermodynamic properties exhibited by supercooled liquids in the vicinity of their glass transition. This suggests that a theory for the kinetic properties of glass-forming systems should be intermingled with equilibrium considerations. In particular, despite still being a source of controversy concerning its ability to actually model the glass transition, a rather successful model for the description of the thermodynamic properties of linear polymers around the glass transition temperature T_g is due to Gibbs and di Marzio [1]. The aim of this paper is to develop a stochastic model for relaxation phenomena in linear polymers whose Hamiltonian is closely related to the one of the Gibbs–di Marzio theory.

As discussed below, the Hamiltonian in our stochastic model is Ising-like. It must be stressed that the use of kinetic Ising models for polymer dynamics to model cooperativity is not new [2, 3]. The novel features introduced in this paper are, on the one hand, the explicit connection with the microscopic parameters of a successful equilibrium model and on the other a ‘rule of transition’ that, while related to the Glauber dynamics [4], also incorporates the basic element of the equilibrium model (the notion of a ‘flex’, to be specified later) into the dynamics.

We are fully aware of the fact that this quasi one-dimensional Ising model can only yield a phase transition at zero temperature. Therefore the explicit consideration of the glass transition cannot lie within the scope of our purposes; the same applies to the question of whether the Gibbs–di Marzio theory is appropriate to discuss glass-like phenomena. Rather, it should be clear from the outset that our main goal is to investigate the importance of a topological concept, namely that associated to the flex, on the dynamical properties of linear polymer chains in the simplest possible way.

The paper is organized as follows. In the next section we present the main characteristics of our model for a linear polymer and derive the time evolution equations for the appropriate moments of the probability distribution function. In section 3.1 we compute the dielectric relaxation response function both for a single dipole and for N non-interacting dipoles in the limit of very long chains. In section 3.2 we calculate the relaxational specific heat. In section 4 we discuss these results, we compare them with experimental data, when possible, and give some concluding remarks.

2. The model Hamiltonian

In this section we present the main features of our model for a linear polymer chain.

The chain is visualized as made up of N segments each of which may be found in two orientations with respect to the axis of the backbone chain. Interactions with the surroundings are responsible for random transitions between both states. In stochastic terms this is described by the use of a time-dependent random variable assuming the values ∓ 1 , designating the two possible states. For the m th segment the assignment of

∓ 1 to $\sigma_m(t)$ would then describe the orientation of segment m at time t . Hence, the configuration of the chain is specified by the set of values $\{\sigma_1, \sigma_2, \dots, \sigma_{N-1}, \sigma_N\}$ at any given time t . The cooperative interaction between adjacent segments is introduced in the model through an Ising-like Hamiltonian of the form

$$\mathcal{H} = -\frac{1}{2}(\varepsilon_2 - \varepsilon_1) \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} + \frac{1}{2}(N-1)(\varepsilon_1 + \varepsilon_2) \quad (1)$$

where ε_1 and ε_2 are the energy parameters in the Gibbs-di Marzio [1] model and $N = x - 2$ with x being the number of 'monomers' in the same model. The second term on the right-hand side of equation (1) has been included in order to recover the equilibrium results of the Gibbs-di Marzio lattice model. A flex occurs in the chain whenever $\sigma_{i-1} = -\sigma_i$. Notice that if we identify

$$f = -\frac{\sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}}{2(N-1)} + \frac{1}{2} \quad (2)$$

as the fraction of flexes with respect to the total number $N-1$ of possible flexes, for a very long chain the energy computed with the Hamiltonian in (1) reduces precisely to the Gibbs-di Marzio total intramolecular energy.

Since flexes play a key role in such a model, we are interested in configurational changes in which a single flex is created or destroyed when a transition takes place. Therefore, we adopt as our 'rule of transition' one in which, if the transition is associated with the i th segment, all previous segments retain their values while the i th and all subsequent segments change sign. Symbolically,

$$T_i\{\sigma_1, \sigma_2, \dots, \sigma_i, \sigma_{i+1}, \dots, \sigma_{N-1}, \sigma_N\} \rightarrow \{\sigma_1, \sigma_2, \dots, \sigma_{i-1}, -\sigma_i, -\sigma_{i+1}, \dots, -\sigma_N\} \quad (3)$$

This rule may appear at first sight as rather restrictive, but on the one hand it is the simplest possible case involving a single flex while on the other its usefulness may be judged *a posteriori*. Other possibilities could be analysed but at the expense of more complicated mathematics not necessarily yielding to analytical results.

Let $P(\{\sigma^N\}, t)$ denote the probability that the chain has the configuration $\{\sigma_1, \sigma_2, \dots, \sigma_N\}$ at time t . Since for $t \rightarrow \infty$ this probability should be proportional to the Boltzmann factor, using detailed balance and following the methods outlined in the papers by Orwoll and Stockmayer [2], Isbister and McQuarrie [3], Glauber [4], Suzuki and Kubo [5] and de Oliveira *et al* [6], one finds that the transition probabilities for our rule (3) are given by

$$W_1 = \alpha' \\ W_i(\sigma_{i-1}, \sigma_i) = \alpha(1 - \beta\sigma_{i-1}\sigma_i) \quad i = 2, 3, \dots, N \quad (4)$$

where α and α' are two proportionality constants which determine the time scale of the motion, $\beta = \tanh((\varepsilon_2 - \varepsilon_1)/2k_B T)$, k_B is Boltzmann's constant and T is the absolute temperature. The form of W_1 takes into account the fact that if segment 1 is the one involved in the transition, although in principle we have a change in configuration, the energy of the chain remains unaltered and no flex is created or destroyed. For simplicity we consider that segment 1 is fixed so that $\alpha' = 0$. As far as α is concerned, for the time being, we will take it as a constant but it must be borne in mind that the time scale of the motion is temperature dependent. Therefore it will come as no

surprise that eventually the temperature dependence of α will be an important factor in our later development. Using the transition probabilities given by (4), with $\alpha' = 0$, one may write a master equation for $P(\{\sigma^N\}, t)$ as

$$\frac{dP(\{\sigma^N\}, t)}{dt} = - \sum_{i=1}^N W_i(\sigma_{i-1}, \sigma_i) P(\{\sigma^N\}, t) + \sum_{i=1}^N W_i(\sigma_{i-1}, -\sigma_i) P(T_i\{\sigma^N\}, t). \quad (5)$$

The solution to (5) would of course contain the most complete description of the system available. However, the dynamical properties we are interested in, require only the knowledge of some moments of the probability $P(\{\sigma^N\}, t)$. Most of our attention will therefore be devoted to discussing such moments. Hence, we now introduce the expectation values $q_i(t)$, $r_{i,k}(t)$ and $c_{i,k}(t', t' + t)$ defined as

$$q_i(t) = \langle \sigma_i(t) \rangle = \sum_{\{\sigma^N\}} \sigma_i P(\{\sigma^N\}, t) \quad (6)$$

$$r_{i,k}(t) = \langle \sigma_i(t) \sigma_k(t) \rangle = \sum_{\{\sigma^N\}} \sigma_i \sigma_k P(\{\sigma^N\}, t) \quad (7)$$

and

$$c_{i,k}(t', t' + t) = \langle \sigma_i(t') \sigma_k(t' + t) \rangle = \sum_{\{\sigma^N\}} \sigma_i \langle \sigma_k(t) \rangle_0 P(\{\sigma^N\}, t') \quad (8)$$

where the sums run over all possible configurations compatible with our rule of motion, and $\langle \sigma_k(t) \rangle_0$ is the expectation value of σ_k for a given configuration at $t = t'$. While $r_{i,k}(t)$ is the equal time equilibrium correlation function, which describes whatever tendency the pairs of segments σ_i and σ_k may have to be correlated in direction at time t , the $c_{i,k}(t', t' + t)$ is the so-called time-delayed correlation function which describes correlation effects extending over an interval of length t . When $t' \rightarrow \infty$, $c_{i,k}(t', t' + t)$ is the equilibrium time-dependent pair correlation function [5, 6]. Multiplying now the master equation by the appropriate quantities and performing later the aforementioned summations, the following equations for the different expectation values are derived

$$\frac{dq_1}{dt} = 0 \quad \frac{dq_j}{dt} = -2\alpha(q_j - \beta q_{j-1}) \quad j = 2, \dots, N \quad (9)$$

and

$$\frac{dr_{1,k}}{dt} = -2\alpha(r_{1,k} - \beta r_{1,k-1}) \quad k = 2, \dots, N$$

$$\frac{dr_{j,k}}{dt} = -2\alpha(2r_{j,k} - \beta(r_{j-1,k} + r_{j,k-1})) \quad j = 2, \dots, N-1 \quad j < k \leq N \quad (10)$$

$$r_{j,k} = r_{k,j} \quad r_{j,j} = 1.$$

These are the required time-evolution equations for the q 's and the r 's. As for the c 's, following Gonçalves and de Oliveira [7] it is convenient to multiply them by a Heaviside step function $\Theta(t)$ for later performing a Fourier transform. Then we obtain

the following equations of motion

$$\frac{dc_{i,1}(t', t' + t)}{dt} = -r_{1,1}(t')\delta(t)$$

$$\frac{dc_{i,k}(t', t' + t)}{dt} = -r_{i,k}(t')\delta(t) - 2\alpha(c_{i,k}(t', t' + t) - \beta c_{i,k-1}(t', t' + t)) \quad (11)$$

$$i = 2, \dots, N-1 \quad k > i$$

The chain dynamical properties may be studied in terms of these equations as we will illustrate for the dielectric response function and the frequency-dependent relaxational specific heat in the following section.

3. Description of relaxation phenomena

3.1. The dielectric relaxation response function

In order to proceed with our calculations, a further simplification may be achieved by considering very long chains so that $N \gg 1$. In such a case, end effects may be neglected and we may ignore in (9) to (11) those involving explicitly a subscript 1. As an immediate consequence of the long-chain assumption, we find in particular that the equilibrium solution for the r 's is given by

$$r_{j,k}^{\text{eq}} = \{(1 - (1 - \beta^2)^{1/2})/\beta\}^{k-j} = \{\tanh((\varepsilon_2 - \varepsilon_1)/4k_B T)\}^{k-j} \quad (12)$$

a result that will be useful later. The second equality in (12) suggests that, in magnetic language, the model we have chosen is equivalent to an Ising model with an effective exchange constant $J/2$, where $J = (\varepsilon_2 - \varepsilon_1)/2$. This is due to our dynamical rule (cf equation (3)) which selects some states for the possible transitions. Since only the formation of a single 'domain wall' is permitted, the energy excitations differ by an integer number of $J/2$, while in the case where all the excitations are allowed, these are constructed from energy excitations J .

Motivated by the work of Isbister and McQuarrie [3], we now place a dipole in segment $[N/2]$ (where the square brackets denote the integer part). Then the dielectric relaxation linear response function may be computed from

$$\psi(\omega) = \frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = 1 - i\omega \int_{-\infty}^{\infty} dt e^{-i\omega t} \frac{\langle \sigma_{[N/2]}(0) \sigma_{[N/2]}(t) \rangle^{\text{eq}}}{\langle \sigma_{[N/2]} \sigma_{[N/2]} \rangle_0}$$

$$= 1 - i\omega \int_{-\infty}^{\infty} dt e^{-i\omega t} \frac{c_{[N/2], [N/2]}^{\text{eq}}(0, t)}{c_{[N/2], [N/2]}}$$

$$= 1 - i\omega \phi(\omega) \quad (13)$$

where $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ is the complex dielectric constant and ε_∞ and ε_0 are the values of the dielectric constant at infinite and zero frequencies, respectively. Furthermore, $\langle \rangle^{\text{eq}}$ denotes an equilibrium average. Since we are interested in calculating bulk properties, we will assume translational invariance, which is a correct procedure provided we consider very long chains. This is equivalent to identifying $r_{j,j+n}^{\text{eq}} = r_n^{\text{eq}}$ and $c_{j,j+n}(t', t' + t) = c_n(t', t' + t)$ in the limit $j \gg 1$. Then the spatial Fourier transform of c_n is given by

$$\langle \sigma_{-q}(t') \sigma_q(t' + t) \rangle = \sum_n e^{-iqn} c_n(t', t' + t). \quad (14)$$

The equilibrium response function $\psi(\omega)$ requires the evaluation of the correlation $\langle \sigma_{-q}(t') \sigma_q(t' + t) \rangle$ in the limit when $t' \rightarrow \infty$. In this limit we may write [7] for the temporal Fourier transform

$$\hat{c}_n(\omega) = \lim_{t' \rightarrow \infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} c_n(t', t' + t). \quad (15)$$

With the aid of (14) and (15) and taking the limit $t' \rightarrow \infty$ in (11) after some algebraic manipulations, we arrive at

$$\langle \sigma_{-q} \sigma_q \rangle_{\omega} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \sigma_{-q}(0) \sigma_q(t) \rangle^{\text{eq}} = \frac{\langle \sigma_{-q} \sigma_q \rangle^{\text{eq}}}{i\omega + 2\alpha(1 - \beta e^{-iq})} \quad (16)$$

where $\langle \sigma_{-q} \sigma_q \rangle^{\text{eq}}$, the (equilibrium) static correlation in q -space, is given by

$$\langle \sigma_{-q} \sigma_q \rangle^{\text{eq}} = \frac{1}{\cosh((\varepsilon_2 - \varepsilon_1)/2k_B T)(1 - \beta \cos q)}. \quad (17)$$

Equations (16) and (17) allow us finally to obtain $\phi(\omega)$ as

$$\phi(\omega) = \hat{c}_0(\omega) = \frac{1}{i\omega + 2\alpha(1 - \beta^2)^{1/2}} \quad (18)$$

which when inserted in (13) yields to the dielectric response, that we will discuss later on.

While the analysis of the relaxation of a single dipole in the chain has the advantage of simplicity, from a physical point of view it does not seem too natural to examine the dynamics of the whole chain in terms of what happens in a particular segment. Therefore we propose a different situation in which we place a dipole in each and every segment of the chain, but neglect dipole-dipole interactions. In this case, we may also compute the dielectric response function as

$$\Psi_N(\omega) = i\omega \frac{\sum_n \int_{-\infty}^{\infty} dt e^{-i\omega t} c_n^{\text{eq}}(0, t)}{\sum_n r_n^{\text{eq}}} = 1 - i\omega \phi_N(\omega). \quad (19)$$

It should be noted that in the previous expression we have neglected the boundary contributions to the relaxation function. Now, performing an analogous calculation to the one leading to (18) we obtain

$$\phi_N(\omega) = \frac{\langle \sigma_0 \sigma_0 \rangle_{\omega}}{\langle \sigma_0 \sigma_0 \rangle_0} = \frac{\sum_n \hat{c}_n(\omega)}{\sum_n r_n^{\text{eq}}} = \frac{1}{i\omega + 2\alpha(1 - \beta)} \quad (20)$$

which is the result for the non-interacting N dipoles case. Both (18) and (20) will be discussed and compared in section 4.

3.2. Relaxational specific heat

Now we turn to the frequency-dependent energetics of the chain as represented by our model. Assuming again translational invariance, equation (10) reduces to

$$\frac{dr_h}{dt} = -4\dot{\alpha} \left(r_h - \frac{\beta}{2}(r_{h-1} + r_{h+1}) \right) \quad (21)$$

where $r_h = r_{i,k}$ with $h = |k - j|$.

Let the chain be in equilibrium with a heat bath at a temperature T_c . Then the equilibrium values of the two segment correlation functions r_h^{eq} are given by (cf equation (12))

$$r_h^{eq} = \left\{ \tanh \left(\frac{\varepsilon_2 - \varepsilon_1}{4k_B T_c} \right) \right\}^h \quad (22)$$

We now subject the system to a periodic temperature perturbation of frequency ω , so that we set

$$\begin{aligned} T &= T_c + \delta T = T_c + \delta T e^{i\omega t} \\ \beta &= \beta_c + \delta\beta = \beta_c - \frac{(\varepsilon_2 - \varepsilon_1)}{2k_B T_c^2} \operatorname{sech}^2 \left(\frac{\varepsilon_2 - \varepsilon_1}{2k_B T_c} \right) \Delta T e^{i\omega t} \\ r_h &= r_h^{eq} + \delta r_h = r_h^{eq} - \frac{(\varepsilon_2 - \varepsilon_1)}{2k_B T_c^2} \operatorname{sech}^2 \left(\frac{\varepsilon_2 - \varepsilon_1}{2k_B T_c} \right) \Delta T e^{i\omega t} s_h(\omega) \end{aligned} \quad (23)$$

$$\alpha = \alpha(T_c) + \delta\alpha = \alpha(T_c) + \left(\frac{\partial \alpha}{\partial T} \right)_{T=T_c} \Delta T e^{i\omega t} = \alpha(T_c) - \frac{(\varepsilon_2 - \varepsilon_1)}{2k_B T_c^2} \operatorname{sech}^2 \left(\frac{\varepsilon_2 - \varepsilon_1}{2k_B T_c} \right) \Delta T e^{i\omega t} \alpha_1$$

where $\beta_c = \tanh((\varepsilon_2 - \varepsilon_1)/2k_B T_c)$ and s_h is the h th response function to the perturbation. Moreover in (23) we have emphasized the temperature dependence of α whose form will be specified below (cf equation (30) with $T = T_c$). Since $dr_h^{eq}/dt = 0$, if terms of order $(\Delta T)^2$ are neglected, substitution of (23) into (22) leads to

$$\left(\frac{i\omega}{2\alpha(T_c)} \mathbf{1} + L_0 \right) \cdot s = r_0 \quad (24)$$

where $\mathbf{1}$ is the identity matrix, $s = (s_1, s_2, \dots, s_{N-1})$

$$L_0 = \begin{bmatrix} 2 & -\beta_c & 0 & 0 & \dots & 0 & 0 & 0 \\ -\beta_c & 2 & -\beta_c & 0 & \dots & 0 & 0 & 0 \\ 0 & -\beta_c & 2 & -\beta_c & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \dots & -\beta_c & 2 & -\beta_c \\ \vdots & \vdots & \vdots & \vdots & \dots & 0 & -\beta_c & 2 \end{bmatrix} \quad \text{and } r_0 = \begin{bmatrix} 1 + r^{eq} \\ r_1^{eq} + r_3^{eq} \\ \vdots \\ \vdots \\ r_{N-3}^{eq} + r_{N-1}^{eq} \\ r_{N-2}^{eq} \end{bmatrix}$$

The relaxational specific heat $C^*(\omega)$, defined as the ratio of the change in energy stored in the chain to the change in temperature, is given by

$$C^*(\omega) = \frac{(\varepsilon_2 - \varepsilon_1)(r_1 - r_1^{eq})}{2\Delta T e^{i\omega t}} = -\frac{(\varepsilon_2 - \varepsilon_1)}{4k_B T_c^2} \operatorname{sech}^2 \left(\frac{\varepsilon_2 - \varepsilon_1}{2k_B T_c} \right) s_1(\omega). \quad (26)$$

Therefore, in order to calculate this quantity we require knowledge of $s_1(\omega)$. We note that (24) and (25) have exactly the same form as (16) and (17) in [8]. Hence, we may make use of the solution found therein for $s_1(\omega)$, which yields

$$C^*(\omega) = -\frac{2}{(2N-1)} \frac{(\varepsilon_2 - \varepsilon_1)^2}{k_B T_c} \operatorname{sech}^2 \left(\frac{\varepsilon_2 - \varepsilon_1}{2k_B T_c} \right) \sum_{m=1}^{N-1} \frac{X(k_m) \alpha(T_c) \omega_{k_m}}{i\omega + 2\alpha(T_c) \omega_{k_m}} \quad (27)$$

where

$$k_m = \frac{2m\pi}{2N-1} \quad X(k_m) = \frac{\sin^2 k_m}{2(1 - \beta_c \cos k_m)^2} \quad \omega_{k_m} = 2(1 - \beta_c \cos k_m). \quad (28)$$

The results embodied in (27) will be evaluated and discussed below.

4. Results and discussion

We start by discussing dielectric relaxation. In both cases that we have examined, the dielectric response function displays a Debye relaxation behaviour, i.e.

$$\psi(t) = e^{-t/\tau_D} \quad (29)$$

where $\tau_D = (2\alpha(1 - \beta^2)^{1/2})^{-1}$ in the single dipole case and $\tau_D = (2\alpha(1 - \beta))^{-1}$, for N non-interacting dipoles. This result, which as pointed out by Bozdemir [9] could be anticipated since we have neglected the interactions between the dipoles, implies that the frequency corresponding to the maximum of the loss curve is $\omega_{\max} = 1/\tau_D$. Since frequently the temperature dependence of the experimental data on dielectric relaxation is presented in terms of the behaviour of $\log \omega_{\max}$ as a function of the inverse of the temperature, the fact that we have derived simple analytical expressions for ω_{\max} is very convenient for comparison with experiment.

Clearly, ω_{\max} depends on temperature through β , but as it was anticipated above, α should also be temperature dependent. The form of this last dependence may be obtained by combining the ideas put forward by Adam and Gibbs [10] connecting the microscopic transition probabilities in the Gibbs-di Marzio model with the inverse of the time scale of the motion, and the recent results by García-Colín *et al* [11, 12] for the temperature dependence of this characteristic time. Thus, if T_0 is the temperature for which the configurational entropy in the Gibbs-di Marzio model goes to zero, α is given by (cf equation (9) in [11])

$$\alpha = \frac{1}{\tau_0} \exp \frac{K}{F(T)(T_0 - T)} \quad (30)$$

where the function $F(T)$ turns out to be [11]

$$F(T) = \frac{A'(T + T_0)}{2TT_0} + B'T - \frac{C'T(T + T_0)}{2} \quad (31)$$

with A' , B' and C' constants whose value depends on the particular material. Values of these constants, calculated from results of di Marzio and Dowell [13] for six different polymers, appear in the table of [12]. Further, $K = 2.303\Delta\mu S_c^*/k_B$ (μ being the chemical potential and S_c^* the critical configurational entropy). This quantity is directly calculable from the equilibrium data of each substance and a table of values appears in [10]. Finally, τ_0 is also a constant whose value would vary from substance to

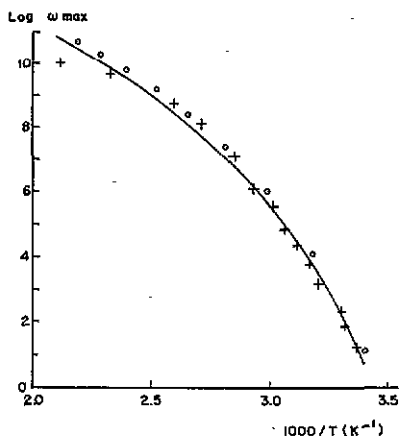


Figure 1. Temperature dependence of ω_{\max} for the β relaxation of PMA. The blobs correspond to the theoretical values for the single dipole model while the continuous line corresponds to the theoretical values for the N non-interacting dipoles model. The crosses are the experimental data from [13].

substance and in the magnetic language it would correspond to a free spin relaxation time. It should be stressed that if ϵ_1 , ϵ_2 , A' , B' , C' and K are known for a given polymer, in a comparison with experimental data τ_0 is the only adjustable parameter remaining in our model.

In figure 1, we show the results of the calculated $\log \omega_{\max}$ versus $1000/T$ for PMA (both for the one dipole and the N non-interacting dipoles) as well as the experimental data for the β relaxation of the same polymer taken from [14] (cf figure 32 and note that we have followed the nomenclature adopted by Bur). In the calculation we have set $\tau_0 = 10^{-16}$ s, computed the value for $\Delta\epsilon = \epsilon_2 - \epsilon_1$ with the prescription given in [13], namely $\Delta\epsilon/k_B T_g = 2.25$, taken the values of T_g , T_0 , A' , B' and C' from the table in [12] and adjusted the value of K ($12.90 \text{ kcal mol}^{-1}$) since no values for $\Delta\mu S_c^*/k_B$ were available for this substance in [10]. It must be stressed though that this value for K is reasonable given corresponding values determined experimentally for other similar polymers, as reported in the table of [10]. As can be clearly seen from the figure, the agreement between the theoretical calculation and the experimental data is very good. This agreement extends over a wide range of frequencies and temperatures and becomes poorer well above T_g , with the N dipole case being slightly better, irrespective of a change in the value of τ_0 .

Figure 2 contains analogous results for another linear polymer, namely PVAC, whose equilibrium properties may also be described by the Gibbs–di Marzio model [13]. For this polymer, the values of all the quantities K , T_g , T_0 , A' , B' and C' have been taken from the table of [12] so the only adjustable parameter is τ_0 , which was now set equal to 2×10^{-16} s, and we have reported only the N -dipoles theoretical result. The experimental data were obtained from figure 1 in [15] and once again we have adopted the terminology of Bur for this relaxation. Clearly, there is also very good agreement between the theoretical calculation and the experimental data for PVAC.

It is remarkable that a Debye behaviour can perform so well in the case of these polymers, since experimentally the description in terms of the kww expression is usually preferred. It could be argued that the Vogel–Fulcher form of (30) is

responsible for the good fits of the data. Nevertheless, it is important to stress that the way it arises in our model, its connection with the parameters of the Gibbs–di Marzio model and the analytical result for the temperature dependence of ω_{\max} that we have obtained could not have been anticipated. Moreover, the form of the dielectric response (equations (18) and (20), respectively) is also a prediction of the present model that could be tested against experiment. Of course the deviations between theoretical values and experimental measurements of ω_{\max} at the higher temperatures and frequencies suggest that most likely the Debye behaviour is lost at a certain crossover point where the dynamics must become more complicated than our simple model predicts.

Another relevant aspect of our results that we have not discussed yet is the fact that if one scales the frequency ω with ω_{\max} , the resulting scaled dielectric response function becomes universal for all polymers that may be described in terms of the Gibbs–di Marzio model. Thus, from values of this function for a given substance computed at a particular frequency and temperature, one may in principle infer corresponding values for the same or for other substance at different frequencies and temperatures, at least in the range where the Debye behaviour holds.

Concerning some of the other limitations of our model, it must be mentioned that it is not able to produce the bimodal distributions typical of dielectric relaxation in amorphous polymers [14]. We are currently investigating if the removal of the long-chain assumption may remedy this deficiency.

With respect to the relaxational heat capacity, as indicated previously we have also made use of (30) for $\alpha(T_c)$. Again, we have considered PMA and PVAc with the values for τ_0 taken from the fits to the dielectric data. The results are displayed graphically in figure 3. In this case, however, we are not aware of the availability of experimental data with which to make comparisons. Therefore, these results are only indicative of the calculation and await future assessment. Nevertheless, the analytical form we have obtained indicates that for this response function the universality observed in the dielectric relaxation does not show up at least in a simple way. We have numerically checked that if one attempts the usual scaling of the frequency by dividing it by the

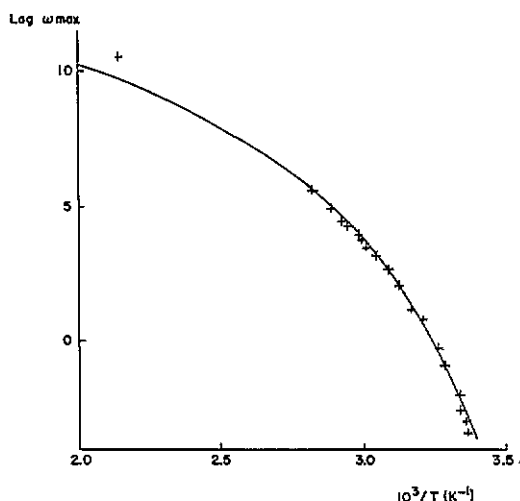


Figure 2. Temperature dependence of ω_{\max} for the β relaxation of PVAc. The continuous line is the theoretical result and the crosses are the experimental data taken from [14].

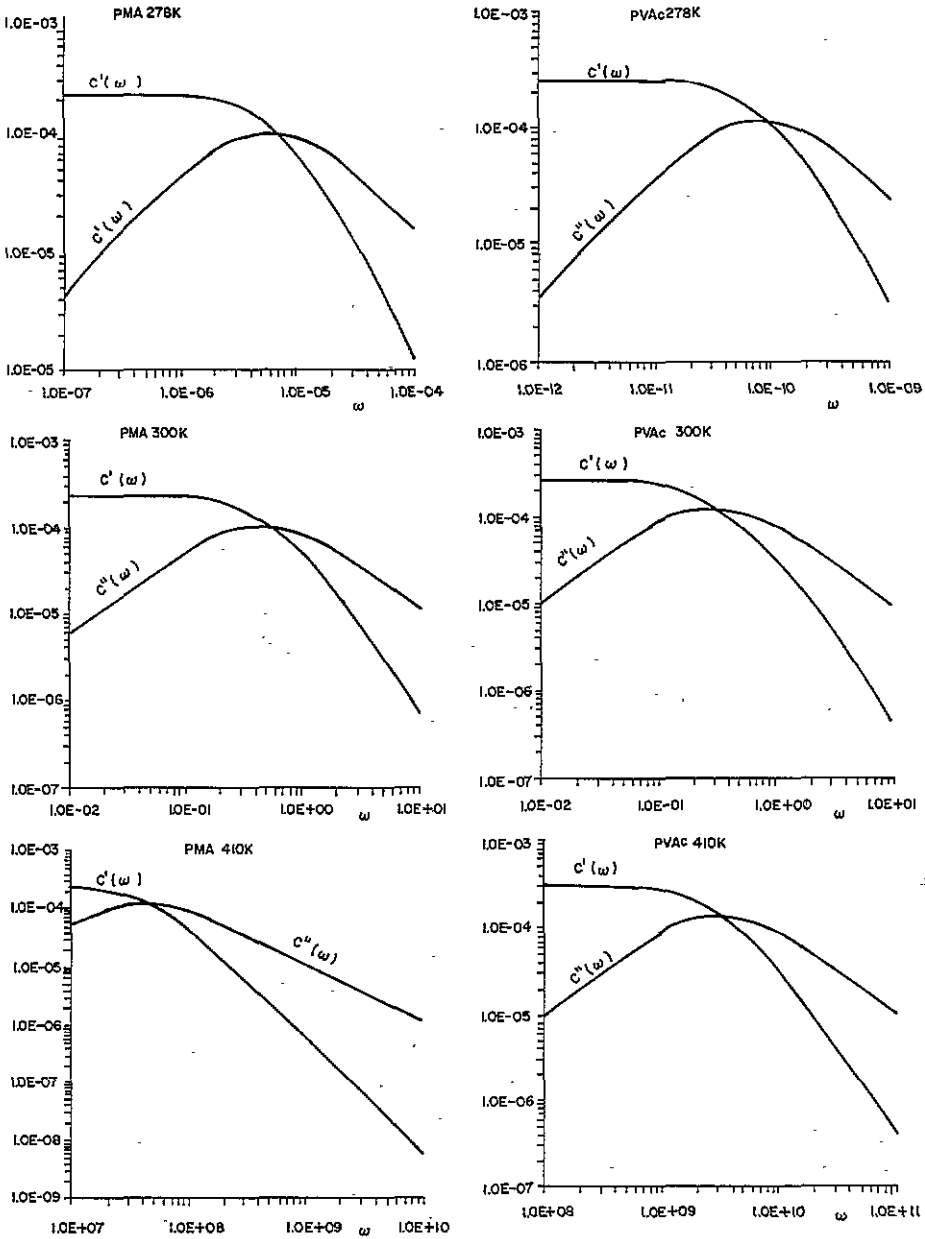


Figure 3. Real ($C'(\omega)$) and imaginary ($C''(\omega)$) components of the relaxational specific heat for PMA and PVAc at different temperatures. Note the impressive change in the position of the maximum of $C''(\omega)$ as one approaches T_g .

one corresponding to the maximum of the loss curve, and simultaneously scales both the real and imaginary parts with their respective maximum values, the apparent universality that holds when the temperatures are not too far apart is destroyed. It is interesting to stress that even in such a simple model, the universality in a wide range that is claimed to be a signature around the glass transition, does not arise immedi-

ately. We are presently investigating whether a Nagel plot [16] would restore the feature of universality.

Finally, we want to point out that our results suggest that the notion of the flex, which is clearly related to topological constraints and of course a key element in the Gibbs-di Marzio model taken over into our stochastic model, seems to play not only an important role in determining the equilibrium properties of linear polymers, but also in the dynamics of these chains. The full assessment of this possibility requires more work on the subject, particularly in view of the fact that our rule of motion is clearly not realistic. This rule of motion nevertheless permits the analysis of the elementary dynamical event, namely the creation or destruction of a single flex, and in particular the derivation of analytical results. Therefore, since no simple modification to account for a realistic motion appears to be feasible, we favour the view of critically assessing the apparent success of this simple and physically appealing model before attempting to engage in more difficult calculations.

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References

- [1] Gibbs J H and di Marzio E A 1958 *J. Chem. Phys.* **28** 373
Concerning the criticism of the Gibbs-di Marzio theory of the glass transition, see:
Bascle J, Garel T and Orland H 1992 *J. Phys A: Math Gen* **25** L1323
For a discussion of the validity and approximations involved in this model, see:
Wittmann H P 1991 *J. Chem. Phys.* **95** 8449
- [2] For reviews of kinetic Ising models in polymer dynamics, see:
Orwoll R A and Stockmayer W H 1969 *Adv. Chem. Phys.* **15** 305
Lacombe R H 1980 *J. Macro. Sci. B* **18**, 697
Other papers that may be of interest in connection with this topic include:
Anderson J E 1970 *J. Chem. Phys.* **52** 2821
Simha R and Lacombe R H 1971 *J. Chem. Phys.* **55** 2936; 1974 *J. Chem. Phys.* **61** 1899
Lacombe R H and Simha R 1973 *J. Chem. Phys.* **58** 1043
Skinner J L and Wolyness P G 1980 *J. Chem. Phys.* **73** 4022
Skinner J L 1983 *J. Chem. Phys.* **79** 1955
Budimir J and Skinner J L 1985 *J. Chem. Phys.* **82** 5232
Fredrickson G H and Andersen H C 1985 *J. Chem. Phys.* **83** 5822
- [3] Isbister D J and McQuarrie D A 1974 *J. Chem. Phys.* **60** 1937
- [4] Glauber R J 1963 *J. Math. Phys.* **4** 294
- [5] Suzuki M and Kubo R 1968 *J. Phys. Soc. Jpn.* **24** 51
- [6] de Oliveira N T, Gonçalves L L, Sá Barreto F C 1985 *Z. Phys. B* **58** 319
- [7] Gonçalves L L and de Oliveira N T 1985 *Can. J. Phys.* **63** 1215
- [8] López de Haro M 1983 *J. Chem. Phys.* **78** 546
- [9] Bozdemir S 1981 *Phys. Status Solidi b* **103** 459; 1982 *Phys. Status Solidi b* **104** 37
- [10] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139

- [11] García-Colín L S, del Castillo L F and Goldstein P 1989 *Phys. Rev. B* **40** 7040
- [12] García-Colín L S, del Castillo L F and Goldstein P 1990 (erratum) *Phys. Rev. B* **41** 4785
- [13] di Marzio E A and Dowell F 1979 *J. Appl. Phys.* **50** 6061
- [14] Bur A J 1985 *Polymer* **26** 963
- [15] Murthy S S N 1990 *J. Chem. Phys.* **92** 2684
- [16] Dixon P K, Wu L, Nagel S R, Williams B D and Carini J P 1990 *Phys. Rev. Lett.* **65** 1108