

Meeting the challenge of the cooperative, non-Arrhenius, non-linear response behaviour of macromolecular materials

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Introduction

One of the authors [1,2] proposed recently a cooperative segmental theory of molecular dynamics (CSTMD), for the time-dependent behaviour of polymers and other materials, at constant volume, when subject to thermal (heating/cooling) or forced (mechanical, dielectrical, etc.) excitations. The theory only assumes that segments may be identified within the structure, which may (individually, or in clusters of random size, $n \geq 1$) contribute to the materials response. For example, in a polypropylene, a segment may be identified as the shortest chain length capable of independent torsion and rotation (within the amorphous phase), as in the crankshaft [3] type of motions (4 adjacent main chain carbon atoms and their associated methyls and hydrogens).

The theory develops from, and extends, Eyring's absolute reaction/physical process rate theory [4,5], and yields the equilibrium frequencies of motion/transition of clusters of any number, n , of individual segments, as functions of the absolute temperature, T , the activation energy at 0 K of a single-segment transition, E_{01} , and a characteristic frequency of vibration of each segment at its activated state, $\nu_1^\#$ (the same for all n cooperatively participating segments of any given cluster),

$$\nu_n(T) = \nu_1^\# \cdot \left(\frac{z_{\#r}}{z} \right) \cdot \frac{\exp\left(-\frac{E_{01} - h\nu_1^\# / 2}{k_B T}\right)}{\sinh\left(\frac{h\nu_1^\#}{2k_B T}\right)} \quad (1)$$

where $(z_{\#r}/z)$, a residual single-segment partition function ratio, may be only slightly temperature-dependent, being here treated as a constant, and h and k_B are Planck's and Boltzmann's constants, respectively. E_{01} , $\nu_1^\#$ and $(z_{\#r}/z)$ will depend on the detailed structure's local energy landscape, which is an extremely powerful and useful concept in condensed matter physics [6].

Equation 1 accounts for two distinct possibilities for the torsion/rotation of each single segment, and directly predicts the existence of a crossover [1,2,7] at a given temperature T_c ($\nu_1^\#$, E_{01}), at which the expression within brackets is exactly 1 [1]), and provides a straightforward measure of the cooperativity within any given cluster, through n .

This paper discusses the physics underlying Equation 1 and extends its predictions to a forced excitation, at constant pressure, such as mechanical creep, showing that they are consistent with those of much simpler dynamic models, e.g. based on chain conformational transitions. A separate contribution to Macro 2004 [8] further discusses and validates the model against experimental amorphous and semi-crystalline polymer creep data [9].

CSTMD's predicted temperature-dependent behaviour

Figure 1 shows plots of a range of cooperative frequencies as functions of temperature, for a typical, moderately flexible macromolecular structure, hypothetically characterized by $E_{01} = 40$ kJ mol⁻¹, and $\nu_1^\# = 10^{6.5}$ Hz [1,10]; the latter is also the crossover frequency, ν_c [1] (cf. Equation 1). The corresponding solid lines would be nearly exactly straight in an Arrhenius ($\ln \nu_n$ vs. $1/T$) diagram [1].

Very briefly, it is important to consider how such a diagram may depict the gradual activation or deactivation of the various structure's modes (corresponding to different n values), when the material is simply heated or cooled, respectively, at controlled rate, without any other excitation. In this case, it may be shown [1,11] that the various modes are activated, one after the other, from $n=1$ up to ∞ , in heating,

and that the whole process is reversed, in cooling. As all the cooperative frequencies increase with temperature, according to Equation 1, the material follows (equivalent frequency) paths such as those illustrated (\square symbols), at the indicated temperature scanning rates [1,11]. However, if the material is subject to a forced dynamic excitation of frequency ν , while it is slowly heated/cooled, Figure 1 may also be used to determine at which temperatures the various modes are activated/deactivated, respectively, from the intersections of a horizontal line at frequency ν with each of the ν_n lines [1,11].

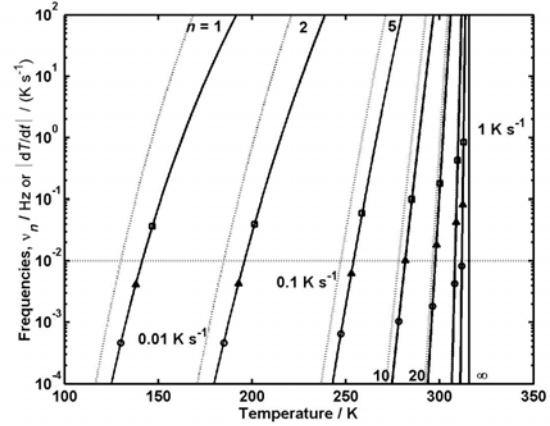


Figure 1. Cooperative frequencies (solid lines), for varying segment cluster sizes, n , as functions of temperature, and equivalent frequency paths (\circ , Δ , \square) followed in thermal scans, at the indicated rates.

In addition, a diagram such as Figure 1 (expanded) and/or the corresponding equations may also be used to obtain the exact range of frequencies that will be active ($\nu_n > \nu$) or just being activated ($\nu_n = \nu$) at any given temperature, at the time-scale defined by ν . In the case of a transient response (e.g. creep) with $\nu = 0$, at constant temperature, the material will then, of course, not be in equilibrium, but the frequencies ν_n (appropriately modified by the applied excitation, e.g. stress, in the case of creep) will nevertheless still be determining the dynamics of the corresponding elementary (first-order, Debye) processes in their approach to equilibrium, by means of their characteristic times $\tau_n \propto 1/(\nu_n^+ - \nu_n^-)$ where the + and - superscripts refer to transitions yielding positive and negative contributions, respectively, to the overall strain increase, assuming that, on average, half of the cluster transitions will positively contribute to that increase (with a decreased activation energy) and half to its decrease (with a correspondingly increased activation energy). It may be shown [11] that this modification will not eliminate the previously predicted, and experimentally found, crossover behaviour [7,10].

CSTMD and a dynamic model of creep

First of all, the above theory may be extended to constant pressure conditions. Full details will be omitted here, but the exponential's argument in Equation 1 will then include a term proportional to the pressure, P , which will yield a positive dependence of T_c (and surely also of the glass transition temperature, T_g) on pressure, as reasonably expected.

To apply the theory to creep (at constant stress), we do not need any new concepts, Eyring's approach [4,5] providing what is needed to correctly formulate the problem, through the classical linear dependence of each cluster effective activation barrier on the applied stress and on its specific activation volume (proportional to n), according to the last paragraph of the preceding section.

Following the procedure outlined above, one may obtain, for the characteristic retardation times, as functions of the applied stress, σ_0 ,

$$\tau_n = \frac{\sigma_0}{c_{0,n} \sinh(\beta_n \sigma_0)} \quad (2)$$

with $c_{0,n} = c_0^\# \nu_n$, where the ν_n are given by Equation 1, as functions of the temperature and relevant structural parameters, and β_n is the

cluster's activation volume divided by $k_B T$. The details of the algebraic manipulation are somewhat involved (but not too cumbersome) and are omitted in this paper. Instead, physical insight may be gained by briefly considering the proof that the above result may be similarly obtained for the set of elementary gauche/trans conformational transitions within a large set of typical, free (non-entangled), polymer chains. Finally, the relative weighing of the whole range of retardation times must also be outlined, to allow the application of the theory to creep compliance predictions.

Conformational transitions and creep of large sets of (non-entangled) free chains

The delayed elastic strain rate of a large number of such chains, at constant stress, σ_0 , may be formulated as

$$\frac{d(\varepsilon' - \varepsilon'_0)}{dt} \propto \alpha_{g^-} e^{-E_0^-/kT} e^{\beta\sigma_0} + \alpha_{g^+} e^{-E_0^+/kT} e^{\beta\sigma_0} - 2\beta_i e^{-E_0^+/kT} e^{-\beta\sigma_0} \quad (3)$$

where ε'_0 is an instantaneous elastic strain, E_0^- and E_0^+ the activation energies of the gauche \rightarrow trans and trans \rightarrow gauche transitions, respectively, and α_{g^-} , α_{g^+} and β_i are the instantaneous population numbers of each type of conformation, subject to the condition that, at $t = 0$, just before (and just after) the stress is applied, they must obey Boltzmann's distribution. β_i , like β_n , is proportional to an activation volume, this time of a single, much smaller, chain segment capable of a gauche/trans transition. Assuming that, as the system creeps, the number of trans conformations will increase, and that of the gauche conformations decrease, in proportion to the increase in strain, the coefficients in the above equation become linearly related to the delayed elastic strain, and so (taking the initial Boltzmann's distribution into account),

$$\frac{d(\varepsilon' - \varepsilon'_0)}{dt} \propto 2\alpha_0 e^{-E_0^+/kT} \cdot \left\{ [1 - a(\varepsilon' - \varepsilon'_0)] e^{\beta\sigma_0} - [1 + a'(\varepsilon' - \varepsilon'_0)] e^{-\beta\sigma_0} \right\} \quad (3a)$$

Finally, bearing in mind that a and a' must obey two relationships - one establishing that the total number of (gauche + trans) conformations must be constant, and the other establishing that, at the very long time ($t \rightarrow \infty$) equilibrium, where the delayed elastic strain (which does not include viscous flow) reaches its plateau value, the derivative of that strain must be zero - both a and a' may be explicitly calculated [9] and Equation 3a integrated to yield the corresponding creep compliance function,

$$D'(t) = D_0' + (D_\infty' - D_0') \left\{ 1 - e^{-[c_0' \sinh(\beta\sigma_0) / \sigma_0] t} \right\} \quad (4)$$

$$\text{with } c_0' \propto e^{-E_0^+/kT} / (D_\infty' - D_0') \quad (4a)$$

which is that of a generalized, non-linear, modified Voigt-Kelvin unit, with retardation time obeying a relationship entirely analogous to Equation 2. Equation 4 provided the basis for our substantially successful modelling of the creep behaviour of polymer materials [8,9]. The combined effect of a wide range of possible contributing elementary processes has been considered in References 8 and 9, and is also considered in the following section.

Cluster size distribution and non-linear retardation time distribution

For an isolated system of N_A segments, or at constant temperature (to within negligible energy fluctuations), the cluster weights or contributions to the total internal energy, F_n , should be proportional to $n \cdot N_A C_n$ which, for extremely large N_A (typically of the order of Avogadro's number), gives $F_n = e^{-1}/(n-1)!$. However, for the clusters' response to forced excitations (each of them expectedly proportional to n), one may assume their relative contributions to be

proportional to $n^2 \cdot N_A C_n$. So, instead of F_n , the resulting weighing function may likewise be shown to be $G_n = n F_n / 2$.

While F_n strongly decreases with n , G_n has a maximum for $n = 2$, being almost completely (99.97 %) confined to the range $n = 1$ to 7. From F_n and G_n , the corresponding frequency distributions, $F(v_n)$ and $G(v_n)$, are easily obtained and plotted. The first approximately yields a power law with a temperature-increasing exponent [1,11], and the second is plotted in Figure 2 (the highest ordinates corresponding to $n = 2$), which shows its compatibility with a truncated log-normal frequency/characteristic time distribution [8,9], very similarly to old but successful views and proposals [12]. Of course, the relevant frequency scale for a forced excitation is stress-dependent and of the order of $v_n^+ - v_n^-$ (cf. above), rather than simply the v_n of Equation 1 shown in Figure 2's abscissas.

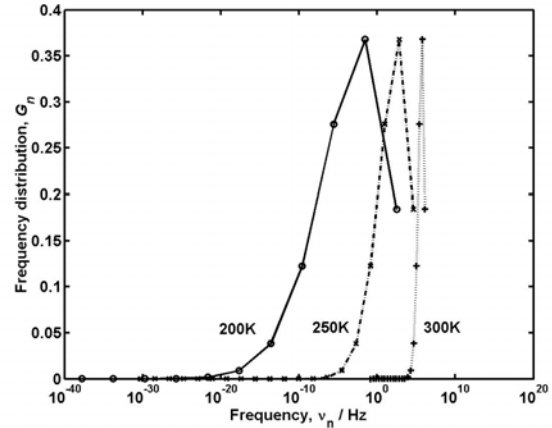


Figure 2. Calculated cooperative segmental frequency distributions, $G_n(v_n)$, in a forced dissipative excitation, at the indicated temperatures.

Accounting for a (not too wide) distribution of E_{01} values, to accommodate the expected diversity of local (segment) environments, constitutes a logical and straightforward improvement of the proposed model, which yields a continuous, rather than a discontinuous, frequency or retardation time spectrum, like those predicted from the interpretation of experimental creep data for a range of different polymers [8,9]. These spectra are responsible for the non-Debye, stretched-exponential behaviour of most viscoelastic materials.

Conclusion

The cooperative, temperature-dependent, non-Arrhenius, non-linear, viscoelastic behaviour of polymers, namely creep, may be meaningfully modelled at the (macro)molecular scale and validated against experimental data for a wide range of materials.

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