The effect of thermodynamic variables on polymer chain dynamics

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1. Background

The low frequency motions of high molecular weight ("entangled") polymers are directly relevant to processing and forming operations and exert a substantial influence on many material properties. The conceptual framework of theoretical studies of the dynamics of entangled chains is invariably the reptation model [1,2], which has been widely accepted in view of its intuitive appeal and reasonable agreement with experimental results [3,4]. Where predictions of the reptation model are wrong, this usually implies that mechanisms other than longitudinal ("snakelike") diffusion are operative [5].

An important aspect of the rheology of polymers is the effect of temperature or pressure on the dynamics. According to the reptation model, at short times the chain segments move freely within a tube of their entanglement constraints. Thus, the motion can be described by the Rouse model [6], which terminates when entanglements begin to manifest themselves. There are two species-dependent parameters, the local (Rouse) friction coefficient, \( \zeta \), and a parameter characterizing the entanglement effect, so that the temperature dependence of the chain dynamics is governed entirely by \( \zeta \). Since \( \zeta \) is the same as the local friction coefficient for the segmental motion, the temperature of the entire dynamics of a polymer from the glass transition zone to the terminal flow regime are predicted to be the same. This leads to the well-known time-temperature superposition principle, which by master curves of viscoelastic properties are constructed, encompassing many decades of time or frequency, from data measured over a much narrower range [6].

Although time-temperature superpositioning is common and often useful, when the data extend into the glass transition (or softening) zone, polymers exhibit thermorheological complexity. The chain dynamics invariably have a weaker dependence on temperature than the local segmental modes underlying the onset of glassy behavior; this causes deviations from time-temperature superpositioning. First discovered in polystyrene by Plazek [7], this breakdown of the superposition principle is observed in all polymers for which data have been obtained under conditions such that both the chain and the local segmental modes simultaneously contribute (i.e., the glass transition zone): poly(vinyl acetate) [8], polypropylene glycol [9], poly(phenylmethyisiloxane) [10], polyisoprene [11], polybutadiene [12], polyisobutylene [13], atactic polypropylene [14], poly(alkyl glycidyl ether) [15], and atactic polypropylene [16].

The proceeding statements concerning the effect of temperature on the behavior of polymers can be extended to pressure, although rheological data are extremely sparse. Dielectric spectroscopy is not a rheological probe per se; however, for polymers with a dipole moment parallel to the chain contour ("type-A" polymers), the dielectric normal mode is determined by the motion of the end-to-end chain vector [17,18]. This means that in the usual case where the dipole moment is weak so that dipole–dipole correlations are negligible, the dielectric response of a type-A polymer can yield the terminal relaxation time, the shape of the terminal relaxation function, and how these vary with thermodynamic variables such as temperature and pressure. Dielectric measurements are especially useful for the latter, since the absence of moving parts facilitates the experiment in comparison to mechanical
measurements [19]. In this review, we describe recent results addressing how temperature and pressure, and in turn volume, underlie the chain dynamics. Notwithstanding the breakdown of time-temperature (or time-pressure) superpositioning, general patterns emerge between the segmental and the chain dynamics, which can be connected to the forces between molecules. There is no universality of the chain dynamics, since these forces are governed by the intermolecular potential, which depends on the chemical structure. However, a simple scaling law, with predictive capability, is shown to be applicable to the dynamics of polymers over the very broad range of their viscoelastic response.

2. Scaling law and universality

The breakdown of time-temperature superpositioning precludes any correspondence between time-temperature shift factors for the segmental versus the global chain motion, even for a single material. The only exception is well above $T_g$, where Arrhenius curves of the relaxation times flatten and become parallel [16]. Comparing different materials, the chain dynamics exhibit similar features, such as molecular weight dependences and the shape of the relaxation function [2,6], since the coarse-graining appropriate to the large length scales diminishes the influence of the local chemical structure. However, the temperature dependence of the terminal relaxation time, $\tau_n$, and viscosity, $\eta$, varies among different polymers, implying different local friction factors. Interestingly, Sokolov et al. [20–22] recently produced master curves of the shift factors for $\tau_n$ and $\eta$ of various polymers plotted versus $T_g/T$, suggesting the existence of a universal $T_g$-normalized temperature dependence of the chain dynamics. This is an intriguing result, implying that a parameter, $T_g$, related to the local

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**Fig. 1.** Local segmental relaxation times (solid symbols) and time-temperature shift factors for the terminal relaxation (open symbols) for atactic polypropylene [16]. The data encompass measurements from dynamic mechanical spectroscopy, transient creep compliance, viscosity, dynamic light scattering, dielectric relaxation, and $^{13}$C NMR. Vertical shifts were applied to the chain mode data to obtain superpositioning, so that the absolute position on the ordinate scale is arbitrary.

**Fig. 2.** Local segmental relaxation times of polymethylphenylsiloxane measured dielectrically: (upper left) as a function of temperature at the indicated pressures [29]; (upper right) as a function pressure at the indicated temperatures [29]; (lower left) data replotted as a function of specific volume; (lower right) superpositioning according to Eq. (2) with $\gamma = 5$ [30].
segmental dynamics can account for differences in the global dynamics. While many polymers conform at least approximately to this universal behavior, it turns out that variations in the \( T_g \)-scaled chain dynamics are evident for a number of materials [23].

The local segmental dynamics directly reflect the forces between segments, and since these forces are governed by the chemical structure, the segmental relaxation properties differ significantly among polymers. A common method of comparing the material response to changes in use of structure, the segmental relaxation properties differ between segments, and since these forces are governed by the chemical structure.

\[ m = T_g \frac{d \log \tau_s}{dT} \mid_{T_g} \]

is called the “fragility” [24], which for polymers fall in the range from \( 46 \leq m \leq 191 \) [25], corresponding to (very large) apparent activation energies, \( \sim 180-1200 \text{kJ/mol} \). The fragility is known to correlate with other properties, such as the breadth of the relaxation dispersion [25] and the separation in time of the segmental and secondary relaxation processes [26].

The above consideration of \( T \)-dependences is restricted to constant (ambient) pressure; extension to the effect of pressure or volume on the dynamics complicates matters. The fragility, for example, decreases with pressure, in the absence of structural changes such as H-bond concentration [27], while the isochoric pressure, extension to the effect of pressure or volume on the dynamics complicates matters. The fragility, for example, decreases with pressure, in the absence of structural changes such as H-bond concentration [27], while the isochoric pressure.

\[ \tau_s = f(TV) \]

in which \( V \) is specific volume and \( \tau \) a material constant. This variable defines the relaxation time, so that a plot versus \( TV \) of \( \tau_s \) for a given polymer measured over a range of \( T \) and \( P \) will superpose to a single, material-specific master curve. This scaling, illustrated in Fig. 2 for a siloxane polymer [29,30], is quite general, having been demonstrated for more than 50 materials [19]. The exponent \( \gamma \) varies from 1.3 to 5.6 [19], reflecting the different influence of volume, relative to temperature, on the local dynamics of different polymers.

Interestingly, when this scaling is extended to the chain dynamics of polymers, as measured by the dielectric normal mode in type-A polymers, the chain relaxation times for a given material also superpose to a single master curve versus \( TV \). Moreover, the scaling exponent \( \gamma \) has the identical value as for the segmental relaxation times, as shown for polypropylene glycol [31], 1,4-polyisoprene [31], and polyoxybutylene (POB) [32]. A similar result was found in molecular dynamic simulations of polybutadiene [33]. The equivalence of the scaling exponent for the segmental and global dynamics arises from the fact that both reflect the magnitude of the local friction coefficient. However, in the same manner that the \( T \)-dependence of the two modes differ, as discussed above, \( \tau_s \) varies more strongly with \( TV \) than does \( \tau_m \). Data for POB [32] showing this behavior are seen in Fig. 3. An explanation for the fact that the segmental and normal mode relaxation times are both functions of \( TV \) with the same \( \gamma \), yet have a difference dependence, is offered by the coupling model [34].

Eq. (2) has been derived from entropy considerations [35], leading to a connection between \( \gamma \) and the Grüneisen parameter [36]. Fundamentally the intermolecular potential governs the molecular motions, so that this exponent must be related to the steepness of the potential. For real materials the latter is difficult to quantify, but recent progress has been made by molecular dynamic simulations (mds).

3. Intermolecular potential

Molecular dynamic simulations of the motion of liquids near \( T_g \) commonly employ a Lennard-Jones (LJ) potential to describe the interactions between molecules [37]

\[ U(r) = 4\epsilon \left( \frac{\sigma^6}{r^6} - \frac{\sigma^6}{r^n} \right) \]

in which \( r \) is the intermolecular distance, \( \epsilon \) and \( \sigma \) are material constants, and the repulsive exponent \( n \) is usually assumed to be 12. For polymers an additional harmonic potential is invoked to account for the intrachain forces [38,39]

\[ U(r) = 4\epsilon \left( \frac{\sigma^6}{r^6} - 2\left( \frac{\sigma^6}{r^n} \right) \right) + k(r - l)^2 \]

in which \( k \) is the backbone force constant and \( l \) the bond length. By applying the scaling relation to simulation data, the connection between the exponent \( \gamma \) and the intermolecular potential can be examined. In fact, by approximating the weak, long-range attractive forces as a spatially uniform background term, Eq. (3) simplifies to a repulsive inverse power law [37]

\[ U(r) \sim r^{-\alpha} + \text{const} \]

When Eq. (5) is applicable, all thermodynamic properties become a function of \( r^n \) or, equivalently \( V^{n/3} \) [40]. This implies that \( n/3 \) can be identified with \( \gamma \). This was borne out in early work that showed approximate collapse using \( \gamma = 4 \) of viscosity [41] and diffusion [42] data for LJ fluids with \( n = 12 \). This connection between the steepness of the repulsive potential and the scaling exponent was investigated further in mds of an LJ liquid in which the exponent of the repulsive term of the potential was varied between 8 and 36 [43]. The calculated diffusion constant conform to the scaling law (Eq. (2)) with the exponent approximately equal to, but systematically larger than, one-third the value of \( n \), the exponent in the repulsive potential. These results, shown in Fig. 4, confirm the connection of the dynamics and its scaling to the repulsive forces between molecules.

![Fig. 3. Dielectric relaxation times for polyoxybutylene (upper) and normal mode (lower) for polyoxybutylene: isobars (\( P \leq 628 \text{MPa} \)) at \( 247 \text{K} \) (inverted triangles), \( 273 \text{K} \) (circles), and \( 297 \text{K} \) (triangles) and an isotherm (197–274 K) at 0.1 MPa (squares) [32].](image-url)
To understand why \( \gamma > n/3 \) requires consideration of the actual shape of the repulsive part of the potential, specifically the effect of the longer-range attractive term in Eq. (3). Shown in Fig. 5 is a representative plot of the intermolecular potential function for \( n = 24 \), along with the corresponding radial distribution function, \( g(r) \) [43]. The radial distribution function gives the probability of finding a particle at a distance \( r \) from another particle; thus, \( g(r) \) describes the effect of intermolecular correlations on the distribution of molecules resulting from the forces between them. It is seen in Fig. 5 that only at very small interparticle distances is the asymptotic region \( U(r) \sim r^{-\gamma} \) attained. At more accessible values of \( r \), close to the minimum in the potential, the potential is steeper. In fact fitting the potential to a power law (Eq. (5)) in the range between 0.95\( r_{\min} \) and 1.01\( r_{\min} \), where \( r_{\min} \) represents the interparticle separation at the minimum in \( U(r) \), yields an \( n \) essentially equal to 3\( \gamma \) (see Table 1) [43]. This range of \( r \) corresponds to the distance of closest approach, as seen in the plot of the radial distribution function in Fig. 5. Budzien et al. [39] also found that inclusion of an attractive term in their simulations increases the value of \( \gamma \) that yields superposition of diffusion data.

These results underscore the idea that the scaling exponent provides direct information about the forces between molecules, in particular in the range of intermolecular separations important for the liquid (or melt) state. The steepness of the repulsive poten-

![Fig. 4](image1.png)

![Fig. 5](image2.png)

**Fig. 4.** Diffusion coefficients for three pressures and a range of temperatures from simulations using the indicated values of the repulsive exponent (Eq. (3)) [43]. Note that the ordinate is the diffusion constant normalized by \( V^{1/3}T^{1/2} \), but the superpositioning is very similar without the normalization.

**Fig. 5.** (top) Radial distribution functions for \( P = 10 \) at the three indicated temperatures of an LJ fluid (Eq. (3)) with a repulsive exponent \( = 24 \); (middle) radial distribution function for the three indicated pressures at the lowest equilibrated temperatures; (bottom) pair potential (solid line) and best-fit IPL (Eq. (5), dashed line) in the range 0.95 \( \leq r \leq 1.01 \) (indicated by the vertical lines in all panels) from Ref. [43].
tial exerts a dominant role in governing the dynamic behavior. However, as stated above, the high concentration of intramolecular bonds in chain molecules means that the intramolecular forces make a substantial contribution. Since intramolecular interactions do not change much with pressure (chains simply move closer together rather than change their radius of gyration) [32], volume effects per se tend to be weaker in polymers than molecular liquids [44,45]. This effect of the intramolecular bonds was evident in mds of Tsoulo et al. [33] on 1,4-polybutadiene. Using Eq. (4) to describe the potential with $n = 12$, relaxation times, for both the segmental and terminal chain dynamics, superposed when plotted according to Eq. (2). The scaling exponent collapsing the various $\tau(T,V)$ data, $\gamma = 2.8$, is less than one-third the value of the repulsive exponent. This is opposite to the results for simple LJ particles (Fig. 5) [43], for which the scaling exponent is larger than $n/3$.

To understand this in Fig. 6 we plot $U(r)$ calculated using representative values for polybutadiene: $\varepsilon = 4.12$ kJ/mol, $\sigma = 4.19 \text{ Å}$, $k = 3.4 \text{ MJ/(molÅ)}^2$, and $l = 1.46 \text{ Å}$ [46]. Similar to the data in Fig. 5, in the limit of small $r$, $U(r)$ has a power law form with a slope equal to 12. However, nearer the minimum the potential is flatter. The line in the figure is for $U(r) \sim r^{-8.5}$, which corresponds to one-third the $\gamma$ yielding superposition of the diffusion data. Thus, the presence of the harmonic term, due to chain stretching and bending motions, softens the effective potential. This result is in keeping with the general observation that volume changes exert a weaker effect on the dynamics of polymers than on the motion of small molecules [19,44,45].

4. Summary

The defining aspect of polymers – the giant size of their constituent molecules – gives rise to relaxation properties not seen in simple molecules. Polymer dynamics encompass a range of length scales, with motions at the various length scales responding differently to changes in thermodynamic variables ($T$, $P$, and $V$). This causes the well-known breakdown of time-temperature superposition in the glass transition zone, where both the chain and segmental modes contribute. Nevertheless, relaxation times for both the global chain and local segmental modes collapse onto (different) respective master curves as a function of the scaling variable $TV$, for the same value of the exponent $\gamma$. Similar to the greater sensitivity of the segmental modes to changes in $T$, $P$, and $V$, $\tau_s$ vary more strongly with $TV$ than do $\tau_p$, notwithstanding the equivalent values of $\gamma$ for the two modes. Molecular dynamics simulations bring out the fact that the magnitude of this scaling exponent reflects the steepness of the intermolecular repulsive potential in the vicinity of the minimum, where the fluctuating segments spend most of their time. The contribution of intramolecular bonds softens the effective potential, leading to smaller values of $\gamma$. This weaker influence of volume in polymers compared to molecular liquids is ironic, given the long-standing reliance on free volume concepts in the interpretation of the physical properties of polymers.

Aside from insights into the intermolecular potential, the scaling relation has practical utility. If the temperature dependence of the relaxation times is known for ambient pressure (the usual case), any arbitrary combination of $T$ and $P$ can be calculated from the equation of state that will correspond to the ambient pressure $T$ and $V$. The two thermodynamic conditions (ambient and elevated $P$) will have the same relaxation time, since they have the same product variable $TV$ (viz. Eq. (2)). Thus, for any measured $\tau_s$ or $\tau_p$ all thermodynamic conditions associated with the same value of relaxation time can be calculated by using the scaling relationship. The only requirement is knowledge of the equation of state. The approach has been verified and used to explore the dynamics of various glass-forming liquids over a range of conditions [27].

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References