



Resolving the Mystery of the Chain Friction Mechanism in Polymer Liquids

Alexei P. Sokolov^{1,*} and Kenneth S. Schweizer²

¹*Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, USA*

²*Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801, USA*

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We propose an explanation for the long-standing puzzles of the microscopic mechanism of chain friction and the failure of time-temperature superposition in polymer melts based on decoupling of macromolecular scale diffusion from local structural relaxation due to spatially heterogeneous dynamics. The proposed physical picture is also relevant for understanding some aspects of dynamic fluctuation and decoupling phenomena in nonpolymeric glass-forming liquids, crystal growth rates, and protein activity in viscous solvents.

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Polymer liquids exhibit unique viscoelastic properties due to their construction as long interpenetrating chains of repeat units. The global chain motion is the basic relaxation process that controls the long time relaxation and macroscopic transport properties of these materials [1]. Despite the success of classic theories for the universal aspects of chain dynamics and its dependence on molecular weight [1–3], the problem of the mechanism of the temperature-dependent local friction remains poorly understood [4]. Traditional models assume the same microscopic frictional process operates on all length and time scales [1–3], and hence segmental relaxation (the analog of structural or α -relaxation in nonpolymeric glass-forming liquids) and chain relaxation should exhibit the same temperature dependence. This assumption is the basis for the widely employed empirical time-temperature superposition (TTS) principle—a cornerstone of polymer physics and rheology [1,4]. However, for more than four decades, it has been known that TTS fails in a material-specific fashion. Specifically, the characteristic relaxation time of chain modes, τ_C , exhibits weaker temperature variations than its segmental analog, τ_S , as the glass transition temperature, T_g , is approached [4,5]. Thus, in contrast to the usual theoretical assumptions, the polymer friction mechanism depends on length scale, a mystery that remains unsolved [4–7] despite a few phenomenological model attempts [4,8].

In this Letter, we propose that the key to understanding the difference in temperature variations of chain and segmental friction is spatially heterogeneous dynamics which modifies local structural relaxation but is averaged out on the chain relaxation length and time scale. This physical picture resolves the two puzzles of TTS failure and the almost universal behavior of the temperature dependence of chain relaxation [6]. Moreover, the ideas are also relevant for some aspects of dynamic decoupling phenomena in nonpolymeric glass-forming liquids, solutions of biological macromolecules, and crystallization kinetics.

Our starting point is the known fact that the macromolecular scale relaxation process is of diffusive origin, driven by many local elementary segment scale jumps, with a characteristic relaxation time [2]

$$\tau_C \propto \frac{R_{ee}^2}{D_{CM}}. \quad (1)$$

Here, $R_{ee}^2 \propto N\sigma^2$ is the mean squared end-to-end distance, N is the degree of polymerization, σ is the statistical segment length, and the center-of-mass diffusion constant is

$$D_{CM} \approx \frac{D_{seg}}{N^X} \propto N^{-X} \sigma^2 \bar{\tau}_S^{-1} \quad (2)$$

where X differs for unentangled and entangled chains [3]. The diffusive nature of chain scale relaxation is in strong contrast to nanometer-scale segmental relaxation which involves *local dynamically heterogeneous* motions. The relevant “segmental” diffusion constant in Eq. (2) involves a *mean* friction constant (with corresponding mean local hopping time, $\bar{\tau}_S$) since in the supercooled regime, the spatial extent (a few nm) and lifetime of dynamic heterogeneities are much shorter than macromolecular size and relaxation time [9–11]. Hence, for the chain dynamics problem, heterogeneity and decoupling effects are spatially and temporally averaged out, as demonstrated for polystyrene melts [12]. On the other hand, for molecular liquids, the Stokes-Einstein relation between the self-diffusion constant and the structural relaxation time (or viscosity and single particle rotational time), $D\tau_\alpha = \text{const}$, fails as T_g is approached [9–16]. Such “translation-rotation decoupling” is experimentally well characterized by a “fractional Stokes-Einstein” (FSE) law [13,14]: $D\tau_\alpha \propto (\tau_\alpha)^\varepsilon$, with the exponent $\varepsilon \sim 0.23, 0.13$, and 0 for orthoterphenyl (OTP) [13], trisnaphthylbenzene (TNB) [14], and silica [17], respectively. We propose the same decoupling effect applies to the relationship between $\tau_C \propto D_{CM}^{-1}$ and τ_S in polymer liquids and can quantitatively explain the difference in their temperature behavior.

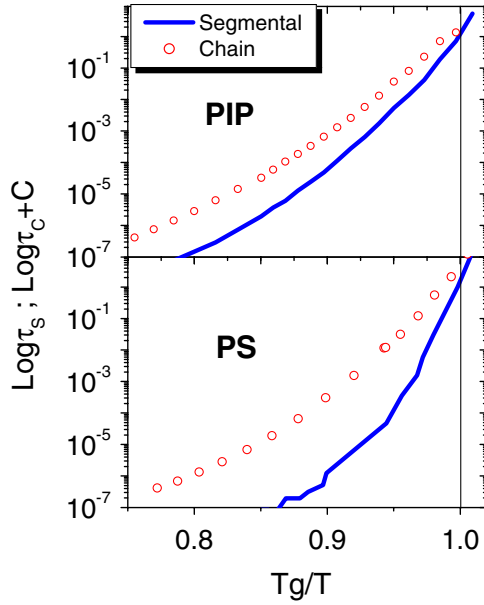


FIG. 1 (color online). Temperature dependence of segmental and chain relaxation in PIP and PS (data from [6]).

Experimental evidence for our proposition is reflected in existing polymer data which reveal a strong similarity between decoupling of the temperature dependence of chain and segmental dynamics and FSE behavior in molecular liquids. Figure 1 shows experimental results for two well-studied polymers, polyisoprene (PIP), and polystyrene (PS) (data from [6], where T_g has been taken as the temperature at which the segmental relaxation time $\tau_s = 1$ second). Both exhibit differences in the temperature variations of τ_c and τ_s , which is much stronger for PS (Fig. 1). The decoupling is quantified via the ratio $R = \tau_c/\tau_s$ (Fig. 2), which for temperatures close to T_g is well approximated by an effective power law, $R \propto (\tau_s)^{-\varepsilon}$. Note that ε varies widely from ~ 0.15 – 0.2 for PIP and poly(oxybutylene) (POB), up to ~ 0.53 for polycarbonate (PC), a far larger range than observed in nonpolymeric liquids. These polymers also exhibit a strong difference in the steepness of the temperature dependence of τ_s close to T_g , as quantified by the so-called dynamic fragility parameter, m , which characterizes the deviation from simple Arrhenius behavior [18]:

$$m = \left. \frac{\partial}{\partial(T_g/T)} \log \tau_s \right|_{T=T_g}. \quad (3)$$

PIP and POB have the lowest fragility while PC has the highest fragility among the polymers presented in Fig. 2 [6]. Figure 3(a) clearly demonstrates that ε is chemical structure dependent and systematically increases with fragility. The fragility values employed are an average of the data presented in Refs. [6,19], and the error-bars are estimated from the difference in these two data sets.

Distinct experimental probes of glassy dynamics in non-polymeric systems display a strong similarity with the

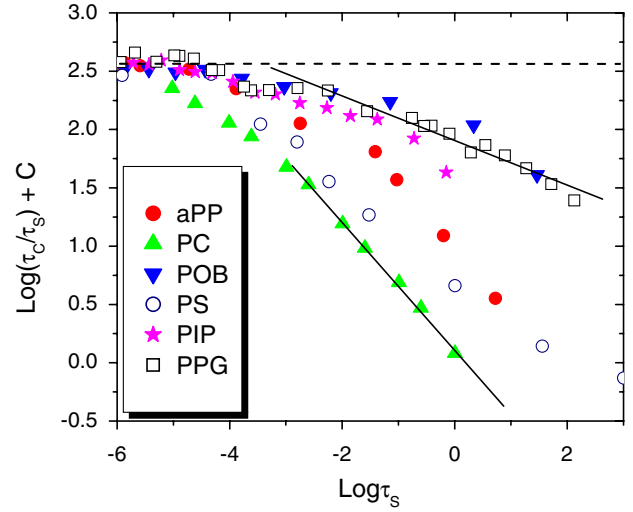


FIG. 2 (color online). The ratio of the chain to the segmental relaxation time $R = \tau_c/\tau_s$, plotted as a function of τ_s for atactic polypropylene (aPP), polycarbonate (PC), polyoxybutylene (POB), PS, PIP, and polypropylene glycol (PPG) (data from [6]). The dashed line shows the behavior expected if segmental and chain friction would have the same mechanism; the solid lines indicate $R \propto \tau_s^{-\varepsilon}$.

decoupling of chain and segmental relaxation in polymer melts. For example, dynamic decoupling of various motions in diverse glass-forming liquids is observed at temperatures approaching T_g . Apparently, this decoupling occurs for both the bulk viscosity and self-diffusion constant, and the single molecule rotational and translational motions [9,10,13–16]. Also, the kinetic factor that enters the crystallization growth rate, which reflects a local diffusive process, exhibits strong decoupling from the bulk viscosity in a fragility-dependent manner [Fig. 3(a)], where empirically $\varepsilon = 0.005m - 0.1$ has been proposed [15]. Moreover, dynamic heterogeneity and FSE behavior has been suggested [20] as a novel mechanism for destabilizing a deeply supercooled liquid against crystallization via its influence on the nucleation rate, which in turn provides a possible resolution of the famous Kauzmann paradox [21].

Several conceptually distinct modern theories of glassy dynamics are qualitatively consistent with an increase in the degree of decoupling and/or apparent exponent ε with fragility, including the entropy crisis Random First Order Phase Transition (RFOT) theory [22], and the family of coarse grained kinetically constrained models based on dynamic facilitation rules [23,24]. Both approaches predict the degree of decoupling grows with increasing fragility, but an explicit result for $\varepsilon(m)$ has not been obtained. Another microscopic approach based on thermally activated barrier hopping does predict the FSE exponent for hard sphere fluids and colloidal suspensions [25,26]. This theory adopts a domain model where fluctuating local density results in a distribution of barrier heights and relaxation times, which gives rise to decoupling of the volume fraction dependence of the alpha relaxation time

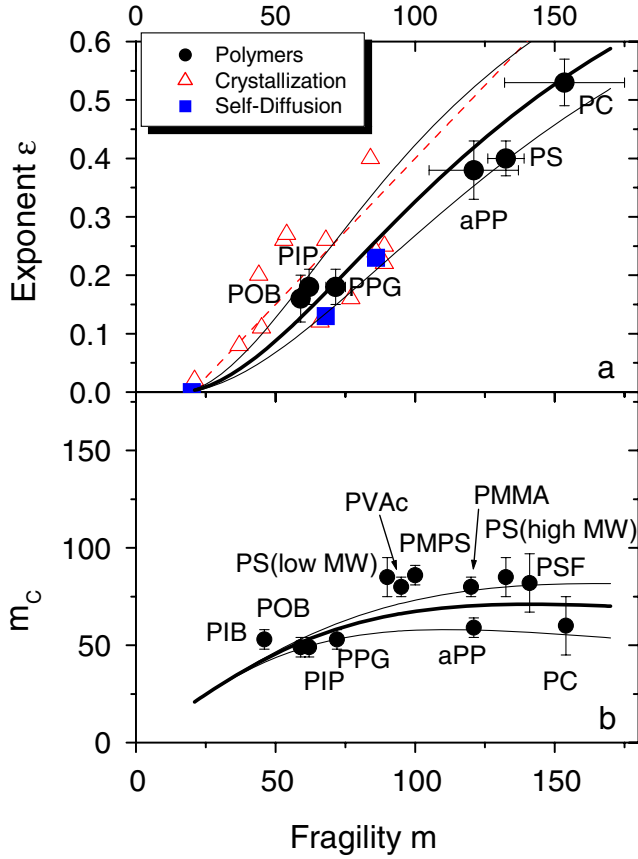


FIG. 3 (color online). (a) The decoupling exponent ε for polymers (closed circles; names indicated) determined using the last 4 decades of data close to T_g in Fig. 2. Open triangles are decoupling exponents estimated from crystal growth rates [15]. Closed squares present self-diffusion data, in order of the increasing fragility: SiO_2 [17], TNB [14], and OTP [13]. The dashed line shows the linear relationship proposed in [15]. The solid lines present the predictions of Eq. (5) for $q = 0.13$ (thick line, best fit through the polymeric data), $q = 0.1$ (the lower thin solid line), and $q = 0.2$ (the upper thin solid line). (b) “Effective fragility” of the chain relaxation as a function of segmental fragility determined using Eq. (4) with $q = 0.13$ (thick solid line), $q = 0.1$ (upper thin solid line), and $q = 0.2$ (lower thin solid line). Symbols show experimental estimates of m_C : the names of the polymers are indicated and include polyisobutylene (PIB), low and high molecular weight PS, poly(methylphenyl siloxane) (PMPS), poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA).

and diffusion constant, and also stretched nonexponential relaxation. The basic ideas can be carried over to thermal polymer melts, and a result analogous in form to that derived in [26] is obtained [27]:

$$D_{\text{CM}}\tau_S \propto \frac{\tau_S}{\tau_C} \propto \frac{\tau_S}{\tau_S} = e^{\sigma_E^2/2} \propto \tau_S^{-\varepsilon}. \quad (4)$$

Here, σ_E^2 is the barrier fluctuation variance (in units of the thermal energy), $\varepsilon = \Delta/(1 + \Delta)$, $\Delta = a_c q$ where a_c is a material-specific local stiffness parameter determined by the (essentially temperature independent) polymer back-

bone characteristic ratio that describes the number of segments on a single chain participating in the barrier crossing event, and $q \equiv \sigma_E^2/2\bar{E}_B$, where \bar{E}_B is the mean activation barrier [25,26]. Based on a domain diameter of $d \sim 3\text{--}4$ particle diameters, a nearly volume fraction independent $q \sim 0.1\text{--}0.2$ is predicted for hard sphere fluids [26]. The same model when applied to polymer melts (where $d \sim 3\text{--}4$ nm) yields a nearly monomer chemistry and temperature independent value of $q \sim 0.1\text{--}0.2$ [27]. Moreover, the polymer melt theory [25] predicts the fragility at T_g closely follows the law: $m \approx 16 + 40.6(a_c)^{0.56}$, consistent with the intuitive idea that fragility grows with increasing chain stiffness. Combining these theoretical elements yields an experimentally testable connection between the decoupling exponent and fragility:

$$\frac{1}{\varepsilon} = 1 + \frac{1}{a_c q} = 1 + \frac{q^{-1}}{[(m - 16)/40.6]^{1/0.56}}. \quad (5)$$

Figure 3(a) shows a fit of the experimental data for polymers to Eq. (5) based on varying the single parameter q . Good agreement is obtained for $q \approx 0.13$, a value consistent with theoretical expectations [26,27]. This agreement strongly supports a connection between the FSE exponent and fragility, and a dynamic heterogeneity origin of the temperature decoupling phenomenon, in polymer liquids.

We now explore other consequences of the proposed physical picture. Consider first the steepness of the temperature dependence of chain relaxation. To leading order, Eq. (4) implies the effective chain relaxation fragility, m_C , is related to its segmental analog as $m_C \approx m(1 - \varepsilon)$. Using this relationship, m_C is computed as a function of segmental fragility [Fig. 3(b)]. The steepness of the chain temperature dependence is predicted to initially grow significantly with fragility, but then to vary weakly for $m > 60\text{--}80$. Figure 3(b) presents data for 12 polymers with significant variations in chemical structure. All data are from [28], except PC (m_C is an average of the three data sets [6,29,30]) and polysulfone (PSF) (m_C is an average of the three data sets [29–31]). They agree qualitatively with the predicted behavior [Fig. 3(b)]. Hence, a logical consequence of the proposed decoupling mechanism is that the effective fragility of chain relaxation is only weakly variable for different polymers, in strong contrast to its segmental scale analog. To the best of our knowledge, this provides the first plausible explanation for the surprising almost universal behavior of chain relaxation observed when temperature is reduced by T_g , and the rather weak (although measurable [28]) dependence of m_C on polymer chemical structure and molecular weight [6,28,32].

Second, the same decoupling scenario applies to diffusion and relaxation in nonpolymeric liquids, including the reduction of translation-rotation decoupling (decrease of the exponent ε) as the fragility decreases [12–17]. For example, it is consistent with the observation that SiO_2 and other low-fragility systems exhibit essentially no, or

very weak, decoupling of various relaxation phenomena, and also provides a physical basis for understanding the material-dependent decoupling of the crystal growth rate from viscosity [15]. As an additional testable prediction, we suggest the steepness of the temperature dependence of diffusion in nonpolymeric liquids should vary weakly with dynamic fragility for $m > 60$ [Fig. 3(b)].

Third, as a more speculative comment, the same decoupling mechanism may be applicable to protein activity in viscous solvents; i.e., the dynamically heterogeneous aspect of solvent relaxation (viscosity) is largely averaged out on the protein length and relaxation time scales, especially in highly fragile solvents at temperatures near T_g . It is known that the temperature dependence of biochemical processes (e.g., ligand escape rate from myoglobin) are often decoupled from solvent viscosity [33], a fact that is also usually described by a FSE law. For example, myoglobin in glycerol-water solutions exhibits $\varepsilon \sim 0-0.2$, while a much larger $\varepsilon \sim 0.5$ occurs in sucrose-water solutions [33]. These observations are consistent with the much higher fragility of sucrose relative to glycerol.

In conclusion, we have proposed that decoupling of the temperature dependence of the local and chain scale relaxation times in polymer liquids is the combined consequence of heterogeneous dynamics on the nanometer segmental scale and the diffusive nature of macromolecular relaxation for which heterogeneities are temporally and spatially averaged out. This idea provides an explanation for the long-standing puzzle of the breakdown of time-temperature superposition in polymer melts [4,5]. Moreover, based on the *observed* relationship between the degree of decoupling and fragility, we propose a physical scenario that explains the almost universal thermal variations of the chain relaxation time and the corresponding relatively modest value of the fragility parameter, m_C , as compared to its segmental analog which varies over the wide range of $m \sim 46-150$. The underlying qualitative idea is that chain relaxation is a mean field process in the sense that heterogeneous dynamics and local chain stiffness effects are (largely) averaged over, in contrast to nanometer-scale segmental relaxation. We emphasize that the proposed ideas may be applicable to dynamics in other complex systems, including molecular liquids and the decoupling of protein activity from solvent viscosity.

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*Contact author: alexei@uakron.edu

- [1] J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley & Sons, New York, 1980), 3rd ed.
- [2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1986).
- [3] T. C. B. McLeish, *Adv. Phys.* **51**, 1379 (2002).
- [4] K. L. Ngai and D. J. Plazek, *Rubber Chem. Technol.* **68**, 376 (1995).
- [5] D. J. Plazek, *J. Phys. Chem.* **69**, 3480 (1965).
- [6] Y. Ding and A. P. Sokolov, *Macromolecules* **39**, 3322 (2006), and references therein.
- [7] A. P. Sokolov and Y. Hayashi, *J. Non-Cryst. Solids* **353**, 3838 (2007).
- [8] B. Ilan and R. F. Loring, *Macromolecules* **32**, 949 (1999).
- [9] M. D. Ediger, *Annu. Rev. Phys. Chem.* **51**, 99 (2000).
- [10] R. Richert, *J. Phys. Condens. Matter* **14**, R703 (2002).
- [11] U. Tracht, M. Wilhelm, A. Heuer, and H. W. Spiess, *J. Magn. Reson.* **140**, 460 (1999).
- [12] O. Urakawa, S. F. Swallen, M. D. Ediger, and E. D. von Meerwall, *Macromolecules* **37**, 1558 (2004).
- [13] M. K. Mapes, S. F. Swallen, and M. D. Ediger, *J. Phys. Chem. B* **110**, 507 (2006).
- [14] S. F. Swallen, K. Traynor, R. J. McMahon, and M. D. Ediger, *J. Phys. Chem. B* (to be published); S. F. Swallen, P. A. Bonvallet, R. J. McMahon, and M. D. Ediger, *Phys. Rev. Lett.* **90**, 015901 (2003).
- [15] M. D. Ediger, P. Harrowell, and L. Yu, *J. Chem. Phys.* **128**, 034709 (2008).
- [16] J. F. Douglas and D. Leporini, *J. Non-Cryst. Solids* **235-237**, 137 (1998).
- [17] M. L. F. Nascimento and E. D. Zanotto, *Phys. Rev. B* **73**, 024209 (2006).
- [18] R. Boehmer and C. A. Angell, *Phys. Rev. B* **45**, 10091 (1992).
- [19] Q. Qin and G. B. McKenna, *J. Non-Cryst. Solids* **352**, 2977 (2006).
- [20] H. Tanaka, *Phys. Rev. E* **68**, 011505 (2003).
- [21] W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).
- [22] V. Lubchenko and P. G. Wolynes, *Annu. Rev. Phys. Chem.* **58**, 235 (2007).
- [23] F. Ritort and P. Sollich, *Adv. Phys.* **52**, 219 (2003).
- [24] Y. Jung, J. P. Garrahan, and D. Chandler, *Phys. Rev. E* **69**, 061205 (2004).
- [25] E. J. Saltzman and K. S. Schweizer, *J. Phys. Condens. Matter* **19**, 205123 (2007).
- [26] K. S. Schweizer and E. J. Saltzman, *J. Phys. Chem. B* **108**, 19729 (2004).
- [27] E. J. Saltzman and K. S. Schweizer (unpublished calculations).
- [28] K. L. Ngai, D. J. Plazek, and C. M. Roland, *Macromolecules* **41**, 3925 (2008).
- [29] A. Alegria, E. Macho, and J. Colmenero, *Macromolecules* **24**, 5196 (1991).
- [30] E. J. Hwang, T. Ionue, and K. Osaki, *Polym. Eng. Sci.* **34**, 135 (1994).
- [31] Y. Hwang and M. D. Ediger, *J. Polym. Sci. B* **34**, 2853 (1996).
- [32] C. Y. Liu, J. S. He, R. Keunings, and C. Bailly, *Macromolecules* **39**, 8867 (2006).
- [33] T. Kleinert and W. Doster *et al.*, *Biochemistry* **37**, 717 (1998).