The application of the energy landscape model to polymers

C. M. Roland, P. G. Santangelo, and K. L. Ngai
Naval Research Laboratory, Washington, DC 20375-5342

The energy landscape model of the glass transition has received increasing attention, due to its potential for providing a thermodynamic interpretation of the dynamics of glass-forming liquids. Herein, the idea that the temperature-dependence of the dynamics near the glass temperature ("fragility") can be related to thermodynamic properties is tested for polymers. Previously, for several homologous series, we found deviations from a proposed correlation between fragility and the heat capacity increment at the glass temperature. A survey of 17 polymers likewise indicates no correlation between these two quantities. More recently, the landscape approach to the dynamics of glass-formers was extended to a proposal that fragility can be determined *a priori* from thermodynamic information. However, for the 11 polymers for which sufficient thermodynamic and relaxation data were available, we find that thermodynamic properties bear no relationship to fragility. Thus, it appears that the status of the glass transition as an important unsolved problem in condensed matter physics remains intact. [S0021-9606(99)51136-7]

I. INTRODUCTION

Interpreting the macroscopic properties of polymers and other complex materials requires an understanding of the underlying microscopic-scale phenomena. Efforts to accomplish this generally focus either on the thermodynamic properties or on dynamics and relaxation; however, establishing a connection between these fundamental aspects of the behavior of glass-forming liquids is an ambitious task. Toward this end, Angell and co-workers have developed an energy landscape model and used it to analyze data on various small molecule glass-formers.[1,2] The central idea of the model is that the manner in which the structure and transport properties of a glass evolve with temperature is governed by the density of configurational states comprising the material's potential energy hypersurface. The topology of this energy landscape (i.e., the number of minima and the barrier heights between them) provides a measure of the steepness of the excitation profile for glass-forming liquids. According to the model, when heated through T_g, fragile liquids readily transition among many configurational states, giving rise to substantial changes in relaxation times and viscosities. This leads to the prediction that fragile behavior is associated with a large heat capacity increment during the glass transition.

Whether or not this landscape interpretation is correct, the classification of liquids and polymers as "strong" and "fragile" has become a common means to classify relaxation in glass-formers. One of the more intriguing aspects of such work is the correlation demonstrated between fragility and the shape of the relaxation function. Specifically, fragile glass-formers have broader relaxation functions than do strong, or less fragile, liquids.[3–7] The breadth, or degree of nonexponentiality, of the dispersion is reflected in the Kohlrausch exponent β

$$\phi_\alpha(t) = \exp\left[-\left(\frac{t}{\tau_\alpha}\right)^\beta\right], \tag{1}$$

where $\varphi(t)$ is the relaxation function and τ_α the relaxation time. The correlation of β with fragility has been expressed quantitatively for a large number of glass-forming liquids as[7]

$$m = 250(\pm 30) - 320\beta, \tag{2}$$

where the fragility parameter, m, is equal to the slope of the T_g-normalized Arrhenius plot of τ_α

$$m = \frac{d\log(\tau_\alpha)}{d(T_g/T)}\Big|_{T=T_g}. \tag{3}$$

For dynamics, the glass temperature is commonly taken to be the temperature at which the relaxation time assumes an arbitrary value, e.g., $\tau_\alpha(T_g) = 100$ s.

The rationale for a correlation between thermodynamic characteristics such as $\Delta C_p(T_g)$ and relaxation properties is the idea that the latter reflect the temperature evolution of the thermodynamic states of the system. If dynamic properties such as m are indeed "rate-of-structural-change metrics,"[8] they will be governed by the response of the energy landscape to temperature; accordingly, other fundamental connections between thermodynamics and relaxation should be evident. These ideas led to the suggestion that the rapidity of the departure of a liquid's configurational entropy from its value at the melting temperature should parallel dynamic measures of fragility such as m.[8–11] A thermodynamic fragility can be defined from the steepness of Kauzmann plots[12] of ΔS, the configurational entropy difference between the liquid and perfect crystal, versus temperature normalized by T_m, the equilibrium melting point. To allow comparison of different glasses, ΔS in a Kauzmann plot is normalized by the value at the melting temperature, $\Delta S(T_m)$.

Our purpose herein is to examine the utility of the landscape model for polymers. Polymers provide a formidable test of this approach, since they encompass a range of relaxation properties including the most fragile behavior, as well as having diverse chemical structures. First, our recent results, comparing $\Delta C_p(T_g)$ and m for polymers having sys-
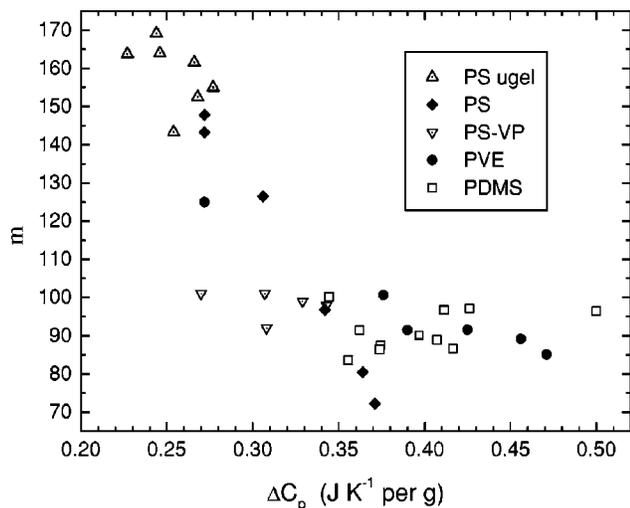
FIG. 1. Fragility versus heat capacity change at T_g for several homologous series of polymers. Following the original works, T_g is taken to be the temperature at which $\tau = 100$ s for PS (Ref. 14) and PS microgels (Ref. 22), while for PDMS (Ref. 16 and PS-VP (Ref. 23), $\tau(T_g) = 1$ s, and for PVE (Refs. 20,21) $\tau(T_g) = 0.16$ s. The observed trends are at odds with the landscape model's prediction that $\Delta C_p(T_g)$ and fragility are directly correlated; to wit: increasing molecular weight reduces $\Delta C_p(T_g)$ for both PS and PDMS, although fragility increases for the former and does not change for the latter. Crosslinking reduces $\Delta C_p(T_g)$, yet the fragility of both PVE networks and of PS microgels increase with crosslink density. The introduction of polar vinyl-phenol moieties into the backbone of PS increases $\Delta C_p(T_g)$, but has no effect on the copolymer's fragility.

tematic variations in structure, are reviewed. We then avail ourselves of literature compilations of the thermal properties of polymers to fully explore whether a relationship between these two quantities exists. Finally, this survey of literature data is extended to a comparison of m with the proposed thermodynamic measure of fragility.

II. HEAT CAPACITY CHANGE DURING THE GLASS TRANSITION

An assessment of the landscape model is obtained by comparing the heat capacity change at T_g for polymers identical in chemical structure, but exhibiting different fragilities. This can be accomplished by systematic variation of molecular weight for a given species. The effect of chain length on m appears to parallel its effect on T_g. For polystyrene (PS), a higher concentration of chain ends (i.e., lower molecular weight) causes a marked decrease in the glass temperature;[13] there is a concomitant reduction in m.[14,15] For more flexible polymers such as polydimethylsiloxane (PDMS), molecular weight has a relatively small effect on both the glass temperature and fragility.[16] Presumably flexible chains realize less benefit from the excess mobility conferred by free ends.

We can compare $\Delta C_p(T_g)$ for polymers differing only in molecular weight. Below some high polymer limit, the heat capacity change at T_g varies inversely with chain length. The expectation from the landscape model is that over this range, m should likewise decrease with increasing molecular weight. As seen in Fig. 1, however, the fragility of PS increases with increasing molecular weight. On the other hand, for PDMS, m is independent of chain length (Fig. 1), not-

withstanding the molecular weight dependence of its $\Delta C_p(T_g)$. Results for both polymers are at odds with the landscape model.

Another variable influencing behavior at the glass transition is crosslinking.[17,18] Networks, when examined using conventional spectroscopies or other bulk measurement techniques, exhibit a distribution of segmental relaxation behaviors.[19] Chain segments in proximity to a network junction experience stronger constraints on their local motion than do more remote segments. This yields a distribution of relaxation behaviors, and a relaxation function that can no longer be described using Eq. (1). Nevertheless, fragility can still be quantified by measuring the change in the mean relaxation time with temperature.

Dielectric relaxation spectra of polyvinylethylene (PVE) networks[20,21] and mechanical spectra of polystyrene microgels[22] have been reported in the literature. In both cases, fragility increases with the concentration of junctions. However, there is a concomitant reduction in the heat capacity change at T_g, due to reduced configurational freedom for the shorter network chains. Thus, as shown in Fig. 1, results for these two networks are opposite to the prediction of the landscape model.

Segmental relaxation behavior can also be altered by introducing different chemical groups into the chain backbone. Figure 1 includes data obtained for polystyrene having varying levels of vinyl–phenol comonomer.[23] While $\Delta C_p(_g)$ increases with vinyl–phenol content, there is almost no change in m with copolymer composition. This represents another example of discrepancy between experimental data and the model.

Actually, experiments on copolymers are not a completely fair test. Changing the chemical structure of the material can alter the energy barrier between configurational states. As Angell pointed out in regard to the exceptional behavior of alcohols[24] and substituted benzenes,[25] a glass-former's access to the available configurations is constrained if high barriers exist between the various energy minima. The implication is that restrictions on molecular rearrangements from hydrogen bonding or other intermolecular associations, might yield fragilities less than expected from the magnitude of $\Delta C_p(T_g)$.[1,2,26] Thus, the ratio of $\Delta C_p(T_g)$ to the barrier heights separating minima on the energy surface would be a better predictor of fragility.[24,25] However, we do not expect energy barriers to vary substantially among the majority of hydrocarbon polymers.[27]

Thus, the trend for every material in Fig. 1 is contrary to the landscape model's prediction that fragility is an increasing function of $\Delta C_p(T_g)$. Beyond these direct assessments of the model, general observations can be made concerning its application to polymers. Wunderlich and co-workers[28–31] surveyed data for polymers both below T_g and in the melt state, and determined that the heat capacity of the solid can be expressed as the sum of an "external contribution," related to thermal and volume expansion coefficients, and a vibrational term, which includes the skeletal vibrational spectrum, as well as contributions for chemical groups comprising the chain. From an evaluation of data for dozens of polymers, Wunderlich et al. concluded that the magnitude of
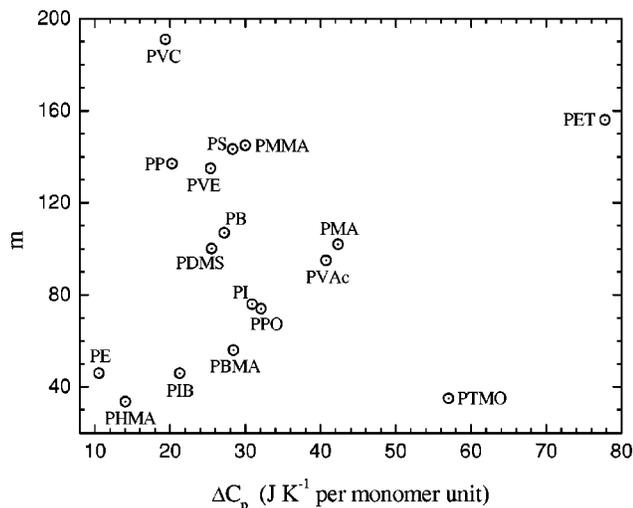
FIG. 2. Fragility versus the heat capacity change at T_g per mole of monomer units for 17 polymers (data from Table I), demonstrating the absence of any correlation between these quantities.

TABLE I. Polymers data, where n is the number of beads per monomer unit. Fragilities were calculated from Eq. (3) with $\tau(T_g) = 100$ s.

Polymer	Symbol	m	$\Delta C_p(T_g)$ (J deg^{1}mol^{-1})	$n^{a,b}$
Polyvinylchloride	PVC	191[c]	19.4[b]	2
Polyethylene terephthalate	PET	156[d,e]	77.8[b]	7
Poly(methylmethacrylate)	PMMA	145[c,f]	30.0[f]	3
Polystyrene	PS	143[g]	28.3[g]	3
Polypropylene	PP	137[h]	20.3[b]	2
Polyvinylethylene	PVE	135[i,j,k]	25.4[l]	2
1,4-polybutadiene	PB	107[j]	27.2[b]	3
Poly(methyl acrylate)	PMA	102[c]	42.33[b]	⋯
Polydimethyl siloxane	PDMS	100[m]	25.5[m]	2
Polyvinylacetate	PVAc	95[c]	40.7[b]	4
Polyisoprene	PI	76[n,o]	30.9[b]	3
Polypropylene oxide	PPO	74[p,q]	32.1[b]	3
Poly(butylmethacrylate)	PBMA	56[f]	28.4[f]	⋯
Polyisobutylene	PIB	46[c]	21.3[b]	2
Polyethylene	PE	46[r,d]	10.5[b]	1
Polytetramethylene oxide	PTMO	35[d,s]	57.0[b]	5
Poly(hexylmethacrylate)	PHMA	34[f]	14.1[f]	⋯

[a]References 31,33.	[k]Reference 45.
[b]Reference 34.	[l]Reference 21.
[c]Reference 7.	[m]Reference 16.
[d]Reference 40.	[n]Reference 4.
[e]Reference 41.	[o]Reference 46.
[f]Reference 42.	[p]Reference 47.
[g]Reference 14.	[q]Reference 48.
[h]Reference 43.	[r]Reference 6.
[i]Reference 20.	[s]Reference 49.
[j]Reference 44.	

the vibrational component of the heat capacity can be accounted for simply from the additive contributions of the various chemical groups. This group additivity approach can quantitatively describe heat capacities of polymers in the solid state.[28–31]

Above T_g, however, there is an additional term due to the conformational freedom available to a polymer in the liquid state. The heat capacity thus depends on bond rotational energies, and the degeneracy of the various conformational states. The important point is that modification of a polymer chain by the introduction of substituent groups does not simply add a term to the liquid heat capacity. Obviously, if additional groups on the polymer chain increase the heat capacity in the glassy state, as indicated by a group additivity rule, then the lack of a corresponding effect on the liquid C_p means that their difference, $\Delta C_p(T_g)$, generally decreases upon addition of substituent groups. We have previously shown that the addition of bulky or inflexible groups to a polymer backbone increases fragility, ascribing the effect to enhanced intermolecular cooperativity from steric constraints among neighboring segments.[4,6,32] In light of the group additivity rule[28–31] implying smaller $\Delta C_p(T_g)$, this increase in fragility upon addition of pendant groups implies a correlation of m with $\Delta C_p(T_g)$ that is opposite to that predicted by the landscape model.

In Fig. 2 we plot fragilities versus $\Delta C_p(T_g)$ for 17 polymers of high molecular weight. These represent all cases for which reliable data for both quantities were available in the literature (see Table I). Clearly, there is no relationship between m and $\Delta C_p(T_g)$ over this broad range of materials. The abscissa in Fig. 2 is the heat capacity increment per mole of repeat units. For polymers which differ only in molecular weight or crosslink density (Fig. 1), the choice of units for $\Delta C_p(T_g)$ is irrelevant. However, for chemically distinct species, the appropriate denominator for the heat capacity increment is not obvious.

From analysis of published data for amorphous polymers, Wunderlich et al. concluded that, when $\Delta C_p(T_g)$ is

normalized to the ''bead size'' of the polymer chain, the heat capacity change at T_g is a near universal constant.[31,33,34] Originally defined as the smallest molecular unit whose movement alters the ''hole equilibrium'' of the liquid,[33] the bead for polymers is the portion of the chain that can be considered rigid. Listed in Table I is n, the number of ''beads'' per repeat unit, for most of the polymers in Fig. 2.

In Fig. 3 we display $\Delta \widetilde{C}_p(T_g)$, the heat capacity increment per bead ($= \Delta C_p(T_g)/n$), for the polymers in Fig. 2. The acrylate polymers are omitted, because of uncertainty regarding the definition of a bead for these structures.[34] The values in Fig. 3 fall within a narrow range, with an average $\Delta \widetilde{C}_p(T_g) = 11.5 \pm 1.7$ J/deg per mole of beads, as reported by Wunderlich.[31,33,34] No support for a correlation with fragility is apparent in Fig. 3, and certainly there is no trend of increasing $\Delta \widetilde{C}_p(T_g)$ with increasing m.

III. THERMODYNAMIC DETERMINATION OF FRAGILITY

Building on the notion that relaxation properties are related to thermodynamics quantities, Angell and co-workers put forth the proposition that fragilities could be determined from thermodynamic data.[8] Experimental results on small-molecule glass-formers,[8] as well as simulation results for a model liquid,[35] have provided some support for this idea. With the availability of data on the temperature dependence of the configurational entropy for various polymers in both
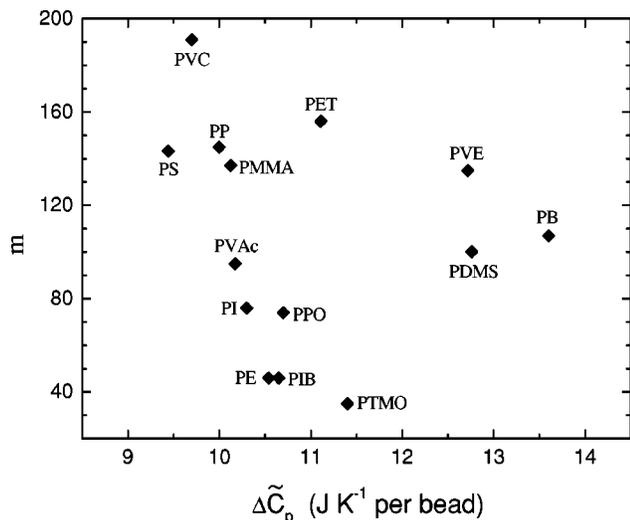
FIG. 3. Fragility versus the heat capacity increment at T_g per bead. This corresponds to Fig. 2 with the abscissa divided by n. These normalized heat capacity values fall within a narrow range (Refs. 31,33,34 while the fragility is widely scattered.

TABLE II. Thermodynamic data for polymers.[a]

Polymer	T_g (K)	T_m (K)	ΔS_m (J K^{-1} mole^{-1})	ΔS_g (J K^{-1} K^{-1} mole^{-1})	F [Eq. (4)]
PVC	354	546	20.1	2.36	0.554
PET	342	553	48.6	22.4	0.164
PB	171	285	32.3	20.4	0.211
PS	373	516	19.4	11.7	0.230
PP	270	461	18.9	11.5	0.107
PMMA	378	450	21.3	15.5	0.226
PDMS	146	219	11.8	2.72	0.362
PI	200	301	14.4	3.98	0.381
PIB	200	317	37.9	29.6	0.091
PE	237	415	9.91	5.57	0.139
PTMO	189	330	43.6	16.6	0.213

[a]Reference 34.

their amorphous and completely crystalline states,[34] the concept of thermodynamic fragility, and its correlation with dynamic fragility, can be tested for polymers.

Figure 4 shows Kauzmann plots for 11 polymers, representing all those for which both fragilities and the necessary configurational entropy data was obtained from the literature. The equilibrium melting points used for normalization are calculated by extrapolation from experimental data.[36–38] These and the other parameters used in constructing Fig. 4 are listed in Table I. The steepness of the Kauzmann plots is a measure of thermodynamic fragility.[8] However, the rank ordering of the curves in Fig. 4 is different from that of the respective m's for these polymers (Table I).

For example, the dynamic behavior of PTMO (also known as polytetrahydrofuran) is among the least fragile (smallest m) of all polymers. This has been ascribed to weak intermolecular constraints on the chain segments, due to the

free rotation afforded by the backbone ether linkages.[6] Nevertheless, the thermodynamic fragility of PTMO is intermediate among the eleven polymers in Fig. 4.

Among the polyalkenes in Table I, the dynamics of PP are by far the most fragile; however, its thermodynamic fragility is intermediate between that of PE and PIB. With the exception of PVC, PI and PDMS have the largest thermodynamic fragilities in Fig. 4, while their dynamic fragility falls in the lower half of the polymers in Table I.

This comparison can be made more explicit by quantifying thermodynamic fragility. A convenient measure is the fractional decrease of the fusion entropy at $T/T_m = 0.8$ (Ref. 8)

$$F = 1 - \frac{\Delta S(0.8 T_m)}{\Delta S(T_m)}, \tag{4}$$

which can be determined without extrapolation for all the polymers in Fig. 4. In Fig. 5 we display this thermodynamic fragility versus dynamic fragility; no correlation between the quantities is apparent.

Finally, Ito et al. have pointed out that Kauzmann plots can be converted to a form analogous to the usual dynamic fragility curves by using T_g for the reference temperature, in

FIG. 4. Kauzmann plots for 11 polymers (see Table II). The steepness reflects the thermodynamic fragility (Ref. 8).
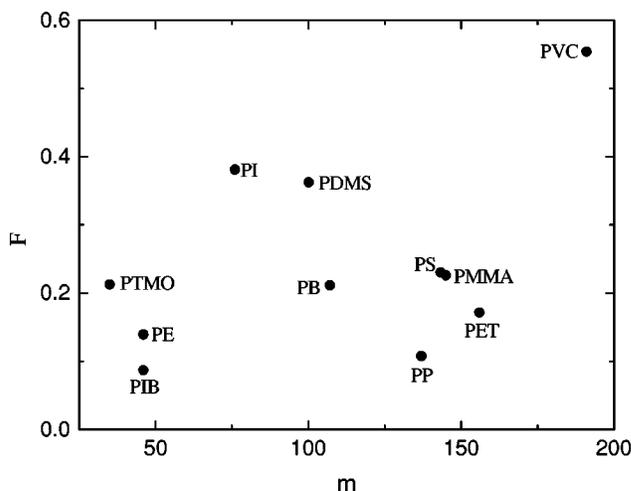
FIG. 5. Thermodynamic fragility, calculated from the data in Fig. 4 using Eq. (4), versus dynamic fragility.

J. Chem. Phys., Vol. 111, No. 12, 22 September 1999

The energy landscape model   5597
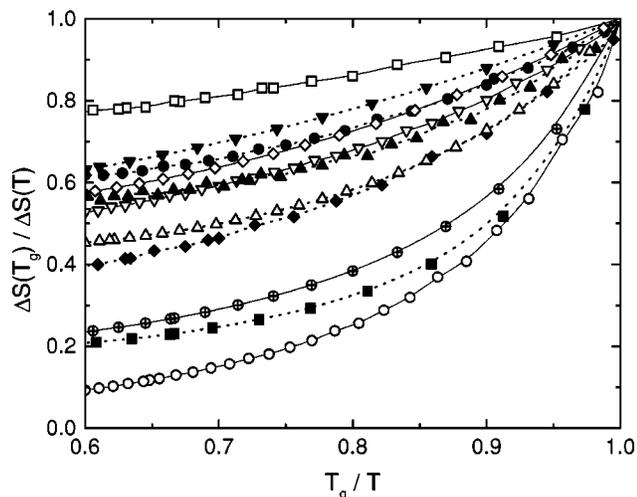
FIG. 6. The data in Fig. 4 replotted in a fashion analogous to dynamic fragility curves. The symbols are identified in Fig. 4.

place of T_m. In Fig. 6, the data in Fig. 4 has been replotted as $\Delta S(T_g)/\Delta S$ versus T_g/T, where $\Delta S(T_g)$ is the configurational entropy at T_g, relative to the perfect crystal. In keeping with the thermodynamic basis for the Kauzmann plot, T_g is taken to be the temperature of half-vitrification at a slow rate of temperature change.[39] This is in contrast to the dynamic measure used for m, e.g., $\tau_\alpha(T_g) = 100$ s.

The curves in Fig. 6 have the qualitative appearance of dynamic fragility. However, from Fig. 6 rank ordering of thermodynamic fragility is

PIB<PB<PP<PE<PMMA<PS<PET

<PTMO<PI<PDMS<PVC,
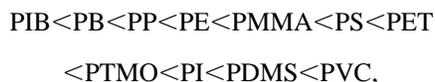
whereas the dynamic fragility for these polymers (Table I) follows the order

PTMO<PE,PIB<PI<PDMS<PB<PP<PS<PMMA

<PET<PVC.

This demonstrates the absence for polymers of any relationship between thermodynamic and dynamic fragilities.

IV. SUMMARY

A theory able to describe the factors which govern dynamics near the glass transition has obvious appeal. Since polymers encompass a broad range of chemical structures, glass temperatures, and fragilities, any theory purporting to explain glass transition behavior must address experimental results on polymers. The energy landscape model makes a valuable contribution by attempting to connect, in a fundamental way, relaxation behavior to the underlying thermodynamics. However, the predicted relationships are absent for polymers. Angell has suggested that polymers may be exceptional, because of intramolecular interactions unique to chain molecules, as well as possibly higher vibrational contributions to the configurational heat capacity.[50,51] We believe the model's failure may indicate the limitations of a description

of the complex dynamics in condensed matter which does not explicitly consider the intermolecular cooperativity inherent therein.

[1] C. A. Angell, J. Non-Cryst. Solids **131-133**, 13 (1991).
[2] C. A. Angell, Science **267**, 1924 (1995).
[3] D. J. Plazek and K. L. Ngai, Macromolecules **24**, 1222 (1991).
[4] C. M. Roland and K. L. Ngai, Macromolecules **24**, 5315 (1991); **25**, 1844 (1992).
[5] C. M. Roland and K. L. Ngai, Macromolecules **25**, 5764 (1992).
[6] K. L. Ngai and C. M. Roland, Macromolecules **26**, 6824 (1993).
[7] R. Bohmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).
[8] K. Ito, C. T. Moynihan, and C. A. Angell, Nature (London) **398**, 492 (1999).
[9] C. A. Angell, Nature (London) **393**, 521 (1998).
[10] R. Richert and C. A. Angell, J. Chem. Phys. **108**, 9016 (1998).
[11] C. A. Angell, J. Res. Natl. Inst. Stand. Technol. **102**, 171 (1997).
[12] W. Kauzmann, Chem. Rev. **43**, 2319 (1948).
[13] T. G. Fox and P. J. Flory, J. Polym. Sci. **14**, 315 (1954).
[14] P. G. Santangelo and C. M. Roland, Macromolecules **31**, 4581 (1998).
[15] A. K. Rizos and K. L. Ngai, Macromolecules **31**, 6217 (1998).
[16] C. M. Roland and K. L. Ngai, Macromolecules **29**, 5747 (1996).
[17] K. L. Ngai and C. M. Roland, Macromolecules **27**, 2454 (1994).
[18] K. L. Ngai, C. M. Roland, and A. F. Yee, Rubber Chem. Technol. **66**, 817 (1993).
[19] C. M. Roland, K. L. Ngai, and D. J. Plazek, Comput. Theor. Polym. Sci. **7**, 133 (1997).
[20] C. M. Roland, Macromolecules **27**, 4242 (1994).
[21] P. G. Santangelo and C. M. Roland, Phys. Rev. B **58**, 14121 (1998).
[22] C. M. Roland, P. G. Santangelo, M. Antonietti, and M. Neese, Macromolecules **32**, 2283 (1999).
[23] M. J. Schroeder, C. M. Roland, and T. K. Kwei, Macromolecules (in press).
[24] C. A. Angell, in *Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (National Technical Information Service, Springfield, VA, 1985), p. 1.
[25] C. Alba-Simionesco, J. Fan, and C. A. Angell, J. Chem. Phys. **110**, 5262 (1999).
[26] C. A. Angell, P. H. Poole, and J. Shao, Nuovo Cimento **16**, 883 (1994).
[27] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Oxford University Press, New York, 1969).
[28] M. Pyda and B. Wunderlich, Macromolecules **32**, 2044 (1999).
[29] B. Wunderlich and U. Gaur, Pure Appl. Chem. **52**, 445 (1980).
[30] B. Wunderlich and H. Baur, Adv. Polym. Sci. **7**, 151 (1970).
[31] B. Wunderlich and L. D. Jones, J. Macromol. Sci., Phys. **B3**, 67 (1969).
[32] C. M. Roland, Macromolecules **25**, 7031 (1992).
[33] B. Wunderlich, J. Phys. Chem. **64**, 1052 (1960).
[34] U. Gaur, H. C. Shu, A. Mehta, S. F. Lau, B. B. Wunderlich, M. Varma-Nair, and B. Wunderlich, J. Phys. Chem. Ref. Data **10**, 89 (1981); **10**, 119 (1981); **10**, 1001 (1981); **10**, 1051 (1981); **11**, 313 (1982); **11**, 1065 (1982); **12**, 29 (1983); **12**, 65 (1983); **12**, 91 (1983); **20**, 349 (1991). See also World Wide Web at URL http://web.utk.edu/~athas/databank/intro.html
[35] S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature (London) **393**, 554 (1998).
[36] J. D. Hoffman and J. J. Weeks, J. Res. Natl. Bur. Stand. **66A**, 13 (1962).
[37] M. Gopalan and L. Mandelkern, J. Phys. Chem. **71**, 3833 (1967).
[38] B. Wunderlich, *Macromolecular Physics* (Academic, New York, 1980), Vol. 3.
[39] B. Wunderlich, in *The Assignment of Glass Transition Temperatures Using Thermomechanical Analysis*, edited by R. J. Seyler, Amer. Soc. Testing and Materials, Philadelphia, PA, 1994), p. 17.
[40] Available data does not extend to sufficiently low frequency for extrapolation to $\tau_\alpha = 100$ s; thus, m evaluated at higher temperature, then scaled using results for another polymer having similar fragility.
[41] K. L. Ngai and C. M. Roland, Macromolecules **26**, 2688 (1993).

[42] E. Hempel, M. Beiner, T. Renner, and E. Donth, Acta Polym. **47**, 525 (1997).

[43] P. G. Santangelo, K. L. Ngai, and C. M. Roland, Macromolecules **29**, 3651 (1996).

[44] R. Zorn, G. B. McKenna, L. Willner, and D. Richter, Macromolecules **28**, 8552 (1995).

[45] J. Colmenero, A. Alegria, P. G. Santangelo, K. L. Ngai, and C. M. Roland, Macromolecules **27**, 407 (1994).

[46] P. G. Santangelo and C. M. Roland, Macromolecules **31**, 3715 (1998).

[47] Entry ''p'' in Table I of Ref. 7 is data for polypropylene oxide, although it is misidentified as polypropylene glycol.

[48] G. Williams, Trans. Faraday Soc. **61**, 1564 (1965).

[49] P. G. Santangelo, K. L. Ngai, and C. M. Roland, Macromolecules **26**, 2682 (1993).

[50] C. A. Angell in *Supercooled Liquids*, ACS Symposium Series 676, edited by J. T. Fourkas, U. Mohanty, D. Kivelson, and K. Nelson (American Chemical Society, Washington, DC, 1997), Chap. 3.

[51] C. A. Agnell, Pure Appl. Chem. **63**, 1387 (1991).