

## Direct computation of characteristic temperatures and relaxation times for glass-forming polymer liquids

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Characteristic temperatures and structural relaxation times for different classes of glass-forming polymer liquids are computed using a revised entropy theory of glass formation that permits the chain backbone and the side groups to have different rigidities. The theory is applied to glass formation at constant pressure or constant temperature. Our calculations provide new insights into physical factors influencing the breadth of the glass transition and the associated growth of relaxation times. © 2005 American Institute of Physics. [DOI: 10.1063/1.2035087]

Numerous observations indicate a strong correlation between glass formation and a rapid drop of fluid entropy upon cooling.<sup>1–4</sup> Gibbs and DiMarzio<sup>5</sup> (GD) first formulated a thermodynamic theory of glass formation in polymer fluids, based on the identification of an “ideal” glass transition with the vanishing of the configurational entropy in a mean-field Flory-Huggins lattice model for a melt of semiflexible polymers. The configuration entropy  $s(T)$  characterizes the number of distinct fluid conformational states and *excludes* the contributions from vibrational motions that are present in the experimentally measured fluid entropy. The lack of a clear relation between  $s(T)$  and the measured entropy has led to persistent uncertainties in experimental tests of the entropy theory of glass formation (see below). Further progress in the entropy theory of glass formation emerged from the Adam–Gibbs (AG) relation between the rate of structural relaxation and the configurational entropy.<sup>3</sup> Despite some idealizations, these theories still provide the foundation for many current ideas about glass formation.

Although the GD theory claims numerous successes in rationalizing trends in the glass transition temperature  $T_g$  with molecular structure,<sup>5</sup> its prediction of a vanishing  $s(T)$  at a finite temperature  $T_0$  has been questioned,<sup>6,7</sup> casting doubt on the existence of an ideal glass transition. In our view, the question of whether  $s(T)$  vanishes for  $T_0 > 0$  K is academic since it is impossible to equilibrate fluids at temperatures below  $T_g$  where the fluid entropy and  $s(T)$  *extrapolate to zero*. Thus, we have developed a new entropy theory that focuses on the temperature regime *above*  $T_g$  where these conceptual difficulties do not arise and where a thermodynamic description of polymer melts is reliable. Our theory does not invoke the existence of an entropy catastrophe to define the glass transition, but still retains the notion of a temperature  $T_0$  at which  $s(T)$  extrapolates to zero as found experimentally for the total fluid entropy. Our entropy theory emphasizes the short-range correlations in the fluid that stem from chain connectivity, semi-flexibility of the chain back-

bone and side groups, and monomer structure. These variables are clearly relevant to describing how molecular structure affects the rate of structural relaxation in real polymer melts. This more realistic treatment of the thermodynamics of polymer melts is achieved through a lattice cluster (LCT) generalization of the Flory theory of semiflexible polymer melts.<sup>8</sup>

According to the Adam–Gibbs theory,<sup>3</sup> the structural relaxation time of a polymer fluid is related to  $s(T)$  through the well-known AG relation,

$$\tau = \tau_o \exp\{\beta \Delta\mu [s^*/s(T)]\}, \quad (1)$$

where  $\tau_o$  is the high-temperature limiting relaxation time in the fluid,  $\Delta\mu$  is a (property and system dependent) activation energy at *high* temperatures, and  $s^*$  is the postulated high-temperature limit of  $s(T)$ . The AG equation for  $\tau$  implies that the “fragility” of glass-forming liquids is related to the rate of change of  $s(T)$  and to the strength of the van der Waals interactions and other microstructure effects through  $\Delta\mu$ .

A crucial modification of the classic entropy theory lies in our *identification* of  $s$  in Eq. (1) with the configurational entropy  $s_c$  *per lattice site* (an entropy density) rather than with the entropy  $s_{c,m}$  per unit mass, as commonly assumed in analyzing experiments.<sup>9</sup> This identification enables us to explain many aspects of the thermodynamics and dynamics of glass formation over the entire temperature range of this process and is consistent with the simulations of diffusion in lattice models of polymer melts by Binder *et al.*<sup>6</sup> Since the complex changes in the dynamics of glass-forming liquids often initiate for  $T > 2T_g$ , it is important to determine the breadth of this transition by estimating the temperatures characterizing the beginning, middle, and end of this broad transition phenomenon. Thus, we not only distinguish between  $T_g$  and the extrapolated temperature  $T_0$ , but also evaluate the onset temperature  $T_A$  for the supercooled regime (below which  $\tau$  no longer displays an Arrhenius temperature dependence) and the crossover temperature ( $T_I$  in our notation) separating well-defined temperature regimes in which both  $s_c$  and  $\tau$  exhibit a rather distinct temperature depen-

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dence. The characteristic temperatures  $T_A$ ,  $T_I$ , and  $T_0$  are determined from the maximum  $s_c^*$  of  $s_c$ , the inflection point in  $s_c(T)T$ , and the extrapolated vanishing of  $s_c(T)$ , respectively. The kinetic glass transition temperature  $T_g$  is calculated from a Lindemann-type relation<sup>10</sup> for the instability of the solid (glass) to liquefaction when the mean interparticle separation increases by 12.5%–15% over the value for the “solid” at  $T_0$ ,

$$\frac{\nu(P, T = T_g) - \nu(P, T = T_0)}{\nu(P, T = T_g)} = \begin{cases} 0.027 & F-S \text{ class} \\ 0.016 & F-F \text{ class}, \end{cases}$$

where  $\nu$  denotes the specific volume and the  $F-S$  and  $F-F$  polymer classes are defined below. Elsewhere, we discuss the application of this Lindemann criterion in detail.<sup>11</sup>

Previous attempts at comparing the entropy theory to experiments are complicated by the difficulty of estimating  $s(T)$  for real fluids. For instance, Richert and Angell<sup>9</sup> suggest that the AG model generally “breaks down” for temperatures 20–30 K above  $T_g$ . On the other hand, molecular-dynamics simulations for model liquids<sup>12</sup> and Monte Carlo simulations of diffusion in lattice polymer fluids<sup>6</sup> both claim consistency with the AG model at temperatures far above  $T_g$ . These conflicting conclusions are perhaps not surprising given that experiments and simulations invoke completely different measures of “configurational entropy.” The experimental studies identify  $s(T)$  of the AG theory with the molar fluid entropy  $S_{\text{exc}}$  relative to the crystalline or low-temperature glass state, while the simulations’ estimate of  $s(T)$  are obtained from the number of accessible configurational states. Since  $S_{\text{exc}}$  contains a substantial vibrational contribution, it is entirely unclear<sup>13</sup> if  $S_{\text{exc}}$  provides a good estimate of the  $s(T)$  that appears in Eq. (1). Below we suggest a simple logical alternative that establishes consistency between experimental and simulated estimates of the configurational entropy.

Experimental studies<sup>14,15</sup> of the structural origin of fragility in polymers suggest that polymers with simple side branch structures (e.g., polybutadienes and many polyolefins) are rather strong, while polymers with bulky, rigid side groups (e.g., polystyrene) are more fragile. Since the relative rigidity of the side groups and the chain backbone is the essential parameter governing the nature of glass formation in polymers, we assign different bending energies  $E_b$  and  $E_s$  for a pair of chain backbone and side group bonds, respectively, when two semiflexible bonds lie in orthogonal directions (*gauche* bonds). Calculations are performed for two generic categories of polymers: chains with flexible backbone and flexible side groups and chains with flexible backbone and rigid side branches, termed the  $F-F$  and  $F-S$  polymer classes, respectively. For simplicity, a common united atom monomer structure (shown in the inset to Fig. 1) is used in both classes. The  $F-F$  class is specified by  $E_b/k_B = E_s/k_B = 400$  K. The same  $E_b/k_B = 400$  K is assigned to the  $F-S$  chains, but a relatively large  $E_s/k_B = 4000$  K represents the stiff side groups. All computations refer to a pressure of  $P = 1$  atm (0.101 325 MPa), unless otherwise specified, and are performed for the nearest-neighbor van der Waals interaction energy  $\epsilon/k_B = 200$  K [a typical value for poly ( $\alpha$ -olefins)] and the unit volume as  $v_{\text{cell}} = a_{\text{cell}}^3 = (2.7)^3 \text{ \AA}^3$ . One *trans* and two *gauche* conformations are assumed for each backbone and side chain bond pair.<sup>8</sup>

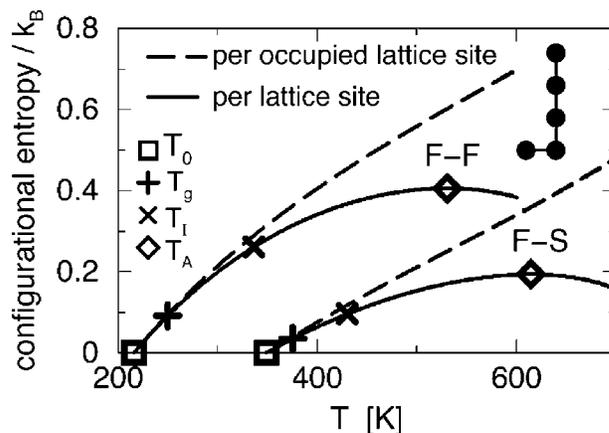


FIG. 1. Comparison of the LCT configuration entropies per site ( $s_c \equiv S_c/N_i$ ) and per united atom group [ $s_{c,m} \equiv S_c/(nM)$ ] for constant pressure  $P = 1$  atm polymer fluids ( $M = 40\,001$ ).  $N_i$ ,  $n$ , and  $M$  are the numbers of lattice sites, polymer chains, and united atom groups in a single chain, respectively. The molar mass is proportional to  $M$ . The inset depicts the monomer structure used in our calculations.

Figure 1 compares  $s_c(T)$  and  $s_{c,m}(T)$  for the  $F-F$  and  $F-S$  polymer classes. Both configurational entropies almost coincide for  $T < T_I$ , but they differ appreciably at higher temperatures. The bifurcation in the configurational entropies in Fig. 1 is remarkably similar in form to the deviation observed between the experimentally determined excess fluid entropy  $S_{\text{exc}}$  and the configurational entropy  $s$ , as estimated by fitting dielectric relaxation-time data<sup>9</sup> to Eq. (1). Because  $s_c(T)$  is an *entropy density*, the maximum in  $s_c(T)$  derives from an interplay between changes in the entropy and the fluid density with temperature.

While Binder *et al.*<sup>6</sup> have previously shown that the AG theory provides a good description of the temperature dependence of diffusion in polymer melts when  $s(T)$  is identified with the site configurational entropy, they do not mention that this choice substantially departs from the use of  $S_{\text{exc}}$  in experimental tests of the AG theory. The tendency of  $s_c$  to increase slowly at high temperatures in the simulations of Binder *et al.* is broadly mirrored in constant volume landscape configurational entropy  $s_{c,L}$  calculations that likewise claim general accord with the AG theory when the  $s(T)$  of Eq. (1) is replaced by  $s_{c,L}$ . Our theory indicates that  $s_c(T)$  can exhibit a maximum at constant pressure, while the entropy at constant volume cannot. These observations strongly suggest that better consistency between the AG theory and experiments might be obtained simply by normalizing  $S_{\text{exc}}$  by the fluid molar volume (i.e., by using the entropy density rather than  $S_{\text{exc}}$  alone). However, even with this change in normalization, the subtraction of the residual vibrational contributions from the fluid entropy is necessary for reliably testing the validity of AG theory.

The temperature dependence of  $s_c$  naturally divides into high- and low-temperature regimes of glass formation, separated by the crossover temperature  $T_I$  in Fig. 1. Below  $T_I$ , the product  $s_c T$  scales nearly proportional to the reduced temperature  $\delta T_0 = (T - T_0)/T_0$ , which in combination with Eq. (1) implies  $\tau = \tau_0 \exp[1/(K_s \delta T_0)]$ , for  $T_g < T < T_I$ , where the constant  $K_s$  characterizes the fragility at low temperatures. The

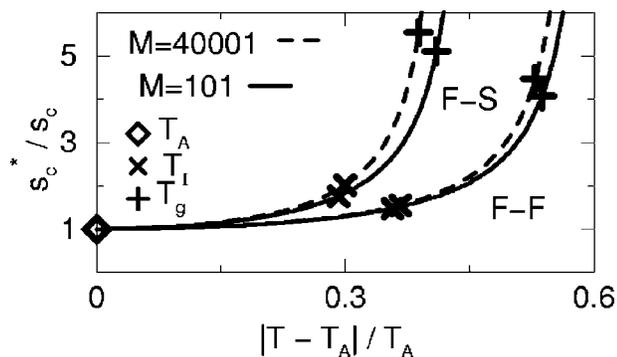


FIG. 2. LCT estimates for the size  $z^* = s_c^*/s_c$  [where  $s_c^* = s_c(T_A)$ ] of the cooperative rearranging regions in constant pressure ( $P=1$  atm) glass-forming polymer fluids as a function of  $\delta T_A \equiv |T - T_A|/T_A$ .

former equation for  $\tau$  is just the well-known Vogel–Fulcher–Tammann–Hesse (VFTH) equation<sup>16</sup> and was theoretically rationalized by Adams and Gibbs.<sup>3</sup> A very different temperature dependence of  $s_c T$  emerges from our calculations for  $T > T_I$ , however.

The ratio  $z^* = s_c^*/s_c(T)$  in Eq. (1) for  $\tau$  is generally interpreted as the average number of monomer elements in the dynamic cooperatively rearranging regions, structures that are hypothesized to form in cooled glass-forming liquids and that are associated with a growing activation energy barrier for transport. Figure 2 presents  $z^*$  as a function of the reduced temperature  $\delta T_A \equiv |T - T_A|/T_A$ . While  $z^*$  is unity at  $T_A$ , it grows upon cooling, becoming about 2 near  $T_I$  and about 4 or 5 near  $T_g$ . The fit to  $z^*$  as a function of  $\delta T_A$  in Fig. 2 is parabolic to a high degree for both polymer classes, i.e.,  $z^* - 1 = C_s (\delta T_A)^2$  for  $T_A - 100 \text{ K} < T < T_A$ , where  $C_s$  depends on polymer mass and polymer class. A similar scaling of  $z^*$  for  $T \approx T_A$  emerges from the theory of Schweizer and Saltzman.<sup>17</sup> Remarkably, the LCT estimates of  $z^*$  are also compatible with recent experimental estimates of the reduced activation energy barrier  $\mathcal{E}/\mathcal{E}(T > T_A)$  for diverse fluids by Kivelson *et al.*,<sup>18</sup> although with a somewhat larger exponent (8/3). Figure 2 shows that  $C_s$  is larger for *F-S* polymers, which in combination with Eq. (1) implies that  $\tau$  has a stronger temperature variation for the more fragile *F-S* polymers. The parameter  $C_s$  provides a measure of fragility in the high-temperature regime of glass formation, complementing the fragility parameter  $K_s$  appropriate to the low-temperature regime of glass formation.

Our extension of the entropy theory is combined with an empirically motivated relation between  $\Delta\mu$  and  $T_I$ , namely,  $\Delta\mu/k_B \approx 6T_I$ , which enables explicit computation of  $\tau$  without adjustable parameters beyond the molecular parameters inherent in the LCT model. The resultant empirical connection between dynamic quantities and microscopic parameters of the LCT also permits us to explore the structural origins of fragility in glass-forming liquids, as will be described elsewhere. The approximate relation  $\Delta\mu/k_B \approx 6T_I$  is based on the molecular-dynamics simulations for both binary Lennard-Jones glass-forming liquids<sup>19</sup> and a Lennard-Jones bead model of polymer melts<sup>20</sup> for which  $T_I$  is identified with the fitted mode-coupling temperature  $T_{mc}$ . Comparisons of direct LCT computations for  $T_I/T_g$  and  $\tau(T=T_I)$  with literature

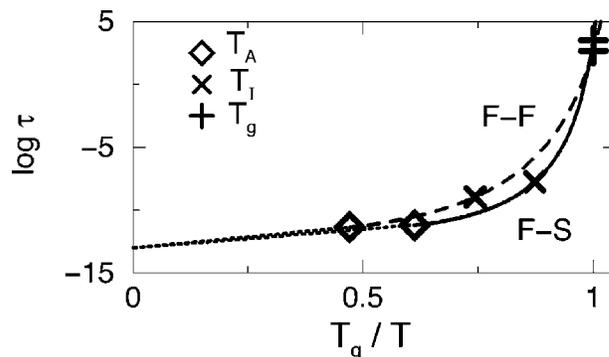


FIG. 3. The calculated structural relaxation time  $\tau$  for  $P=1$  atm high molar mass ( $M=40\,001$ ) *F-S* and *F-F* polymer fluids as a function of  $T_g/T$ . Dotted lines refer to the high-temperature regime  $T > T_A$ , where an Arrhenius relation applies. The high temperature limiting  $\tau$  is taken as  $\tau_o = 10^{-13}$  s.

estimates<sup>21,22</sup> of  $T_{mc}/T_g$  and  $\tau(T=T_{mc})$ , respectively, confirm this identification of  $T_I$  with  $T_{mc}$ . The relation is also supported by viscosity data for a wide range of glass-forming salts,<sup>23</sup> where the high-temperature regime above  $T_I$  is experimentally accessible.

The revised entropy theory also provides detailed predictions for the dependence of  $\tau$  on temperature, pressure, molar mass, and monomer structure over the entire glass-formation temperature region from  $T_0$  to  $T_A$ . Figure 3 illustrates the computed  $\tau$  as a function of the reduced inverse temperature  $T_g/T$  for *F-S* and *F-F* polymer class fluids at  $P=1$  atm. We predict that  $\tau(T=T_A)$  at the onset of glass formation is on the order of a few picoseconds for both polymer classes, while  $\tau(T=T_I)$  is generally a few orders of magnitude larger, i.e.,  $\mathcal{O}(10^{-8\pm 1}$  s). The predictions in Fig. 3 agree reasonably well with recent tabulated estimates<sup>22</sup> of  $\tau$  at the nominal mode-coupling temperature (the analog of  $T_I$ ) for a wide variety of glass-forming liquids where  $\tau$  is  $\mathcal{O}(10^{-7\pm 1}$  s).<sup>24</sup> Figure 3 further exhibits  $\tau$  as increasing rapidly for  $T < T_I$ , with  $\tau(T=T_g)$  becoming as large as  $10^3$  s, as is typical for glass-forming liquids.<sup>22</sup> [Alternatively,  $T_g$  could be defined by  $\tau(T_g) = 10^3$  s, and the resulting  $T_g$  could be used to derive the Lindemann criterion.] For both *F-F* and *F-S* polymer classes,  $\tau$  varies similarly with temperature, although the steepness of the rise in  $\tau$  at low temperatures is less pronounced for *F-F* polymers, reflecting the “stronger” nature of this class of fluids.

Glass formation can also be induced by increasing pressure at constant temperature.<sup>25,26</sup> Specifically, an empirical pressure analog of the VFTH equation has been used to describe data for  $\tau(P, T = \text{const})$  at variable pressures.<sup>25,26</sup> This pressure analog,  $\tau(P) = \tau(P=1 \text{ atm}) \exp[aP/(P_0 - P)]$ , where  $a = a(T)$  is a constant, exhibits an apparent singularity at a critical pressure  $P_0$  which is the counterpart of the “Vogel temperature”  $T_\infty = T_0$  of the original VFTH equation. We represent  $\tau$  at fixed  $T$  and variable  $P$  as a generalization of Eq. (1) by  $\tau(P) = \tau_o \exp[\beta \mathcal{E}_{AG}(P)]$ , with  $\mathcal{E}_{AG}(P)$  written equivalently as

$$\mathcal{E}_{AG}(P) = \Delta\mu [s_c^*/s_{c,o}] [s_{c,o}/s_c(T, P)], \quad (2)$$

where  $s_{c,o} \equiv s_{c,o}(T)$  is the site configurational entropy at  $P=1$  atm and where a weak pressure dependence of  $\Delta\mu$  and  $s_c^*$

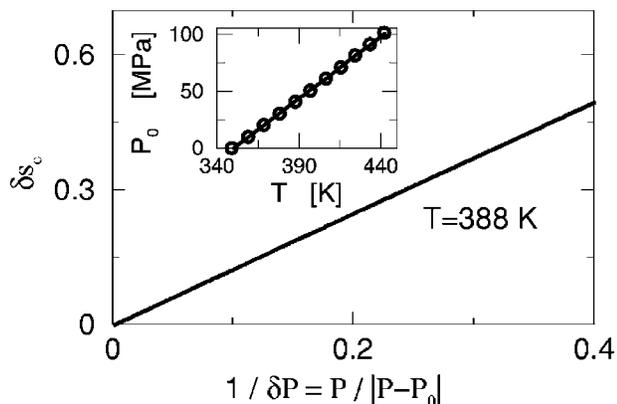


FIG. 4. LCT computations for the  $\delta s_c$  of Eq. (3) as a function of the reciprocal of  $\delta P = |P - P_0|/P$  for a high molar mass ( $M=40\,001$ )  $F$ - $S$  polymer fluid at  $T=388$  K. The inset illustrates the temperature dependence of  $P_0$  (symbols). The line is a least-squares fit  $P_0 = a + bT$  with  $a = -378.6$  MPa and  $b = 1.0825$  MPa/K.

is neglected.<sup>27</sup> The equation for  $\tau(P)$  can be rearranged as

$$\tau(P) = \tau(P = 1 \text{ atm}) \exp[\beta \mathcal{E}_{AG}(P = 1 \text{ atm}) \delta s_c], \quad (3)$$

where  $\delta s_c \equiv [s_{c,o}/s_c(T, P)] - 1$ . The consistency of Eq. (3) with the empirical correlation for  $\tau(P)$  requires that  $\delta s_c$  is inversely proportional to the reduced pressure  $\delta P = |P - P_0|/P$  as shown in Fig. 4 for an isothermal  $F$ - $S$  polymer melt. Thus, the origin of the pressure analog of the VFTH equation<sup>25</sup> naturally follows from the entropy theory. The inset to Fig. 4 presents the critical pressure  $P_0$  as scaling linearly with temperature, in agreement with experiments.<sup>28</sup> Generally  $P_0$  is a function of  $T, \epsilon, E_b, E_s$ , and monomer structure.

In summary, our analytic theoretical framework for both equilibrium and relaxation properties of glass-forming polymers provides a recipe for calculating the multiple characteristic temperatures of glass formation in polymer fluids and generates an understanding of the regularities observed in the magnitude of  $\tau$  at these temperatures. This is the first analytical theory describing these aspects of glass formations in polymer fluids. Moreover, the theory is the first to explain

the impact of different side group and backbone chain rigidities on glass formation and provides a theoretical basis for the pressure analog of the VFTH equation for  $\tau$ .

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- <sup>1</sup>W. Kauzmann, Chem. Rev. (Washington, D.C.) **43**, 219 (1948).
- <sup>2</sup>C. A. Angell, Science **267**, 1924 (1995).
- <sup>3</sup>G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965); see also U. Mohanty, I. Oppenheim, and C. H. Tanbes, Science **266**, 425 (1994).
- <sup>4</sup>S. Sastry, Nature (London) **409**, 164 (2001).
- <sup>5</sup>J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. **28**, 383 (1958).
- <sup>6</sup>K. Binder, J. Baschnagel, and W. Paul, Prog. Polym. Sci. **28**, 115 (2003).
- <sup>7</sup>H.-P. Wittmann, J. Chem. Phys. **95**, 8449 (1991).
- <sup>8</sup>K. F. Freed, J. Chem. Phys. **119**, 5730 (2003).
- <sup>9</sup>R. Richert and C. A. Angell, J. Chem. Phys. **108**, 9016 (1998).
- <sup>10</sup>F. A. Lindemann, Phys. Z. **11**, 609 (1910).
- <sup>11</sup>J. Dudowicz, K. F. Freed, and J. F. Douglas, J. Phys. Chem. B, "The Glass Formation Temperature of Polymer Melts" (online).
- <sup>12</sup>A. Scala, F. W. Starr, E. La Nave, H. E. Stanley, and F. Sciortino, Nature (London) **406**, 166 (2000); S. Mossa, E. H. E. Stanley, C. Donati, F. Sciortino, and P. Tartaglia, Phys. Rev. E **65**, 041205 (2002).
- <sup>13</sup>D. Prevosto, S. Capaccioli, M. Lucchesi, D. Leporini, and P. Rolla, J. Phys.: Condens. Matter **16**, 6597 (2004).
- <sup>14</sup>K. L. Ngai and C. M. Roland, Macromolecules **26**, 6824 (1993); P. G. Santangelo and C. M. Roland, *ibid.* **31**, 4581 (1998).
- <sup>15</sup>D. M. Colucci and G. B. McKenna, Mater. Res. Soc. Symp. Proc. **455**, 171 (1997).
- <sup>16</sup>H. Vogel, Phys. Z. **22**, 645 (1921).
- <sup>17</sup>K. S. Schweizer and E. J. Saltzman, J. Chem. Phys. **119**, 1181 (2003); **121**, 1984 (2003).
- <sup>18</sup>D. Kivelson, G. Tarjus, X. Zhao, and S. A. Kivelson, Phys. Rev. E **53**, 751 (1996).
- <sup>19</sup>S. Sastry, P. G. Debedenetti, and F. H. Stillinger, Nature (London) **393**, 554 (1998).
- <sup>20</sup>F. W. Starr and J. F. Douglas (unpublished).
- <sup>21</sup>C. A. Angell, J. Res. Natl. Inst. Stand. Technol. **102**, 171 (1997).
- <sup>22</sup>V. N. Novikov and A. P. Sokolov, Phys. Rev. E **67**, 031507 (2003).
- <sup>23</sup>A. Voronel, E. Veliynlin, T. Grande, and H. A. Oye, J. Phys.: Condens. Matter **9**, L247 (1997).
- <sup>24</sup>V. N. Novikov and A. P. Sokolov, Nature (London) **431**, 961 (2004).
- <sup>25</sup>M. Paluch, A. Patkowski, and E. W. Fischer, Phys. Rev. Lett. **85**, 2140 (2000).
- <sup>26</sup>K. Mpoukouvalas and G. Floudas, Phys. Rev. E **68**, 031801 (2003).
- <sup>27</sup>D. Tabor, Philos. Mag. A **57**, 217 (1988).
- <sup>28</sup>G. Floudas (private communication).