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Does equilibrium polymerization describe the dynamic heterogeneity of glass-forming liquids?

Jack F. Douglas

Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Jacek Dudowicz and Karl F. Freed^{a)}

The James Franck Institute, The University of Chicago, Chicago, Illinois 60637 and Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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A significant body of evidence indicates that particles with excessively high or low mobility relative to Brownian particles form in dynamic equilibrium in glass-forming liquids. We examine whether these “dynamic heterogeneities” can be identified with a kind of *equilibrium polymerization*. This correspondence is first checked by demonstrating the presence of a striking resemblance between the temperature dependences of the configurational entropy s_c in both the theory of equilibrium polymerization and the generalized entropy theory of glass formation in polymer melts. Moreover, the multiple characteristic temperatures of glass formation are also shown to have analogs in the thermodynamics of equilibrium polymerization, supporting the contention that both processes are varieties of rounded thermodynamic transitions. We also find that the average cluster mass (or degree of polymerization) varies in nearly inverse proportionality to s_c . This inverse relation accords with the basic hypothesis of Adam-Gibbs that the number of particles in the cooperatively rearranging regions (CRR) of glass-forming liquids scales inversely to s_c of the fluid. Our identification of the CRR with equilibrium polymers is further supported by simulations for a variety of glass-forming liquids that verify the existence of stringlike or polymeric clusters exhibiting collective particle motion. Moreover, these dynamical clusters have an exponential length distribution, and the average “string” length grows upon cooling according to the predictions of equilibrium polymerization theory. The observed scale of dynamic heterogeneity in glass-forming liquids is found to be consistent with this type of self-assembly process. Both experiments and simulations have revealed remarkable similarities between the dynamical properties of self-assembling and glass-forming liquids, suggesting that the development of a theory for the dynamics of self-assembling fluids will also enhance our understanding of relaxation in glass-forming liquids. © 2006 American Institute of Physics. [DOI: 10.1063/1.2356863]

I. INTRODUCTION

Many recent experimental and computational studies provide firm evidence for the presence of transient clusters of particles both with excessively high or low particle mobilities (relative to simple Brownian motion) in supercooled and in concentrated colloidal glass-forming fluids.^{1–21} An elucidation of the origin and geometrical nature of these “dynamically heterogeneous structures” and their impact on the fluid’s relaxation remains a challenge for any theory of glass formation. Because the popular mode coupling theory of glass formation assumes from the onset that glass-forming liquids are *homogeneous*, this theory is incapable of describing the thermodynamic origin of this clustering. The mean field theory of Klein and co-workers^{2,22–24} indicates, however, that the homogeneity assumption is not intrinsic to mean field theory. Specifically, their theory predicts a thermodynamic instability (at a finite wave vector q) corresponding to the formation of fluid heterogeneities (“clumps” or relatively high density regions) that exist in a state of dy-

namic equilibrium, so that inhomogeneous structures are constantly forming and disintegrating. The formation of clumps or “entropic droplets” of *mobile* particles in glass-forming liquids is also emphasized by the mean field “random first order transition” model of supercooled liquids developed by Xia and Wolynes.²⁵ Simulations of fluids with interactions that are consistent with mean field theory confirm the existence of dynamic structures that have been predicted by Klein and co-workers^{2,22} and that remarkably resemble simulated micelles.^{26,27} Molecular dynamics simulations of a glass-forming binary Lennard-Jones fluid in two dimensions yield limited evidence supporting this immobile particle clump picture of glass formation, but no strong evidence has yet been reported for simulations of a three-dimensional glass-forming fluid with physically realistic intermolecular interactions. As mentioned before, reports of dynamical clusters of excessively mobile particles in both simulations and experiments accord qualitatively with the picture of Xia and Wolynes.²⁵

Although the evidence is fragmentary, these attempts at describing dynamic heterogeneity in glass-forming liquids as an equilibrium clustering process appear attractive. In the

^{a)}Electronic mail: k-freed@uchicago.edu

present paper, we test the consistency of this proposed origin of dynamic heterogeneity in glass-forming liquids by comparing to a well-defined particle clustering process (equilibrium polymerization) whose behavior seems to agree particularly well with the established phenomenology of glass-forming liquids. We also compare equilibrium polymerization theory with the generalized entropy theory of glass formation²⁸ to provide a better understanding of thermodynamic aspects of the glass transition and assumptions invoked by the classical Adam-Gibbs and Gibbs-DiMarzio theories of glass formation.

As mentioned before, mobile particle clusters appear in simulations of cooled glass-forming liquids,^{3,4,16,17} concentrated colloidal fluids,^{11–13} and atomic clusters.²⁹ Simulations of glass-forming binary Lennard-Jones (LJ) fluids, water at low temperatures, and model polymer glass-forming liquids all exhibit the existence of *polymerlike* clusters of mobile particles that form and disintegrate in a state of dynamic equilibrium.^{3,4,30} Polymeric clusters of mobile particles have also been identified in suspensions of spherical colloid particles at high concentrations^{11–14} and in experiments for shaken granular systems.³¹ Collective particle motion has also been inferred in time-of-flight neutron scattering measurements.³² These observations, taken together, motivate our investigation of whether equilibrium polymerization, in particular, provides an appropriate model for describing the dynamic heterogeneity of glass-forming liquids.

Donati *et al.*³ quantify the geometrical and statistical characteristics of these “strings” of mobile particles in a binary LJ fluid and find that these transient polymeric structures exhibit a nearly exponential size distribution, a characteristic feature of equilibrium polymerization.³³ Donati *et al.* also tentatively suggest³ that these stringlike structures should be identified with the cooperatively rearranging regions (CRRs) of the Adam-Gibbs theory and that the apparent activation energy E for the fluid’s structural relaxation is consistent with a proportionality to the average string length, as required by the identification of the strings with the CRR. Later simulations reveal that E for a model of supercooled water is nearly proportional to the mass of the mobile particle clusters,³⁰ an observation stimulating serious interest in the interrelation between E and stringlike motion in cooled liquids. Recent simulations by Aichele *et al.*³⁴ demonstrate that the average string length L in the Dzugutov model of a glass-forming liquid is consistent with the scaling relation $E \sim L \sim 1/s_{c,L}$, where the “landscape configurational entropy” $s_{c,L}$ is estimated by sampling the number of potential energy minima of this fluid under constant volume conditions.³⁰ A similar inverse scaling between L and the configurational entropy $s_c(T)$ (per site) applies to “living” equilibrium polymers or, equivalently, to equilibrium polymerization with a chemical initiator.³³ Below, we study this scaling behavior for more general equilibrium polymerization models that are better suited for modeling glass formation.³³ While our findings are all consistent with identifying the CRR of the Adam-Gibbs (AG) entropy theory with equilibrium polymers,^{3,30,33} it is necessary to test whether the basic phenomenology of

glass formation is consistent with describing the CRR polymerization process by using equilibrium polymerization theory.

The broad nature of glass formation that emerges from the generalized entropy theory of glass formation and from experiments clearly points to a rounded transition, as emphasized previously by Gordon *et al.*³⁵ The simplest models of equilibrium polymerization that postulate the formation of linear polymer chains display the essential characteristics of rounded transitions, as is evident from the temperature variation of the configurational entropy. In particular, we briefly review in Sec. II those results from the theory of equilibrium polymerization that pertain to the phenomenology of glass formation. The dynamic polymers of equilibrium polymerization are then identified with the interpenetrating mobile or immobile particle clusters^{2,18} that coexist in supercooled liquids and that grow in a parallel fashion upon cooling. The comparison between equilibrium polymerization and glass-forming liquids allows us to examine the AG hypothesis of an inverse relation between the configurational entropy and the size z^* of the dynamic clusters in the cooled liquid, a central assumption of the AG theory of structural relaxation in glass-forming liquids. Section III provides a summary of those aspects of the generalized entropy theory of glass formation that are used in the comparison with equilibrium polymerization theory in Sec. IV. We also examine evidence showing a commonality of the dynamics of solutions exhibiting equilibrium polymerization and of glass-forming liquids.

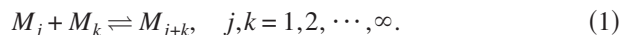
II. FLORY-HUGGINS THEORY OF EQUILIBRIUM POLYMERIZATION

Our theory of equilibrium polymerization employs the standard Flory-Huggins (FH) lattice model to describe the thermodynamics of polydisperse polymer solutions by imposing the thermodynamic condition of chemical equilibrium between polymer species of different sizes. The treatment here is based on the simplified version of this theory³⁶ that neglects the fluid’s compressibility, but this restriction may be lifted if necessary.³⁷ The present section defines our equilibrium polymerization model and describes its basic characteristics that are compared with those obtained from the entropy theory of glass formation.

Our systematic equilibrium polymerization theory has been derived for three general models of association: a model with unrestricted equilibrium polymerization in which all particles can associate democratically at equilibrium [termed the free association (FA) model], a model in which particles must become thermally activated to initiate polymerization (A model), and the “living” polymerization or I model where chain growth is induced by a chemical “initiator.” (The I model is not, however, used in the present study since there is no evident analog to chemical initiation in glass formation.) This basic classification scheme for equilibrium polymerization follows the approach introduced long ago by Tobolsky and Eisenberg³⁸ and encompasses the main classes of equilibrium polymerization encountered in practice.

A. Free association model

The FA system is composed of solvent molecules and monomers of species M that can “freely associate” into polymers once the free energy for this process is negative. The resulting polymers form and disintegrate in dynamic equilibrium. Chain growth may proceed either by the addition of a single monomer or by the linkage of two chains. Alternatively, chains may break in the middle, or segments may dissociate from the chain ends. These two modes of polymerization and depolymerization can be represented by the single kinetic equation,³⁶



The equilibrium constant K_p for the polymerization reaction in Eq. (1) is assumed to be same for all j and k and, thus, is expressed in terms of a single free energy Δf_p of polymerization as $K_p = \exp(-\Delta f_p/k_B T)$, with k_B designating Boltzmann's constant and T being the absolute temperature. The basic thermodynamic properties of free association solutions that are employed in our comparative analysis of equilibrium polymerization and glass formation include the extent of polymerization Φ (the fraction of monomers converted into polymers, an “order parameter” for this assembly process), the average degree of polymerization L , and the configurational entropy s_c . These basic properties are functions on the initial monomer concentration ϕ_1^0 , the temperature T , and the energy Δh_p and entropy Δs_p of polymerization.³⁶ We quote expressions³⁶ for these basic equilibrium polymer solution properties that are used in the present calculations,

$$L \equiv \frac{\sum_{i=1}^{\infty} \phi_i}{\sum_{i=1}^{\infty} \phi_i/i} = \frac{\phi_1^0}{\phi_1^0 - CA^2/(1-A)^2}, \quad (2)$$

$$\Phi \equiv \frac{\phi_1^0 - \phi_1}{\phi_1^0} = \frac{1}{\phi_1^0} \frac{CA^2(2-A)}{(1-A)^2}, \quad (3)$$

$$\frac{s_c}{k_B} = -(1 - \phi_1^0) \ln(1 - \phi_1^0) - \phi_1^0 \ln \phi_1 + \frac{CA^2}{(1-A)^2} \left[\frac{\Delta h_p}{k_B T} - 1 \right]. \quad (4)$$

The factor C is defined as,

$$C = \frac{z}{2\alpha K_p}, \quad (5)$$

where the coefficient α is equal to unity for stiff chains and to $(z-1)$ for fully flexible chains. The variable $A \equiv \phi_1 K_p$ is determined from the mass conservation constraint,

$$\phi_1^0 = \phi_1 + \frac{CA^2(2-A)}{(1-A)^2}, \quad (6)$$

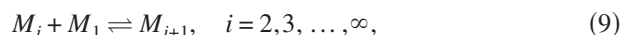
which must, in general, be solved numerically. The polymerization transition temperature T_p is defined as the temperature where $\Phi(T)$ exhibits an inflection point. For the FA

model, this definition departs from the other estimate based on the maximum of the specific heat $C_V(T)$. In Eqs. (2)–(4) and (6), z designates the lattice coordination number and ϕ_1 denotes the equilibrium volume fraction of *unpolymerized* monomers. Because there is no vibrational contributions within the Flory-Huggins lattice model, the entropy of Eq. (22) of Ref. 39 is also the configurational entropy.

The continuum equivalent of the FA model is considered in many previous studies of equilibrium polymerization.^{39,40} While the formation of dynamic chains is well treated by the FA model, other models of equilibrium polymerization describe the behavior of some systems. Due to the absence of constraints on chain growth, the polymerization transition is especially broad in the FA model, and the next subsection describes a model where the transition sharpness can be varied and the two definitions of T_p coincide.

B. Activated equilibrium polymerization

The simplest model of activated polymerization is described by the reaction scheme,³⁶



where the activated species M_1^* reacts *only* with nonactivated monomers M_1 to form dimers, but *does not* participate in the successive chain propagation processes. An alternative model, in which dimers are formed by linking two activated monomers M_1^* and chain growth occurs exclusively through the addition of M_1^* to the resulting polymers, is mathematically isomorphic³⁶ to that described by Eqs. (7)–(9). The simplest activation model of Eqs. (7)–(9) is specified by designating $\Delta f_a = \Delta h_a - T\Delta s_a$ and $\Delta f_p = \Delta h_p - T\Delta s_p$ as the free energies of activation and polymerization, respectively. In order to minimize the number of parameters, both the enthalpies Δh_p and entropies Δs_p associated with dimer formation [Eq. (8)] and with the propagation process [Eq. (9)], respectively, are taken as identical. The free energy parameters Δh_a and Δs_a for monomer activation regulate the sharpness of the polymerization transition, as discussed extensively in our previous papers^{33,36,41,42} and in the earlier works of Wheeler *et al.*⁴³

We distinguish two extreme cases of low and high equilibrium constants $K_a(T_p) = \exp[-(\Delta h_a - T\Delta s_a)/k_B T_p]$ for the activation process. A small $K_a(T_p)$ implies low (relatively high) concentrations of activated (nonactivated) monomers at the transition temperature T_p . Within the reaction scheme defined by Eqs. (7)–(9) for the A model, the activated species M_1^* reacts only with unactivated monomers M_1 to form dimers, but M_1^* does not participate in further propagation steps. Chain growth is taken as occurring exclusively through the addition of M_1 to existing polymers M_i ($i \geq 2$). Thus, the resulting degree of polymerization in the fully polymerized state is relatively high for the low activation model. In contrast, the high activation model is characterized by an equilibrium constant $K_a(T_p)$ that exceeds unity, which implies

that almost all monomers become converted into the activated state, so that chain growth is impeded due to the low concentration of the unactivated M_1 species. Consequently, the degree of polymerization is limited in this model.

The expressions for L and Φ for the A model of equilibrium polymerization are formally identical to those in Eqs. (2) and (3) for the free association FA model, but factor C involves the equilibrium constant K_a for monomer activation,

$$C_a = \frac{zK_a}{2\alpha K_p}. \quad (10)$$

Similarly, the mass conservation constraint contains the extra term $\phi_1^* = \phi_1 K_a$ that is absent from Eq. (6),

$$\phi_1^0 = \phi_1(1 + K_a) + \frac{C_a A^2(2 - A)}{(1 - A)^2}, \quad (11)$$

and the configurational entropy is represented by a more lengthy formula,

$$\begin{aligned} \frac{s_c}{k_B} = & -(1 - \phi_1^0) \ln(1 - \phi_1^0) - \phi_1^0 \ln \phi_1 \\ & + \frac{C_a A^2}{(1 - A)^2} \left[\frac{\Delta h_p}{k_B T} - \frac{\Delta h_a}{k_B T} - 1 \right] + (\phi_1^0 - \phi_1) \frac{\Delta h_a}{k_B T}. \end{aligned} \quad (12)$$

III. GLASS FORMATION AND GENERALIZED ENTROPY THEORY OF POLYMER GLASS FORMATION

A. Basic components of the generalized entropy theory of polymer glass formation

Our recent approach to understanding the fundamental molecular nature of glass formation builds on the original entropy theory for glass formation in polymers, developed by Gibbs and DiMarzio,⁴⁴ and on the Adam-Gibbs relation⁴⁵ between the rate of long wavelength structural relaxation τ in glass-forming liquids and the fluid's configurational entropy. The configurational entropy s_c of a polymer melt is calculated based on the lattice cluster theory generalization^{46,47} of the FH mean field approximation for semiflexible polymer fluids. This generalization enables us to treat models of polymers with explicit backbone and side group molecular structures and with variable flexibility and molecular interactions for these chain portions, as well as the dependence of thermodynamic properties on pressure and the addition of solvent, etc.²⁸ The new entropy theory permits the direct computation of all characteristic temperatures of glass formation,^{48,49} variations of fragility with polymer structure,⁵⁰ and the explicit computation of τ as a function of molecular parameters, such as the monomer structure and disparate flexibilities of different portions of the monomers.⁴⁸

B. Characteristic temperatures of glass formation

Experimental studies have established that long wavelength (large scale) structural relaxation times τ of glass-forming liquids display a nearly Arrhenius temperature dependence at sufficiently high temperatures, but this "universal" high temperature behavior of liquids "breaks

down" at a temperature T_A well above the glass transition temperature T_g where structural arrest of the fluid occurs (T_A can exceed $2T_g$).

The thermodynamic path to glass formation is marked by other characteristic temperatures besides T_A . These characteristic temperatures are universal in glass-forming liquids and serve to define the breadth and nature of glass formation. The temperature T_c (or a narrow temperature range about this reported temperature) appears below T_A and signals the occurrence of singular changes in the properties of glass-forming liquids. For example, a bifurcation of structural relaxation times τ into fast (β -relaxation) and slow (α -relaxation) modes becomes conspicuous⁵¹ for $T \approx T_c$, and a breakdown in the Stokes-Einstein relation between the diffusion coefficient and the fluid shear viscosity η has been reported^{1,52-54} below T_c . Inspired by mode coupling theory, numerous experimental and computational studies estimate T_c by fitting data for τ in the temperature range $T_g \ll T < T_A$ to the relation⁵⁵ $\tau \sim (T - T_c)^{-\gamma}$, where T_c and γ are adjustable parameters. Although τ definitely does not diverge for $T = T_c$, the fitted temperature T_c clearly has some physical significance for glass formation since it consistently demarks a narrow temperature range in which numerous properties of the glass-forming fluid change. However, the theoretical foundation for determining T_c from mode coupling theory is rather uncertain. Elsewhere, we suggest⁵⁰ that the experimentally determined T_c can directly be estimated from the inflection point in the product of temperature and the configurational entropy that is calculated from our generalized entropy theory of glass formation. Hence, this temperature T_c should more properly be interpreted as a *crossover temperature* separating high and low temperature regimes of glass formation, each with a differing temperature dependence of τ .⁴⁸

The glass transition temperature T_g is the most commonly studied characteristic of glass-forming liquids, but the physical meaning of this temperature continues to provoke discussion. Operationally, T_g is often determined from the maximum in the specific heat from measurements performed at a fixed temperature scanning rate. In reality, these experiments do not provide strictly thermodynamic information, and the "observed" T_g varies with the temperature scan rate and other system constraints. Alternatively, T_g is often fixed by the prescription that η at T_g achieves the threshold value of $\eta \approx 10^{14}$ Pa s or by the condition that τ has the order of magnitude of $\tau \sim O(10^2 - 10^3$ s). Although these criteria are somewhat rough, a narrow temperature range definitely exists near the experimentally determined calorimetric T_g where structural arrest tends to occur and below which glass-forming liquids exhibit a strong tendency to fall out of equilibrium and to display noticeable drifts in properties with time. Thus, nonequilibrium "aging" phenomena become prevalent below T_g , where a thermodynamic description becomes inadequate.

The strong temperature dependence of τ below T_c serves to define another characteristic temperature of glass formation, the Vogel temperature T_∞ . An astoundingly large class of liquids (ionic, polymeric, biological materials, colloidal dispersions, emulsions, etc.) exhibit an apparent essential

singularity in the *extrapolated* temperature dependence of their structural relaxation time and other transport properties at low temperatures, i.e.,

$$\tau \sim \tau_{\infty} \exp[D/(T - T_{\infty})], \quad T_g < T < T_c.$$

Of course, this phenomenology^{52,56–61} does not imply that τ *actually diverges* as $T \rightarrow T_{\infty}$, any more than the definition of the “mode coupling temperature” or crossover temperature by a power law scaling for $T > T_c$ implies that τ actually diverges at T_c . Nevertheless, the temperature T_{∞} is subject to a well-defined experimental determination and has general significance for characterizing the dynamics of glass-forming liquids. Within the generalized entropy theory, the temperature T_{∞} coincides with the calculated temperature T_0 where s_c extrapolates to zero.

In summary, our theory implies that glass formation involves a relatively broad *thermodynamic transition* between a simple fluid behavior at high temperatures and a nonequilibrium solid at low temperatures. More specifically, the temperature T_A defines the *onset temperature* for this transformation, while the solidification process is basically “finished” for T_0 where extrapolated relaxation times become astronomical in magnitude. The temperature T_c (designated as T_l in Ref. 28) demarks a boundary between distinct high and low temperature regimes of glass formation. The glass transition temperature T_g is clearly some kind of “kinetic instability temperature” at which the fluid becomes “stuck” and below which it is difficult for the system to achieve equilibrium.

The generalized entropy theory of glass formation and its main results are summarized in recent publications.^{28,48–50,62} Here, we discuss only those predictions of this theory that are required for comparison with the theory of equilibrium polymerization. In the next section, for example, we compare the temperature dependence of the configurational entropy in supercooled polymer liquids and equilibrium polymer solutions and analyze the relation between the “fragility” of glass-forming liquids and the sharpness of the polymerization transition, which can correspondingly be tuned by varying the equilibrium constant K_a for monomer activation. The identification in the next section of the CRR with equilibrium polymers enables us to explore the basic postulate of AG theory that the size of the CRR scales inversely to the configurational entropy of glass-forming liquids. A direct computation of the average degree L of polymerization, which is the analog of the average number z^* of cooperating particles in AG theory, provides a simple means of checking the consistency of this hypothesis.

The configurational entropy of glass-forming polymers is computed with the lattice cluster theory from Eq. (20) of Ref. 28 for melts of model polymers that differ in the relative stiffness of the chain backbone and the side groups. A single monomer of these polymer chains is modeled by a structure that is equivalent to a united atom representation of a 1-pentene unit (see inset to Fig. 1 of Ref. 49). The lattice cluster theory expression for the free energy of a system of polymers with structured monomers has the form of a high temperature expansion whose coefficients depend on the fractions f_b and f_s of *gauche* bonds in the backbone and side

groups, respectively. The configurational entropy s_c of the polymer fluid is determined in this theory following Gibbs and DiMarzio⁴⁴ as the microcanonical ensemble entropy $S(E)$ evaluated for $E = E(T)$. The fractions f_b and f_s are chosen to maximize the entropy at fixed temperature and pressure in these computations. While lengthy analytic expression exists for s_c as a function of composition ϕ and f_b and f_s for a melt of semiflexible polymers with structured monomers, there is no closed analytic expression for the maximized s_c at constant pressure, so the equations involved must be solved numerically. The illustrative calculations of the present paper follow the same procedure as detailed in Ref. 28 and earlier papers.^{48–50}

IV. STRINGS, DYNAMICAL COOPERATIVELY REARRANGING REGIONS, AND EQUILIBRIUM POLYMERIZATION

As mentioned above, a wide range of experimental and simulation evidence indicates the existence of dynamic clustering of mobile and “immobile” particles in cooled liquids. In the present section, we consider the possibility of modeling this clustering phenomenon in terms of equilibrium polymerization theory and compare this modeling with the predictions of the generalized entropy theory of glass formation, which does not in its present form directly address fluctuation effects on molecular scales. A first internal consistency check concerns the temperature dependence of the configurational entropy for these two theories of fluid “ordering” where crystallization is not an option.

The inverse proportionality between cluster size z^* and the configurational entropy is a basic postulate of the AG description of relaxation in glass-forming liquids and is also found to be a general property of equilibrium polymerization, regardless of the constraints (e.g., thermal activation or chemical initiation) that regulate the temperature range over which the polymerization transition occurs. We next show that both the polymerization transition and glass formation are governed by corresponding sets of characteristic temperatures.

Once the qualitative correspondence between these thermodynamic transitions is established, we directly compare our equilibrium polymerization theory to simulation data of Donati *et al.*³ for the temperature dependence of the mass distribution of mobile clusters in supercooled liquids. The resultant quantitative description of the simulation data by equilibrium polymerization theory provides encouraging support for our interpretation of the stringlike clusters in cooled liquids as equilibrium polymers. Ramifications of this correspondence are analyzed to understand regularities in the size of the CRR (which has been reported for temperatures $T \approx T_c$), the spatial scale of dynamic heterogeneities of glass-forming liquids, and other basic aspects of glass-forming liquids.

A. Configurational entropy and dynamic cluster size distribution in equilibrium polymerization and glass-forming liquids

We begin our comparison of the thermodynamics of equilibrium polymerization solutions and glass-forming

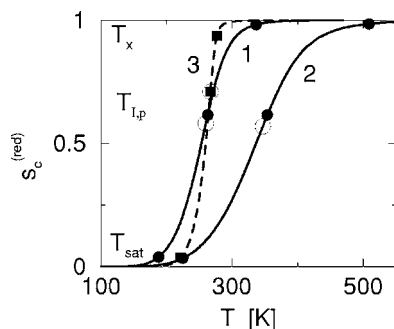


FIG. 1. Temperature dependence of the reduced configurational entropy per lattice site $s_c^{(\text{red})}$ for an incompressible equilibrium polymerization solution. s_c for the FA and A models of equilibrium polymerization is calculated from Eqs. (4) and (12), respectively, and this quantity is shown in the reduced form specified by Eq. (13). These illustrative calculations (as well as those in Figs. 2–6) are performed for completely flexible chains. Curves 1 and 2 refer to the FA model with the enthalpy Δh_p and entropy Δs_p of polymerization chosen as $\Delta h_p = -35$ kJ/mol and $\Delta s_p = -105$ J/(mol K), and $\Delta h_p = -35$ kJ/mol and $\Delta s_p = -70$ J/(mol K), respectively. The third curve corresponds to the activated equilibrium polymerization model A_1 that is specified by $\Delta h_a = \Delta h_p = -35$ kJ/mol, $\Delta s_a = -160$ J/(mol K), and $\Delta s_p = -105$ J/(mol K) (with Δh_a and Δs_a being the enthalpy and the entropy of activation, respectively). The above free energy estimates are consistent with previous studies of equilibrium polymerization (Refs. 33, 41, 42, and 73), and the initial monomer concentration ϕ_1^0 is taken as $\phi_1^0 = 0.05$ for specific comparison to string formation in glass-forming liquids (see text). Solid symbols denote the calculated saturation temperature T_{sat} , the inflection point temperature T_{Lp} where $s_c^{(\text{red})}(T)T$ exhibits an inflection point, and the crossover temperature T_x . All temperatures are defined in the text. Open circles designate the polymerization transition temperatures T_p estimated from the maximum of the specific heat $C_V(T)$.

polymer liquids with an analysis of the temperature dependence of the configurational entropy in these two systems. Figure 1 presents the computed temperature dependence of the dimensionless configurational entropy $s_c^{(\text{red})}$ of an incompressible solution of associating species undergoing equilibrium polymerization upon cooling in the FA and $A_1 \equiv A (\sigma \equiv \Delta h_a / \Delta h_p = 1)$ models. This dimensionless quantity $s_c^{(\text{red})}(T)$ is related to the system's configurational entropy (per lattice site) $s_c(T)$ [Eq. (4) for the FA model and Eq. (12) for the A_1 model] as

$$s_c^{(\text{red})}(T) = [s_c(T) - s_c^{(0)}] / [s_c^{(\infty)} - s_c^{(0)}], \quad (13)$$

where $s_c^{(0)}$ and $s_c^{(\infty)}$ denote the low and high temperature limiting values of $s_c(T)$, respectively, so that $s_c^{(\text{red})}$ by definition varies from zero to unity. Since factors that influence the sharpness of the polymerization transition are crucial in the corresponding case of glass formation, the variation of $s_c^{(\text{red})}$ in Fig. 1 is presented for three different cases. Curves 1 and 2 correspond to the FA model where the “entropy gap” $\Delta s_c^* = s_c^{(\infty)} - s_c^{(0)}$ has been varied, while the dashed curve 3 refers to the A_1 model where $K_a \approx 0.03$ at the polymerization temperature $T_p = 267$ K. The free energy parameters Δh_p and Δs_p are taken to be the same for cases 1 and 3 [$\Delta h_p = -35$ 000 J/mol and $\Delta s_p = -105$ J/(mol K)], but Δs_p is -70 J/(mol K) for case 2. The latter reduces the entropy gap $\Delta s_c^* / k_B$ in the FA model from 0.82 to 0.62 in case 2. As discussed below, such a reduction of the entropy gap is characteristic of a more rapid variation of s with temperature and thus of increased glass fragility in the generalized entropy theory.^{28,48,50,62} (Roughly speaking, fragility defines the rela-

tive rate with which the shear viscosity, the diffusion coefficient, and the rate of structural relaxation vary with temperature, and a more rapid change corresponds to a more fragile behavior.) Inspection of Fig. 1 indicates that this reduction of Δs_c^* (or equivalently Δs_p since Δs_c^* scales in high proportionality to Δs_p) in the FA model leads to a substantial increase of the polymerization transition temperature T_p , a general property of equilibrium polymerization and other equilibrium self-assembly processes.

Figure 1 also illustrates another general effect. Reducing K_a from a value on the order of unity, characteristic of the FA model ($\Delta h_a = \Delta s_a = 0$), *sharpens* the polymerization transition.^{33,36,41–43} The polymerization transition is characterized³³ by two additional temperatures, T_x and T_{sat} , which correspond to the beginning and end of the polymerization transition, respectively, and which are designated by filled symbols in Fig. 1. The crossover temperature T_x is defined in our previous paper³³ as the temperature at which Φ , the fraction of monomers converted into polymers, is 5%, while the saturation temperature T_{sat} refers to the temperature where the entropy $s(T)$ of the equilibrium polymer solution approaches within 5% of its limiting low temperature value, $s_c^{(0)}$.³³ Figure 1 also includes the crossover temperature T_{Lp} (solid symbols) at which the product $s_c^{(\text{red})} T$ exhibits an inflection point (solid symbols), since the corresponding temperature has special significance (see Sec. IV B) in the generalized entropy theory of glass formation.^{28,48–50} Figure 1 exhibits T_{Lp} as close to the polymerization temperature T_p for the FA model and coincident with T_p for the A_1 model. The multiple temperatures in Fig. 1 are characteristic of *rounded* thermodynamic transitions, and we show below that similar characteristic temperatures arise in glass formation.

As demonstrated in Fig. 1, the overall sharpness of the polymerization transition is governed by Δs_p (or, equivalently, by Δs_c^*), although this effect is diminished if $s_c^{(\text{red})}(T)$ is viewed in terms of a reduced temperature scale T/T_p . Changes in the temperature dependence of $s_c^{(\text{red})}$ in the high temperature regime above T_p are particularly interesting in comparison with glass-forming liquids since ratios of the characteristic temperatures of glass formation are related to the fragility of glass-forming liquids.^{50,62} Changing Δs_p from -105 J/(mol K) to -70 J/(mol K), corresponding to curves 1 and 2, respectively, modifies T_x/T_p from 1.28 to 1.44. Little alteration in this temperature ratio is found, however, for the A_1 model, where T_x/T_p remains almost invariant upon introducing the above shift in Δs_p .

The tendency of the reduced configurational entropy $s_c^{(\text{red})}$ to drop sharply upon cooling (see Fig. 1) has a counterpart in the variation of the configurational entropy density $s_c(T)$ (i.e., per unit volume) of glass-forming liquids, as computed from the generalized entropy theory of polymer glass formation [see Eq. (20) of Ref. 28]. The trend illustrated in Fig. 2 corresponds to two extreme types of high molar mass polymer glass formers: F–F polymer chains (containing both flexible backbone and side groups) that exhibit relatively strong glass formation and F–S polymers (characterized by flexible backbone and stiff side groups) that undergo a rather fragile glass formation.^{48–50} The entropy gap for glass formation $\Delta s_c^* \equiv s_c(T_A) - s_c(T_0)$ for the F–F and F–S polymers is

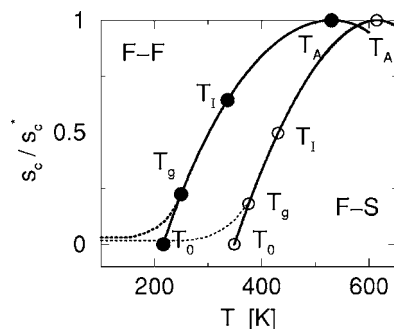


FIG. 2. The configurational entropy s_c calculated from the generalized entropy of glass formation as a function of temperature T for representative high molar mass F-F and F-S polymer fluids at a constant pressure of $P = 1$ atm (0.101 325 MPa) (Ref. 48). The configurational entropy s_c is normalized by its maximum value s_c^* and is determined from Eq. (20) of Ref. 28. The characteristic temperatures of glass formation, T_0 , T_g , T_i , and T_A , are indicated in the figure. The dotted line schematically depicts a correction to the mean field configurational entropy. As noted by Wolfgardt *et al.* (Ref. 62), s_c does not vanish, but instead achieves a small plateau value at low temperatures. An individual monomer of the F-F and F-S polymers contains two backbone segments and one side group with three units (like the united atom representation of 1-pentene) (Refs. 48 and 50). The F-F and F-S polymers represent chains with a flexible chain backbone and flexible side groups, and flexible chain and stiff side branches, respectively, as described in our schematic model of glass formation in polymer melts (Refs. 48–50). The bending energies E_b and E_s and the van der Waals interaction energy are chosen as $E_b/k_B = E_s/k_B = 400$ K (F-F polymers), $E_b/k_B = 400$ K, and $E_s/k_B = 4000$ K (F-S polymers), while the van der Waals energy ϵ is selected to be common for these two polymer classes as $\epsilon/k_B = 200$ K. The volume v_{cell} associated with a single lattice site and the lattice coordination number are taken as $v_{\text{cell}} = (2.7)^3 \text{ \AA}^3$ and $z = 6$, respectively. Each backbone and side chain semiflexible bond pair is further taken to have of one *trans* and two *gauche* configurations.

computed⁶² as $\Delta s_c^*/k_B = 0.41$ and $\Delta s_c^*/k_B = 0.19$, respectively, so that Δs_c^* is diminished for more fragile glass-forming liquids. The overall shapes of the curves in Figs. 1 and 2 are quite similar, except for the *maximum* that occurs at high temperatures for $s_c(T)$ in glass-forming polymer fluids. The temperature dependence of $s_c(T)$ is somewhat stronger in the F-S case, which is the origin of the increased fragility for this class of polymers. The maximum in s_c arises because the fluid is assumed to be compressible in our glass-forming polymer liquid model.^{28,48} This maximum would not appear under the *constant volume* conditions often considered in simulations of glass-forming liquids.

We suspect that the vanishing of s_c at a finite temperature T_0 in Fig. 2 is an artifact of mean field theory since our theory of the thermodynamics of polymer systems is implicitly based on a high temperature series expansion.²⁸ This interpretation would imply that T_0 only has meaning as an extrapolation temperature using data obtained above T_g . To emphasize this viewpoint, we introduce a dashed line to indicate the “expected” temperature dependence of s_c .^{63,64} Monte Carlo simulations of glass formation in a lattice model of a polymer melt by Wolfgardt *et al.*⁶³ support the suggestion that s_c levels off at low temperatures, rather than vanishing at a finite temperature T_0 . (Unfortunately, the difficulty of performing equilibrium simulations at temperatures below T_g makes it problematic, if not impossible, to prove this point by simulation.) Thus, we expect the similarity of the temperature dependence of $s_c(T)$ in equilibrium polymer-

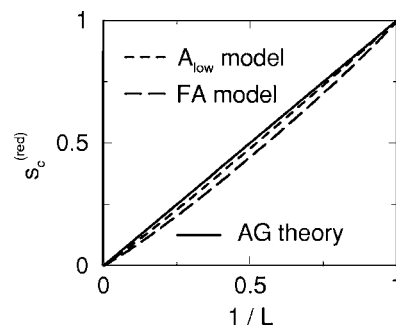


FIG. 3. The reduced configurational entropy $s_c^{(\text{red})}$ of Eq. (13) as a function of the reciprocal of the average degree of polymerization L for an incompressible solution of associating species undergoing equilibrium polymerization. The free energy parameters are the same as those employed in Fig. 1 (curve 1), while the enthalpy (Δh_a) and entropy (Δs_a) for monomer activation in the low probability activation model A_{low} are chosen as $\Delta h_a = 0$ and $\Delta s_a = \Delta s_p = -105 \text{ J/(mol K)}$ (Ref. 36). The solid line presents $s_c^{(\text{red})} = 1/L$ corresponding to the AG hypothesis of an inverse proportionality between the configurational entropy and the size z^* of the cooperatively rearranging regions (CRR) in glass-forming liquids.

ization solutions and glass-forming polymeric liquids to extend to low temperatures, so that s_c/s_c^* for glass-forming polymeric liquids has a similar sigmoidal shape as a function of temperature as $s_c^{(\text{red})}$ for equilibrium polymerization.

Next, we consider the relation between L and $s_c^{(\text{red})}$ to determine if equilibrium polymerization theory is consistent with the central, and most debatable, hypothesis of the AG theory, namely, that the average size z^* of the CRR is inversely proportional to s_c . Figure 3 depicts $s_c^{(\text{red})}$ versus the reciprocal of the average degree of polymerization L for both the FA model and a variant of the equilibrium polymerization A model (the A_{low} model).^{36,65} The A_{low} model is defined by the condition that the equilibrium constant K_a for activation is small and independent of temperature ($K_a = 3.2 \times 10^{-6}$ rather than equal to unity as in the FA model). A small K_a implies that the polymerization transition is “close” to being a second order phase transition and is, thus, much sharper than the extremely broad transition found for the FA model. Figure 3 indicates that L [see Eq. (2)] is indeed nearly inversely proportional to $s_c^{(\text{red})}$ for both these extreme models of equilibrium polymerization, in close accord with the Adam-Gibbs hypothesis. The variation of L with $s_c^{(\text{red})}$ thus resembles the variation of z^* with $s_c(T)$ for glass-forming liquids (see solid line in Fig. 3), with the linear relation becoming increasingly accurate for smaller K_a , such that this relation apparently holds *exactly* in the limit of a second order polymerization phase transition ($K_a \rightarrow 0$). The scaling behavior $s_c^{(\text{red})} \propto L^{-1}$ also applies³³ for the living polymerization I model where the initiator concentration is small and the polymerization transition is as sharp as for the A_{low} model illustrated in Fig. 3. Thus, the approximate scaling $L \sim 1/s_c$ seems to be a general property of equilibrium polymerization and probably applies generally to mean field theories of self-assembling particle systems since differences in cluster connectivity are irrelevant in a mean field theory. The proposed identification of equilibrium polymers with the CRR in glass-forming liquids is not only plausible, but also provides insight into the thermodynamic origins and significance of the AG hypothesis that s_c scales inversely to the

mass of dynamic clusters (CRR) that supposedly form in glass-forming liquids.

The AG model is based on the additional hypothesis that the apparent activation energy E for structural relaxation in glass-forming liquids equals $E = L\Delta\mu$, where $\Delta\mu$ is the activation energy in the fluid at high temperatures where relaxation is presumed to be noncooperative (i.e., $L=1$).^{28,45,48,50,62} This scaling relation is consistent with the statistical independence of binary particle exchange events, so that the probability that n particles participate in a joint collective exchange event is the n th power of the probability for an “elementary” single particle exchange event.⁶⁶ In the equilibrium polymerization model, L is the average value of the polymerization index n which, in turn, corresponds to the average string polymerization index in the structures appearing in glass-forming liquids. The identification of the strings with equilibrium polymers implies that the probability of a string of length n is the n th power of the probability of a string of length unity (i.e., the string length distribution is predicted to be exponential), again in accord with the Adam-Gibbs model.⁴⁵ Section IV summarizes literature results obtained from molecular dynamics simulations for a variety of liquids that support this general relation. The assumptions $E \sim L\Delta\mu$ and $L \sim 1/s_c$ correspond to the entire physical content of the AG model, and we conclude that these hypotheses can apparently be justified if the stringlike collective motion of glass-forming liquids is identified as an equilibrium polymerization process and if the strings are identified with the dynamic clusters of the AG model.

B. Characteristic temperatures of polymerization and glass formation

As mentioned before, the broad thermodynamic transition predicted by equilibrium polymerization theory^{33,41} in Fig. 1 can be described by three main characteristic temperatures: an onset temperature T_x where polymers first begin to form, a polymerization temperature T_p where the configurational specific heat has a maximum,⁶⁷ and a “saturation temperature” T_{sat} where s_c nearly saturates to its low temperature limit.^{33,36} Strictly speaking, no phase transition of finite order (first or second order transition) occurs in the FA model or in the A model for nonzero K_a since all derivatives of the free energy remain bounded at finite temperatures. In other words, the behavior in Fig. 1 is a classic example of a rounded or “infinite order” thermodynamic transition.³⁶ The corresponding multiplicity of characteristic temperatures in glass formation (see Fig. 2) is certainly suggestive of a similar rounded thermodynamic transition.

The wide temperature range between T_{sat} and T_x is a measure of the extent of transition rounding in the polymerization transitions depicted in Fig. 1, and the counterpart of this transition rounding is the fragility of glass-forming liquids (see Appendix A). The characteristic temperatures of equilibrium polymerization, T_x , T_p , and T_{sat} , correspond to the characteristic temperatures T_A , T_I , and T_0 , respectively, of the generalized entropy theory of glass formation. The temperature gaps $T_x - T_{\text{sat}}$ and $T_A - T_0$ between the onset and end of these broad polymerization transitions define their breadth, and the inflection point in $s_c T$ in each case demarks

a reasonable estimate of the crossover temperature T_I separating the high and low temperature transition regimes. The temperatures ratios (T_A/T_I , T_A/T_0 , T_I/T_g , etc.) provide useful measures of transition sharpness (fragility), and these ratios are discussed at length in our previous papers on glass formation.^{28,48–50} The ratios T_x/T_p , T_x/T_{sat} , and T_p/T_{sat} should provide similar measures of transition rounding for self-assembly transitions.

A full comparison of all the ratios of characteristic temperature for glass formation and equilibrium polymerization is hampered by an apparent lack of an analog to the glass transition temperature T_g in equilibrium polymerization. Figure 2 demonstrates that the temperature T_g occurs for both F–F and F–S polymers when $s_c(T)/s_c^* \sim O(0.1)$, suggesting a possibility for defining such a temperature for self-assembling fluids. Our former work estimates T_g based on a Lindemann criterion⁶⁸ that relates T_g to a critical value of the fluid’s excess free volume (defined in terms of the specific volume) that is necessary for fluidlike motion to exist and for structural relaxation to occur on reasonable time scales.^{28,49} Because s_c has been argued to be directly proportional to the mean square particle displacement $\langle u^2 \rangle$ in the fluid,⁶² the determination of T_g from a criterion involving s_c is plausible.⁶⁹ As particle localization within very long lived clusters is likewise characteristic of the dynamic cluster formation in equilibrium polymerization when the conversion fraction becomes large, it is reasonable to consider whether the criterion [i.e., $s_c^{(\text{red})}(T) \sim O(0.1)$] also describes an instability condition (or “softening transition”) for self-assembling particle systems.

Experimental tests of this proposed instability for self-assembled structures are complicated by the difficulty of estimating s_c . A similar problem exists for glass-forming liquids where the observed entropy contains large vibrational contributions that are difficult to estimate.^{50,62} Figures 4(a) and 4(b) compare $s_c^{(\text{red})}$ to the more experimentally accessible variable, the extent of polymerization Φ , the order parameter for the polymerization process. The comparison is made for both FA and A₁ models with the same interaction parameters as prescribed in Fig. 1. The broad transition for the FA model produces the approximate relation $s_c^{(\text{red})} \approx (1 - \Phi)^{1/2}$, while for the relatively sharp transition in the A₁ model we find $s_c^{(\text{red})} \approx (1 - \Phi)$. Thus, s_c and Φ are clearly related, although the relation is somewhat model dependent.

Starr and Sciortino⁷⁰ have recently estimated an instability criterion for the self-assembly of DNA functionalized particles that form an associated network, thereby allowing for a tentative comparison with our proposed instability criterion for self-assembled structures. They describe the DNA assembly process in terms of an order parameter, the fraction Φ of DNA strands that are bonded into the network, which likewise can be considered as the “extent of polymerization” or the “extent of assembly.” Starr and Sciortino find that Φ governs the network dynamics and that relaxation becomes extremely sluggish when $(1 - \Phi)$ becomes sufficiently small, i.e., $(1 - \Phi) \sim 0.1$. Specifically, it is no longer possible to determine the diffusion coefficient for $(1 - \Phi) \approx 0.3$, and these systems have difficulty to equilibrate for smaller $(1 - \Phi)$. The self-assembly transition in DNA is quite sharp,

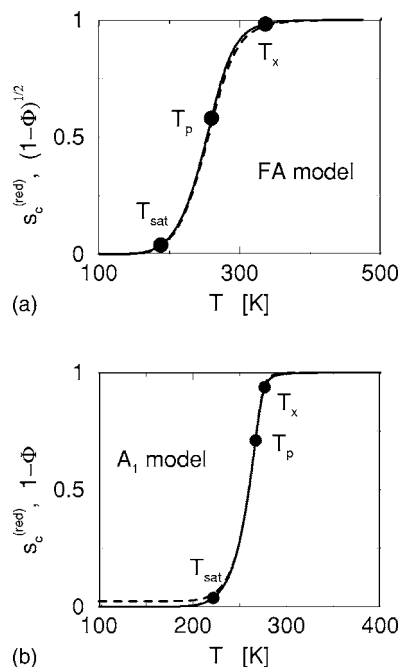


FIG. 4. (a) The reduced configurational entropy $s_c^{(red)}$ (solid line) and $\sqrt{1-\Phi}$, where Φ is the extent of polymerization, (dashed line) as functions of temperature for the FA equilibrium polymerization model. Solid symbols indicate the calculated saturation temperature T_{sat} , the polymerization temperature T_p , and the crossover temperature T_x . The free energy parameters and the initial monomer concentration ϕ_1^0 are the same as in Fig. 1 (curve 1). (b) The reduced configurational entropy $s_c^{(red)}$ (solid line) and $(1-\Phi)$, where Φ is the extent of polymerization, (dashed line) as functions of temperature for the activated equilibrium polymerization A_1 model. Solid symbols indicate the calculated saturation temperature T_{sat} , the polymerization temperature T_p , and the crossover temperature T_x . The free energy parameters and the initial monomer concentration ϕ_1^0 are the same as in Fig. 1 (curve 3).

as in the A_1 model (see Figs. 1 and 4(b)), so that the approximations $s_c \approx 1-\Phi$ and $s_c(T_g) \approx 0.1$ are expected to apply to their DNA data as well. This tentative estimate of the instability condition supports our suggestion that the concept of a glass transition temperature can be extended to self-assembling systems. In further accord with this observation, experiments for equilibrium polymer systems also indicate a sensitivity to the cooling history⁷¹ and the presence of aging phenomena, features normally associated with the “glass transition” in supercooled liquids. Further computational and experimental tests will be required to confirm the significance of a well-defined instability temperature in assembling systems that directly parallels T_g in glass-forming liquids. Perhaps, the most direct means to probe for this temperature is through measurement of the mean square particle displacement $\langle u^2 \rangle$ within the self-assembled clusters. The instability condition for melting and glass formation signals a softening process (at T_m and T_g , respectively) and is prescribed by the requirement that the ratio of $\langle u^2 \rangle^{1/2}$ relative to the interparticle separation in the ordered state be on the order $O(0.1)$.^{25,49,68} Correspondingly, we can define an “instability temperature” for self-assembling structures by the condition that $\langle u^2 \rangle^{1/2}$ relative to the average distance to another particle in the cluster is on the order (0.1). This criterion is a generalization of the Lindemann instability condition for crystal melting and glass softening and can be tested in simulations,

in neutron and x-ray scatterings from molecular fluids, and in particle tracking measurements for assembling colloidal fluids.

C. The analog of “fragility” in equilibrium polymerization

In addition to a dependence on the free energy parameters Δh_p and Δs_p , the sharpness of polymerization transitions depends on *constraints* on how the clusters grow (initiation of growth from the chain ends,⁷² thermal activation,³⁶ branching, confinement, etc.). Thus, the analog of fragility in systems undergoing equilibrium polymerization can be adjusted by varying these additional regulatory constraints on the assembly process.^{52,56,57,61} As a particularly concrete example, the rate of change of the viscosity of equilibrium polymer solutions [e.g., poly(α -methylstyrene)] with temperature can be *tuned continuously* by varying the polymerization initiator concentration,^{72,73} a parameter controlling the sharpness of the equilibrium polymerization transition,^{36,43} in a fashion directly analogous to changing K_a in the A model.^{33,36,41–43} The suggested correspondence between equilibrium polymerization and glass formation provides clear hints about the physical factors that affect the variation of fragility in glass-forming liquids. For example, energetically unfavorable (unstable) regions that form spontaneously by thermal fluctuations could play the role of an initiator or activated species in catalyzing collective liquid motion, as suggested previously for water.⁷⁴

D. Comparison of size distribution of equilibrium polymers and strings of cooperative motion

The prediction that the mobile particles of glass-forming liquids should exhibit the statistical properties of flexible equilibrium polymers (see Appendix B) has first been verified by Donati *et al.*³ In particular, they find a nearly exponential size distribution of linear chains of mobile particles, whose conformational shapes resemble random flight polymers.³ Figure 5 compares the string length distribution of Donati *et al.* for a glass-forming model of binary Lennard-Jones mixture to the chain length distribution $P(n)$ predicted for equilibrium polymerization in the FA model.⁷⁵ The solid lines in Fig. 5 are the fits obtained from our equilibrium polymerization theory expressions for $P(n)$,

$$P(n \geq 2) = \frac{CA^n}{\phi_1 + CA^2/(1-A)} \quad (14)$$

and

$$P(n=1) = \frac{\phi_1}{\phi_1 + CA^2/(1-A)}, \quad (15)$$

where $P(n=1)$ is the probability that a particle is in the monomeric state, A , C , and ϕ_1 are defined following Eq. (5), and $z=6$ is appropriate for a cubic lattice. [Equations (14) and (15) are generalizations of the expressions for $P(n)$ given in Eq. (40) of Ref. 33 for the I model of equilibrium polymerization.] Our identification of the strings in glass-forming liquids with equilibrium polymers is based on the concept that fluctuations in the interparticle packing in the

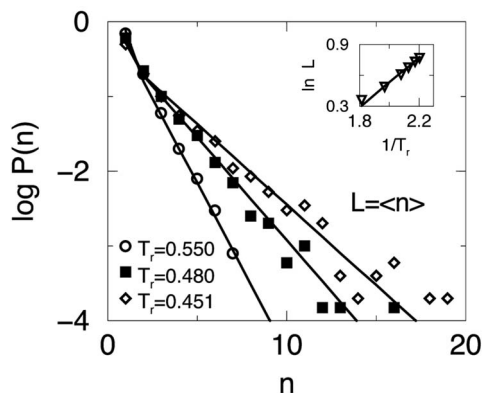


FIG. 5. Comparison of the size distribution $P(n)$ of strings from simulations of supercooled liquids and from calculations for equilibrium linear polymers in the free association (FA) model [see Eqs. (14) and (15)]. Symbols denote the simulation data of Donati *et al.* (Ref. 3) for three different reduced temperatures $T_r \equiv k_B T / \epsilon_{LJ} = 0.550, 0.480$, and 0.451 , while lines are the fits to the simulation data obtained from the FH equilibrium polymerization theory. The initial monomer concentration is taken as the maximum concentration (5%) of mobile Lennard-Jones particles in the simulated glass-forming liquid. The fitted values of the enthalpy and entropy of polymerization are $\Delta h_p / \epsilon_{LJ} = -3.55$ and $\Delta s_p / k_B = -3.91$, respectively. The inset presents a comparison of simulation data (Ref. 3) (triangles) for the logarithm of the average string length L vs the inverse reduced temperature $1/T_r$. The predictions (solid line) of the equilibrium polymerization theory are generated for the same free energy parameters and initial monomer concentration as used in the fits shown in the main figure.

fluid lead to corresponding fluctuations in the local interactions felt by any given particle and arising from the presence of surrounding particles. This effective many-body interaction potential can be anisotropic due to nonlocal packing constraints, so that the symmetry properties of the original interparticle potential may be broken in dense fluids. The formation of polymeric structures is a natural consequence of the resulting anisotropy in the effective interactions.⁷⁶ This proposed explanation of the physical origin of strings requires critical examination in future simulation studies.

The total volume fraction ϕ_1^0 of particles that can undergo association is chosen as $\phi_1^0 = 0.05$ based on simulations by Donati *et al.*³ In particular, simulations for both small molecule and polymer glass-forming model liquids indicate that the volume fraction of mobile particles generally lies in the range^{3,17,77} of 5%–7%, *regardless of temperature*.⁷⁸ For simplicity, the free association FA model of equilibrium polymerization is used to obtain the fits in Fig. 5 from Eqs. (14) and (15) since the temperature range is limited and since the FA model contains the fewest adjustable parameters. The inset to Fig. 5 again demonstrates agreement between simulation data for $L(T)$ and equilibrium polymerization theory and confirms the exponential character of the average string length $L(T)$ as a function of temperature. Using the free energy parameters specified in the caption of Fig. 5, the average degree of polymerization at the transition temperature T_p then equals 2.3, which is rather close to the magnitude of the polymerization index $z^*(T_c) \approx 2$ of the CRR near the experimental crossover temperature T_c of glass formation.⁵¹ (The temperature T_c is identified in our previous papers^{28,48–50} with the temperature T_l of the generalized entropy theory of glass formation, and the equilibrium polymerization analog

of T_l almost coincides with T_p ; see Fig. 1.) Simulations by Aichele *et al.*³⁴ for the temperature dependence of L in a model *polymeric* glass-forming liquid are consistent with an exponential string length distribution (see Fig. 10 of Ref. 34) and the simple scaling $L \propto \exp(\delta/T)$ (where δ is a constant³⁴), results emerging from the simple FA equilibrium polymerization model in a continuum limit approximation in which the analytic theory simplifies.^{40,79}

String formation has also been examined in detail for the Dzugutov fluid¹⁸ (a model of supercooled metallic liquids) where the string length n distribution is likewise found to be exponential. Moreover, the average string length $L \equiv \langle n \rangle$ has been shown to scale in near inverse proportionality to the landscape configurational entropy $s_{c,L}$ and in near proportionality to the activation energy for structural relaxation, providing a striking confirmation of the validity of the AG model for structural relaxation. Exponential string length distributions also emerge from recent simulations of glass-forming liquids with or without antiplasticizing additives that reduce T_g while increasing the density and stiffness of the glass.⁸⁰ The relative length of the strings at fixed reduced temperature T/T_g becomes smaller as the antiplasticizer additives render the glass formation stronger (i.e., more Arrhenius).⁸⁰ We conclude that all computationally investigated fluids considered so far consistently exhibit an exponential length distribution of stringlike mobile particles, as in the original work of Donati *et al.*³ In each instance, the variation of the average string mass and other thermodynamic properties agrees with equilibrium polymerization theory, predicted thermodynamic relations from the AG theory, and the identification of strings with the CRR. This finding is striking given the diverse range of fluids investigated, thereby strongly suggesting that the string formation is a *universal property* of cooled glass-forming liquids.

Stephensen *et al.*⁸¹ have recently suggested that the stringlike clusters identified in the simulations should transform into the compact clusters predicted by the random first order transition model as the glass transition is approached. While their arguments offer an interesting potential reconciliation between the predicted droplet structures of the mean field theory and the observed stringlike structures found in equilibrated simulations, it does not appear possible to test these predictions computationally since equilibrium simulations cannot be performed much below T_c where the strings are still evident. Stephensen *et al.*⁸¹ suggest that the mobile particle clusters found at high temperatures ($T > T_c$) are somewhat like percolation clusters, but the power law mass distribution of these clusters under near critical conditions⁸² is incompatible with the exponential distribution of strings observed in the simulations. However, it is possible that the strings themselves might cluster into more compact clusters at low temperatures, a trend already observed in previous studies at high temperatures where the “mobile particle clusters” are found to have a branched polymer form with a power law mass distribution,¹⁷ consistent with the mass distribution of percolation clusters. These mobile particle clusters are composed of *ensembles of strings* and might reasonably be taken to correspond to the structures discussed by Stephensen *et al.* However, the temperature dependence of

these mobile particle clusters (string clusters) is quite different from that of the strings in the simulations of Donati *et al.*³ In particular, the mass of the mobile clusters seems to diverge near the crossover temperature T_c in the binary LJ fluid,¹⁷ while the average string length L does not exhibit a singular behavior as T_c is approached.⁸³ This temperature dependence of the mobile particle clusters (string clusters) would appear to make them unsuitable for the identification with the CRR of the AG theory. This point requires further investigation, however, given the observations of Refs. 30 and 34 which indicate that the structural relaxation time of water and the Dzugutov fluid can approximately be related to the mass of mobile particle clusters over a limited temperature range.

Langer and Lemaitre⁸⁴ have also proposed a model for the stringlike motion observed by Donati *et al.*³ in terms of “thermally activated chains of small atomic displacements” with the geometrical form and statistical properties of linear polymer chains. While this model addresses geometrical features of the strings, it does not consider their dynamic nature and fails to reproduce the characteristic exponential string length distribution. An interesting aspect of the work of Langer and Lemaitre is the suggestion that stringlike motion might be identified with the defect structures that are important in the plastic flow of amorphous nonequilibrium solids. In accord with this possibility, Zhang *et al.*⁸⁵ observe stringlike atomic motion to be prevalent in the grain boundary motion of simulated polycrystalline materials under steady strain.

E. Saturation of the self-assembly process at low temperatures and its implications

The FA model is a rather special limit of the activation model of equilibrium polymerization when $K_a \equiv 1$. Figure 2 demonstrates that glass formation is a broad transition phenomenon that can potentially be interpreted in terms of the A model of equilibrium polymerization, provided that $K_a \sim O(1)$. Hence, the use of the FA model to describe glass-forming polymer liquids can only be a first approximation. Significant changes in the temperature dependence of L occur if K_a becomes small, as for sulfur and many other real polymerizing systems.^{36,65} Hence, it is worth discussing some features that could lead to behavior not captured by the simplest FA model and that have ramifications for the interpretation of glass formation based on the equilibrium polymerization viewpoint.

Figure 6 presents the temperature dependence of L for the A_1 model and indicates that $L(T)$ approaches a *finite value* L^* at low temperatures, a process we term “saturation.” (This is something that never occurs in the FA model.)⁸⁶ Thus, the activation equilibrium constant K_a not only serves to regulate the *broadness* of the polymerization transition (the analog of glass fragility in equilibrium polymerization theory), but also the ultimate size of the polymer chains that form at low temperatures. A limiting constant L at low temperatures and the identification of strings with equilibrium polymers corresponding to the A_1 model would mean that the structural relaxation returns to an Arrhenius law at low

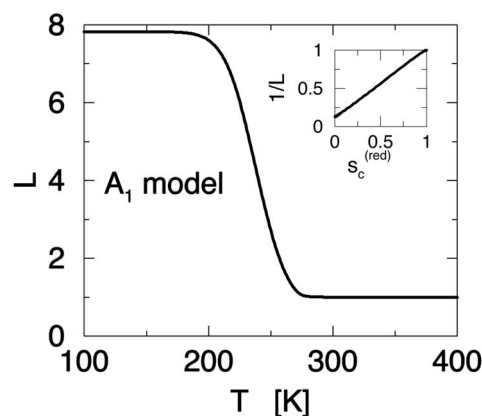


FIG. 6. Temperature variation of the average degree of polymerization L for the A_1 model of activated equilibrium polymerization that is illustrated in Fig. 1 (see curve 3). The inset presents the reciprocal of L as a function of the reduced configurational entropy $s_c^{(\text{red})}$ of Eq. (13).

temperatures, albeit with an apparent activation energy that is L^* times its value at high temperatures where $L=1$. (The inset to Fig. 6 shows that L is still approximately proportional to $1/s_c$ in the A_1 model, but the slope differs from unity.) Numerous experimental and computational studies claim that the temperature dependence of the structural relaxation time τ becomes Arrhenius at low temperatures,^{87–89} suggesting that an activation process might be influencing the formation of stringlike structures in glass-forming liquids. According to the equilibrium polymer-string analogy, these activation processes lie at the heart of understanding the fragility of glass-forming liquids.

F. Two-state models of glass formation and self-assembly

Another type of chemical equilibrium model of supercooled liquids bears close mathematical and physical relations to the equilibrium polymerization models discussed in this section. Angell and Rao and Moyinihan and Angell⁹⁰ have considered a simplified “excitation model” for the fluid where fluid particles transform back and forth between normal and excited (mobile) fluid states under the constraint of equilibrium. The temperature dependence of s_c for this model is rather similar to that obtained for the FA equilibrium polymerization model (see Fig. 1). Our model of “polymeric excitations” may be understood as a generalization of the “two-state” model of Angell and Rao and Moyinihan and Angell⁹⁰ which accounts for the interactions between the excitations responsible for collective particle movement. Simplified two-state models, in which particles are abstractly assigned to “associated” or “dissociated” states, have also been applied to describe self-assembly of DNA functionalized particles into network⁹¹ and other self-assembly systems. While these two-state models capture many aspects of the thermodynamics of the excitation or assembly processes and lead to reasonable estimates of the thermodynamic parameters (Δh and Δs) governing these thermodynamic transitions, they provide no information about the scale and geometry of the dynamical heterogeneity as the transition develops.

G. Size of cooperatively rearranging regions and the average degree of polymerization: Evidence for universality at the crossover temperature T_c

The proposed analogy between the CRR and equilibrium polymers has implications for the number of particles involved in these structures and the size of these dynamically heterogeneous regions. Both experiments and the generalized entropy theory estimate the size z^* of the CRR near the crossover temperature (our T_f) to be about 2 for fragile glass-forming liquids.⁵¹ [Specifically, $z^*(T_f) = 1.55$ and 2.02 for high molar mass F-F and F-S polymers, respectively.] As discussed in Ref. 28, this regularity in the magnitude of z^* is ultimately responsible for the nearly universal magnitude of the structural relaxation time at the crossover temperature T_f ,⁹² thereby providing clear evidence that the glass transition process is not purely a kinetic phenomenon since the fluid at T_f is effectively at equilibrium.

The average polymerization index L at the polymerization temperature T_p also happens to lie close to 2 in the FA model (L equals 1.92 and 2.02 for cases 1 and 2, respectively, in Fig. 1). This value of 2 compares well with the average polymer string length $L \approx 2.2$ of mobile particles (calculated from MD simulation data for binary LJ glass-forming liquids)^{3,4} in the vicinity of the empirical mode coupling temperature T_c , which provides a specific estimate of the crossover temperature T_f . Recent experiments and simulations for associating dipolar fluids also reveal the presence of a transition involving the formation of equilibrium polymer chains, and L at T_p is again in the broad range of 2–4 for simulations in both three and two spatial dimensions and for a real self-assembling magnetic particle system in quasi-two-dimensions.^{93,94} The near universality of z^* in the neighborhood of T_f ,⁵¹ the direct observation of transient polymer clustering in simulations of glass-forming liquids,³ and the corresponding predictions from theories and simulations of fluids exhibiting equilibrium polymerization^{36,93,94} provide good further supporting evidence that the clusters undergoing cooperative motion in structural glasses involve a kind of equilibrium polymerization.

The suggested correspondence between equilibrium polymers and the CRR of the Adam-Gibbs model allows us to estimate the spatial extent of these hypothetical transient clusters. Using the generalized entropy theory prediction²⁸ that z^* at T_g is about 4–5 (depending on the polymer class) and taking the size of a molecule or monomer to be on the order of 0.5–1 nm in a typical glass-forming liquid, such as orthoterphenyl,⁹⁵ the average size of a CRR at the glass transition temperature should likewise have nanometer dimensions. Specifically, if we assume that the root-mean square end-to-end distance R_{rms} of the CRR grows with the square root of the degree of polymerization⁹⁶ [i.e., $R_{\text{rms}} \sim (z^*)^{1/2}$], the average CRR size would be roughly in the range of 1–2 nm [using⁴⁸ $z^*(T_g) \approx 4$ –5]. Of course, random walk scaling models³ represent an idealization for such short chains, and a wormlike chain model may provide a more realistic estimate for the mean dimensions of the CRR polymeric clusters.⁶⁵ An upper bound for R_{rms} can be inferred by assuming rodlike CRR chains, with R_{rms} then ranging from 2 to 5 nm. A realistic value of R_{rms} should then lie midway

between the upper and lower bounds, so that 2–3 nm is probably a typical order of magnitude for R_{rms} . This equilibrium polymer estimate is quite consistent with experimental estimates for the *average cluster dimensions* of the CRR,^{7,95,97} and much larger clusters may occur due to the intrinsic mass polydispersity of equilibrium polymers. Moreover, since different measurements are governed by *different averages* of the cluster polydispersity, experimental determinations of the CRR can be anticipated to vary somewhat with the measurement method, a well known phenomenon for the properties of polydisperse polymer solutions.

H. Equilibrium polymerization of immobile particle clusters

Although the presence of particles with excessively high mobility relative to the Brownian motion represents a conspicuous feature of the supercooled fluid state, this mobile particle population is not responsible for the divergence of the viscosity that is characteristic of solidification. (Indeed, mobile particles reduce the viscosity!) This situation creates no conceptual difficulties because the formation of mobile particle clusters is accompanied by the emergence of immobile particle clusters that interpenetrate the space occupied by the mobile particle. The existence of these immobile particle clusters broadly accords with the clump model of Klein and co-workers.^{2,22} Molecular dynamics studies by Klein and co-workers² of these clusters of immobile and locally well packed particles in a two-dimensional binary Lennard-Jones glass-forming fluid reveal that the immobile clusters grow upon cooling as described above for the mobile particle clusters. The size distribution for the immobile clusters is, however, consistent with branched equilibrium polymerization rather than with the formation of linear chains. Thus, the immobile cluster mass distribution involves a power law with an exponential cutoff. Similar clusters of *immobile and well packed* particles have been observed in simulations of the Dzugutov fluid in three dimensions.¹⁸ Using the language of equilibrium polymerization, the fraction of immobile particles in the study of Dzugutov *et al.* corresponds to their extent of polymerization Φ , and about 12% of the particles are observed to be in an immobile and well packed state at low temperatures, a similar order of magnitude to the mobile particle strings. Unfortunately, the size distribution for the immobile particle clusters in the Dzugutov fluid is not available for a quantitative comparison with equilibrium polymerization theory.

I. Equilibrium polymerization and Fisher clusters in glass-forming liquids

In addition to the presence of nanometer scale heterogeneities in glass-forming liquids, reports exist of heterogeneities with dimensions more than two orders of magnitude larger.⁹⁸ While these structures are apparently transient, the large structures can persist for as much as 10^4 – 10^7 times the structural relaxation time of the fluid.⁹⁸ The presence of these structures apparently depends on sample history.

We can rationalize the “Fisher clusters” and the ultraslow diffusive modes associated with them^{98,99} as arising

from the formation of large scale, low energy clusters in the glass state. These clusters can resist disintegration at higher temperatures where the clusters are thermodynamically unstable. A similar phenomenon exists for equilibrium polymers where long chains persist when the fluid is returned to a thermodynamic regime where the monomeric form is thermodynamically stable.¹⁰⁰ The disintegration of the high molar mass and presumably entangled polymers can be extremely sluggish, unless the temperature is varied sufficiently to erase the “memory” of these structures. This type of asymmetry in the assembly-disassembly kinetics is prevalent in numerous self-assembling biological systems, such as viral capsids¹⁰¹ and the amyloid fibers arising in neurodegenerative diseases.¹⁰² Singh and Zlotnick¹⁰¹ have recently demonstrated that this hysteresis phenomenon in viral capsid organization can be understood in terms of kinetic modeling consistent with equilibrium polymerization of shell-like polymer capsid structures. We therefore attribute the formation of the large scale Fisher clusters to the formation of “frozen” polymeric clusters that are trapped in long-lived metastable states of this general kind.

J. Implications of correspondence between equilibrium polymerization and glass formation for understanding the dynamics of associating fluids

If the dynamic clusters of glass-forming liquids can really be identified with a kind of equilibrium polymerization, then associating fluids should share many phenomenological properties of glass-forming liquids. Recent work has established that the thermodynamic and relaxation properties of self-assembly fluids indeed have many features in common with glass-forming liquids. For example, Monte Carlo simulations by Kumar and Douglas¹⁰³ for a fluid of associating polymers that form a thermally reversible gel at low temperatures exhibit many of the classic signatures of glass formation: transient caging of particle motion, growth of the non-Gaussian parameter, and a very strong temperature dependence of the diffusion coefficient and the rate of structural relaxation that is similar in functional form to that observed in glass-forming liquids. These findings have been further amplified by molecular dynamics simulations²⁶ of a telechelic polymer solution that forms micelles at low temperatures. These associating fluids exhibit a bifurcation of relaxation times due to the clustering transition and display a breakdown of the Stokes-Einstein relation associated with the onset of this “dynamic heterogeneity.” A recent work by Guo and Luijten¹⁰⁴ further confirms the observation of a breakdown of the Stokes-Einstein relation near the gelation transition in another telechelic polymer fluid exhibiting thermally reversible gelation. Correspondingly, Lu and Solomon¹⁰⁵ observe a breakdown of particle tracking estimates for the rheological properties of associating fluids that rely on the assumption of the validity of Stokes-Einstein relation. All these findings are consistent with our expectation that the dynamic heterogeneity of glass-forming liquids is a general phenomenon with important ramifications for associating fluids as well.

V. CONCLUSIONS

Recent simulations^{3,4,16,17} and experiments^{11–13} for colloidal fluids both suggest that the CRRs of the AG theory take the form of stringlike structures. This viewpoint clearly motivates comparing the thermodynamics of cooled glass-forming polymer melts to the thermodynamics of polymeric clusters arising from equilibrium polymerization upon cooling (not necessarily as linear chains¹⁰⁶). These two classes of complex fluids indeed exhibit remarkable similarities in their thermodynamic behavior. In each case, the broad thermodynamic transition is accompanied by a drop of the configurational entropy to a low temperature residual value. Both are demarked by temperatures where this drop initiates (T_x in equilibrium polymerization³³ versus T_A in glass formation⁴⁸) and ends (T_{sat} in equilibrium polymerization³³ versus T_0 in glass formation⁴⁸), and in both these complex fluid models there is an inflection point in $s_c T$ at an intermediate temperature (T_l vs $T_{l,p}$) separating high and low temperature regimes of these rounded thermodynamic transitions. This resemblance strongly suggests that glass formation involves thermodynamic particle clustering transition of some kind (not necessarily the simplest free association model of equilibrium polymerization).

As a precise test of the correspondence between glass formation and equilibrium polymerization, we analyze the relation between s_c and the average size z^* of the CRR (which is proportional to the average chain length in the equilibrium polymerization model). Adam and Gibbs hypothesize that these quantities should be inversely related to each other, and explicit calculations for two different models of equilibrium polymerization (where z^* is taken as corresponding to the average degree of polymerization L) indicate that such a relation holds to a good approximation. This inverse relation provides another striking confirmation of the hypothesis that the CRR are themselves both polymeric and dynamic by nature. The idea that cooled liquids are composed of dynamic polymeric structures whose degree of polymerization z^* changes with temperature has long been advocated as a qualitative description of cooled liquids, so the general idea is certainly not new.¹⁰⁷

The polymeric interpretation of “excitation structures” in glass-forming liquids also provides insights into the dynamical origins of variations of fragility in supercooled liquids. It is well known that chemical initiation and thermal activation ultimately regulate the extent of polymer growth in polymerizations that proceed upon cooling, as well as the sharpness (the analog of fragility in glass-forming liquids) of the resulting transitions.³⁶ It is reasonable to imagine that highly energetically unstable regions form in cooled liquids through thermal fluctuations and that these events serve as “catalysts” for collective motions.⁷⁴ In accordance with this analogy, the rate of change of the viscosity with temperature and the extent of polymerization in living polymerization solutions can be tuned by varying the initiator concentration.^{71–73}

The suggested correspondence between glass formation and equilibrium polymerization also provides a tentative framework for comprehending many nonequilibrium rheological properties of glass-forming materials. Physical aging

can naturally be understood by the slow growth of the polymer chains into their equilibrium populations of dynamic clusters upon lowering the temperature, and the effect is naturally expected in equilibrium polymer solutions as well. The viscosity and relaxation times grow as these structures form, and the properties cease to evolve once equilibrium is achieved. Experimental measurements for equilibrium polymerization solutions become dependent on the scanning rate when the temperature is varied too rapidly compared to the equilibration time. Similar nonequilibrium history effects are also characteristic of glass-forming liquids. Strong shear thinning is prevalent in both glass-forming liquids and polymerizing liquids since shear tends to break down these structures, and aging naturally follows this “rejuvenating” process as these fluids recover their equilibrium populations. The equilibrium polymerization model of glass formation offers a prospective tool for investigating the non-Newtonian physical properties of these complex fluids and the drift of their properties over time.

Given the success of equilibrium polymerization model in rationalizing many of the thermodynamic aspects of glass formation, it would clearly be of interest to develop a systematic theory of structural relaxation in fluids undergoing equilibrium polymerization. This would allow a direct comparison to detailed aspects of the time dependence of structural relaxation in glass-forming liquids. Douglas and Hubbard¹⁰⁶ long ago hypothesized that the dynamic heterogeneity of supercooled liquids could be explained in terms of equilibrium polymerization, and they provide specific estimates for the viscoelastic properties of these solutions based on this physical model. The time has come to develop this tentative model of structural relaxation in glass-forming liquids in a systematic fashion, consistent with the long wavelength entropy theory of glass formation.

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APPENDIX A: OBJECTIVE MEASURES OF FRAGILITY AND AN ORDER PARAMETER FOR GLASS FORMATION

Although the general concept of “fragility” as a measure of the strength of the temperature dependence of structural relaxation times and associated transport properties is unequivocal, some suggested specific measures of fragility, such as E/T_g , where E is the apparent activation energy (for structural relaxation) at T_g , seem to lack a fundamental significance.¹⁰⁸ In particular, these definitions depend on the range of the particle interactions since E depends on the cohesive energy density, even at high temperatures where $E(T \rightarrow \infty) \approx \Delta\mu$, and on molecular parameters, such as the bond rotational energy in polymers, etc.^{62,109} The sensitivity of T_g to cooling rate also raises fundamental questions about definitions of fragility based on this temperature. Estimates of the fragility parameter D in the Vogel-Fulcher-Tammann-Hesse equation for τ can vary widely depending on the temperature range chosen,¹¹⁰ so this definition of fragility can

also be problematic. Ratios of characteristic temperatures of glass formation appear to provide objective measures of transition broadness and thus fragility, but the apparent lack of a fundamental thermodynamic significance of T_g engenders concern about this measure of fragility as well. The combination of equilibrium polymerization theory, the generalized entropy theory of glass formation, and the identification of the strings with the CRR of AG offers the prospect of a more fundamental definition of fragility.

Our goal lies in introducing a more fundamental definition for the strength of the temperature dependence of transport properties that is not subject to the criticism just mentioned and that equally applies to the high and low temperature regimes of glass formation. This extension is especially needed for the analysis of simulations since the low temperature regime is generally inaccessible in equilibrated simulations of glass-forming liquids.

The “differential” fragility χ_g of a glass-forming fluid at a temperature T may be defined through the derivative of the normalized activation energy for structural relaxation,

$$\chi_g = d[E(T)/E(T \rightarrow \infty)]/dT. \quad (A1)$$

This quantity describes how much the temperature dependence of structural relaxation deviates from an Arrhenius behavior, which is the most basic concept embodied by the term “fragility.” Within the AG theory, χ_g exactly equals

$$\chi_{g,AG} = d[z^*(T)]/dT, \quad (A2)$$

where z^* is the average number of particles in the cooperatively rearranging regions (CRR). Further, the identification of the CRR with strings implies,

$$\chi_{g,L}(\text{strings} \equiv \text{CRR}) = d[L(T)]/dT. \quad (A3)$$

It is apparent that χ_g corresponds to a kind of “susceptibility” associated with this type of rounded transition, and the term “glass susceptibility” might be a better term than “fragility.” At any rate, these measures of glass fragility imply that the fluid transport properties are “strong” at high temperatures. The differential fragility then gradually increases upon cooling below an onset temperature T_A for glass formation. The rate of change of χ_g becomes largest around T_g and then becomes smaller again at lower temperatures where a return to an Arrhenius behavior has often been reported.^{87,89,111} This variation in χ_g is a natural consequence of the sigmoidal temperature dependence of s_c/s_c^* presented in Fig. 2.

Our definition of fragility should be supplemented by further information indicating the relative *location* of the fluid state within this broad thermodynamic transition. Thus, we also seek an objective measure of the relative breadth for this type of transition. The extent Φ of string polymerization provides a natural *order parameter for glass formation* (i.e., an “extent of glass formation”) that quantifies the degree to which this transition has developed. In a previous paper,³³ we show that Φ can be approximately related to L in the I model of equilibrium polymerization by $\Phi \approx (L-1)/L$ or $L \approx 1/(1-\Phi)$, so that the ratio $(L-1)/L$ might also serve as an effective order parameter for glass formation. Both of these quantities vanish in the high temperature homogeneous fluid state and approach unity at low temperatures where the clus-

tering process is finished. Consequently, either Φ or L can then serve as objective measures of the extent of glass formation. A measure of the breadth of the polymerization or glass transition can also be obtained by considering the variance of L or Φ , or the absolute value of the derivative of Φ with respect to temperature, $|d\Phi(T)/dT|$. The half-width of these peaked functions provides an intrinsic measure of transition broadness. These measures of transition susceptibility, extent of ordering, and transition breadth apply equally well to equilibrium polymerization and self-assembly as to glass formation. Collectively, these measures offer a unified description of the characteristics of rounded transitions.

APPENDIX B: MOBILE PARTICLE IN GLASS-FORMING FLUIDS AND EQUILIBRIUM POLYMER SOLUTIONS

The existence of mobile particle strings having the characteristic of equilibrium polymers has been predicted by Douglas¹¹² before the pioneering paper of Donati *et al.*³ This prediction is based on a field theory description of the hydrodynamics of suspensions, developed earlier by Kholodenko and Douglas,¹¹³ which indicates the emergence of hydrodynamic screening in particle suspensions by a mechanism similar to the emergence of superconductivity in metallic solids, where the hydrodynamic interactions of the fluid play a role analogous to the elastic interactions in superconductors. The introduction of further approximations by Douglas¹¹² leads to a formal mathematical correspondence between hydrodynamic screening in suspensions and superfluidity, a phenomenon closely related to the theory of superconductivity. The prediction of string formation in supercooled liquids then follows from a well-known equilibrium polymerization model of the superfluidity transition introduced by Feynman.^{114,116}

Although heuristic, these arguments suggest many specific predictions concerning the nature of dynamic heterogeneities in glass-forming liquids, influencing the interpretation of the simulation data. In particular, the model just mentioned predicts the strings of *mobile* particles to grow upon cooling and that the strings exhibit an exponential length distribution. (See Ceperley and Pollock¹¹⁵ for a discussion of the “quantum analog” of the string distribution considered by Donati *et al.*³). Other predictions concern the breakdown of the Stokes-Einstein relation seen in both glass-forming liquids and superfluids, a roton feature in the dispersion relation for density fluctuations in glass-forming liquids, an order-disorder condition governed by a Lindemann criterion, etc. These results suggest that the molecular dynamics of classical cooled liquids have much in common with cooled quantum liquids such as He⁴. Both types of model fluids at low temperatures exhibit an ordering that is appropriately described by a two-fluid formalism where particles of extremely high mobility coexist with “normal” fluid particles and where the entropy of the fluid drops to very small values by virtue of collective particle motion. Ironically, the particle permutational “stirring motion” suggested by Feynman¹¹⁶ has never been confirmed in dense quantum fluids.

¹M. T. Cicerone, F. R. Blackburn, and M. D. Ediger, J. Chem. Phys. **102**, 471 (1995).

- ²G. Johnson, A. I. Mel'cuk, H. Gould, W. Klein, and R. D. Mountain, Phys. Rev. E **57**, 5707 (1998); A. I. Mel'cuk, R. A. Ramos, H. Gould, W. Klein, and R. D. Mountain, Phys. Rev. Lett. **75**, 2522 (1995).
- ³C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **80**, 2338 (1998). There are interesting earlier suggestions of stringlike or tunnel-like motion in molecular, colloidal, and granular fluids. See A. Rahman, J. Chem. Phys. **45**, 2585 (1966); R. Zwanzig and M. Bishop, *ibid.* **60**, 295 (1974); and Refs. **13**, **19**, **20**, **29**, and **31**.
- ⁴C. Bennemann, C. Donati, J. Baschnagel, and S. C. Glotzer, Nature (London) **399**, 246 (1999).
- ⁵E. V. Russell and N. E. Israeloff, Nature (London) **408**, 695 (2000); E. V. Russell, N. E. Israeloff, L. E. Walther, and H. A. Gomariz, Phys. Rev. Lett. **81**, 1461 (1998).
- ⁶K. Schmidt-Rohr and H. W. Spiess, Phys. Rev. Lett. **66**, 3020 (1991).
- ⁷U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, and H. W. Spiess, Phys. Rev. Lett. **81**, 2727 (1998).
- ⁸I. Chang, F. Fujara, B. Geil, G. Heuberger, T. Mangel, and H. Sillescu, J. Non-Cryst. Solids **172–174**, 248 (1994); I. Chang and H. Sillescu, J. Phys. Chem. B **101**, 8794 (1997).
- ⁹M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **103**, 5684 (1995); **104**, 7210 (1996).
- ¹⁰S. A. Reinsberg, X. H. Qui, M. Wilhelm, H. W. Spiess, and M. D. Ediger, J. Chem. Phys. **114**, 7299 (2001).
- ¹¹A. H. Marcus, J. Schofield, and S. A. Rice, Phys. Rev. E **60**, 5725 (1999); B. Cui, B. Lin, and S. A. Rice, J. Chem. Phys. **114**, 9142 (2001).
- ¹²E. R. Weeks, J. C. Crocker, A. C. Levitt, A. Schofield, and D. A. Weitz, Science **287**, 627 (2000).
- ¹³C. A. Murray and R. A. Wenk, Phys. Rev. Lett. **62**, 1643 (1989); C. A. Murray, D. H. Van Winkle, and R. A. Wenk, Phase Transitions **21**, 93 (1990); C. A. Murray and D. H. Van Winkle, Phys. Rev. Lett. **58**, 1200 (1987).
- ¹⁴W. K. Kegel and A. van Blaaderen, Science **287**, 290 (2000).
- ¹⁵D. Thirumalai and R. D. Mountain, Phys. Rev. E **47**, 479 (1993).
- ¹⁶W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **79**, 2827 (1997).
- ¹⁷C. Donati, S. C. Glotzer, P. H. Poole, W. Kob, and S. J. Plimpton, Phys. Rev. E **60**, 3107 (1999).
- ¹⁸M. Dzugutov, S. I. Simdyankin, and F. H. M. Zetterling, Phys. Rev. Lett. **89**, 195701 (2002); F. H. M. Zetterling, M. Dzugutov, and S. I. Simdyankin, J. Non-Cryst. Solids **293–295**, 39 (2001).
- ¹⁹Y. Hiwatari and T. Muranaka, J. Non-Cryst. Solids **235–237**, 19 (1998); H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, J. Chem. Phys. **88**, 3879 (1988).
- ²⁰D. N. Perera and P. Harrowell, J. Non-Cryst. Solids **235–237**, 314 (1998); G. Wahnström, Phys. Rev. A **44**, 3752 (1991).
- ²¹R. Yamamoto and A. Onuki, Phys. Rev. E **58**, 3515 (1998).
- ²²W. Klein, H. Gould, R. A. Ramos, I. Clejan, and A. I. Mel'cuk, Physica A **205**, 738 (1994); N. Grewe and W. Klein, J. Math. Phys. **18**, 1735 (1979); J. W. Haus and P. H. E. Meijer, Phys. Rev. A **14**, 2285 (1976).
- ²³W. Klein and A. D. J. Haymet, Phys. Rev. B **30**, 1387 (1984).
- ²⁴W. Klein and N. Grewe, J. Chem. Phys. **72**, 5456 (1980).
- ²⁵X. Xia and P. G. Wolynes, Proc. Natl. Acad. Sci. U.S.A. **97**, 2990 (2000).
- ²⁶D. Bedrov, G. D. Smith, and J. F. Douglas, Europhys. Lett. **59**, 384 (2002).
- ²⁷C. Ayyari, D. Bedrov, and G. D. Smith, J. Chem. Phys. **123**, 124912 (2005); D. C. Rapport, Phys. Rev. E **70**, 051905 (2004); see Fig. 18.
- ²⁸J. Dudowicz, K. F. Freed, and J. F. Douglas, J. Chem. Phys. **124**, 064901 (2006).
- ²⁹J. Jellinek, T. L. Beck, and R. S. Berry, J. Chem. Phys. **84**, 2783 (1986).
- ³⁰N. Giovambattista, S. V. Buldyrev, F. W. Starr, and H. E. Stanley, Phys. Rev. Lett. **90**, 085506 (2003).
- ³¹B. Pouligny, R. Malzbender, P. Ryan, and N. A. Clark, Phys. Rev. B **42**, 988 (1990); R. V. Chamberlin and D. W. Kingsbury, J. Non-Cryst. Solids **172–174**, 318 (1994).
- ³²M. Russina, F. Mezei, R. Lechner, S. Longeville, and B. Urban, Phys. Rev. Lett. **84**, 3630 (2000).
- ³³J. Dudowicz, K. F. Freed, and J. F. Douglas, J. Chem. Phys. **111**, 7116 (1999).
- ³⁴M. Aichele, Y. Gebremichael, F. W. Starr, J. Baschnagel, and S. C. Glotzer, J. Chem. Phys. **119**, 5290 (2003).
- ³⁵M. Gordon, K. Kapadia, and A. Malakis, J. Phys. A **9**, 751 (1976).
- ³⁶J. Dudowicz, K. F. Freed, and J. F. Douglas, J. Chem. Phys. **119**, 12645 (2003).

- ³⁷ P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).
- ³⁸ A. V. Tobolsky and A. Eisenburg, *J. Am. Chem. Soc.* **81**, 780 (1959); **81**, 2302 (1959); **82**, 289 (1960); *J. Colloid Sci.* **17**, 49 (1962).
- ³⁹ Y. Rouault and A. Milchev, *Phys. Rev. E* **51**, 5905 (1995); A. Milchev and D. P. Landau, *ibid.* **52**, 6431 (1995).
- ⁴⁰ M. E. Cates and S. J. Candau, *J. Phys.: Condens. Matter* **2**, 6892 (1990).
- ⁴¹ J. Dudowicz, K. F. Freed, and J. F. Douglas, *J. Chem. Phys.* **113**, 434 (2000).
- ⁴² J. Dudowicz, K. F. Freed, and J. F. Douglas, *J. Chem. Phys.* **112**, 1002 (2000).
- ⁴³ J. C. Wheeler, S. J. Kennedy, and P. Pfeuty, *Phys. Rev. Lett.* **45**, 1748 (1980); S. J. Kennedy and J. C. Wheeler, *J. Chem. Phys.* **78**, 953 (1983).
- ⁴⁴ J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.* **28**, 373 (1958).
- ⁴⁵ G. Adam and J. H. Gibbs, *J. Polym. Sci.* **40**, 121 (1959); *J. Chem. Phys.* **43**, 139 (1965).
- ⁴⁶ K. F. Freed, *J. Chem. Phys.* **119**, 5730 (2003).
- ⁴⁷ K. W. Foreman and K. F. Freed, *Adv. Chem. Phys.* **103**, 335 (1998).
- ⁴⁸ J. Dudowicz, K. F. Freed, and J. Douglas, *J. Chem. Phys.* **123**, 111102 (2005).
- ⁴⁹ J. Dudowicz, K. F. Freed, and J. Douglas, *J. Phys. Chem. B* **109**, 21285 (2005).
- ⁵⁰ J. Dudowicz, K. F. Freed, and J. Douglas, *J. Phys. Chem. B* **109**, 21350 (2005).
- ⁵¹ K. L. Ngai, *J. Chem. Phys.* **111**, 3639 (1999); *J. Phys. Chem. B* **103**, 5895 (1999).
- ⁵² M. D. Ediger, C. A. Angell, and S. R. Nagel, *J. Phys. Chem.* **100**, 13200 (1996).
- ⁵³ F. Fujara, B. Geil, H. Sillescu, and G. Fleischer, *Z. Phys. B: Condens. Matter* **88**, 195 (1992).
- ⁵⁴ M. D. Ediger, *Annu. Rev. Phys. Chem.* **51**, 99 (2000).
- ⁵⁵ W. Götze and L. Sjogren, *Rep. Prog. Phys.* **55**, 241 (1992).
- ⁵⁶ C. A. Angell, *Science* **267**, 1924 (1995).
- ⁵⁷ C. A. Angell, *J. Non-Cryst. Solids* **131-133**, 13 (1991).
- ⁵⁸ J. L. Green, K. Ito, K. Xu, and C. A. Angell, *J. Phys. Chem. B* **103**, 3991 (1999).
- ⁵⁹ G. B. McKenna, in *Comprehensive Polymer Science*, edited by C. Booth and C. Price (Pergamon, Oxford, 1989), Vol. 2, p. 311.
- ⁶⁰ K. L. Ngai, *J. Non-Cryst. Solids* **275**, 7 (2000).
- ⁶¹ P. G. Debenedetti and F. H. Stillinger, *Nature (London)* **410**, 259 (2001).
- ⁶² J. Dudowicz, K. F. Freed, and J. F. Douglas, *Adv. Chem. Phys.* (in press).
- ⁶³ M. Wolfgardt, J. Baschnagel, W. Paul, and K. Binder, *Phys. Rev. E* **54**, 1535 (1996).
- ⁶⁴ H.-P. Wittmann, *J. Chem. Phys.* **95**, 8449 (1991).
- ⁶⁵ K. Rah, K. F. Freed, J. Dudowicz, and J. F. Douglas, *J. Chem. Phys.* **124**, 144906 (2006).
- ⁶⁶ Even before the original work of Adam and Gibbs (Ref. 45) was published, R. P. Feynman [*Phys. Rev.* **91**, 1291 (1953)] argued in the context of modeling the superfluidity transition in liquid He⁴ that the probability of an n -particle collective particle displacement is on the order of the n th power of the probability of an elementary binary exchange event.
- ⁶⁷ Vibrational contributions to the fluid's internal energy can obscure this feature.
- ⁶⁸ F. A. Lindemann, *Phys. Z.* **11**, 609 (1910); J. J. Gilvarry, *Phys. Rev.* **102**, 308 (1956).
- ⁶⁹ The criterion $s_c(T_g) \sim O(0.1)$ would imply that *all* the characteristic temperatures of glass formation can be inferred from s_c in the entropy theory of glass formation (i.e., T_A , T_c , T_0 , and T_g are defined by the maximum in s_c , the inflection point in $s_c T$, the vanishing of s_c , and the condition $s_c^{(red)} \approx 0.1$, respectively).
- ⁷⁰ F. S. Starr and F. Sciortino, *J. Phys.: Condens. Matter* **18**, L347 (2006).
- ⁷¹ A. Plois Andrews, K. P. Andrews, S. C. Greer, F. Boue, and P. Pfeuty, *Macromolecules* **27**, 3902 (1994).
- ⁷² J. Ruiz-Garcia and S. C. Greer, *J. Mol. Liq.* **71**, 209 (1997).
- ⁷³ S. C. Greer, *J. Phys. Chem. B* **102**, 5413 (1998); *Adv. Chem. Phys.* **94**, 261 (1996).
- ⁷⁴ F. Sciortino, A. Geiger, and H. E. Stanley, *Nature (London)* **354**, 218 (1991); *Phys. Rev. Lett.* **65**, 3452 (1990); *J. Chem. Phys.* **96**, 3857 (1992).
- ⁷⁵ The equilibrium theory does not address the dynamical process by which the particle clusters form and disintegrate in dynamic equilibrium.
- ⁷⁶ K. Van Workum and J. F. Douglas, *Phys. Rev. E* **73**, 031502 (2006).
- ⁷⁷ Y. Gebremichael, T. B. Schroder, F. W. Starr, and S. C. Glotzer, *Phys. Rev. E* **64**, 051503 (2001).
- ⁷⁸ This regularity is frankly not understood.
- ⁷⁹ J. P. Wittmer, A. Milchev, and M. E. Cates, *Europhys. Lett.* **41**, 291 (1998).
- ⁸⁰ R. A. Riggelman, K. Yoshimoto, J. F. Douglas, and J. J. de Pablo, *Phys. Rev. Lett.* **97**, 045502 (2006).
- ⁸¹ J. D. Stephensen, J. Schmalian, P. G. Wolynes, *Nat. Phys.* **2**, 268 (2006).
- ⁸² D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd ed. (Taylor and Francis, Washington DC, 1992).
- ⁸³ The average string length L seems to extrapolate to infinity at much lower temperatures, close to T_0 . Specifically, the data for $L(T)$ of Donati and co-authors (Ref. 3) displayed in the inset to Fig. 5 can be fitted by $L \sim [(T-T_0)/T_0]^{-0.52}$, where $T_0=0.35$. B. Coluzzi [*J. Chem. Phys.* **112**, 2933 (2000)] estimate the Kauzmann temperature, where the landscape configurational entropy extrapolates to zero, to be roughly equal to 0.32 in the binary LJ model considered by Donati and co-authors (Ref. 3). The average mass M of the mobile particle clusters (Ref. 17) on the other hand, exhibits the scaling relation $M \sim [(T-T_c)/T_c]^{-0.62}$, where T_c is the fitted mode coupling temperature ($T_c=0.435$) and where the analysis is based on the same MD data as considered for the string analysis.
- ⁸⁴ J. S. Langer and A. Lemaître, *Phys. Rev. Lett.* **94**, 175701 (2005); J. S. Langer, *Phys. Rev. E* **73**, 041504 (2006).
- ⁸⁵ H. Zhang, D. Srolovitz, J. F. Douglas, and J. A. Warren, *Phys. Rev. B* **74**, 115404 (2006).
- ⁸⁶ The overall shape of the $L(T)$ curve is similar to that found for the I model of living polymerization, where the concentration of chemical initiator controls (Ref. 33) the magnitude of $L(T)$ at low temperatures.
- ⁸⁷ P. A. O'Connell and G. B. McKenna, *J. Chem. Phys.* **110**, 11054 (1999).
- ⁸⁸ J. Horbach and W. Kob, *Phys. Rev. E* **64**, 041503 (2001).
- ⁸⁹ I. Saika-Voivod, P. H. Poole, and F. Sciortino, *Nature (London)* **412**, 514 (2001).
- ⁹⁰ C. A. Angell and R. J. Rao, *J. Chem. Phys.* **57**, 470 (1972); C. T. Moynihan and C. A. Angell, *J. Non-Cryst. Solids* **274**, 131 (2000).
- ⁹¹ S. Y. Park and D. Stroud, *Phys. Rev. B* **67**, 212202 (2003); M.-P. Valignat, D. Theodoly, J. C. Crocker, W. B. Russel, and P. M. Chaikin, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 4275 (2005).
- ⁹² V. N. Novikov and A. P. Sokolov, *Phys. Rev. E* **67**, 031507 (2003); I. M. Hodge, *J. Non-Cryst. Solids* **202**, 164 (1996).
- ⁹³ J. Stambaugh, K. Van Workum, J. F. Douglas, and W. Losert, *Phys. Rev. E* **72**, 031301 (2005).
- ⁹⁴ K. Van Workum and J. F. Douglas, *Phys. Rev. E* **71**, 031502 (2005).
- ⁹⁵ O. Yamamuro, I. Tsukushi, A. Lindqvist, S. Takahara, M. Ishikawa, and T. Matsuo, *J. Phys. Chem. B* **102**, 1605 (1998).
- ⁹⁶ More precise methods of calculating R_{ms} are given in Ref. 65.
- ⁹⁷ C. T. Moynihan and J. Schroeder, *J. Non-Cryst. Solids* **160**, 52 (1993).
- ⁹⁸ E. W. Fisher, *Physica A* **201**, 183 (1993).
- ⁹⁹ K. Kawasaki, *Physica A* **217**, 124 (1995).
- ¹⁰⁰ J. D. Pardee and J. A. Spudich, in *Methods in Enzymology: Structural and Contractile Proteins*, edited by D. W. Frederiksen and L. D. Cunningham (Academic, New York, 1982), Vol. 85, Pt. B, pp. 164-181.
- ¹⁰¹ S. Singh and A. Zlotnick, *J. Biol. Chem.* **278**, 18249 (2003).
- ¹⁰² D. R. Booth, M. Sunde, V. Bellotti *et al.*, *Nature (London)* **385**, 787 (1997); C. Li, J. Orbulescu, G. Sui, and R. M. Leblanc, *Langmuir* **20**, 8641 (2004); T. R. Serio, A. G. Cashikar, A. S. Kowal, G. J. Sawicki, J. J. Moslehi, L. Serpell, M. F. Arnsdorf, and S. L. Lindquist, *Science* **289**, 1317 (2000).
- ¹⁰³ S. Kumar and J. F. Douglas, *Phys. Rev. Lett.* **87**, 188301 (2001).
- ¹⁰⁴ L. Guo and E. Luijten, *J. Polym. Sci., Part B: Polym. Phys.* **43**, 959 (2005).
- ¹⁰⁵ Q. Lu and M. J. Solomon, *Phys. Rev. E* **66**, 061504 (2002); See also J. van der Gucht, N. A. M. Besseling, W. Knoben, L. Bouteiller, and M. A. Cohen-Stuart, *Phys. Rev. E* **67**, 051106 (2003).
- ¹⁰⁶ J. F. Douglas and J. B. Hubbard, *Macromolecules* **24**, 3163 (1991).
- ¹⁰⁷ J. De Guzman, *An. R. Soc. Esp. Fis. Quim.* **11**, 353 (1913); J. M. Burgers, *Introductory Remarks on Recent Investigation Concerning the Structure of Liquids*, Second Report on Viscosity and Plasticity (North Holland, Amsterdam, 1938), p. 34; G. Hägg, *J. Chem. Phys.* **3**, 42 (1935); D. O. Miles and A. S. Hamamoto, *Nature (London)* **119**, 644 (1962); A. A. Vlasov, *Theor. Math. Phys.* **5**, 1228 (1970); M. A. Floriano and C. A. Angell, *J. Chem. Phys.* **91**, 2537 (1989); M. Wilson and P. A. Madden, *Mol. Phys.* **92**, 197 (1970); P. A. Madden and M. Wilson, *J. Phys.: Condens. Matter* **12**, A95 (2000).
- ¹⁰⁸ G. P. Johari, *Philos. Mag.* **86**, 1567 (2006).
- ¹⁰⁹ This criticism would not apply if it is ultimately found that $\Delta\mu \propto T_g$ with a universal constant of proportionality.

- ¹¹⁰S. F. Swallen, P. A. Bonvallet, R. J. McMahon, and M. D. Ediger, Phys. Rev. Lett. **90**, 015901 (2003).
- ¹¹¹P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, NJ, 1996).
- ¹¹²J. F. Douglas (unpublished).
- ¹¹³A. Kholodenko and J. F. Douglas, Phys. Rev. E **51**, 1081 (1995). Only

results pertaining to the collective diffusion coefficient are reported in this paper.

- ¹¹⁴R. P. Feynman, Phys. Rev. **90**, 1116 (1953); D. M. Ceperley and E. L. Pollock, Phys. Rev. B **39**, 2084 (1989).
- ¹¹⁵D. M. Ceperley and E. L. Pollock, Phys. Rev. B **39**, 2084 (1989).
- ¹¹⁶R. P. Feynman, Phys. Rev. **92**, 262 (1954).