

Entropy theory of polymer glass formation revisited. I. General formulationJacek Dudowicz^{a)} and Karl F. Freed^{b)}*The James Franck Institute, The University of Chicago, Chicago, Illinois 60637 and Department of Chemistry, The University of Chicago, Chicago, Illinois 60637*Jack F. Douglas^{c)}*Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

(Received 30 September 2005; accepted 16 December 2005; published online 8 February 2006)

A generalized entropy theory of glass formation is developed by merging the lattice cluster theory for the thermodynamics of semiflexible polymer melts at constant pressure with the Adam-Gibbs relation between the structural relaxation time and the configurational entropy. Since experimental studies have suggested that the relative rigidity of the chain backbone and the side groups is an essential parameter governing the nature of glass formation in polymers, we incorporate this rigidity disparity parameter, along with monomer structure, into our new theoretical description of the polymer fluid thermodynamics. Our entropy theory is compared with alternative theories that describe the rate of structural relaxation in glass-forming liquids in terms of an activated rate process. © 2006 American Institute of Physics. [DOI: 10.1063/1.2166391]

I. INTRODUCTION

Glass formation^{1–5} has been central to fabrication technologies since the dawn of civilization. Glasses not only encompass window panes, the insulation of our homes, the optical fibers supplying our cable TV, and vessels for eating and drinking, but they also include a vast array of “plastic” polymeric materials in our environment.^{1–5} The mechanical and rheological properties of polymer solids and fluids are primarily controlled by the physics of glass formation. The impressively slow dynamics of cooled polymer systems is also characteristic of many biological materials, so that an understanding of polymer glass formation is also essential to designing technological processes aimed at preserving foods, drugs, and tissues.^{2,6–8} Despite the fundamental nature of glass formation and the many regularities observed in this process, a generally accepted theoretical description of this ubiquitous and conceptually vexing form of matter remains elusive.

While new theories of glass formation are constantly being introduced, some ideas remain invariant for qualitatively understanding the nature of this phenomenon. Since the works of Simon⁹ and Kauzmann,¹⁰ it has generally been appreciated that the rapid increase in viscosity η and structural relaxation times τ associated with glass formation is accompanied by a drop in the fluid entropy S (e.g., increases of η by 14 orders of magnitude are often observed over modest temperature ranges of a couple of hundred of degrees). The drops in S upon lowering temperature T are indeed so rapid that extrapolations of S to low temperatures would lead to a negative S at a nonzero temperature (the Kauzmann paradox). While a negative entropy is patently absurd for a system in equilibrium, this situation is acceptable for nonequilibrium materials, so that the interpretation of this trend in the entropy remains unclear. Since the work of Batchinski,¹¹ Doolittle,¹² and Cohen and co-workers,¹³ it is also generally recognized that a reduction of “free volume” (loosely the space available for molecular motion) normally accompanies these dramatic changes in the transport properties of “cooled” liquids. However, the manner in which the changes in S and free volume are interrelated has never been adequately assessed. Because of the controversy surrounding the multiplicity of different interpretations of the previous entropy theories, we now review those essential aspects of the classic entropy approach to glass formation used in our formulation before introducing our generalization of this theory.

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A. Strengths and weaknesses of the Gibbs-DiMarzio theory

Gibbs and DiMarzio¹⁴ (GD) first developed a systematic statistical mechanical theory of glass formation in polymer fluids, based on experimental observations and on lattice model calculations by Meyer, Flory, and Huggins.¹⁵ Apart from providing a clear physical picture of glass formation upon cooling as arising from a vanishing number of accessible configurational states due to the increasing rigidity of polymer chains,^{14,16} this theoretical approach has produced a wide array of quantitative predictions regarding glass formation, and numerous successes of the theory are reviewed by DiMarzio and Yang.^{17,18} The main focus of GD theory is the “configurational entropy” S_c , which is that portion of the fluid entropy relating to the number of distinct configurational states of the fluid alone, with vibrational contributions being excluded. Unfortunately, the conceptual clarity of the notion of configurational entropy S_c is not matched by any direct method for determining this quantity experimentally. Consequently, comparisons of GD theory with experiment often involve uncontrolled approximations associated with

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attempts to evaluate S_c .¹⁹ On the other hand, recent progress in estimating S_c from numerical simulations has been achieved by determining the number of accessible minima in the potential-energy surface describing the glass-forming liquid.^{20–24} While this numerical estimate of the configurational entropy must be closely related to the S_c calculated from the entropy theory, the exact relation between them has not yet been established. In spite of this uncertainty, both of these quantities are designated by the term configurational entropy.

In addition to the fundamental difficulties of estimating S_c , strong criticism has been raised against fundamental tenets of GD theory. For example, there has been widespread disagreement concerning GD's identification of a vanishing of S_c with a second-order phase transition and of the glass transition temperature with the temperature of this hypothetical transition.²⁵ Moreover, even the vanishing of S_c has been suggested to be an artifact of the inaccuracy of the mean-field calculation of S_c for dense polymer fluids.²⁶ In the final assessment, however, the *qualitative picture* of polymer glass formation as stemming from an "entropy catastrophe" remains a viable conceptual model.²⁷ For instance, recent mean-field calculations for spin models of glass formation have converged with results generated from GD theory, suggesting that the entropy catastrophe concept has broad applicability.²⁸

Simulations²⁹ have recently provided some insights into the formal limit $S_c \rightarrow 0$ predicted by mean-field lattice model theories of glass formation. While Monte Carlo estimates of τ for a Flory-Huggins (FH) lattice model of a semiflexible polymer melt extrapolate to infinity near the "ideal" glass transition temperature T_0 where S_c extrapolates to zero, the values of S_c computed from GD theory are too low by roughly a constant compared to the simulation estimates, and this constant shift is suggested to be sufficient to prevent S_c from strictly vanishing.^{29,30} Hence, we can reasonably infer that S approaches a small, but finite asymptotic low-temperature limit and that S_c similarly becomes *critically small* near T_0 . The possibility of a constant residual configurational entropy at low temperatures is briefly mentioned in the original paper by GD and has recently been emphasized again by DiMarzio.¹⁸ Thus, while the *literal* prediction of a vanishing S_c at a finite temperature T_0 is suspect, this formal extension of the thermodynamic theory still retains its value as an indicator of an "entropy crisis" that is identifiable from *extrapolations* of both thermodynamic (e.g., specific heat) and dynamic (e.g., viscosity and diffusion) properties. By considering the configurational entropy of the lattice model to represent the excess configurational entropy relative to the entropy of the glass, the conceptual difficulties of the original GD theory can largely be eliminated.

The original GD theory of glass formation in polymer liquids involves a number of other assumptions and approximations that significantly limit the predictive capacity of the theory. Firstly, the theory is preoccupied with the general philosophical problem of locating and explaining the conceptual basis for an "ideal glass transition temperature" T_0 . Unfortunately, a fluid cannot remain in equilibrium near T_0 because of the astronomical magnitude of the structural

relaxation time near this temperature. Hence, a comparison of GD theory with experiment is necessarily indirect. Notably, the experimental glass transition temperature T_g (determined from the maximum in the specific heat or from a change in the slope of the density as a function of temperature^{2,7,10}) normally occurs^{6,31} above the Kauzmann temperature T_K where the excess fluid entropy S_{exc} extrapolates to zero, and the difference between T_0 and T_g is neglected by GD theory.³² Secondly, the theory is based on a highly simplified description of polymer chains as semiflexible self-avoiding walks composed of structureless monomer units. Thus, little can be said about how monomer and solvent structure affect glass formation. In particular, recent experiments^{33–35} have established that more subtle aspects of glass formation, such as "fragility" (the relative rate at which η and τ vary with temperature),³⁶ depend significantly on the geometry and the degree of rigidity of the polymer side groups. Thirdly, since the complex changes in the dynamics of glass-forming liquids often initiate at temperatures exceeding $2T_g$, it is important to determine the breadth of this transition by estimating temperatures characterizing the beginning, middle, and end of this broad transition phenomenon. Evidently, these issues are beyond the predictive capacity of the classic GD theory.

B. Strengths and weaknesses of the Adam-Gibbs theory

The AG model³⁷ for the dynamics of glass-forming liquids essentially postulates that the drop in S upon lowering temperature is accompanied by collective motion and that the fluid's structural relaxation times τ are activated with a barrier height \mathcal{E} that is proportional³⁸ to the number z^* of polymer segments within hypothetical "cooperatively rearranging regions" (CRR). (These elements do not necessarily belong to an individual chain, so that similar dynamic structures presumably also arise in low molar mass glass-forming fluids.) At high temperatures, the molecular displacements at an atomic scale are taken to be entirely noncollective, and the AG barrier height \mathcal{E}_{AG} reduces to a (constant) Arrhenius activation energy $\Delta\mu$. More generally, τ is estimated as $\tau = \tau_0 \exp(\beta\mathcal{E}_{\text{AG}})$, where $\mathcal{E} \approx \mathcal{E}_{\text{AG}} \equiv \Delta\mu z^*$ and τ_0 is a constant. Extensive experimental estimates of $\Delta\mu$ exist for both small molecule³⁹ and polymer liquids.⁴⁰ For instance, data for the viscosity and tracer diffusion in weakly supercooled alkane liquids indicate a nearly linear dependence of $\Delta\mu$ on polymer mass for a relatively low molar mass range (6–16 carbon atoms).^{41,42} A proportional increase of the apparent activation energy with polymer molar mass has also been found recently in reactive polymerization systems,⁴³ supporting the plausibility of this first AG hypothesis that the barrier height \mathcal{E} increases with the CRR "polymerization index" z^* .

The final link between this generalized Arrhenius description for the precipitous increase of relaxation times in cooled liquids and GD theory of glass formation is achieved through a second, less evident, hypothesis of the AG model that z^* is simply inversely proportional to the configurational entropy.⁴⁴ This relation is partially motivated by earlier observations by Bestul and Chang that an entropic barrier

height \mathcal{E} in a generalized Arrhenius relation varies nearly inversely^{45,46} to the fluid entropy S (relative to that of the glass) at low temperatures near T_g . Thus, the second AG hypothesis also has a reasonable basis, at least at a phenomenological level. As discussed below, the second AG hypothesis is consistent with the widely utilized relation for the temperature-dependent activation energy of Volger-Fulcher-Tammann-Hesse (VFTH) over a wide temperature range near T_g , perhaps providing the strongest argument in favor of the second AG hypothesis.¹⁻⁵

Despite the heuristic nature of the reasoning involved, the AG model has held up remarkably well over the last 40 years in comparisons with numerous experiments⁴⁷⁻⁵⁰ and with recent simulations of diverse glass-forming fluids^{20-24,51} (e.g., silica, binary Lennard-Jones mixtures, water, and orthoterphenyl). Recent studies by Mohanty *et al.*,⁴⁴ Lubchenko and Wolynes,⁵² and by Bouchaud and Biroli⁵³ have sought to place the AG model on a sounder theoretical foundation. Good agreement with the AG model has been reported for simulations performed at temperatures well above T_g , where the configurational entropy is estimated through the “energy landscape” or “inherent structure” construction of Stillinger and Weber,⁵⁴ rather than from the fluid’s excess entropy S_{exc} , which is determined from specific-heat measurements as the difference between the fluid entropy S and that of the crystal or glass.⁵⁵ On the other hand, deviations from the AG relation have been claimed⁴⁷ in real glass-forming liquids at temperatures 20–30 K above T_g . It is unclear whether these deviations arise from a “failure” of the AG model or from uncertainties associated with estimating S_c from specific heat data given that the excess entropy S_{exc} is not really equivalent to S_c of the GD and AG theories. The basis for these claims of a failure of the AG model at elevated temperatures is explained in our recent note⁵⁶ and is briefly mentioned below for completeness.

C. Lattice cluster theory extension of the entropy theory for glass-forming polymer fluids

A generalized entropy theory of polymer glass formation has been developed by merging the Adam-Gibbs (AG) relation between the rate of structural relaxation and the configurational entropy with the lattice cluster theory (LCT) for the thermodynamics of semiflexible polymer melts. Section II provides the derivation of this entropy theory that has been used in Refs. 56–58 and that is one of the main components of the present paper. The generalized entropy theory involves a significant extension of the scope of earlier theories of glass formation by Gibbs and DiMarzio¹⁴ and by Freed,⁵⁹ which are entirely preoccupied with computing S_c and thereby estimating an ideal glass transition temperature T_0 where the configurational entropy extrapolates to zero. This new approach focuses instead on computing several thermodynamic properties for temperatures much higher than T_0 , on establishing a theoretical framework for calculating the variation of the fragility of polymer fluids with molecular structure, and on the explicit determination of the rate of long wavelength structural relaxation for these fluids at any temperature where an equilibrium theory generates an appropriate description. The new theory also takes cognizance of

experimental evidence³³⁻³⁵ that the relative rigidity of the chain backbone and the side groups is a relevant variable in the realistic modeling of glass formation in real polymer fluids, an effect entirely neglected in the GD (Ref. 14) and Freed⁵⁹ theories. Section II describes how this disparity between the rigidities of different portions of a polymer chain is incorporated in the generalized entropy theory, along with the specific dependence of glass-formation process on the monomer molecular structure. Section II and the Introduction are designed to motivate the framework for our theory and to discuss important conceptual pitfalls in the entropy theory that should be recognized in its comparison to experiments and simulations. In order to place our new theoretical formulation in perspective for comparison with other theories and to provide some essential definitions, Sec. III includes a brief review of some earlier results.⁵⁶⁻⁵⁸ Section IV compares our theory with other theories of glass formation that are based on the concept of a temperature-dependent activation energy. In particular, we discuss free-energy barrier model of Schweizer and Saltzman,^{75,76} the frustrated-limited cluster model of Kivelson and co-workers,⁸⁰ the “shoving model” of Dyre *et al.*,⁷⁷ and the Buchenau-Zorn model,⁸⁴ which relates the energy barrier for structural relaxation to Debye-Waller factors.

II. THEORETICAL BACKGROUND

A. Lattice cluster theory of glass formation in polymer melts

The LCT for glass formation in polymers is based on the evaluation of the system’s configurational entropy. Following Gibbs-DiMarzio theory,^{14,16} we define S_c in terms of the logarithm of the microcanonical ensemble (fixed N , V , and U) density of states $\Omega(U)$,

$$S_c(T) = k_B \ln \Omega(U)|_{U=U(T)}, \quad (1)$$

where $U(T)$ is the internal energy at temperature T , and k_B is Boltzmann’s constant. From its definition, $S_c(T)$ must be a monotonically increasing function of T . The LCT presumes the existence of a polymer melt and does not account for the possibility of forming a solid through crystallization, so that the term *equilibrium* in this paper designates an *equilibrated fluid*.

The site configurational entropy s_c is related to the total (microcanonical) entropy S_c as

$$s_c = S_c/N_l, \quad (2)$$

where N_l is the total number of lattice sites (proportional to the system volume V). The quantity s_c , therefore, can be considered as an “entropy density” S_c/V , which need not be monotonic in T .

The density of states $\Omega(U)$, in turn, is connected with the canonical partition function $Z(T)$ through the formal weighted sum over states,

$$Z(T) = \int_0^\infty dU \Omega(U) \exp[-U/(k_B T)]. \quad (3)$$

The computation of the density of states within the LCT is nontrivial since the LCT free energy $F(T) = -\beta \ln Z(T)$ is

derived as a power series in the product of the van der Waals interaction energies $\{\epsilon\}$ and $\beta=1/(k_B T)$. This series for semiflexible polymer systems has been developed^{59,60} through second order in β ,

$$\beta F/N_l = A + B\beta - C\beta^2, \quad (4)$$

where the coefficients A , B , and C are functions of the volume fractions and molecular masses of the system's components, the van der Waals interaction energies $\{\epsilon\}$, the dimensional conformational energy differences $\beta\{E\}$ between *trans* and *gauche* conformations (i.e., the chain stiffness), as well as a set of geometrical indices that reflect the chemical structure of the system's constituents. Since the LCT has been formulated for hypercubic lattices ($z=2d$), the *trans* conformation is defined as that for a pair of collinear successive bonds, while the *gauche* conformation arises when the two successive bonds lie along orthogonal directions.⁶⁰ The inclusion of energy differences between *trans* and *gauche* conformations into the theory, i.e., the treatment of the polymers as semiflexible, greatly enhances the complexity of the evaluation of $s_c(T)$ because A , B , and C of Eq. (4) then become functions of $\{\exp(-\beta E)\}$.

The truncation of the high-temperature series in Eq. (4) at order β^2 is a valid concern when applying the theory at low temperatures. This concern also extends to GD theory which implicitly involves a truncation at order β . At some point, these perturbative treatments must simply fail, but we expect that these lattice theories to identify faithfully the location of the entropy crisis at low temperatures, based on numerous previous comparisons between measurements and GD theory. Experience⁶¹ with the LCT theory in describing equation of state⁶² and miscibility⁶³ data indicates that this approach gives sensible and often accurate estimates of thermodynamic properties over wide ranges of temperatures and pressures. In light of these limitations, this paper focuses on the temperature range above T_g where our theory is more reliable.

1. One-bending energy model

The individual monomers are represented in terms of a set of united atom groups that each occupies a single lattice site, so that each monomer spreads out over several neighboring lattice sites to reflect its size and shape. All united atom groups are assumed, for simplicity, to interact with a common monomer averaged van der Waals interaction energy ϵ , and a common *gauche* energy penalty E is ascribed to all *gauche* semiflexible bond pairs, regardless of whether the *gauche* bonds belong to the backbone or to side chains. The description of a one-component monodisperse polymer system involves the use of only one composition variable ϕ and one site occupancy index M (proportional to the molar mass M_{mol}), which is defined as the number of united atom groups in a single chain. Under these general conditions, the functional dependence of the coefficients A , B , and C of Eq. (4) can be formally written as

$$A(E) = A_0 + A_1(E) = A_0(\phi, M, N_{2i}) + A_1(\phi, M, \{N_{\alpha}\}, \epsilon, g_E), \quad (5)$$

$$B(E) = B(\phi, M, \{N_{\alpha}\}, \epsilon, g_E), \quad (6)$$

$$C(E) = C(\phi, M, \{N_{\alpha}\}, \epsilon, g_E), \quad (7)$$

where A_0 and $A_1(E)$ represent the athermal and nonathermal portions of $A(E)$, respectively, $\{N_{\alpha}\}$ are the geometrical indices that specify a given monomer's structure, and g_E is the bending energy factor,^{59,60}

$$g_E = \frac{q \exp[-\beta E]}{1 + (q-1)\exp[-\beta E]}. \quad (8)$$

Explicit formulas for A , B , and C for multicomponent polymer systems are given in Ref. 59 (with corrections in Appendix A). The factor g_E plays the role of the "order parameter" for chain semiflexibility and is defined in terms of the dimensionless bending energy βE and the total number q of *trans* and *gauche* conformations for a given monomer species. Note that q is simply a measure of the orientational entropy associated with a pair of consecutive flexible bonds. The form of Eq. (8) is obtained by assuming the existence of one *trans* and $(q-1)$ *gauche* conformations for a pair of successive bonds between united atom groups. If $E=0$, the bonds are fully flexible, whereas the bonds are completely rigid in the $E \rightarrow \infty$ limit. The quantity A_0 of Eq. (5) contains the combinatorial portion (see below) of the free energy $\beta F/N_l$, and N_{2i} designates the number of bond pairs in a single chain that can be assigned as being either in *trans* or *gauche* conformations.⁶⁰

Given the above model and assumptions, Freed⁵⁹ has recently shown that the LCT configurational entropy $s_c(T)$ of a polymer melt is given by the expression,

$$\frac{s_c(T)}{k_B} = - \left[\mathcal{A}_0(f=f_0) + \mathcal{A}_1(f=f_0) + \frac{[\beta B(f=f_0) - \beta u(T) + \beta E f_0 N_{2i}/M]^2}{4\beta^2 C(f=f_0)} \right], \quad (9)$$

where f and f_0 are defined below. In Eq. (9), $u(T)$ is the specific internal energy which is derived from Eq. (4) as

$$\begin{aligned} \beta u \equiv \beta U(T)/N_l &= \beta B - 2\beta^2 C - \frac{\beta E g_E^2}{q \exp[-\beta E]} \\ &\times \frac{\partial}{\partial g_E} [A + \beta B - \beta^2 C], \end{aligned} \quad (10)$$

$\mathcal{A}_0(f)$ is equal to

$$\begin{aligned} \mathcal{A}_0(f) &= \frac{\phi}{M} \ln \left(\frac{2\phi}{z'M} \right) + \phi \left(1 - \frac{1}{M} \right) + (1-\phi) \ln(1-\phi) \\ &+ \phi \frac{N_{2i}}{M} [-f \ln(q-1) + f \ln f + (1-f) \ln(1-f)], \end{aligned} \quad (11)$$

and $\mathcal{A}_1(f)$, $\mathcal{B}(f)$, and $\mathcal{C}(f)$ are generalizations of A_1 , B , and C in Eqs. (5)–(7), obtained by replacing the bending energy factor g_E from Eq. (8) with the variable,

$$g_f = f \frac{q}{q-1}. \quad (12)$$

The quantity f in Eq. (12) represents the ratio of the total number of gauche bond pairs to the maximum number of gauche bond pairs (N_{2i} per chain) in the system; l in Eq. (11) designates the number of subchains in a single chain; z is the lattice coordination number ($z=2d=6$ for a simple cubic lattice). Each subchain is defined as a combination of successive bonds that may reside in either trans or gauche conformations.⁶⁰ A gauche energy penalty E is not assigned to successive bonds that belong to different subchains.^{59,60} The quantities \mathcal{A}_1 , \mathcal{B} , and \mathcal{C} are analogs of Eqs. (5)–(7) that are defined in terms of f ,

$$\mathcal{A}_1(f) = A_1(\phi, M, \{N_\alpha\}, \epsilon, g_f), \quad (13)$$

$$\mathcal{B}(f) = B(\phi, M, \{N_\alpha\}, \epsilon, g_f), \quad (14)$$

$$\mathcal{C}(f) = C(\phi, M, \{N_\alpha\}, \epsilon, g_f). \quad (15)$$

Quantities computed in terms of the fraction f of gauche bonds are obtained within a constrained ensemble that we term the “ f ensemble,” while those computed in terms of g_E are said to be derived from the “ E ensemble.”

The f_0 that appears in Eq. (9) is determined as the value of f that maximizes the configurational entropy $s_c(T)$, i.e., from the condition

$$\left. \frac{\partial}{\partial f} \left[\mathcal{A}_0(f) + \mathcal{A}_1(f) + \frac{[\beta\mathcal{B}(f) - \beta u + \beta E_f N_{2i}/M]^2}{4\beta^2\mathcal{C}(f)} \right] \right|_{\phi, T} = 0. \quad (16)$$

While Eqs. (9)–(16) provide a recipe for evaluating $s_c(T)$ for constant volume (V) systems (i.e., constant ϕ), they can be easily applied to constant pressure systems by computing ϕ for a given pressure P and temperature T from the equation of state. For internal consistency, this equation of state must be derived from the free-energy \mathcal{F} expression appropriate to the f ensemble,

$$P = - \left. \frac{\partial \mathcal{F}(f_0)}{\partial V} \right|_{n, T} = - \frac{1}{a_{\text{cell}}^3} \left. \frac{\partial \mathcal{F}(f_0)}{\partial N_l} \right|_{n, T}, \quad (17)$$

where n is the total number of polymer chains, a_{cell}^3 is the volume associated with a single lattice site, and the free energy $\mathcal{F}(f)$ is given by

$$\beta\mathcal{F}(f) = N_l[\mathcal{A}_0(f) + \mathcal{A}_1(f) + \beta\mathcal{B}(f) - \beta^2\mathcal{C}(f)]. \quad (18)$$

Other thermodynamic properties are similarly evaluated from $\mathcal{F}(f_0)$.

2. Two-bending energy model

The above mean-field treatment of s_c represents an extension of GD theory to a melt of semiflexible, interacting polymers composed of structured monomers. Equations (9)–(11) and (16)–(18) maintain their general validity when different united atom groups within the individual monomers interact with different van der Waals energies, but they are *restricted* to the case of a single-bending energy E for the whole molecule. While the assumption of a common gauche energy penalty E for all bond pairs is a natural starting point, this assumption is clearly an oversimplification for treating many “real” polymers, such as polystyrene, where the side groups are rather rigid. Since the different rigidities of the backbone and side groups are expected to affect the strength of the temperature dependence of $s_c(T)$ (and thus the fragility of the glass-formation process^{33–35}), here we extend the theory to a model polymer melt in which the gauche energy penalty E_b in the chain backbone *differs* from the gauche energy penalty E_s in the side groups. The existence of two bending energies E_b and E_s leads to the appearance of two separate gauche bond fractions f_b and f_s in the theory, where the subscripts b and s indicate backbone and side chains, respectively. The extension of the theory also implies a partitioning of the geometrical indices $\{N_\alpha\}$ into three groups $\{N_\alpha^{(b)}\}$, $\{N_\alpha^{(s)}\}$, and $\{N_\alpha^{(bs)}\}$. These three groups refer to classes of configurations with pairs of semiflexible bonds belonging to the chain backbone, the side group, and both. (For instance, $N_{2i} = N_{2i}^{(b)} + N_{2i}^{(s)}$ and $N_{4+} = N_{4+}^{(s)} + N_{4+}^{(bs)}$, where N_{4+} is the number of sets of four bonds that meet at a common united atom group).⁵⁹ Consequently, there are two bending energy factors g_{E_b} and g_{E_s} defined as

$$g_{E_b} = \frac{q_b \exp[-\beta E_b]}{1 + (q_b - 1) \exp[-\beta E_b]}, \quad (19)$$

$$g_{E_s} = \frac{q_s \exp[-\beta E_s]}{1 + (q_s - 1) \exp[-\beta E_s]},$$

where q_b and q_s denote total numbers of trans and gauche conformations for a pair of consecutive bonds in the backbone and side chains, respectively. In general, q_b and q_s may differ, but we assume a single trans conformation and two gauche conformations.

The configurational entropy $s_c(T)$ for the two-bending energy model is expressed in the form,

$$\frac{s_c(T)}{k_B} = - \mathcal{A}_0(f_b = f_b^0, f_s = f_s^0) - \mathcal{A}_1(f_b = f_b^0, f_s = f_s^0) - \frac{[\beta\mathcal{B}(f_b = f_b^0, f_s = f_s^0) - \beta u(T) + \beta E_b f_b^0 N_{2i}^{(b)}/M + \beta E_s f_s^0 N_{2i}^{(s)}/M]^2}{4\beta^2\mathcal{C}(f_b = f_b^0, f_s = f_s^0)}, \quad (20)$$

where

$$\begin{aligned} \mathcal{A}_0(f_b, f_s) &= \frac{\phi}{M} \ln \left(\frac{2\phi}{z^l M} \right) + \phi \left(1 - \frac{1}{M} \right) + (1 - \phi) \ln(1 - \phi) \\ &+ \phi \frac{N_{2i}^{(b)}}{M} [-f_b \ln(q_b - 1) + f_b \ln f_b] \\ &+ (1 - f_b) \ln(1 - f_b) + \phi \frac{N_{2i}^{(s)}}{M} [-f_s \ln(q_s - 1) \\ &+ f_s \ln f_s + (1 - f_s) \ln(1 - f_s)], \end{aligned} \quad (21)$$

and the polynomials,

$$\mathcal{A}_1(f_b, f_s) = \mathcal{A}_1(\phi, M, \{N_\alpha^{(b)}\}, \{N_\alpha^{(s)}\}, \{N_\alpha^{(bs)}\}, \epsilon, g_{f_b}, g_{f_s}), \quad (22)$$

$$\mathcal{B}(f_b, f_s) = \mathcal{B}(\phi, M, \{N_\alpha^{(b)}\}, \{N_\alpha^{(s)}\}, \{N_\alpha^{(bs)}\}, \epsilon, g_{f_b}, g_{f_s}), \quad (23)$$

$$\mathcal{C}(f_b, f_s) = \mathcal{C}(\phi, M, \{N_\alpha^{(b)}\}, \{N_\alpha^{(s)}\}, \{N_\alpha^{(bs)}\}, \epsilon, g_{f_b}, g_{f_s}), \quad (24)$$

with

$$g_{f_b} = f_b \frac{q_b}{q_b - 1}, \quad g_{f_s} = f_s \frac{q_s}{q_s - 1} \quad (25)$$

are generated from Eqs. (13)–(15) by partitioning the geometrical factors $\{N_\alpha\}$ into three groups $\{N_\alpha^{(b)}\}$, $\{N_\alpha^{(s)}\}$, and $\{N_\alpha^{(bs)}\}$ and by multiplying them by the corresponding statistical weights involving, respectively, g_{f_b} , g_{f_s} , and $g_{f_b}g_{f_s}$ (see Appendix B for more details).

The specific internal energy βu of Eq. (20) is given by

$$\begin{aligned} \beta u &= \beta B(E_b, E_s) - 2\beta^2 C(E_b, E_s) - \frac{\beta E_b g_{E_b}^2}{q_b \exp[-\beta E_b]} \frac{\partial}{\partial g_{E_b}} \\ &\times [A(E_b, E_s) + \beta B(E_b, E_s) - \beta^2 C(E_b, E_s)] \\ &- \frac{\beta E_s g_{E_s}^2}{q_s \exp[-\beta E_s]} \frac{\partial}{\partial g_{E_s}} \\ &\times [A(E_b, E_s) + \beta B(E_b, E_s) - \beta^2 C(E_b, E_s)], \end{aligned} \quad (26)$$

where the functions $A(E_b, E_s) = A_0 + A_1(E_b, E_s)$, $B(E_b, E_s)$, and $C(E_b, E_s)$ are the E -ensemble counterparts of \mathcal{A} , \mathcal{B} , and \mathcal{C} , respectively.

The values f_b^0 and f_s^0 of Eq. (20) are obtained by solving the set of equations,

$$\left. \frac{\partial}{\partial f_b} \left[\mathcal{A}_0(f_b, f_s) + \mathcal{A}_1(f_b, f_s) + \frac{[\beta B(f_b, f_s) - \beta u + \beta E_b f_b N_{2i}^{(b)}/M + \beta E_s f_s N_{2i}^{(s)}/M]^2}{4\beta^2 C(f_b, f_s)} \right] \right|_{\phi, T} = 0, \quad (27)$$

$$\left. \frac{\partial}{\partial f_s} \left[\mathcal{A}_0(f_b, f_s) + \mathcal{A}_1(f_b, f_s) + \frac{[\beta B(f_b, f_s) - \beta u + \beta E_b f_b N_{2i}^{(b)}/M + \beta E_s f_s N_{2i}^{(s)}/M]^2}{4\beta^2 C(f_b, f_s)} \right] \right|_{\phi, T} = 0. \quad (28)$$

In analogy to Eq. (17), the equation of state is derived from the corresponding free-energy expression in the f ensemble,

$$\begin{aligned} \beta \mathcal{F}(f_b, f_s) &= N_l [\mathcal{A}_0(f_b, f_s) + \mathcal{A}_1(f_b, f_s) + \beta \mathcal{B}(f_b, f_s) \\ &- \beta^2 \mathcal{C}(f_b, f_s)], \end{aligned} \quad (29)$$

by taking the appropriate derivative,

$$P = - \left. \frac{\partial \mathcal{F}(f_b^0, f_s^0)}{\partial V} \right|_{n, T} = - \frac{1}{a^3} \left. \frac{\partial \mathcal{F}(f_b^0, f_s^0)}{\partial N_l} \right|_{n, T}. \quad (30)$$

The generalization of Eqs. (19)–(30) to a polymer melt with arbitrary numbers of distinct bending energies in both backbone and side chains is straightforward.

The equation of state $P = P(T, \phi)$ enables the computation of the isothermal compressibility κ_T ,

$$\kappa_T = - \left. \frac{1}{V} \frac{\partial V}{\partial P} \right|_T, \quad (31)$$

and the specific volume v ,

$$v(T, P) = \frac{1}{\phi} \frac{a_{\text{cell}}^3 r N_{\text{Av}}}{M_{\text{mol}}}, \quad (32)$$

where r denotes the number of lattice sites occupied by a single monomer, M_{mol} is its molar mass, and N_{Av} is Avogadro's number. Both κ_T and $v(T, P)$ play an important role in analyzing glass formation.^{57,58} All other thermodynamic properties at constant T , P may readily be evaluated from \mathcal{F} of Eq. (29). We consider this two-bending energy model as a general schematic model (SM) for glass formation in polymeric liquids, based on the physical motivation described in the next subsection.

B. General classes of glass-forming polymers

Our focus on the two-bending energy version of the LCT is motivated by the idealized view⁶⁴ that polymers can be classified approximately into three basic categories: chains with a flexible backbone and flexible side groups; chains that have a flexible backbone and rigid side branches; chains with a relatively stiff backbone and flexible side groups. We term them as the flexible-flexible (F-F), flexible-stiff (F-S), and stiff-flexible (S-F) class polymers, respectively. The F-F

polymers are an idealization of polydimethylsulfoxide (PDMS), polyisobutylene (PIB), polyisoprene (PI), polyethylene (PE), and other species having both flexible backbone and side groups. The F-S polymers of the second class are intended to model molecules, such as polystyrene, poly(α -methylstyrene), etc., where the side groups are spatially extended and relatively stiff on average, compared to the bonds in the chain backbone. Finally, the S-F chains describe polymers, such as poly(n -alkyl methacrylates), polycarbonates, and other polymers for which the chain backbone is comprised of aromatic or other rigid bulky groups. Polymers of these three general classes can be schematically represented by chains having different bending energies E_b and E_s . This simplified model contains a minimal set of physical parameters (E_b , E_s , and ϵ) and therefore ignores monomer shape, tacticity, variability of interaction and bending energies with chemically different united atom groups, etc. Although a comparative study of the different polymer classes is crucial to characterize the variation of fragility with monomer structure,⁵⁷ our theory is illustrated here for the representative case of F-S polymers.

C. Adam-Gibbs relation between the configurational entropy s_c and relaxation in glass-forming liquids

As discussed in the introduction, the Adam-Gibbs³⁷ model of relaxation in cooled liquids relates the structural relaxation times τ , associated with long wavelength relaxation processes (viscosity, translational diffusion, rates of diffusion-limited chemical reactions, etc.), to the configurational entropy s_c through the generalized Arrhenius relation,

$$\tau = \tau_0 \exp[\beta \mathcal{E}_{AG}], \quad \mathcal{E}_{AG} \equiv \Delta\mu [s_c^*/s_c(T)], \quad (33)$$

where τ_0 is the high-temperature limiting relaxation time τ in the fluid, $\Delta\mu$ is a (property and system-dependent) activation energy at high enough temperatures, such that an Arrhenius dependence of τ approximately holds (i.e., $\tau = \tau_0 \exp[\beta \Delta\mu]$), and s_c^* is the high-temperature limit of $s_c(T)$ (assumed constant in the AG model). For simple atomic fluids, we expect $\tau_0 \sim \mathcal{O}(10^{-14}$ s), while τ_0 may be somewhat larger⁶⁵ [$\tau_0 \sim \mathcal{O}(10^{-13}$ s)] for more complex molecules, such as polymers, since the mobile fluid elements (monomers) are larger. The average activation energy \mathcal{E}_{AG} grows upon cooling as particle motion becomes more collective. A measure of the number of particles in the dynamic clusters (called “cooperative rearranging regions” or CRR) embodying this collective motion is provided by the ratio $z^* \equiv s_c^*/s_c(T)$. In the AG theory, this ratio generates the enhancement of the activation energy (\mathcal{E}_{AG}) relative to its high-temperature value $\Delta\mu$ [see Eq. (33)]. The configurational entropy of the AG model is identified here with the entropy per lattice site s_c of the LCT, since the use of the entropy density is the only normalization condition that leads to a sensible variation of τ at high temperatures in the AG model (see below and Ref. 56). The experimental counterpart of the site entropy in the lattice model theory is the molar entropy $S_c^{(\text{mol})}$ (or $S_{\text{exc}}^{(\text{mol})}$) divided by the fluid molar volume $V^{(\text{mol})}$. [Superscripts (mol) denote molar quantities.]

The experimental inaccessibility of the configurational entropy poses no problem for the LCT, apart from a consideration of whether to normalize the configurational entropy per lattice site or per monomer in order to provide a better representation of experiment within the AG model. Once s_c has been identified as the only appropriate and physically consistent choice, then τ can be calculated from Eq. (33) as a function of temperature T , molar mass M_{mol} , pressure P , monomer structure, backbone and side group rigidities, etc., provided that $\Delta\mu$ is specified.⁵⁷

Unfortunately, reliable experimental estimates of the configurational entropy are not available to enable explicit application of the AG model for polymer fluids. Instead, the temperature dependence of τ in polymer melts is often analyzed in terms of the empirical VFTH equation,⁶⁶

$$\tau = \tau_{\text{VFTH}} \exp \left[\frac{DT_\infty}{T - T_\infty} \right], \quad (34)$$

where T_∞ is the “Vogel temperature” at which structural relaxation times τ and the shear viscosity η extrapolate to infinity, D is a “fragility constant”^{67,68} describing the strength of the temperature dependence of τ , and τ_{VFTH} is an adjustable parameter. In the recent literature,⁵¹ the inverse of D has been advocated as a more suitable definition of fragility since $K \equiv 1/D$ is larger for more fragile fluids. Equation (34) is consistent with Eq. (33) if $s_c T$ varies linearly near T_0 as $s_c T \sim (T - T_0)$, and below we reiterate the conditions under which this behavior holds.

III. CONFIGURATIONAL ENTROPY AND CHARACTERISTIC TEMPERATURES FOR GLASS FORMATION IN POLYMERIC FLUIDS

According to the classical GD theory of glass formation,¹⁴ an “ideal glass transition” can be identified with a thermodynamic event, the vanishing of the configurational entropy. The vanishing is a physically natural condition because a system must have a multiplicity of accessible configurational states to achieve equilibrium. In analogy to GD theory, our LCT configurational entropy s_c also extrapolates to zero at a temperature T_0 . As discussed in the introduction, we interpret T_0 as the temperature at which the difference between the fluid’s configurational entropy and the entropy of the glass extrapolates to zero, reflecting the sparseness of accessible configurational states. Thus, T_0 can be identified with the VFTH temperature T_∞ at which structural relaxation times τ extrapolate to infinity, in agreement with AG theory. While, T_0 is not generally equal^{69,70} to the Kauzmann temperature T_K at which the excess molar entropy S_{exc} extrapolates to zero, T_K and T_∞ are often found to be very close to each other.⁴⁹ The next subsection analyzes the temperature dependence the LCT site configurational entropy $s_c(T)$ and the characteristic temperatures of glass formation that are determined from the LCT expression for s_c when the latter is combined with the AG relation (33).

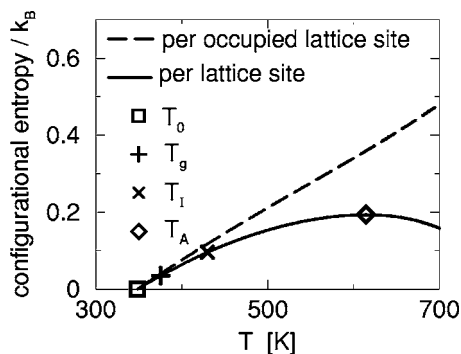


FIG. 1. Comparison of the site and mass configurational entropies calculated from the LCT as a function of temperature T for a representative high molar mass F-S polymer fluid at constant pressure of $P=1$ atm (0.101 325 MPa). The characteristic temperatures of glass formation, T_0 , T_g , T_I , and T_A , are indicated in the figure by \square , $+$, \times , and \diamond , respectively. An individual monomer of the F-S polymers contains two backbone segments and one side group with three units (like the united atom representation of 1-pentene). The bending energies E_b and E_s and the van der Waals interaction energy are chosen as $E_b/k_B=400$ K, $E_s/k_B=4000$ K, and $\epsilon/k_B=200$ K, while the unit cell volume v_{cell} associated with a single lattice site and the lattice coordination number is taken as $v_{\text{cell}}=2.7 \times 10^3 \text{ \AA}^3$ and $z=6$, respectively. We further assume the presence of one *trans* and two *gauche* configurations for each backbone and side chain semiflexible bond pair [i.e., $q_b=q_s=3$; see Eq. (19)]. The same values of E_b , E_s , ϵ , v_{cell} , z , q_b , and q_s are used in the computations presented in Figs. 2 and 3.

A. Temperature dependence of the configurational entropy s_c

The configurational entropy per occupied lattice site (i.e., per unit mass) is *by definition* a monotonic function of temperature, and, of course, the fluid entropy deduced from calorimetric measurements also has this monotonic property. Figure 1 compares the mass and site configurational entropies as a function of temperature T . These two types of configurational entropy nearly coincide for temperatures lower than T_I (defined in next paragraph), but they differ appreciably at higher temperatures. The bifurcation in the configurational entropies in Fig. 1 is remarkably similar in form to the deviation observed between the experimentally determined excess fluid entropy $S_{\text{exc}}^{(\text{mol})}$ and the configurational entropy as estimated from fits of relaxation data to the AG relation for τ .⁴⁷ Since these observations have a large impact on the interpretation of the generalized entropy theory, we discuss them in further detail.

Richert and Angell⁴⁷ sought to assess the accuracy of the AG relation by fitting its basic parameters to precise dielectric relaxation data over a wide range of temperatures. They find that an assumed AG expression for the relaxation time τ of model glass-forming fluids (salol and 2-methyl tetrahydrofuran) represents the data well, provided that the fitted configurational entropy has a *maximum* at high temperatures (occurring at $1.6T_K$ and $1.7T_K$, respectively). This comparison clearly shows that estimates of the configurational entropy based on AG theory *deviate qualitatively* from the excess entropy S_{exc} obtained from specific-heat measurements at high temperatures, and this deviation is often cited^{47,71} as evidence for a serious “breakdown” of the AG model. This conclusion, however, is difficult to reconcile with the fact that virtually all of the equilibrated simulation studies^{20–24,51,72} indicating agreement with the AG model are

restricted to relatively high temperatures where Richert and Angell⁴⁷ claim that the AG model fails!

The disparate trends between the excess fluid entropy S_{exc} and the AG-based estimate of the configurational entropy from dielectric data have their counterparts in comparisons between simulation estimates of the configurational entropy and S_{exc} . The configurational entropy determined by energy landscape calculations^{20–24,51} (denoted below as $s_{c,L}$), as well as the nonvibrational fluid (site) entropy obtained from molecular-dynamics (MC) simulations,^{29,72,73} both tend to approach approximately *constant values* at high temperatures,⁷⁴ while the molar excess entropy $S_{\text{exc}}^{(\text{mol})}$ *does not* behave in this fashion, as made explicit from the measurements of Richert and Angell. Direct LCT calculation of the molar configurational entropy $S_c^{(\text{mol})}$ for a constant pressure fluid of semiflexible polymers confirms that $S_c^{(\text{mol})}$ does not saturate at any reasonably high temperature (see below). In contrast, the computed entropy per site s_c varies similarly to trends found for the site configurational entropy in the MC simulations of Wolfgardt *et al.*²⁹ over the glass transformation temperature range. A resolution of these discrepancies between the various estimates of configurational entropy potentially offers the key to the extension of the AG model to higher temperatures, thereby avoiding the apparent breakdown of the AG model indicated by Richert and Angell.

The configurational entropy appearing in the AG relation (33) is, therefore, identified with the site entropy s_c of the LCT as the only physically sensible choice.⁵⁶ This modification is consistent with the analysis of simulation data for diffusion in lattice models of polymer melts by Binder *et al.*,⁷² although they do not mention the significant departure of this identification from the use of S_{exc} in experimental tests of the AG model.

A maximum in $s_c(T)$ is understandable since s_c is an *entropy density* that reflects a competitive interplay between changes in the entropy and fluid density as the temperature is varied. Hence, the fits of Richert and Angell indicating the existence of a maximum in the configurational entropy cannot be dismissed as unphysical. The maximum in $s_c(T)$ defines the onset temperature T_A of glass formation where orientational correlations arising from chain semiflexibility first start to develop and the structural relaxation time no longer exhibits an approximately Arrhenius temperature dependence. Notably, the maximum in $s_c(T)$ *disappears* in the limit of an incompressible fluid, which physically corresponds to the limit of infinite pressure. A maximum in the configurational entropy is not expected for fluids under the constant volume conditions that are normally considered in molecular-dynamics simulations used to estimate $s_{c,L}$.

B. High- and low-temperature regimes of glass formation

It is apparent from Fig. 1 that s_c exhibits a different temperature dependence at low temperatures near T_0 than at high temperatures near T_A , and these disparities serve to define low- and high-temperature regimes of glass formation. Specifically, s_c at low temperatures ($T \approx T_0$) varies nearly linearly with T , while at high temperatures ($T \approx T_A$), s_c is

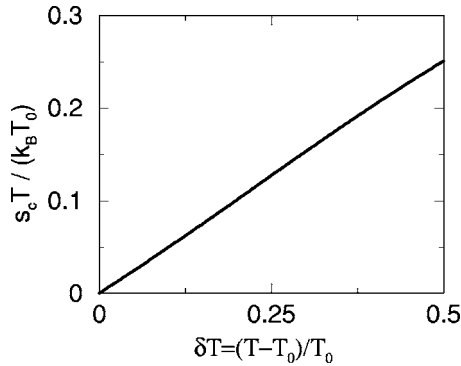


FIG. 2. Test of the correspondence between the AG and VFTH equations for τ . Calculations of $s_c T$ are performed for a representative high molar mass F-S polymer fluid at constant pressure of $P=1$ atm. The product $s_c T$ is normalized by the thermal energy $k_B T_0$ at the ideal glass transition temperature T_0 , and the reduced temperature δT is defined as $\delta T \equiv (T - T_0)/T_0$. The linear scaling of $s_c T$ with δT persists for arbitrary molar mass and for the other two polymer classes, verifying the correspondence between the AG and VFTH relations over the temperature range indicated.

nearly parabolic in T . This difference in the temperature dependence of s_c translates into a rather distinct temperature dependence of τ within the entropy theory, and we next focus on the temperature dependence of s_c in more detail.

Adam and Gibbs argued in their pioneering work³⁷ that their expression for τ [see Eq. (33)] reduces to the VFTH equation (34) if the configurational entropy appearing in the former is approximated by the excess entropy $S_{\text{exc}}^{(\text{mol})}$ estimated from specific-heat measurements. These arguments rely heavily on empiricism and on the uncertain identification of s_c with $S_{\text{exc}}^{(\text{mol})}$.

The mutual consistency of the AG and VFTH equations for the rate of structural relaxation requires that $s_c(T)T$ is linear in $T - T_0$, where T_0 corresponds to the VFTH temperature in the entropy theory. Correspondingly, we plot $s_c T / (k_B T_0)$ versus the reduced temperature $(T - T_0)/T_0$ in Fig. 2 for the representative case of high molar mass F-S polymers and find that a linear relation $s_c T \sim (T - T_0)$ indeed holds to a good approximation over a broad temperature range (up to at least 100 K above T_0), thus providing a strict analytical test of the approximation suggested by Adam and Gibbs. It must be emphasized that replacing s_c by $S_{\text{exc}}^{(\text{mol})}$ still leads to good linearity over the temperature range indicated.

Our observations above indicate that there is a limit to the temperature range over which the AG and VFTH equations approximate each other. A plot of $s_c T$ versus T reveals that $s_c T$ has a well-defined *inflection point* T_I that defines the boundary between the low ($T_0 < T < T_I$)- and high ($T_I < T < T_A$)-temperature regimes of glass formation. The correspondence between the AG and VFTH equations is strictly limited to the low-temperature regime of glass formation.

The temperature dependence of s_c in the high-temperature regime of glass formation is examined by considering the reduced activation energy $\mathcal{E}_{\text{AG}}/\Delta\mu = z^* \equiv s_c^*/s_c(T)$. Figure 3 demonstrates that z^* is accurately described by a parabolic function of temperature over a broad temperature range about the onset temperature T_A . In particular, we find the relation,

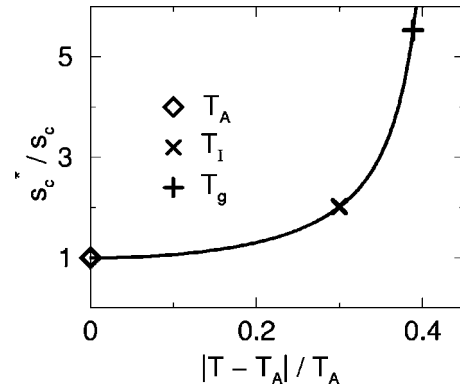


FIG. 3. Relative activation energy $z^* = s_c^*/s_c$ as a function of temperature for a representative high molar mass F-S polymer fluid at constant pressure ($P=1$ atm). The temperature dependence of z^* is expressed in terms of the reduced temperature $\delta T_A \equiv |T - T_A|/T_A$ for the high-temperature region of glass formation. The characteristic temperatures of glass formation, T_g , T_I , and T_A , are designated in the figure by +, \times and \diamond , respectively.

$$z^* - 1 = C_s \left[\frac{|T - T_A|}{T_A} \right]^\alpha, \quad \alpha = 2, \quad (35)$$

$$T_I < T_A - 100 \text{ K} < T < T_A,$$

which holds to an accuracy better than 0.1% over the stated temperature range (where C_s is a constant). The same functional form emerges for all polymer classes considered and for all molar masses, so that this scaling seems to be “universal.” A somewhat larger exponent α is obtained if the fitting is extended to temperatures lower than $T_A - 100$ K, but this extended range compromises the simplicity and generality of Eq. (35). Insertion of Eq. (35) into the AG equation for τ (and taking $\Delta\mu$ as constant) clearly yield a form different from the VFTH equation. We advocate elsewhere that C_s can be used as a measure of glass fragility in the high-temperature regime of glass formation.⁵⁷

The entropy theory of glass formation thus predicts the existence of two distinct regimes of glass formation and allows the direct calculation of the three characteristic temperatures that specify these regimes, the onset temperature T_A , the crossover temperature T_I , and the VFTH temperature T_0 . The remaining characteristic temperature of glass formation, the kinetic glass transition temperature T_g , can be estimated based on the LCT and a Lindemann instability criterion.⁵⁸

IV. ALTERNATIVE ACTIVATION ENERGY THEORIES OF DYNAMICS IN GLASS-FORMING LIQUIDS

Because s_c is not directly measurable, it is natural to inquire into whether other thermodynamic properties exhibit useful approximate relations to s_c that allow us to express the entropy theory in terms of these more accessible variables. Schweizer and Saltzman^{75,76} (SS) have recently developed an ambitious treatment of glass formation based upon a thermodynamic barrier concept in which the barrier height \mathcal{E} is expressed in terms of the fluid isothermal compressibility κ_T rather than the configurational entropy. (This creative approach incorporates ideas taken from a combination of mode-coupling theory, density-functional theory, and acti-

vated rate theory in order to provide an analytical estimate^{75,76} for \mathcal{E} .) Other reasonably successful phenomenological descriptions of relaxation in glass-forming liquids propose⁷⁷ a proportionality between \mathcal{E} and the high-frequency shear modulus G_∞ (shoving model⁷⁷). The present section describes these alternative “activation energy” theories of glass dynamics and their approximate relation to our entropy theory of glass formation. In particular, our estimate of the entropic barrier height \mathcal{E}_{AG} is compared below with the corresponding estimate^{75,76} of \mathcal{E} by SS, which leads to an approximate scaling relation between s_c and κ_T . A similar scaling is then derived between s_c and the mean-square particle displacement $\langle u^2 \rangle$, based on an analysis of G_∞ .

A. Relation to Schweizer and Saltzman theory

According to SS, the structural relaxation time of a glass-forming liquid is described by a generalized Arrhenius expression,

$$\tau = \tau_A \exp(F_B), \quad (36)$$

where τ_A is the relaxation time at high temperatures, which is given in our notation by

$$\tau_A = \tau_0 \exp(\beta \Delta \mu), \quad (37)$$

and F_B in Eq. (36) is a dimensionless barrier height that quantifies the increase of τ from its counterpart τ_A for non-collective motion. The barrier height F_B , in turn, is specified in terms of dimensionless compressibility ratio,

$$F_B \equiv 1/S(0) = 1/(\kappa_T/\kappa_T^0) = \kappa_T^0/\kappa_T, \quad (38)$$

where $\kappa_T^0 = 1/(\rho k_B T)$ denotes the isothermal compressibility of an “ideal gas” of polymers and κ_T refers to the polymer melt. [A philosophically similar expression to Eq. (38) has been suggested for sheared foams and other jammed materials.⁷⁸] From comparisons with experimental data at high temperatures, SS introduce the approximate relation,^{75,76}

$$\kappa_T^0/\kappa_T \approx A^2[(T - T^*)/T]^2, \quad (39)$$

where $T^* = B/A$ and A and B are constants.⁷⁹

Equation (33) implies that the counterpart of the barrier height F_B in the entropy theory equals $(z^* - 1)(\beta \Delta \mu)$ and emerges from the LCT with the corresponding temperature dependence,

$$(z^* - 1)(\beta \Delta \mu) = (C_s \beta \Delta \mu) \left(\frac{T - T_A}{T_A} \right)^2, \quad (40)$$

which applies over the broad (high) temperature range $T_A - 100 \text{ K} < T < T_A$. The above analysis reveals that the barrier heights estimated from the LCT and the SS theory scale with temperature near T_A in a strikingly similar fashion. We emphasize, however, that the prefactor in Eq. (40) depends on the temperature range considered, so that the exact correspondence between Eqs. (39) and (40) only holds for $T \approx T_A$. The SS theory does not describe the temperatures T_0 , T_g , and T_I that characterize glass-forming liquids at low temperatures, nor does it form a basis for readily comprehending the VFTH expression for τ . An expression mathematically

equivalent to Eq. (40), except for a larger exponent (8/3 rather than 2), has been proposed by the “frustration-limited cluster” model of Kivelson and co-workers⁸⁰ This model, like the AG model, attributes the increasing barrier height to the growing size of dynamic clusters in cooled liquids.

B. Relation to shoving model and Buchenau relation

Another class of thermodynamic barrier theories focuses on the large increases in the elastic constants that accompany glass formation. (These theoretical approaches seem especially appropriate to polymer fluids below the crossover temperature T_f .) In particular, the barrier height \mathcal{E} governing particle displacement in the shoving model⁷⁷ is taken to be on the order of the elastic energy $G_\infty V_0$ required to displace a particle on a scale comparable to the interparticle distance,

$$\mathcal{E} \sim G_\infty V_0, \quad (41)$$

where V_0 is an unspecified “critical” volume of molecular dimensions. Note that if we further invoke the approximation⁸¹ $G_\infty \sim 1/\kappa_T$, then Eq. (41) exhibits the same scaling with κ_T , as suggested by SS (i.e., $\mathcal{E} \sim 1/\kappa_T$).

A further development is possible by noting that the high-frequency shear modulus G_∞ is related to the mean-square particle displacement $\langle u^2 \rangle$ of caged fluid particles (monomers) that are transiently localized on time scales ranging between an average molecular collision time and the structural relaxation time τ . Specifically, if the viscoelasticity of a supercooled liquid is approximated below T_I by a simple Maxwell model in conjunction with a Langevin model for Brownian motion, then $\langle u^2 \rangle$ is given by⁸²

$$\langle u^2 \rangle = 2\beta/(\pi R G_\infty), \quad (42)$$

where R denotes the particle (monomer) radius. Although this is a rather idealized model, we anticipate that the inverse scaling between $\langle u^2 \rangle$ and G_∞ should be preserved in more complex treatments of the viscoelasticity of glass-forming fluids. The formal correspondence between $\mathcal{E}_{AG} \approx (s_c^*/s_c) \Delta \mu$ and \mathcal{E} of Eq. (41) then implies the scaling relation,

$$s_c T \sim \langle u^2 \rangle, \quad (43)$$

between the configurational entropy s_c and the Debye-Waller factor $\langle u^2 \rangle$ characterizing the amplitude of molecular displacements within the fluid at very short times (e.g., typically nanoseconds in elastic neutron scattering measurements). Both the landscape configurational energy $s_{c,L} T$ and $\langle u^2 \rangle$ have been found⁸³ to scale linearly with $\delta T = (T - T_0)/T_0$, and the equivalent form of Eq. (43) in terms of the landscape entropy, $s_{c,L} T \sim \langle u^2 \rangle$, has been suggested previously based on molecular-dynamics simulations.⁸³ A direct test of the approximate relation (43) is unavailable at the moment. However, Starr *et al.*⁸³ note that $\langle u^2 \rangle$ can be considered as a molecular scale measure of excess free volume, so that the common extrapolation of $s_c T$ and $\langle u^2 \rangle$ to zero at T_0 is quite natural. The combination of the AG equation (33) with Eq. (43) yields the Buchenau relation⁸⁴ between $\langle u^2 \rangle$ and τ ,

$$\tau \sim \tau_0 \exp(\langle u^2 \rangle_0 / \langle u^2 \rangle), \quad (44)$$

where $\langle u^2 \rangle_0$ is a constant. The relation in Eq. (44) has been found to describe relaxation data for a variety of glass-forming liquids^{84–86} and has been verified in molecular-dynamics simulations of a supercooled polymer melt.⁸³

C. Relation to mode-coupling theory and reduced temperature representation of τ

Mode-coupling theory⁸⁷ predicts that the structural relaxation time τ has the power-law form,

$$\tau = A(T - T_{mc}^{exp})^{-\gamma}, \quad (45)$$

where T_{mc}^{exp} is the mode-coupling temperature that is usually determined from fits of Eq. (45) to experimental data and A and γ are constants. We find that Eq. (45) describes the entropy theory predictions for τ with an accuracy better than 0.15% over the temperature ranges 379–451 and 463–520 K and with the *apparent exponent* γ equaling 2.08 ± 0.01 and 2.78 ± 0.01 for the F-F and F-S polymer classes, respectively. These exponents are consistent with the literature values that lie in the broad range between 2 and 3 for a wide variety of glass-forming liquids (ionic, metallic, organic, water, etc.).^{88,89} Moreover, the fits are obtained for $T_{mc}^{exp} = T_I$, reinforcing this identification from our earlier papers.^{56,57} Of course, the entropy theory predicts that τ remains finite at T_{mc}^{exp} and only diverges at a far lower temperature T_0 .

We next show that the quantitative difference in the temperature dependence of τ between strong (F-F) and fragile (F-S) glass-forming polymers is largely *eliminated* by scaling with a modified reduced temperature involving the variable $T_I/(T_I - T_g)$ that characterizes the breadth of glass formation. Rössler *et al.*⁹⁰ have found that the temperature dependence of the viscosity $\eta(T_g/T)$ exhibits a nearly universal representation for all fragile and strong polymer fluids when η is normalized by $\eta(T_x)$ and T_g/T is multiplied by $(T_x - T)/(T_x - T_g)$, where the crossover temperature T_x is chosen as “close” to the fitted mode-coupling temperature T_{mc}^{exp} . Correspondingly, we apply a similar scaling to our computed curves for $\tau(T_g/T)$ in Fig. 4(a) by again identifying T_{mc}^{exp} with the crossover temperature T_I .^{56,57} Specifically, Fig. 4(b) presents the normalized relaxation time $\tau/\tau(T_I)$ versus $(T_g/T) \times (T_I - T)/(T_I - T_g)$. The resulting scaled curves for the F-S and F-F polymer classes are almost indistinguishable from each other over the entire glass-formation temperature range $T_g < T < T_A$. The reduction in Fig. 4(b) provides additional theoretical support for the empirical scaling introduced by Rössler *et al.*,⁹⁰ as well as for the new entropy theory.

V. CONCLUSIONS

The lattice cluster theory (LCT) of glass formation in polymer melts has been extended to allow for different rigidities of the chain backbone and side groups and to enable the evaluation of all thermodynamic properties as a function of temperature and pressure. The present paper provides the derivation of this theory that has been used in recent short communications^{56–58} to show how the LCT may be combined with venerable concepts from the Gibbs-DiMarzio

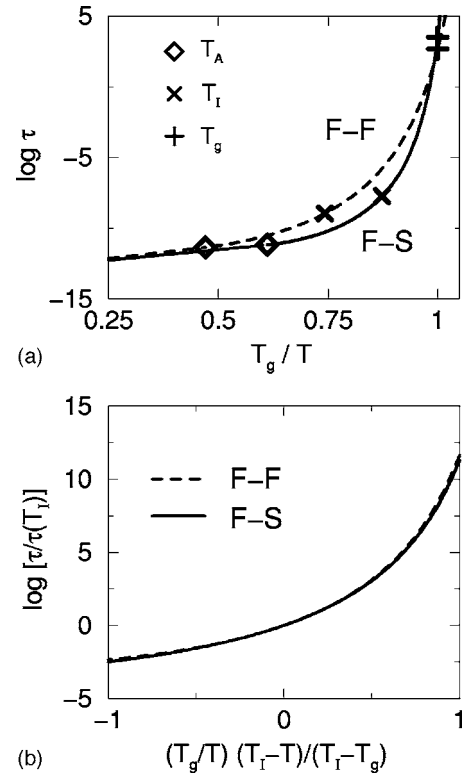


FIG. 4. (a) Structural relaxation times τ for high molar mass ($M=40001$) F-S and F-F polymer fluids at $P=1$ atm as calculated from the generalized entropy theory as a function of the inverse temperature $1/T$ multiplied by the glass transition temperature T_g . The characteristic temperatures of glass formation, T_g , T_I , and T_A , are designated as in Fig. 3. We choose $\tau_0 = 10^{-15}$ s, and the molecular parameters for the F-F polymers are the same as for the F-S polymer class except for the bending energy E_s in the side groups, which is taken to be identical to the bending energy E_b in the chain backbone, $E_s/k_B = E_b/k_B = 400$ K. (b) Structural relaxation times τ of (a) [for constant pressure ($P=1$ atm) high molar mass F-S and F-F polymer fluids] replotted as the ratio $\tau/\tau(T_I)$ vs the scaled temperature variable $(T_g/T)(T_I - T)/(T_I - T_g)$, where T_g denotes the glass transition temperature and T_I designates the crossover temperature.

(GD) and Adam-Gibbs (AG) theories of glass formation in order to define and relate the characteristic temperatures of glass formation within a unified theoretical framework. These characteristic temperatures include the onset temperature T_A for the supercooled regime (below which the structural relaxation time τ no longer displays an Arrhenius temperature dependence), the crossover temperature T_I (separating well-defined high- and low-temperature regimes of glass formation in which both s_c and τ exhibit a rather distinct temperature dependence), and the “ideal” glass transition temperature T_0 (at which the fluid configurational entropy s_c extrapolates to zero). While the concepts of the configurational entropy s_c and the “ideal” transition temperature T_0 intrinsically follow from GD theory, the AG postulate of a specific relation between τ and s_c allows the self-consistent definition of both T_A and T_I in terms of the s_c computed from the LCT. This progress in the predictive capacities of the entropy theory of glass formation arises, in part, because the LCT generates analytical expressions for thermodynamic properties that include the effects of short-range correlations stemming from chain connectivity, different flexibilities of the chain backbone and side groups, and monomer structure,

molecular factors that cannot be described by the classic GD theory. Because GD theory exclusively focuses on computing the temperature T_0 , which occurs well below the kinetic T_g , GD theory is much more limited in scope than our entropy theory.

A wide variety of theories have been proposed to describe glass formation, ranging from thermodynamic theories, such as the entropy and free volume models, to kinetic theories, such as mode-coupling theory, that emphasize particle localization as the origin of structural arrest.^{3,5,7} Each of these theories captures aspects of glass formation in real fluids, and it is thus natural to expect some interrelations between these alternative approaches to glass formation and the entropy theory. For example, a previous paper⁵⁷ shows that the usual phenomenological free volume expression for the rate of structural relaxation of glass-forming fluids at low temperatures (the low-temperature regime of glass formation) and constant pressure is recovered from the entropy theory. Our comparative analysis in Sec. IV between the entropy theory and other theories establishes that many conceptual and predictive characteristics are shared by these approaches. The correspondences are particularly clear in models of glass formation that are based on the concept of an activation energy that depends on thermodynamic properties. The discussion in Sec. IV begins with the recent model of Schweizer and Saltzman^{75,76} (SS) who append an activation barrier to mode-coupling theory to describe hopping processes in the fluid that augment the caging process emphasized in earlier versions of mode-coupling theory. The barrier is of a thermodynamic nature and specifically depends on the bulk isothermal compressibility. The generalized entropy theory is found to produce an identical temperature dependence as the S-S theory for the activation energy in the high-temperature regime (before Arrhenius behavior ensues). At intermediate temperatures, both the S-S and entropy theories display the Rössler scaling⁹⁰ when the crossover temperature T_x is treated as an adjustable parameter, and T_x is replaced by T_f , respectively. The striking parallels between the SS and generalized entropy theories of glass formation support an approximate relation between the isothermal compressibility and the product of the temperature and the configurational entropy, a relation that arises from the formal equating of Eqs. (36)–(38) with Eq. (33). A consideration of the relation between the configurational entropy and the isothermal compressibility, in turn, leads naturally to a connection of the entropy theory with the “shoving model” in which glass formation is driven by the sharply increasing elastic constants as the fluid is cooled. Lastly, the Buchenau relation⁸⁴ (consistent with the entropy theory) determines a link between thermodynamics (the configurational entropy) and particle localization, a viewpoint also emphasized by mode-coupling theory. In particular, Eq. (44) relates the structural relaxation

times and Debye-Waller factors and, thereby, provides yet another connection with free volume type models since the mean-square amplitude $\langle u^2 \rangle$ of particle motion determines a local free volume. Thus, the new entropy theory unifies these seemingly disparate concepts within a single framework that permits quantitative computations for the dependence of melt properties on monomer structure over temperature ranges in which the system can be equilibrated in the fluid state.

Because the AG model implicitly focuses on large scale structural relaxation processes, we are currently unable to describe relaxation processes in the nonzero wave vector q limit. This restriction to long wavelengths precludes treating many aspects of glass formation, such as the q dependence of the structural relaxation time, the bifurcation of relaxation times, etc. Thus, an important direction for the future extension of the entropy theory involves adding a square gradient contribution to the free energy (modeling the energetic cost of density fluctuations in the polymer melt) in order to describe the rate of structural relaxation at finite length scales.

ACKNOWLEDGMENTS

This work is supported, in part, by PRF (Grant No. 37939-AC7) and NSF (Grant No. CHE 0416017). We also thank Jai Pathak for a critical reading of the manuscript.

APPENDIX A: ONE BENDING ENERGY MODEL

The correct forms of Eqs. (31a), (31b), (31c), (32), (33), and (34) of Ref. 59 are, respectively,

$$-A(\{f_s\}) = \cdots z^{-1}[\alpha_1^2 - \alpha_{t2} + 2\alpha_{4+}^{(2)} - 4\alpha_{4+}^{(1)} + 2\alpha_{4+}] + z^{-2}[\alpha_{t2}^2 + \cdots - \alpha_{4dd} + 2\alpha_{4+}^{(1)} - 2\alpha_{4+}^{(2)}] \quad (\text{A1a})$$

$$-B(\{f_s\}) = \cdots + B_0\{(z/2) + \alpha_1 + z^{-1}[\alpha_{t3} + \cdots]\} + \cdots \quad (\text{A1b})$$

$$C(\{f_s\}) = \cdots + C'_0[-(z/2) - 2\alpha_1 + \alpha_{t2} - 2\alpha_1^2] + C_{0,1}(2 + 4\alpha_1) + \cdots \quad (\text{A1c})$$

$$E(T) = \cdots - \sum_s \frac{E_{b,s} g_s^2}{z' \exp(-\beta E_{b,s})} \frac{\partial}{\partial g_s} \times [A(\{E_{b,s}\}) + \beta B(\{E_{b,s}\}) - \beta^2 C(\{E_{b,s}\})] \quad (\text{A2})$$

$$\frac{\partial}{\partial f_s} \left[A(\{f_s\}) + \frac{[B(\{f_s\}) - E(T) + \sum_{s'} E_{b,s'} f_{s'} N_{2s,s'} / M_{s'}]^2}{4C(\{f_s\})} \right] = 0 \quad (\text{A3})$$

$$S_c/(kN_l) = -A(\{f_s^0\}) - \frac{[B(\{f_s^0(E)\}) - E(T) + \sum_{s'} E_{b,s'} f_{s'}^0(E) N_{2s,s'} / M_{s'}]^2}{4C(\{f_s^0\})}. \quad (\text{A4})$$

In addition to these corrections, Eq. (26) of Ref. 59 should not have the $(\phi_s \ln z)$ term, and the product $z^{L_s} M_s$ should be replaced by $z^{L_s} M_s$.

APPENDIX B: TWO BENDING ENERGY MODEL

The polynomials $\mathcal{A}_1(f_b, f_s)$, $\mathcal{B}(f_b, f_s)$, and $\mathcal{C}(f_b, f_s)$ in Eqs. (22)–(24) of the two-bending energy model are generated from Eqs. (31a)–(31c) of Ref. 59 by introducing the following replacements:

$$\begin{aligned} u_{2i} g_f &\rightarrow u_{2i}^{(b)} g_{f_b} + u_{2i}^{(s)} g_{f_s}, & u_{2i} g_f^2 &\rightarrow u_{2i}^{(b)} g_{f_b}^2 + u_{2i}^{(s)} g_{f_s}^2, \\ u_{3ii} g_f^2 &\rightarrow u_{3ii}^{(b)} g_{f_b}^2 + u_{3ii}^{(s)} g_{f_s}^2, & u_{3id} g_f &\rightarrow u_{3id}^{(b)} g_{f_b} + u_{3id}^{(s)} g_{f_s}, \\ u_{4iii} g_f^3 &\rightarrow u_{4iii}^{(b)} g_{f_b}^3 + u_{4iii}^{(s)} g_{f_s}^3, & u_{4iid} g_f^2 &\rightarrow u_{4iid}^{(b)} g_{f_b}^2 + u_{4iid}^{(s)} g_{f_s}^2, \\ u_{4idi} g_f &\rightarrow u_{4idi}^{(b)} g_{f_b} + u_{4idi}^{(s)} g_{f_s}, \\ u_{4idi} g_f^2 &\rightarrow u_{4idi}^{(bs)} g_{f_b} g_{f_s}, & u_{4did} g_f &\rightarrow u_{4did}^{(b)} g_{f_b} + u_{4did}^{(s)} g_{f_s}, \\ u_{4idd} g_f &\rightarrow u_{4idd}^{(b)} g_{f_b} + u_{4idd}^{(s)} g_{f_s}, \\ u_{4+} g_f &\rightarrow u_{4+}^{(b)} g_{f_b} + u_{4+}^{(s)} g_{f_s}, & u_{4+} g_f^2 &\rightarrow u_{4+}^{(s)} g_{f_s}^2 + u_{4+}^{(bs)} g_{f_b} g_{f_s}, \end{aligned}$$

where $u_\alpha \equiv N_\alpha / M$, $\alpha \equiv 2i, 3ii, 3id, 4iii, 4iid, 4idi, 4did, 4idd$, and $4+$, $u_\alpha^{(x)} \equiv N_\alpha^{(x)} / M$ with $x \equiv b, s, bs$, and g_f, g_{f_b} , and g_{f_s} are defined by Eqs. (12) and (25). The variable g_f is denoted in Ref. 59 as $g(f_s)$ with s labeling the species of a multicomponent system. For a polymer melt, this index is irrelevant, and is instead used in the present paper to designate the side groups. Sets of four bonds that meet at a common united atom groups (+) or sequential four bond patterns (*idi*) in which successive bond pairs lie along one subchain, two different subchains, and one subchain, respectively, are the examples of bond configurations that can contain bonds belonging to both chain backbone and side groups. The latter class is denoted by the superscript (*bs*).

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