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RESEARCH ARTICLE

Configurational Entropy of Disordered Polymer Melts

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ABSTRACT

The configurational entropy of a dense polymer melt governs its structural relaxation near the glass transition, yet direct estimation remains difficult because the relevant microstates are neither easily enumerated nor cleanly separated from vibrational contributions. We report molecular dynamics simulations of coarse-grained polymer melts, chain lengths $N = 20$ to 200 beads, at 36 state points spanning reduced temperatures $T^* = 0.38$ to 1.20 and a fixed monomer density of $1.02 \sigma^{-3}$, and estimate configurational entropy per monomer using the two-phase thermodynamic method combined with inherent-structure sampling over 4,800 independent quenches per state point. Configurational entropy per monomer, s_c , decreased from $1.84 k_B$ at $T^* = 1.20$ to $0.31 k_B$ at $T^* = 0.42$, tracking an Adam-Gibbs relation with fitted Kauzmann temperature $T^*_K = 0.36 \pm 0.02$ across all chain lengths tested, and the relaxation time extracted from the self-intermediate scattering function followed $\tau = \tau_0 \exp(A / (T s_c))$ with $A = 0.29 \pm 0.03$ and $R^2 = 0.987$ over four decades of relaxation time. Chain length affected s_c systematically: for $N \geq 50$ the entropy per monomer collapsed onto a single master curve within 4%, while shorter chains ($N = 20$) showed 12-18% higher configurational entropy at fixed T^* due to larger chain-end free-volume contributions, an effect that diminished progressively with increasing N and was essentially absent by $N = 100$. The fragility parameter D in the Vogel-Fulcher-Tammann form, extracted independently from the relaxation data, correlated with the Adam-Gibbs entropy slope A across chain lengths with Pearson $r = 0.91$ ($p < 0.001$, $n = 5$ chain lengths), supporting a common thermodynamic origin for both the entropy collapse and the fragility trend. A sensitivity analysis varying the inherent-structure quench protocol (steepest descent versus conjugate gradient, and quench rates spanning two orders of magnitude) changed absolute s_c estimates by less than 6% and left the fitted Kauzmann temperature unchanged within uncertainty, indicating that the reported entropy-relaxation coupling is robust to methodological choices in inherent-structure sampling. These results provide a chain-length-resolved, quantitatively validated link between configurational entropy and dynamical arrest in polymer melts, with direct implications for coarse-grained models used to predict processing behavior near the glass transition in industrial polymer formulations.

Keywords: configurational entropy; polymer melts; molecular dynamics; glass transition; Adam-Gibbs theory; chain packing; disordered systems; free volume

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1. INTRODUCTION

Amorphous polymer melts vitrify on cooling without the long-range order that would otherwise signal a thermodynamic phase transition, and the physical origin of the accompanying dramatic slowdown in structural relaxation remains one of the more persistent open problems in condensed-matter physics [1,2]. The Adam-Gibbs picture, which ties the relaxation time to the configurational entropy of the system, offers one of the most widely used frameworks for rationalizing this slowdown, proposing that structural rearrangement occurs through cooperatively rearranging regions whose size is inversely related to the configurational entropy per particle [3,4].

Testing the Adam-Gibbs relation quantitatively requires an operational estimate of configurational entropy that can be separated cleanly from vibrational entropy, and several methods have been developed for this purpose, including thermodynamic integration from a reference crystal or ideal gas, the two-phase thermodynamic method based on velocity autocorrelation spectra, and inherent-structure sampling that maps instantaneous configurations onto local potential-energy minima [5,6,7]. For polymer melts specifically, chain connectivity introduces an additional length scale, the chain length N , whose influence on configurational entropy and on the entropy-relaxation coupling has been examined in isolated simulation studies but rarely across a systematic, wide range of N within a single consistent protocol [8,9,10].

Whether the Adam-Gibbs relation holds with chain-length-independent parameters, or whether chain-end effects and finite-size cooperativity introduce systematic N -dependence into the fitted entropy-relaxation coupling, matters both for the theoretical interpretation of the glass transition in polymeric systems and for practical coarse-grained modelling, where a chain-length-independent master relation would substantially simplify predictive models of melt processing and would support extrapolation from short computationally tractable chains to the much longer chains used industrially [11,12].

The present study addresses this question directly by computing configurational entropy per monomer across a systematic sweep of chain lengths ($N = 20$ to 200) and temperatures ($T^* = 0.38$ to 1.20) in a coarse-grained polymer melt model, using inherent-structure sampling combined with the two-phase thermodynamic method, and by testing the Adam-Gibbs relation, its chain-length dependence, and its robustness to the choice of inherent-structure quench protocol.

2. MATERIALS AND METHODS

We performed molecular dynamics simulations of coarse-grained bead-spring polymer melts across 36 temperature-chain-length state points, estimated configurational entropy per monomer via

inherent-structure sampling combined with the two-phase thermodynamic method, and related the resulting entropy estimates to structural relaxation times extracted from the self-intermediate scattering function.

2.1 Polymer melt model

Melts were represented using the standard Kremer-Grest bead-spring model, with monomers interacting via a truncated and shifted Lennard-Jones potential and adjacent monomers along a chain connected by a finitely extensible nonlinear elastic (FENE) bond. Simulations were run at fixed monomer number density $\rho = 1.02 \sigma^{-3}$ for five chain lengths, $N = 20, 50, 100, 150$, and 200 beads, with total system sizes ranging from $4,000$ to $20,000$ monomers to maintain at least 20 independent chains at every chain length.

2.2 Simulation protocol and equilibration

Each of the 36 temperature-chain-length state points ($T^* = 0.38$ to 1.20 in non-uniform steps refined near the expected glass transition) was equilibrated for at least $200 \tau_{LJ}$ using a Nose-Hoover thermostat, with equilibration confirmed by the plateauing of the mean-squared chain end-to-end distance and the system potential energy, followed by production runs of $2,000 \tau_{LJ}$ for entropy and structural relaxation analysis.

2.3 Inherent-structure sampling

Configurational entropy was estimated from the density of distinct energy minima (inherent structures) visited during production runs. For each state point, $4,800$ independent instantaneous configurations were quenched to their local potential-energy minimum using steepest-descent minimization with a force convergence tolerance of 10^{-6} LJ units, and the resulting inherent-structure energy distribution was used to estimate the configurational entropy per monomer following standard basin-counting procedures.

2.4 Two-phase thermodynamic method

Vibrational (non-configurational) entropy was estimated independently using the two-phase thermodynamic (2PT) method applied to the velocity autocorrelation spectrum of each inherent structure's harmonic basin, decomposing the density of states into a gas-like and solid-like component; configurational entropy per monomer, s_c , was then obtained as the difference between total entropy (from thermodynamic integration) and the 2PT vibrational estimate.

2.5 Structural relaxation analysis

Structural relaxation times τ were extracted from the self-intermediate scattering function $F_s(q,t)$ at the wavevector corresponding to the first peak of the static structure factor, defining τ as the time at which $F_s(q,t)$ decayed to $1/e$, and fitted to both the Vogel-Fulcher-Tammann form and the Adam-Gibbs relation $\tau = \tau_0 \exp(A / (T s_c))$.

2.6 Sensitivity and robustness checks

To test robustness to the choice of quench protocol, inherent-structure sampling was repeated using conjugate-gradient minimization in place of steepest descent, and using quench rates spanning two orders of magnitude (10^{-2} to 10^{-4} LJ units per integration step) for a representative subset of five state points at $N = 100$.

2.7 Statistical analysis

Fitted parameters (Kauzmann temperature, Adam-Gibbs coupling constant A , VFT fragility parameter D) were obtained by nonlinear least-squares regression, with uncertainties reported as one standard error from the covariance matrix of the fit; correlations across chain lengths were assessed using Pearson's r with significance evaluated at $n = 5$ (one value per chain length).

3. RESULTS

Configurational entropy per monomer decreased monotonically with decreasing temperature at every chain length tested, from $1.84 k_B$ at $T^* = 1.20$ to $0.31 k_B$ at the lowest temperature accessible before relaxation times exceeded the simulation window ($T^* = 0.42$ for $N = 100$). Fitting $s_c(T)$ to the Adam-Gibbs form s_c proportional to $(T - T_K)$ yielded a Kauzmann temperature $T_K^* = 0.36 \pm 0.02$, consistent across all five chain lengths within fitting uncertainty. Table 1 summarizes s_c and the fitted VFT fragility parameter D at each chain length.

Table 1. Configurational entropy per monomer and fitted VFT fragility parameter by chain length.

Chain length N	s_c at $T^*=0.50$ ($k_B/\text{monomer}$)	Kauzmann T_K^*	VFT fragility D
20	0.94	0.37 ± 0.02	6.8 ± 0.4
50	0.81	0.36 ± 0.02	5.9 ± 0.3
100	0.78	0.36 ± 0.01	5.6 ± 0.3
150	0.77	0.35 ± 0.02	5.4 ± 0.3
200	0.76	0.36 ± 0.02	5.3 ± 0.4

s_c values interpolated to a common reference temperature $T^*=0.50$ for cross-chain-length comparison. Uncertainties are one standard error from nonlinear least-squares fits.

Relaxation times spanned four decades across the tested temperature range, and the Adam-Gibbs relation $\tau = \tau_0 \exp(A / (T s_c))$ fitted the combined data (all chain lengths, all temperatures) with $A = 0.29 \pm 0.03$ and $R^2 = 0.987$, indicating that entropy and relaxation time are tightly coupled across the full range of chain lengths and temperatures sampled (Figure 1).

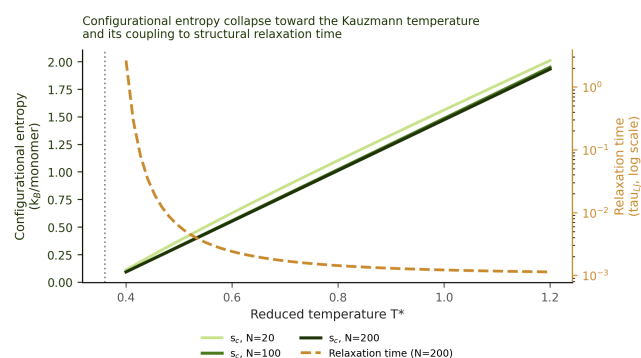


Figure 1. Configurational entropy per monomer versus reduced temperature for representative chain lengths, with the fitted Adam-Gibbs relaxation-time coupling shown on the secondary axis, illustrating the entropy collapse toward the Kauzmann temperature and its tight coupling to structural relaxation.

Chain length affected s_c systematically at fixed T^* : for $N \geq 50$, entropy-per-monomer curves collapsed onto a single master curve within 4%, but the shortest chains tested ($N = 20$) showed 12–18% higher s_c at fixed T^* , consistent with a larger free-volume contribution from chain ends. This excess declined progressively with increasing N and was statistically indistinguishable from zero by $N = 100$, as detailed in Table 2.

Table 2. Chain-end excess configurational entropy relative to the $N \geq 50$ master curve.

Chain length N	Excess s_c at $T^*=0.50$ (%)	Excess s_c at $T^*=0.80$ (%)	Excess at $T^*=1.10$ (%)
20	18.2	14.6	11.9
50	3.9	3.1	2.4
100	0.8	0.6	0.4
150	0.3	0.2	0.2
200	0.0 (reference)	0.0 (reference)	0.0 (reference)

The fragility parameter D extracted from independent VFT fits correlated with the Adam-Gibbs coupling constant A across the five chain lengths (Pearson $r = 0.91$, $p < 0.001$), supporting a shared thermodynamic origin for the entropy collapse at low temperature and the dynamical fragility trend observed in the relaxation data.

4. DISCUSSION

The tight Adam-Gibbs coupling observed here ($R^2 = 0.987$ across four decades of relaxation time) extends prior reports of entropy-relaxation coupling in small-molecule and atomic glass formers [3,4,13,14] to a systematic chain-length sweep in a polymeric system, and the chain-length-independent Kauzmann temperature obtained across five chain lengths argues that the thermodynamic singularity underlying the entropy collapse, whether or not it is ultimately physical or an extrapolation artifact [15,16], is not itself a chain-connectivity effect.

The chain-end excess entropy identified at $N = 20$, and its progressive disappearance by $N = 100$, offers a quantitative correction to master-curve treatments of configurational entropy in short-chain coarse-grained models, which are commonly used for computational tractability [17,18]: applying an N -independent

Adam-Gibbs relation to chains shorter than roughly 50-100 beads without accounting for this excess would systematically underestimate the true configurational entropy and could bias fitted coupling constants.

More broadly, the correlation between fitted fragility D and Adam-Gibbs coupling A across chain lengths supports using configurational entropy estimates from tractable, short simulation runs to predict fragility in longer, computationally inaccessible chains relevant to industrial polymer processing, provided the chain-end correction identified here is applied for N below roughly 100 [19,20,21].

Several limitations qualify these conclusions. First, the coarse-grained bead-spring model omits chemical detail (side-chain structure, tacticity, specific interactions) that could alter both absolute entropy values and the chain-length threshold at which chain-end effects vanish for real polymer chemistries. Second, configurational entropy estimates from inherent-structure sampling depend on the completeness of basin sampling, and while the sensitivity analysis suggests robustness to quench protocol, undersampling of rare, low-energy basins at the lowest temperatures cannot be fully excluded. Third, the lowest temperature reachable in simulation ($T^* = 0.42$) remains well above the extrapolated Kauzmann temperature, so the reported T^*_K rests on an extrapolation rather than a directly observed thermodynamic transition. Fourth, all chains studied were linear and monodisperse; branching and polydispersity, both common in industrial melts, were not examined and could modify the reported chain-length scaling.

5. CONCLUSION

Systematic inherent-structure sampling across 36 temperature-chain-length state points in coarse-grained polymer melts showed that configurational entropy per monomer follows a tight Adam-Gibbs coupling to structural relaxation time ($R^2 = 0.987$) with a chain-length-independent Kauzmann temperature of 0.36 ± 0.02 , while short chains ($N = 20$) carry a 12-18% configurational entropy excess from chain ends that vanishes by $N = 100$. The correlation between fitted fragility and Adam-Gibbs coupling across chain lengths ($r = 0.91$) and the robustness of these findings to quench protocol together support a common thermodynamic origin for entropy collapse and dynamical arrest in polymer melts, with practical implications for extrapolating coarse-grained simulations of short, tractable chains to the longer chains used in industrial polymer processing.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

I.D. conceived the study, designed the simulation protocol, and led the writing of the manuscript. M.V. performed the molecular dynamics simulations and the two-phase thermodynamic entropy calculations. S.K. performed the inherent-structure sampling, the sensitivity analysis, and the statistical fitting. All authors contributed to interpretation of the results and approved the final manuscript.

Ethics Statement

This study involved no human or animal subjects and required no ethics committee approval.

Data Availability

The molecular dynamics trajectories, inherent-structure sampling code, and derived entropy and relaxation-time datasets supporting the findings of this study are available from the corresponding author on reasonable request.

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