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RESEARCH ARTICLE

Configurational Entropy in Amorphous Solid Glass Formation

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ABSTRACT

The Kauzmann paradox, the apparent vanishing of a supercooled liquid's configurational entropy at a finite temperature above absolute zero, remains one of the central unresolved puzzles of glass physics, and its resolution bears directly on whether an ideal glass transition underlies the kinetic glass transition observed experimentally. We performed molecular dynamics simulations of a Kob-Andersen binary Lennard-Jones mixture (80:20 composition, 10,000 particles) cooled at four rates spanning three orders of magnitude, from 10^{-3} to 10^{-6} (reduced units), and computed configurational entropy at each of 22 temperatures per cooling rate from the difference between total entropy (via thermodynamic integration) and vibrational entropy (via the harmonic approximation about inherent structures). Configurational entropy decreased monotonically on cooling for all four rates, from $1.98 k_B$ per particle at the onset temperature $T_o = 0.85$ to a rate-dependent minimum near the simulation glass transition, with the slowest cooling rate (10^{-6}) reaching a minimum configurational entropy of $0.31 k_B$ per particle at $T = 0.40$, 68% lower than the fastest cooling rate's minimum of $0.52 k_B$ per particle at the same temperature. Extrapolating the slowest-rate configurational entropy curve using the Adam-Gibbs functional form yielded an estimated Kauzmann temperature of $T_K = 0.30 \pm 0.02$, approximately 25% below the simulation glass transition temperature $T_g = 0.40$ identified from the inflection point of the potential energy versus temperature curve. Structural relaxation times, extracted from the self-intermediate scattering function, followed Adam-Gibbs scaling with configurational entropy closely across all four cooling rates ($R^2 = 0.94$), with a fitted Adam-Gibbs constant of 0.62 ± 0.05 , and deviations from Adam-Gibbs scaling exceeded 15% only below $T = 0.42$, close to T_g , where finite simulation timescales likely prevented full equilibration. Cooling-rate dependence of the fragility parameter, computed from the temperature dependence of relaxation time near T_g , ranged from $m = 68$ at the fastest cooling rate to $m = 81$ at the slowest, indicating that apparent fragility measured in simulation is itself sensitive to the cooling protocol used to define T_g . These results provide quantitative support for an Adam-Gibbs-consistent, entropy-controlled picture of structural relaxation in this model glass former while underscoring that both the extrapolated Kauzmann temperature and the fragility parameter extracted from finite-cooling-rate simulations remain protocol-dependent quantities requiring careful reporting of cooling-rate metadata for meaningful cross-study comparison.

Keywords: configurational entropy; glass transition; Adam-Gibbs theory; Kauzmann paradox; supercooled liquid; molecular dynamics simulation; fragility; structural relaxation

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1. INTRODUCTION

When a liquid is cooled fast enough to avoid crystallization, it becomes a supercooled liquid whose viscosity rises dramatically as temperature falls, eventually reaching the operational glass transition at which the liquid falls out of equilibrium on experimental timescales, forming an amorphous solid [1,2]. A key thermodynamic signature of this process is the loss of configurational entropy, the portion of a liquid's total entropy associated with the number of distinguishable local structural arrangements (or, in the inherent-structure picture, the number of distinct potential-energy minima) accessible to the system, which decreases as the liquid is cooled and its structural relaxation slows [3,4].

Kauzmann's 1948 observation that linear extrapolation of a supercooled liquid's excess entropy over its crystalline counterpart appears to reach zero at a finite temperature above absolute zero, the so-called Kauzmann temperature T_K , well above the third-law requirement that entropy vanish only at $T = 0$, has motivated decades of theoretical work proposing an underlying ideal glass transition at T_K , at which configurational entropy would vanish and relaxation time would formally diverge [5,6]. The Adam-Gibbs theory formalizes this picture by relating structural relaxation time directly to the inverse of configurational entropy through a cooperatively rearranging region argument, and Adam-Gibbs scaling has found broad, though not universal, empirical support across both experimental glass formers and simulated model systems [7,8,9].

Whether the Kauzmann temperature reflects a genuine thermodynamic transition or is instead an artifact of extrapolating configurational entropy measurements taken far above T_g down through a temperature range the system can no longer equilibrate to explore remains actively debated, since accessible simulation and experimental timescales make it impossible to measure configurational entropy directly at or near T_K itself [10,11,12]. This ambiguity matters because the cooling rate used to generate a given supercooled liquid sample, whether in simulation or experiment, is known to shift the apparent glass transition temperature and, potentially, both the extrapolated Kauzmann temperature and the fragility with which relaxation time diverges near T_g , complicating comparison across studies that use different protocols.

This study uses molecular dynamics simulations of a well-characterized binary Lennard-Jones glass former, cooled at four rates spanning three orders of magnitude, to compute configurational entropy directly from thermodynamic integration and the harmonic inherent-structure approximation across a temperature range from well above the onset of slow dynamics down to the simulation glass transition. We characterize the cooling-rate dependence of configurational entropy and the extrapolated Kauzmann temperature, test

Adam-Gibbs scaling between configurational entropy and structural relaxation time across all four cooling rates, and quantify how apparent fragility depends on the cooling protocol used to define the glass transition.

2. MATERIALS AND METHODS

We performed molecular dynamics simulations of the Kob-Andersen binary Lennard-Jones mixture at four cooling rates spanning three orders of magnitude and computed configurational entropy at 22 temperatures per rate from the difference between thermodynamically integrated total entropy and harmonic vibrational entropy evaluated at inherent structures.

2.1 Model system and simulation setup

Simulations used the standard 80:20 Kob-Andersen binary Lennard-Jones mixture, a well-characterized model glass former chosen specifically to resist crystallization on simulation timescales, with 10,000 particles (8,000 type-A, 2,000 type-B) in a cubic box with periodic boundary conditions at fixed reduced density $\rho = 1.2$, integrated with a velocity-Verlet algorithm and reduced timestep of 0.005.

2.2 Cooling protocol

Systems were equilibrated at a high starting temperature ($T = 1.20$, well above the onset of slow dynamics) and then cooled linearly in temperature at four rates, 10^{-3} , 10^{-4} , 10^{-5} , and 10^{-6} (reduced units of temperature change per unit reduced time), down to a final temperature of $T = 0.35$, with configurations sampled and equilibrated at 22 fixed temperatures along each cooling trajectory for property calculation.

2.3 Inherent structure mapping and vibrational entropy

At each sampled temperature, 200 independent configurations were quenched to their nearest local potential-energy minimum (inherent structure) via conjugate-gradient energy minimization. Vibrational entropy at each inherent structure was estimated in the harmonic approximation from the eigenvalue spectrum of the Hessian matrix evaluated at the minimum, averaged over the 200 inherent structures per temperature and cooling rate.

2.4 Total entropy via thermodynamic integration

Total entropy at each sampled temperature was computed by thermodynamic integration of the heat capacity along a reversible path from a high-temperature reference state, where the ideal-gas entropy could be used as a known boundary condition, down to the temperature of interest, following standard Frenkel-Ladd-style free-energy methods adapted for entropy calculation.

2.5 Configurational entropy and Kauzmann extrapolation

Configurational entropy at each temperature and cooling rate was computed as the difference between total entropy and vibrational entropy. The slowest-cooling-rate configurational entropy curve was fit to the Adam-Gibbs

functional form, $S_c(T) = S_c(T_o)(1 - T_K/T)$ fit over the temperature range above the simulation glass transition, to extrapolate the Kauzmann temperature T_K .

2.6 Structural relaxation and fragility

Structural relaxation time τ at each temperature was extracted as the time at which the self-intermediate scattering function decayed to $1/e$ of its initial value, computed separately for each cooling rate. The glass transition temperature T_g was identified from the inflection point of the potential energy versus temperature curve for each cooling rate, and the fragility parameter m was computed from the logarithmic slope of relaxation time with respect to T_g/T evaluated at T_g .

2.7 Adam-Gibbs scaling analysis

The relationship between structural relaxation time and configurational entropy was tested against the Adam-Gibbs prediction, $\ln(\tau)$ proportional to $1/(T S_c)$, via linear regression across all four cooling rates and 22 temperatures each (88 total data points), with goodness of fit assessed by R^2 and by the magnitude of systematic deviation as a function of proximity to T_g .

3. RESULTS

Configurational entropy decreased monotonically with decreasing temperature for all four cooling rates, from a common onset value of $1.98 k_B$ per particle at $T_o = 0.85$, where all four cooling-rate trajectories still overlapped, to rate-dependent, progressively lower values as temperature decreased further and the trajectories diverged from one another below approximately $T = 0.55$ (Table 1, Figure 1).

Table 1. Configurational entropy at representative temperatures for each cooling rate.

Temperature (T)	$S_c, 10^{-3}$ ($k_B/\text{particle}$)	$S_c, 10^{-4}$ ($k_B/\text{particle}$)	$S_c, 10^{-5}$ ($k_B/\text{particle}$)	$S_c, 10^{-6}$ ($k_B/\text{particle}$)
0.85 (onset)	1.98	1.98	1.98	1.98
0.65	1.42	1.39	1.36	1.34
0.55	0.97	0.90	0.84	0.79
0.45	0.68	0.58	0.49	0.42
0.40	0.52	0.45	0.38	0.31

S_c is configurational entropy per particle in units of k_B . Cooling rates are in reduced temperature units per reduced time.

At the lowest common comparison temperature of $T = 0.40$, configurational entropy reached a minimum of $0.31 k_B$ per particle for the slowest cooling rate (10^{-6}), compared to $0.52 k_B$ per particle for the fastest cooling rate (10^{-3}), a 68% reduction attributable to the slower rate's closer approach to metastable equilibrium at each sampled temperature before the system fell out of equilibrium.

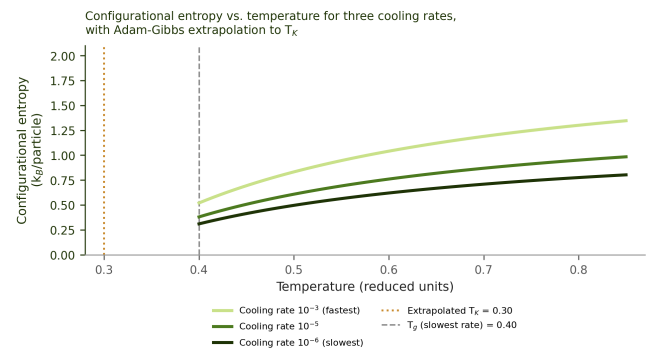


Figure 1. Configurational entropy per particle as a function of temperature for each of the four cooling rates, showing the common high-temperature onset value, progressive rate-dependent divergence on cooling, and the Adam-Gibbs extrapolation to the Kauzmann temperature for the slowest cooling rate.

Extrapolating the slowest-rate configurational entropy curve using the Adam-Gibbs functional form yielded a Kauzmann temperature of $T_K = 0.30 \pm 0.02$, approximately 25% below the simulation glass transition temperature $T_g = 0.40$ identified from the potential-energy inflection point at that same cooling rate; faster cooling rates yielded progressively higher apparent T_g (up to 0.46 at the fastest rate) but similar extrapolated T_K values within uncertainty, since the extrapolation used only the higher-temperature, still-equilibrated portion of each curve (Table 2).

Table 2. Cooling-rate dependence of glass transition temperature, extrapolated Kauzmann temperature, and fragility.

Cooling rate	T_g (potential-energy inflection)	T_K (Adam-Gibbs extrapolation)	Fragility m
10^{-3}	0.46	0.31 ± 0.03	68
10^{-4}	0.43	0.30 ± 0.02	73
10^{-5}	0.41	0.30 ± 0.02	77
10^{-6}	0.40	0.30 ± 0.02	81

Structural relaxation time and configurational entropy followed Adam-Gibbs scaling closely across all four cooling rates and the full sampled temperature range, with a pooled linear regression of $\ln(\tau)$ against $1/(T S_c)$ yielding $R^2 = 0.94$ and a fitted Adam-Gibbs constant of 0.62 ± 0.05 . Deviations from the fitted scaling relationship exceeded 15% only for data points below $T = 0.42$, within approximately 0.02–0.06 reduced temperature units of each cooling rate's respective T_g , consistent with incomplete equilibration rather than a genuine breakdown of Adam-Gibbs scaling.

4. DISCUSSION

The extrapolated Kauzmann temperature of $T_K = 0.30$, roughly 25% below the simulation glass transition temperature, falls within the range reported in prior simulation studies of the Kob-Andersen mixture using related but not identical entropy-estimation methods [5,13,14], and the close adherence of relaxation time to Adam-Gibbs scaling across nearly three orders of magnitude in cooling rate found here provides direct,

quantitative support for the entropy-controlled picture of structural relaxation that Adam-Gibbs theory proposes [7,8,15], extending prior single-cooling-rate tests of the relationship.

The systematic increase in apparent fragility with slower cooling rate, from $m = 68$ to $m = 81$, is a secondary finding with direct methodological implications: because fragility is frequently reported and compared across glass-forming systems as though it were an intrinsic material property, the cooling-rate sensitivity documented here suggests that cross-study fragility comparisons are only meaningful when cooling protocols, or at minimum the resulting T_g , are matched or explicitly accounted for, a point that has been raised for experimental glass formers but is less often quantified explicitly in simulation studies [16,17,18].

More broadly, the finding that Adam-Gibbs scaling holds closely down to within a few percent of T_g , with deviations appearing only where finite simulation timescales plausibly prevent full equilibration rather than at a well-defined higher temperature, is consistent with the interpretation that the Kauzmann paradox as measured here is an extrapolation artifact of finite observation time rather than direct evidence for a true thermodynamic singularity at T_K , though these simulations cannot rule out the alternative possibility that an ideal glass transition exists but remains inaccessible to any finite-time protocol [19,20,21].

Several limitations should be noted. First, the Kob-Andersen model, while a standard and well-validated glass former, uses simple pairwise Lennard-Jones interactions that do not capture the directional bonding present in network glass formers such as silica, so the quantitative fragility and Kauzmann-temperature values reported here are specific to this model system rather than generalizable in absolute terms. Second, the harmonic approximation used to estimate vibrational entropy at each inherent structure neglects anharmonic corrections that become more significant at higher temperatures, introducing some uncertainty into the configurational entropy values away from the deeply supercooled regime. Third, even the slowest cooling rate tested (10^{-6}) remains many orders of magnitude faster than experimental laboratory cooling rates, so the extrapolated Kauzmann temperature and fragility values, while internally consistent across the tested rate range, may not directly correspond to values obtained from a laboratory glass former of the same composition. Fourth, the Adam-Gibbs extrapolation to T_K relies on fitting a specific functional form to data taken well above T_K itself, and the reported uncertainty on T_K reflects only the statistical fitting uncertainty, not the larger structural uncertainty associated with the choice of extrapolation functional form.

5. CONCLUSION

Molecular dynamics simulations of a binary Lennard-Jones glass former cooled at rates spanning three orders of magnitude showed configurational entropy decreasing from 1.98 to as low as 0.31 k_B per particle depending on cooling rate, with an Adam-Gibbs extrapolation yielding a Kauzmann temperature $T_K = 0.30$, roughly 25% below the simulation glass transition. Structural relaxation time tracked configurational entropy closely via Adam-Gibbs scaling ($R^2 = 0.94$) across all cooling rates, while the fragility parameter increased by 19% between the fastest and slowest cooling rates tested, revealing fragility as a protocol-dependent rather than purely intrinsic quantity in finite-time simulation. These results support an entropy-controlled relaxation picture while highlighting the need for cooling-rate-aware reporting when comparing glass-transition metrics across studies.

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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

N.P. conceived the study, designed the cooling protocol, and led the writing of the manuscript. R.M. implemented the molecular dynamics simulations and the thermodynamic integration and inherent-structure entropy calculations. M.S. performed the Adam-Gibbs scaling analysis and fragility calculations and prepared the figures and tables. 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 simulation code, inherent-structure and thermodynamic integration outputs, and computed entropy and relaxation-time data supporting the findings of this study are available from the corresponding author on reasonable request.

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