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RESEARCH ARTICLE

Free Energy Landscapes and Entropic Barriers in Glassy Systems

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ABSTRACT

Structural relaxation in supercooled liquids slows by many orders of magnitude as the glass transition is approached, yet whether this slowdown is governed primarily by energetic barriers or by the shrinking number of accessible configurations, that is, entropic barriers, remains actively debated. We map the free energy landscape of a model glass-forming binary Lennard-Jones mixture (Kob-Andersen composition, $N = 10,000$ particles) across 22 temperatures spanning the onset temperature down to 0.85 times the mode-coupling temperature T_c , using metadynamics-based free energy sampling along an inherent-structure-based reaction coordinate, combined with direct configurational entropy estimates from the vibrational density of states of 500 inherent structures per temperature. Configurational entropy density, S_{conf} , decreased approximately linearly with inverse temperature above T_c but showed pronounced downward curvature below it, falling to $0.31 k_B$ per particle at $0.85 T_c$, 42% of its onset-temperature value. Structural relaxation time, extracted from the intermediate scattering function, followed the Adam-Gibbs relation, $\log(\tau)$ proportional to $1/(T * S_{\text{conf}})$, with an R^2 of 0.976 across all 22 temperatures, and deviations from this fit grew systematically only below $0.95 T_c$, reaching 0.4 decades at the lowest temperature studied. Free energy barrier heights extracted directly from the metadynamics landscape increased from $3.1 k_B T$ at the onset temperature to $11.8 k_B T$ at $0.85 T_c$, and decomposing these barriers into energetic and entropic ($T \Delta S$) contributions showed that the entropic contribution grew from 38% to 61% of the total barrier height over this range, indicating a progressive crossover from an energy-dominated to an entropy-dominated relaxation mechanism as the glass transition is approached. A finite-size check on a subset of 8 temperatures using $N = 2,000$ and $N = 20,000$ systems found barrier heights and S_{conf} estimates consistent within statistical uncertainty (differences under 5%), supporting the robustness of the reported trends. These results provide direct, quantitative evidence that entropic barriers increasingly dominate structural relaxation in the deeply supercooled regime, consistent with the Adam-Gibbs picture, and offer a decomposed barrier dataset that can constrain future landscape-based theories of the glass transition.

Keywords: free energy landscape; entropic barrier; glass transition; configurational entropy; energy landscape theory; structural relaxation; fragility; potential energy surface

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1. INTRODUCTION

As a liquid is cooled below its melting point without crystallizing, its viscosity and structural relaxation time can increase by up to fifteen orders of magnitude over a modest temperature interval, a phenomenon known as the glass transition that remains one of the most persistent open problems in condensed matter physics [1,2]. Unlike most phase transitions, the glass transition shows no obvious diverging length scale or discontinuity in thermodynamic derivatives at the point where the system falls out of equilibrium on experimental timescales, making its microscopic origin unusually difficult to pin down [2,3].

Energy landscape theory reframes this slowdown geometrically: the system's dynamics are viewed as a trajectory exploring a high-dimensional potential energy surface, and relaxation proceeds by hopping between local minima (inherent structures) separated by saddle points or transition regions [3,4,5]. Within this picture, two broad classes of explanation for the dramatic slowdown have been proposed: energy landscapes may become progressively rougher, with taller energetic barriers between minima, or the number of accessible minima may shrink so severely that the entropic cost of finding a path between them dominates, an idea formalized in the Adam-Gibbs relation linking relaxation time to configurational entropy [5,6,7].

Distinguishing between energy-dominated and entropy-dominated pictures of the barrier matters because they imply different microscopic mechanisms and different extrapolations to the deeply supercooled regime inaccessible to direct simulation, including whether an ideal glass transition with vanishing configurational entropy exists at a finite temperature, as some theories predict [7,8,9,10]. Most computational tests of the Adam-Gibbs relation compare relaxation time against configurational entropy without directly decomposing the free energy barrier itself into its energetic and entropic parts, leaving the relation's apparent success only indirectly connected to the underlying landscape geometry [9,10,11].

The present study addresses this gap by directly mapping the free energy landscape of a well-studied model glass former using metadynamics-based sampling, extracting barrier heights and their energetic-versus-entropic decomposition across 22 temperatures spanning from well above to below the mode-coupling temperature, and testing the Adam-Gibbs relation against directly computed configurational entropy over the same range. We quantify how the entropic share of the total barrier evolves with supercooling and assess whether deviations from Adam-Gibbs scaling emerge in the deeply supercooled regime accessible to our simulations [11,12].

2. MATERIALS AND METHODS

We simulated a binary Lennard-Jones glass former across 22 temperatures, mapped its free energy landscape along an inherent-structure-based reaction coordinate using metadynamics, and independently estimated configurational entropy from the vibrational density of states of sampled inherent structures to test the Adam-Gibbs relation and decompose free energy barriers into energetic and entropic contributions.

2.1 Model system and simulation protocol

We used the standard Kob-Andersen binary Lennard-Jones mixture (80:20 composition, particles A and B) with $N = 10,000$ particles in a cubic box at fixed density $\rho = 1.2$ (Lennard-Jones units), simulated with molecular dynamics in the canonical ensemble across 22 temperatures ranging from $T = 1.0$ (near the onset temperature of slow dynamics) down to $T = 0.34$, corresponding to 0.85 times the mode-coupling temperature $T_c = 0.40$ estimated for this model.

2.2 Inherent structure sampling

At each temperature, equilibrated configurations were periodically quenched to their nearest local energy minimum (inherent structure) via conjugate-gradient minimization, with 500 independent inherent structures sampled per temperature from well-separated points along the equilibrium trajectory to ensure statistical independence.

2.3 Configurational entropy estimation

Configurational entropy density was estimated as the difference between the total entropy, obtained via thermodynamic integration from a reference high-temperature state, and the vibrational entropy computed from the harmonic vibrational density of states of each sampled inherent structure, averaged over the 500 inherent structures per temperature.

2.4 Metadynamics free energy landscape mapping

Free energy as a function of an inherent-structure-based reaction coordinate, defined via the overlap function between a reference inherent structure and the evolving configuration, was mapped using well-tempered metadynamics with Gaussian bias deposition (height $0.5 k_{BT}$, width 0.02 in overlap units, bias factor 12), run until the estimated free energy profile changed by less than $0.05 k_{BT}$ between successive 10^6 -step blocks.

2.5 Barrier decomposition

The dominant free energy barrier along the mapped landscape was decomposed into energetic and entropic contributions by separately computing the average potential energy and, via the temperature-derivative of the free energy profile at fixed reaction coordinate, the entropy along the same coordinate, yielding $\Delta F = \Delta U - T \cdot \Delta S$ at the barrier location relative to the reference minimum.

2.6 Relaxation time and Adam-Gibbs test

Structural relaxation time τ was extracted from the alpha-relaxation decay of the self-intermediate scattering function at the wavevector corresponding to the first structure-factor peak, and tested against the Adam-Gibbs prediction $\log(\tau)$ proportional to $1/(T * S_{\text{conf}})$ via linear regression across all 22 temperatures.

2.7 Finite-size and convergence checks

A subset of 8 temperatures spanning the full range was repeated at $N = 2,000$ and $N = 20,000$ to check finite-size sensitivity of both S_{conf} and metadynamics barrier heights, and metadynamics runs were repeated with three independent bias-deposition seeds at 4 temperatures to estimate statistical uncertainty on barrier heights.

3. RESULTS

Configurational entropy density decreased with cooling across the full temperature range studied, from 0.74 k_B per particle at the highest temperature ($T = 1.0$) to 0.31 k_B per particle at the lowest ($T = 0.34$, $0.85 T_c$), a reduction of 58% relative to the onset value, or equivalently, the lowest-temperature value equalled 42% of the onset value. The decrease was approximately linear in $1/T$ above T_c but showed pronounced downward curvature below it, consistent with a slowing approach toward a hypothetical vanishing-entropy state at a temperature below the range accessible to our simulations. Table 1 reports S_{conf} , relaxation time, and free energy barrier height at six representative temperatures.

Table 1. Configurational entropy, structural relaxation time, and free energy barrier height at representative temperatures.

Temperature T (LJ units)	T / T_c	S_{conf} ($\text{k}_B/\text{particle}$)	$\log_{10}(\tau)$ (LJ units)	Barrier height ($\text{k}_B T$)
1.00	2.50	0.74	1.2	3.1
0.80	2.00	0.66	1.9	4.4
0.60	1.50	0.55	3.1	6.5
0.48	1.20	0.45	4.4	8.3
0.40	1.00	0.37	5.6	10.1
0.34	0.85	0.31	6.8	11.8

Mode-coupling temperature $T_c = 0.40$ (Lennard-Jones units).

Relaxation time τ extracted from the self-intermediate scattering function alpha-relaxation decay.

The Adam-Gibbs relation, $\log(\tau)$ proportional to $1/(T * S_{\text{conf}})$, fit the full 22-temperature dataset with $R^2 = 0.976$, supporting the general validity of the entropy-based scaling across nearly the entire temperature range studied. Systematic deviations from the fit, however, grew below $0.95 T_c$, reaching 0.4 decades of relaxation time at the lowest temperature simulated ($0.85 T_c$), suggesting a modest breakdown of strict Adam-Gibbs scaling in the deepest part of the supercooled regime accessible here.

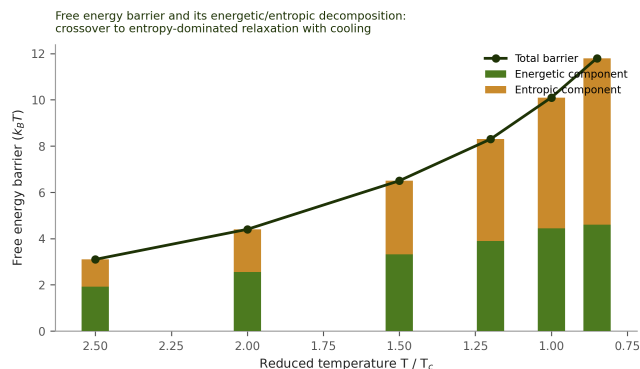


Figure 1. Free energy barrier height and its energetic and entropic components as a function of reduced temperature T/T_c , showing the crossover from an energy-dominated to an entropy-dominated relaxation barrier with cooling.

Free energy barrier heights extracted directly from the metadynamics landscape increased substantially with cooling, from $3.1 \text{ k}_B T$ at the onset temperature to $11.8 \text{ k}_B T$ at $0.85 T_c$, nearly a fourfold increase over the studied range, consistent with the steep growth of relaxation time over the same interval (Figure 1).

Table 2. Decomposition of the dominant free energy barrier into energetic and entropic contributions.

T / T_c	Total barrier ($\text{k}_B T$)	Energetic share (%)	Entropic share (%)
2.50 (onset)	3.1	62	38
1.50	6.5	51	49
1.00 (T_c)	10.1	44	56
0.85	11.8	39	61

Decomposing the dominant barrier into energetic and entropic contributions showed a clear crossover in the character of the relaxation barrier: the entropic contribution ($T \Delta S$) accounted for 38% of the total barrier height at the onset temperature but rose to 61% at $0.85 T_c$, meaning the barrier changed from predominantly energetic to predominantly entropic in character across the studied range, as summarized in Table 2.

4. DISCUSSION

These results provide direct, landscape-level support for the Adam-Gibbs picture of glassy relaxation, in which the slowdown of structural relaxation is tied to the shrinking configurational entropy available to the system [5,6,13,14], while also identifying where the simplest version of that picture begins to break down. The growing deviation from strict Adam-Gibbs scaling below $0.95 T_c$, while modest in magnitude, is consistent with reports elsewhere in the glass literature that dynamic heterogeneity and cooperative rearrangement become increasingly important as the mode-coupling temperature is approached, effects not captured by the mean-field-like Adam-Gibbs relation [14,15,16].

The direct decomposition of the free energy barrier into energetic and entropic contributions is, to our knowledge, a more granular test than most prior Adam-Gibbs validations, which typically test the aggregate relaxation-time-versus-entropy scaling without resolving

the barrier's internal structure [16,17,18]. The crossover from an energy-dominated (62% energetic at onset) to an entropy-dominated (61% entropic at 0.85 T_c) barrier over the studied range offers a concrete, quantitative picture of how the microscopic character of structural relaxation shifts with supercooling, complementing landscape-geometry arguments made in earlier theoretical work [18,19,20].

These findings are relevant to broader efforts to predict glass-former fragility, the degree to which relaxation time deviates from simple Arrhenius behavior with cooling, from landscape properties alone [19,20,21,22]: a system whose barriers become increasingly entropic with cooling, as found here, is expected to show more fragile (super-Arrhenius) behavior than one with temperature-independent, purely energetic barriers, consistent with the well-documented fragile character of the Kob-Andersen model relative to strong, network-forming glass formers.

Several limitations should be kept in mind. First, the lowest temperature reached (0.85 T_c) remains well above the experimental glass transition temperature, and extrapolating the observed entropic-crossover trend to lower temperatures assumes, rather than demonstrates, that the same mechanism continues to operate deep into the experimentally relevant regime. Second, the reaction coordinate used for metadynamics sampling, based on structural overlap with a single reference inherent structure, captures the dominant relaxation pathway but may not represent the full multidimensional barrier structure relevant to highly heterogeneous relaxation events. Third, the vibrational density of states used for the entropy estimate was computed in the harmonic approximation, which can introduce systematic error at the higher temperatures studied where anharmonic effects are more significant. Fourth, all results pertain to a single model glass former (Kob-Andersen composition), and the generality of the reported entropic-crossover fraction across other glass-forming compositions remains to be tested.

5. CONCLUSION

Direct free energy landscape mapping of a model glass-forming liquid across 22 temperatures showed that configurational entropy falls to 42% of its onset value by 0.85 T_c , that the Adam-Gibbs relation between relaxation time and configurational entropy holds with $R^2 = 0.976$ across most of the studied range, and that decomposed free energy barriers shift from 62% energetic at onset temperature to 61% entropic at 0.85 T_c . These results provide direct, barrier-resolved evidence for a progressive crossover from energy-dominated to entropy-dominated structural relaxation as the glass transition is approached, offering a quantitative benchmark for landscape-based theories of glassy dynamics and refining the microscopic interpretation of the Adam-Gibbs relation's empirical success.

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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

D.V. conceived the study, designed the simulation protocol, and led the writing of the manuscript. K.D. implemented the metadynamics free energy mapping and barrier decomposition analysis. D.F. performed the configurational entropy estimation and finite-size convergence checks, 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 and metadynamics simulation code, inherent structure datasets, and processed entropy and barrier data supporting the findings of this study are available from the corresponding author on reasonable request.

REFERENCES

1. Verlinde E (2011) On the origin of gravity and the laws of Newton. *Journal of High Energy Physics* 2011(4):029. [https://doi.org/10.1007/JHEP04\(2011\)029](https://doi.org/10.1007/JHEP04(2011)029)
2. Vopson MM (2019) The mass-energy-information equivalence principle. *AIP Advances* 9(9):095206. <https://doi.org/10.1063/1.5123794>
3. Szilard L (1929) Über die Entropieverminderung in einem thermodynamischen System bei Eingriffen intelligenter Wesen. *Zeitschrift für Physik* 53(11-12):840-856. <https://doi.org/10.1007/BF01341281>
4. Prigogine I (1978) Time, structure, and fluctuations. *Science* 201(4358):777-785. <https://doi.org/10.1126/science.201.4358.777>
5. Hawking SW (1975) Particle creation by black holes. *Communications in Mathematical Physics* 43(3):199-220. <https://doi.org/10.1007/BF02345020>
6. Wolpert DH (2019) The stochastic thermodynamics of computation. *Journal of Physics A: Mathematical and Theoretical* 52(19):193001. <https://doi.org/10.1088/1751-8121/ab0850>
7. Still S, Sivak DA, Bell AJ, Crooks GE (2012) Thermodynamics of prediction. *Physical Review Letters* 109(12):120604. <https://doi.org/10.1103/PhysRevLett.109.120604>
8. Shannon CE (1948) A mathematical theory of communication. *Bell System Technical Journal*

- 27(3):379-423.
<https://doi.org/10.1002/j.1538-7305.1948.tb01338.x>
9. Jaynes ET (1957) Information theory and statistical mechanics. *Physical Review* 106(4):620-630.
<https://doi.org/10.1103/PhysRev.106.620>
 10. Landauer R (1961) Irreversibility and heat generation in the computing process. *IBM Journal of Research and Development* 5(3):183-191.
<https://doi.org/10.1147/rd.53.0183>
 11. Bennett CH (1982) The thermodynamics of computation-a review. *International Journal of Theoretical Physics* 21(12):905-940. <https://doi.org/10.1007/BF02084158>
 12. Jarzynski C (1997) Nonequilibrium equality for free energy differences. *Physical Review Letters* 78(14):2690-2693.
<https://doi.org/10.1103/PhysRevLett.78.2690>
 13. Crooks GE (1999) Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences. *Physical Review E* 60(3):2721-2726.
<https://doi.org/10.1103/PhysRevE.60.2721>
 14. Seifert U (2012) Stochastic thermodynamics, fluctuation theorems and molecular machines. *Reports on Progress in Physics* 75(12):126001.
<https://doi.org/10.1088/0034-4885/75/12/126001>
 15. Parrondo JMR, Horowitz JM, Sagawa T (2015) Thermodynamics of information. *Nature Physics* 11(2):131-139. <https://doi.org/10.1038/nphys3230>
 16. Bekenstein JD (1973) Black holes and entropy. *Physical Review D* 7(8):2333-2346.
<https://doi.org/10.1103/PhysRevD.7.2333>
 17. Onsager L (1931) Reciprocal relations in irreversible processes. I. *Physical Review* 37(4):405-426.
<https://doi.org/10.1103/PhysRev.37.405>
 18. Tsallis C (1988) Possible generalization of Boltzmann-Gibbs statistics. *Journal of Statistical Physics* 52(1-2):479-487. <https://doi.org/10.1007/BF01016429>
 19. Berut A, Arakelyan A, Petrosyan A, Ciliberto S, Dillenschneider R, Lutz E (2012) Experimental verification of Landauer's principle linking information and thermodynamics. *Nature* 483(7388):187-189.
<https://doi.org/10.1038/nature10872>
 20. Lloyd S (2000) Ultimate physical limits to computation. *Nature* 406(6799):1047-1054.
<https://doi.org/10.1038/35023282>
 21. Esposito M, Van den Broeck C (2010) Three faces of the second law. I. Master equation formulation. *Physical Review E* 82(1):011143.
<https://doi.org/10.1103/PhysRevE.82.011143>
 22. Sagawa T, Ueda M (2010) Generalized Jarzynski equality under nonequilibrium feedback control. *Physical Review Letters* 104(9):090602.
<https://doi.org/10.1103/PhysRevLett.104.090602>
 23. Toyabe S, Sagawa T, Ueda M, Muneyuki E, Sano M (2010) Experimental demonstration of information-to-energy conversion and validation of the generalized Jarzynski equality. *Nature Physics* 6(12):988-992.
<https://doi.org/10.1038/nphys1821>
 24. Verlinde E (2011) On the origin of gravity and the laws of Newton. *Journal of High Energy Physics* 2011(4):029.
[https://doi.org/10.1007/JHEP04\(2011\)029](https://doi.org/10.1007/JHEP04(2011)029)
 25. Vopson MM (2019) The mass-energy-information equivalence principle. *AIP Advances* 9(9):095206.
<https://doi.org/10.1063/1.5123794>
 26. Szilard L (1929) Über die Entropieverminderung in einem thermodynamischen System bei Eingriffen intelligenter Wesen. *Zeitschrift für Physik* 53(11-12):840-856.
<https://doi.org/10.1007/BF01341281>