

Temperature-density dependent hidden order of amorphous carbon

Corresponding Author: Professor Gao Tinghong

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this manuscript, the authors reported the temperature-density dependent hidden order in amorphous carbons, constructing a temperature-density phase diagram that revealed the hidden order obscured by structural disorder. The temperature was unveiled as an independent topological order parameter to play a critical role in governing the phase transitions in amorphous carbons, in addition to density. Two representative phase transition pathways and the pressure-controlled nucleation of diamond were further uncovered. The manuscript offers a good theoretical perspective on the hidden order and microstructural features of amorphous carbon, which is recommended for publication after minor revisions.

1. This study investigated the microstructures of amorphous carbons across a wide range of density, from ~ 0.5 to ~ 3.5 g/cm³. However, Fig. 1e contains only the sp³ fraction of the high density structures ranging from 3.0 to 3.5 g/cm³. The sp³ fraction of other densities is recommended to be included in the manuscript.

2. On page 7, the authors mentioned that traditional empirical potentials (such as EDIP) have previously failed to reproduce Diaphite in simulations. However, EDIP has shown good capability to describe the mixed-hybrid microstructures and complex phase interfaces of a-DGs and Diaphite (Natl. Sci. Rev. 11, nwa051 (2024); ACS Nano 18, 34312 (2024); Sci. Adv. 11, ead5007 (2025)). The relevant discussion should be corrected.

3. Current manuscript lacks a clear description of the differences between a-DG and Diaphite in Fig. 2. In previous studies, Diaphite is mainly divided into two types according to their distinct phase interfaces (Nano Lett. 20, 3611 (2020)). The authors are recommended to add more discussion to define their simulated structures and distinguish their differences and correlations between existing studies.

4. At sufficiently high temperatures and densities, the diamond nuclei with various orientations continue to grow and eventually evolve into NPD. The similar temperature-dependent nucleation and growth of paracrystalline diamond grains was also mentioned in previous study (Nano Lett. 24, 312 (2024)). How does the authors define the difference between p-D and NPD? Are there clear boundaries, such as crystalline atom proportions, to distinguish these structures?

Reviewer #2

(Remarks to the Author)

The paper investigates the hidden topological order of amorphous carbon (a-C) by employing machine learning-based NEP and large-scale MD simulations. The study explored the annealing process of a-C under varying temperatures and densities, identifying nine representative structures. By constructing a temperature-density phase diagram, the authors revealed two topological phase boundaries with discontinuous structural transitions, and the critical temperature increases approximately linearly with density. The reviewer finds this work interesting and recognizes it as a piece of timely work. Here are some suggestions and comments.

1) Line 60: There appears to be a punctuation error: the sentence ends with both a period and a comma.

2) Line 169 (around "The formation mechanism of a-G..."): The current explanation focuses on the role of temperature in overcoming kinetic barriers. While this addresses the kinetic aspect, it would be helpful to explain why the system preferentially evolves along the a-G pathway rather than toward other amorphous or crystalline structures. In other words, what makes the a-G configuration energetically or structurally favorable under the simulated conditions?

- 3) Line 271 (regarding the statement "It is expected that more precise physical parameters..."): While it is reasonable to acknowledge the limitations of current structural descriptors, the statement would benefit from more concrete suggestions on how these limitations might be addressed in future studies. For example, proposing potential computational or experimental strategies to refine structural classification (e.g., using machine-learned order parameters, localized electronic descriptors, or topological invariants) would make the discussion more insightful and forward-looking.
- 4) Line 279: The statement that "temperature acts as a topological order parameter independent of density" appears overly definitive. Since this conclusion is drawn from simulations under specific models and approximations, it should be presented more cautiously. A better phrasing would describe this finding as an observed computational trend or model-specific behavior, rather than asserting it as a universal physical principle. Softening this claim would improve scientific rigor and avoid overinterpretation of the results.
- 5) Line 385 (regarding the statement "temperature serves as a topological order parameter independent of density..."): Similar to the previous comment. This statement is overly absolute in drawing conclusions based on the simulation results.
- 6) While this study is theoretical, the authors might acknowledge recent experimental advances in synthesizing amorphous carbon materials via CVD. Citing recent reports [e.g., ACS Nano 17, 24468, 2023; Chin. Phys. Lett. 40, 056101, 2023; Adv. Funct. Mater. 2424751, 2025; RSC Adv. 14, 17032, 2024] would strengthen the link between the simulations and practical experiments. This would emphasize the real-world significance of the observed amorphous carbon structures and suggest potential applications for the identified structural motifs.

Reviewer #3

(Remarks to the Author)

This manuscript employs large-scale machine-learned molecular dynamics simulations to uncover the hidden topological order in amorphous carbon by mapping the temperature–density phase diagram. It highlights the critical role of temperature in the transformation pathways of amorphous carbon. The study is well-organized, clearly written, and provides convincing evidence supporting its conclusions. However, I have the following comments and suggestions that should be addressed before publication:

- The authors developed a new machine-learned potential for disordered carbon in this work. However, several MLIPs for amorphous carbon already exist in the literature (e.g., Wang et al., Phys. Rev. B, 2025, 111, 9). As far as I know, the NEP potential developed by Wang et al. is also capable of reproducing most of the structural features reported here. It is recommended that the authors clearly discuss the advantages of their NEP over the existing potential by Wang et al., and justify the necessity of developing a new potential.
- The manuscript discusses the pore size distribution and N-membered rings of the disordered graphene network (DGN). However, a more relevant and direct comparison would be with the work of Wang et al. (Chem. Mater., 34, 617–628, 2022), which provides detailed analysis of such properties in amorphous carbon.
- In line 62, the authors claim that the empirical EDIP potential fails to predict experimentally observed sp^3/sp^2 ratios. However, according to my knowledge and the findings of Zhang et al. (Sci. Adv., 11, eadx5007, 2025), EDIP performs reasonably well and even comparable to machine-learned potentials in describing the structural characteristics of amorphous carbon. The authors should revisit this statement and provide a more balanced discussion supported by up-to-date references.
- Minor corrections and typos:
 - 1) A redundant full stop appears in line 61 of the Introduction and should be removed.
 - 2) In Fig. 2, panel (i), the term "Nano-polycrystalline (NPD)" is misspelled and needs correction.
 - 3) The reference to Fig. 4C in line 268 appears to be incorrect and should likely refer to Fig. 4b. Please check and correct this reference.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The author has provided a very satisfactory response to the questions, and the manuscript is recommended to be published in its current form.

Reviewer #2

(Remarks to the Author)

I have reviewed the revised manuscript entitled "Temperature-density dependent hidden order of amorphous carbon" along with the authors' responses to the previous round of comments. I would like to express my appreciation to the authors for their comprehensive and thoughtful revisions, which have addressed all my earlier concerns in a satisfactory manner. The additional analyses provided have substantially strengthened the manuscript and enhanced its scientific arguments. The manuscript now presents a clear, robust, and compelling study that fulfills the high publication standards of Communications Physics. I am fully satisfied with its current form and recommend its acceptance.

Reviewer #3

(Remarks to the Author)

The issues I raised have been satisfactorily resolved by the authors. and I agree that the revised version is suitable for publication.

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Each of the raised questions and comments (*quoted in italic*) is addressed below. For those responses requiring manuscript revisions, the relevant changes have been provided in **red text**.

Comments and Author reply

Reviewer Comments:

Reviewer 1 (Remarks to the Author):

Comments: *In this manuscript, the authors reported the temperature-density dependent hidden order in amorphous carbons, constructing a temperature-density phase diagram that revealed the hidden order obscured by structural disorder. The temperature was unveiled as an independent topological order parameter to play a critical role in governing the phase transitions in amorphous carbons, in addition to density. Two representative phase transition pathways and the pressure-controlled nucleation of diamond were further uncovered. The manuscript offers a good theoretical perspective on the hidden order and microstructural features of amorphous carbon, which is recommended for publication after minor revisions.*

Response: We sincerely thank the reviewer for carefully reviewing our work and for providing a positive view of our work.

Comment 1.1: *This study investigated the microstructures of amorphous carbons across a wide range of density, from ~ 0.5 to ~ 3.5 g/cm³. However, Fig. 1e contains only the sp³ fraction of the high density structures ranging from 3.0 to 3.5 g/cm³. The sp³ fraction of other densities is recommend to be included in the manuscript.*

Response: We sincerely thank the reviewer for this valuable suggestion. We have incorporated the sp³ fractions of amorphous carbon structures across the full density range from 0.5 to 3.0 g·cm⁻³, as recommended. The updated results are now presented in the revised Fig. 1e (also marked as Fig. R1 in the response letter), which demonstrate good agreement between our NEP predictions and experimental values, thereby supporting the high fidelity of the developed potential. We also found that EDIP performs well in reproducing experimental and DFT results at higher densities, which is consistent with the

recent study by Zhang et al¹. Although EDIP is capable of capturing the sp^3 fraction, its lack of long-range van der Waals (vdW) interactions and insufficient penalization of isolated sp^2 bonds have been previously shown to limit its accuracy in simulating low-density carbon structures²⁻⁴. Additionally, we have updated the main text accordingly and added relevant references in the revised manuscript.

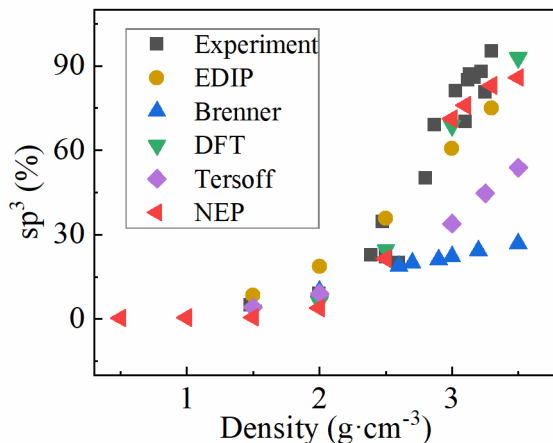


Fig. R1. Comparison of sp^3 content in amorphous carbon prepared by different methods.

The relevant modifications to the main text are as follows:

“Fig. 1e presents a comparative analysis of the sp^3 fraction of amorphous carbon across a wide density range (0.5–3.5 g·cm⁻³), as predicted by the NEP potential at 2000 K. These results are benchmarked against both experimental data and theoretical predictions from DFT and classical empirical potentials such as EDIP, Tersoff, and Brenner. The NEP predictions exhibit excellent agreement with experimental measurements and DFT calculations, accurately capturing the increase in sp^3 content with density. In contrast, in addition to the EDIP potential, other traditional empirical potentials substantially underestimate the sp^3 fraction, especially in the high-density regime. Although the EDIP potential exhibits limitations in describing long-range vdWs interactions and isolated sp^2 bonds, its capability in representing sp^3 bonding is comparable to that obtained from experiments and DFT calculations, which is consistent with recent literature report. This comparison highlights the accuracy of the NEP potential in simulating the structural evolution of amorphous carbon during annealing.” (Page 5, line 122-134)

Comment 1.2: On page 7, the authors mentioned that traditional empirical potentials (such as

EDIP) have previously failed to reproduce Diaphite in simulations. However, EDIP has shown good capability to describe the mixed-hybrid microstructures and complex phase interfaces of a-DGs and Diaphite (Natl. Sci. Rev. 11, nwae051 (2024); ACS Nano 18, 34312 (2024); Sci. Adv. 11, eadx5007 (2025)). The relevant discussion should be corrected.

Response: We thank the reviewer for pointing out this detail. After carefully reading the literature provided by the reviewer, we fully agree with the reviewer's opinion. Therefore, we have revised the discussion of this detail in the manuscript and added relevant literature citations. The revisions to the manuscript are as follows:

“Notably, traditional empirical potentials such as EDIP have recently been successfully applied to describe mixed-hybrid microstructures and complex phase interfaces involving Diaphite, as demonstrated in recent studies. The NEP developed in this study also successfully reproduces this experimentally observed Diaphite structure. This result confirms the capability of the present NEP to accurately describe this complex carbon phase.” (Page 8, line 196-201)

Comment 1.3: *Current manuscript lacks a clear description of the differences between a-DG and Diaphite in Fig. 2. In previous studies, Diaphite is mainly divided into two types according to their distinct phase interfaces (Nano Lett. 20, 3611 (2020)). The authors are recommended to add more discussion to define their simulated structures and distinguish their differences and correlations between existing studies.*

Response: We thank the reviewer for this insightful question. To clarify the differences between a-DG and Diaphite, we analyzed the structures obtained from annealing amorphous carbon with a density of $3.1 \text{ g}\cdot\text{cm}^{-3}$ at different temperatures. At 2700 K, the structure exhibits a mixed phase of amorphous diamond and multilayer graphene (a-DG), as shown in Fig. R2a. At a higher temperature of 3600 K, the structure transforms into a mixture of crystalline diamond and multilayer graphene (Diaphite), as illustrated in Fig R2b. Both structures exhibit distinct phase-separated interfaces.

Furthermore, atomic coordination coloring (yellow for sp^3 and dark purple for sp^2) in Figs. R2c and R2d reveals that the primary difference lies in **whether the sp^3 -hybridized**

carbon atoms form extensive crystalline diamond domains. As the reviewer mentioned, previous studies have reported both a-DG and Diaphite structures⁵. We have added the following discussion to the revised manuscript to elaborate on their differences and correlations:

“In previous simulation studies, Zhu et al. discovered a-DG structures via MD simulations, revealing that they consist of disordered diamond-like regions mixed with graphene layers, where the local graphitic structure imparts medium-range order. They also identified a-DG as an intermediate state during the transformation from compressed multilayer graphene to diamond. Garvie et al. observed Diaphite structures in meteorites using HRTEM, showing they consist of few-layer graphene domains embedded within crystalline diamond, with topological correspondence at the interfaces. Nemeth et al. further proposed a classification framework for this new class of hybrid materials. Both a-DG and Diaphite are hybrid structures consisting of layered sp^2 and bonded sp^3 carbon domains, distinguished primarily by whether the sp^3 -hybridized atoms form well-ordered crystalline diamond.” (Page 8, line 186-196)

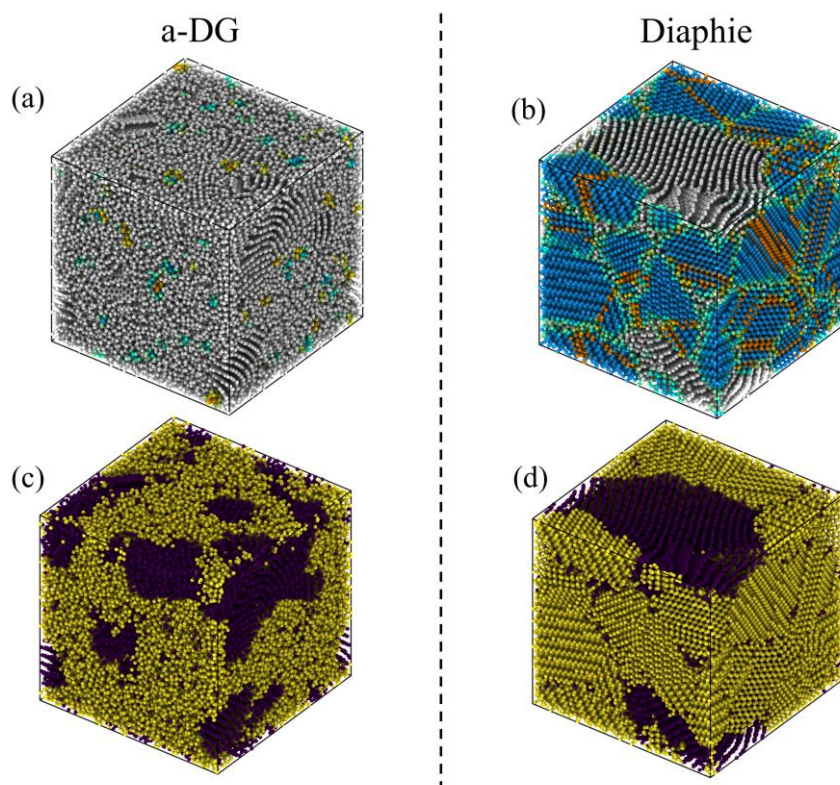


Fig R2. Structures formed by annealing amorphous carbon with a density of $3.1 \text{ g}\cdot\text{cm}^{-3}$ at different

temperatures. Panels (a) and (c) show the a-DG structure obtained at 2700 K, while panels (b) and (d) show the Diaphite structure formed at 3600 K. In (a) and (b), atoms are colored using the “Identify Diamond Structure” modifier in OVITO: blue and orange represent atoms in cubic and hexagonal diamond, respectively (see Fig. S4 in the Supplementary Material for detailed color definitions). Panels (c) and (d) correspond to (a) and (b), respectively, but colored by atomic coordination number: yellow denotes sp^3 -hybridized carbon atoms with fourfold coordination, and dark purple indicates sp^2 -hybridized atoms with threefold coordination.

Comment 1.4: *At sufficiently high temperatures and densities, the diamond nuclei with various orientations continue to grow and eventually evolve into NPD. The similar temperature-dependent nucleation and growth of paracrystalline diamond grains was also mention in previous study (Nano Lett. 24, 312 (2024)). How does the authors define the difference between p-D and NPD? Are there clear boundaries, such as crystalline atom proportions, to distinguish these structures?*

Response: We thank the reviewer for in-depth attention to this issue. The structural differences between paracrystalline diamond (p-D) and nanopolycrystalline diamond (NPD) are indeed significant.

From a structural perspective, p-D consists of nanoscale, diamond-like clusters (including both cubic and hexagonal motifs) embedded in an amorphous carbon matrix, lacking long-range periodicity. In contrast, NPD is composed of larger, well-defined diamond grains that exhibit clear long-range order. This difference is visually demonstrated in the microstructural comparison shown in Fig. R3. Experimentally, the first synthesis of p-D was achieved by applying high temperature and high pressure to a C_{60} precursor⁶. In practice, several methods—such as analysis of the structure factor and XRD profiles—have proven effective in distinguishing p-D from NPD^{6, 7}. Both approaches are adopted in our work and illustrated in Fig. 3 of the main text. Furthermore, as the reviewer mentioned, the recent study by Zhang et al.⁸ reported the temperature-dependent growth of p-D grains. This groundbreaking work suggests that p-D and NPD correspond to distinct local minima on the free energy surface, separated by a substantial energy barrier, indicating that they are thermodynamically distinct phases.

Regarding whether a quantitative boundary can be defined based on the proportion of crystalline atoms, to the best of our knowledge, no consensus or well-defined threshold has been established in the current literature. We consider it insufficiently rigorous to differentiate these two structures solely on the basis of crystalline atom fraction. Instead, employing structural descriptors such as XRD patterns, structure factor analysis, and thermodynamic free energy landscapes offers a more robust and physically meaningful means of distinction.

We have made the relevant corrections in the main text:

“It is worth noting that p-D and NPD exhibit clear structural differences. Structurally, p-D consists of small-grained containing both cubic and hexagonal motifs, which are randomly embedded within an amorphous matrix. In contrast, NPD is composed of larger crystalline grains that exhibit well-defined long-range structural coherence.” (Page 9, Line 207-211)

“The p-D domains exhibit significant lattice distortion relative to ideal diamond structures, with the degree of deformation comparable to that observed in grain boundary atoms of ultrafine NPD.” (Page 10, Line 221-223)

“In addition to calculating XRD curves and structural factors, recent studies have also been able to distinguish between p-D and NPD by calculating the free energy surface.” (Page 11 Line 256-258)

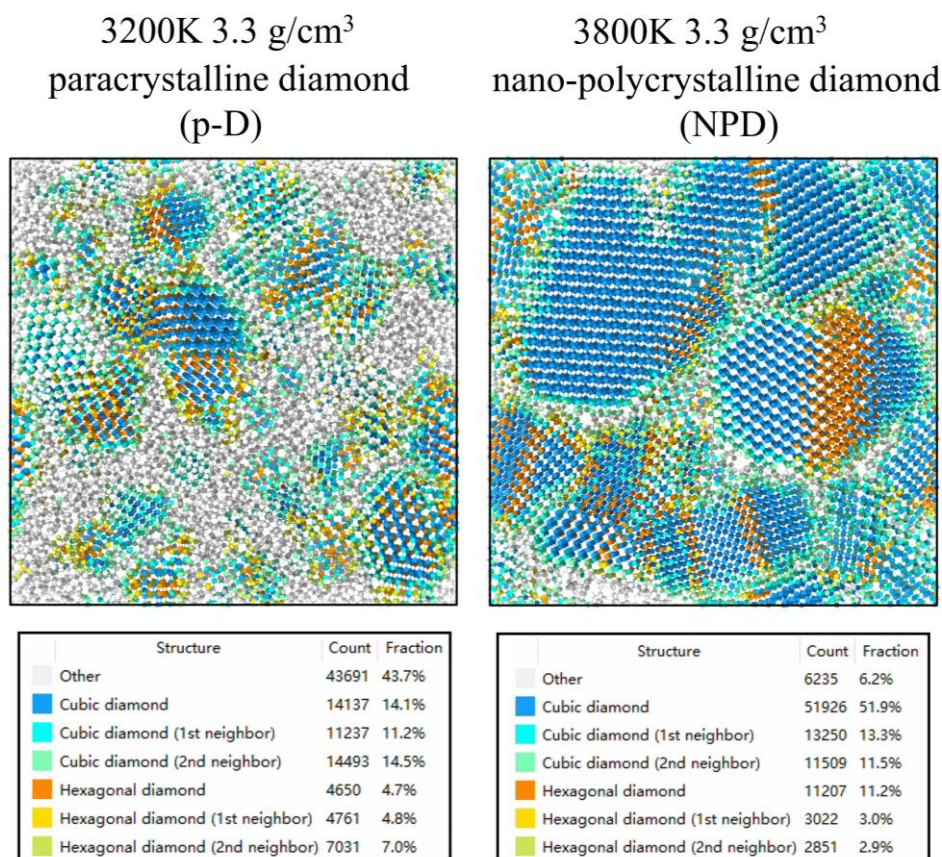


Fig. R3. Comparison of the microstructures of p-D and NPD. An 8 Å-thick sliced slab model is employed for visualization and statistical analysis of atomic species using the OVITO software⁹.

Reviewer #2 (Remarks to the Author):

Comments: *The paper investigates the hidden topological order of amorphous carbon (a-C) by employing machine learning-based NEP and large-scale MD simulations. The study explored the annealing process of a-C under varying temperatures and densities, identifying nine representative structures. By constructing a temperature-density phase diagram, the authors revealed two topological phase boundaries with discontinuous structural transitions, and the critical temperature increases approximately linearly with density. The reviewer finds this work interesting and recognizes it as a piece of timely work. Here are some suggestions and comments.*

Response: We thank the reviewer for the positive feedback and thoughtful suggestions that helped improve the manuscript, and for devoting considerable time and effort to reviewing

our work.

Comment 2.1: *Line 60: There appears to be a punctuation error: the sentence ends with both a period and a comma.*

Response: We thank the reviewer for pointing out the punctuation error. We have removed the period in the revised manuscript. For details, please refer to the manuscript (Page 3, Line 59).

Comment 2.2: *Line 169 (around "The formation mechanism of a-G..."): The current explanation focuses on the role of temperature in overcoming kinetic barriers. While this addresses the kinetic aspect, it would be helpful to explain why the system preferentially evolves along the a-G pathway rather than toward other amorphous or crystalline structures. In other words, what makes the a-G configuration energetically or structurally favorable under the simulated conditions?*

Response: We thank the reviewer for the insightful comment. Under the current simulation conditions, the system preferentially evolves into an a-G structure rather than other amorphous or crystalline structures. Our observations suggest that this behavior arises from a combination of thermodynamic stability, kinetic pathways, and density-related constraints.

(1) From a thermodynamic perspective, under standard atmospheric pressure, the sp^2 -hybridized graphite structure represents the global minimum energy phase of carbon¹⁰, with a standard formation enthalpy of zero and a standard molar entropy of 5.740 J/(K·mol). In contrast, diamond has a higher formation enthalpy of 1.895 kJ/mol and a lower standard molar entropy of 2.377 J/(K·mol)¹¹.

(2) From a kinetic standpoint, high-temperature conditions significantly enhance the entropy-driven effect of the sp^2 network, enabling the sp^2 network dominated by hexagonal carbon rings to more easily overcome local energy barriers and expand into larger ordered structural domains¹².

(3) The applied density range of 2.0–2.9 g·cm⁻³ also plays a crucial role in guiding the structural evolution. On one hand, it provides an ideal interlayer spacing (~3.0–3.4 Å)

that supports van der Waals stabilization between adjacent layers; on the other hand, it suppresses the nucleation and growth of the diamond phase. As a result, both energetic and structural constraints synergistically drive the system toward the formation of an a-G structure with graphitic character.

We have added new discussion on the formation of a-G in the main text. Please refer to the manuscript for details.

“The preferential formation of the a-G structure under our simulation conditions arises from the combined effects of thermodynamics, kinetics, and density constraints. Thermodynamically, sp^2 -hybridized graphite is the most stable carbon phase at ambient pressure, with a lower formation enthalpy and higher entropy than diamond. Kinetically, high-temperature conditions significantly enhance the entropy-driven effect of the sp^2 network, enabling the sp^2 network dominated by hexagonal carbon rings to more easily overcome local energy barriers and expand into larger ordered structural domains. Additionally, the applied density range ($2.0\text{--}2.9\text{ g}\cdot\text{cm}^{-3}$) provides favorable interlayer spacing for van der Waals interactions while suppressing diamond nucleation. These factors drive the system toward forming a-G with graphitic features.” (Page 13, Line 284-293)

Comment 2.3: *Line 271 (regarding the statement "It is expected that more precise physical parameters..."): While it is reasonable to acknowledge the limitations of current structural descriptors, the statement would benefit from more concrete suggestions on how these limitations might be addressed in future studies. For example, proposing potential computational or experimental strategies to refine structural classification (e.g., using machine-learned order parameters, localized electronic descriptors, or topological invariants) would make the discussion more insightful and forward-looking.*

Response: We sincerely thank the reviewer for the valuable comment. In the revised manuscript, we have expanded the sentence to propose several potential computational and experimental strategies, such as the use of machine-learned structural order parameters, local electronic structure descriptors, and topological invariants. These approaches may help to better classify and distinguish various types of amorphous carbon structures, and to

refine the phase diagram accordingly.

“It is expected that more precise physical parameters will be proposed in future studies to distinguish between the nine types of amorphous carbon structures and to achieve a more accurate description of the phase diagram. Possible strategies include the development of machine-learned structural order parameters trained on local atomic environments, the use of localized electronic structure descriptors, and topological invariants derived from ring statistics or Voronoi-based tessellation. These methods may provide higher sensitivity to subtle local differences and thus enhance structural classification accuracy.” (Page 14, Line 313-320)

Comment 2.4: *Line 279: The statement that “temperature acts as a topological order parameter independent of density” appears overly definitive. Since this conclusion is drawn from simulations under specific models and approximations, it should be presented more cautiously. A better phrasing would describe this finding as an observed computational trend or model-specific behavior, rather than asserting it as a universal physical principle. Softening this claim would improve scientific rigor and avoid overinterpretation of the results.*

Response: We sincerely appreciate the reviewer’s insightful comment. The original statement may appear overly definitive and could be misinterpreted as a universally valid conclusion beyond the scope of the employed simulation model. In response, we have revised the sentence to present the observation more cautiously, emphasizing that it reflects a computational trend observed in our simulation model. We also acknowledge the model-specific nature of this finding and avoid overgeneralization by softening the tone in the revised manuscript. The changes to the main text are as follows:

“This indicates that, within our simulation, temperature acts as a topological order parameter largely independent of density. This model-specific finding contrasts with conventional density-driven phase transition mechanisms and underscores the significant role of thermal effects in the local structural evolution of amorphous carbon.” (Page 14, Line 324-328)

Comment 2.5: *Line 385 (regarding the statement "temperature serves as a topological order parameter 386 independent of density..."): Similar to the previous comment. This statement is overly absolute in drawing conclusions based on the simulation results.*

Response: Thank you for the helpful comment. The sentence has been revised to present the conclusion more cautiously, emphasizing that the observation is based on our simulation model and does not claim universal applicability. We now describe the result as a model-specific trend that may provide new insight into the role of temperature in topological transitions, while avoiding overinterpretation.

“A model-specific trend in which temperature appears to act as a topological order parameter largely decoupled from density, suggesting a potential deviation from the traditionally held view that phase transitions are primarily driven by density;” (Page 19, Line 436-438)

Comment 2.6: *While this study is theoretical, the authors might acknowledge recent experimental advances in synthesizing amorphous carbon materials via CVD. Citing recent reports [e.g., ACS Nano 17, 24468, 2023; Chin. Phys. Lett. 40, 056101, 2023; Adv. Funct. Mater. 2424751, 2025; RSC Adv. 14, 17032, 2024] would strengthen the link between the simulations and practical experiments. This would emphasize the real-world significance of the observed amorphous carbon structures and suggest potential applications for the identified structural motifs.*

Response: We sincerely thank the reviewer for this valuable suggestion. The recommended experimental studies represent important and timely advances in the synthesis of amorphous carbon materials via CVD, and they greatly help bridge the gap between theoretical modeling and practical realization. We have now cited these key references at appropriate locations in the manuscript to better highlight the relevance of our simulated structures to experimental observations and potential applications. Please refer to the revised manuscript for details.

“Their research team developed a bottom-up atom-by-atom atomic manufacturing

technology based on the CVD method, achieving a pioneering approach to controlling physical properties through disorder^{9, 10}.” (Page 2, Line 41-43)

“These different amorphous carbon structures suggest that it may be possible in the future to regulate their microstructure for use in semiconductor information devices, silicon-based integrated circuits, gas sensors, and other applications^{61,62}.” (Page 11, Line 263-265)

Reviewer #3 (Remarks to the Author):

Comments: *This manuscript employs large-scale machine-learned molecular dynamics simulations to uncover the hidden topological order in amorphous carbon by mapping the temperature–density phase diagram. It highlights the critical role of temperature in the transformation pathways of amorphous carbon. The study is well-organized, clearly written, and provides convincing evidence supporting its conclusions. However, I have the following comments and suggestions that should be addressed before publication:*

Response: We sincerely thank the reviewer for the positive and constructive comments.

Comment 3.1: *The authors developed a new machine-learned potential for disordered carbon in this work. However, several MLIPs for amorphous carbon already exist in the literature (e.g., Wang et al., Phys. Rev. B, 2025, 111, 9). As far as I know, the NEP potential developed by Wang et al. is also capable of reproducing most of the structural features reported here. It is recommended that the authors clearly discuss the advantages of their NEP over the existing potential by Wang et al., and justify the necessity of developing a new potential.*

Response: We sincerely appreciate the reviewer’s valuable comments. We fully acknowledge the excellent performance of the NEP potential developed by Wang et al.¹³ (hereafter referred to as NEP-Wang) in modeling porous and amorphous carbon systems. Through systematic comparison, we believe that the NEP potential developed in the present work exhibits significant distinctions and necessity in the following two aspects:

1. The NEP-Wang potential is built upon the amorphous carbon GAP model (GAP17) proposed by Deringer et al.¹⁴, incorporating bilayer graphene, low-density nanoporous carbon (NP-C), and glassy carbon configurations into its training dataset. In contrast, our

proposed NEP potential is based on the more general carbon potential GAP20 developed by Rowe et al.¹⁵, and innovatively includes structural data obtained through long-time annealing using both AIMD and classical MD simulations across a wide density range (1.5–3.5 g·cm⁻³). This design emphasizes capturing the structural evolution of amorphous carbon under specific density and temperature conditions. A detailed comparison is provided in Table R1. While NEP-Wang demonstrates superior performance in describing highly disordered structures such as porous carbon, our study targets systems that include both amorphous and partially crystalline phases, making our training dataset more tailored to the intended simulation applications.

2. The NEP potential developed in this work is not intended as a universal model covering the entire configurational space of carbon materials, but rather is specifically designed for simulating the long-timescale annealing evolution of carbon structures under varying density conditions. Although its applicability is narrower than that of NEP-Wang—e.g., it does not extend to properties such as thermal conductivity—it achieves higher structural fidelity in the targeted task. As shown in Table R1, the training accuracy of our NEP model is slightly superior to that of NEP-Wang. While both models exhibit comparable fitting performance in terms of energy and force, our model yields a lower force RMSE for the training structures, indicating a potentially better approximation of the DFT-calculated results when applied to large-scale MD simulations for structural modeling.

In summary, we believe that developing a task-specific NEP potential tailored for carbon annealing, based on existing models, not only carries clear physical significance but also provides a valuable tool for investigating the thermodynamic and kinetic evolution mechanisms of amorphous carbon structures.

Table R1 Comparison between NEP-Wang and the NEP proposed in this work across different aspects.

	NEP-Wang	NEP (This paper)
	GAP-17	GAP-20
Composition of the dataset	bilayer graphene	Structures obtained via AIMD annealing at varying densities
	low-density NP-C	Structures obtained via EDIP annealing

	Glassy carbon	in LAMMPS at varying densities Carbon dimers, as well as perturbed structures of graphite and diamond
Number of structures	7187	7889
RMSE of energy (eV/atom)	45	49.02
RMSE of force(eV/Å)	732	565.5
RMSE of virial(eV/Å)	106	107.29

The main text already includes a comparison with the NEP potential proposed by Wang et al. For details, please refer to the manuscript. (Page 4, Line 108-109)

Comment 3.2: *The manuscript discusses the pore size distribution and N-membered rings of the disordered graphene network (DGN). However, a more relevant and direct comparison would be with the work of Wang et al. (Chem. Mater., 34, 617–628, 2022), which provides detailed analysis of such properties in amorphous carbon.*

Response: We thank the reviewer for this valuable suggestion. We have carefully reviewed the work of Wang et al. (Chem. Mater. 34, 617–628, 2022), which provides a comprehensive analysis of structural features, pore size distributions, and elastic properties of nanoporous carbon over a density range of 0.5–1.7 g·cm⁻³. Their findings show strong relevance to our study, particularly in the following aspects:

1. At low densities, the carbon network exhibits large open pores. As the density increases, the pore size decreases while the number of pores increases. At higher densities, graphene fragments begin to stack locally, leading to the formation of elongated channel-like pores between stacked layers.
2. In terms of ring statistics, the structure exhibits a high degree of graphitization, characterized by a dominant population of six-membered rings, followed by fewer five- and seven-membered rings—indicative of a well-organized sp² network.

We have incorporated a comparison with this work into the revised manuscript in the discussion of the disordered graphene network (DGN).

“Similar features have been reported by Wang et al., who showed that increasing density in nanoporous carbon leads to smaller, more numerous pores and the formation of elongated voids between stacked graphene fragments. Their ring statistics also revealed a six-membered ring–dominated topology, consistent with the highly graphitized sp^2 network observed in our DGN structures.” (Page 7, Line 154-158)

Comment 3.3: *In line 62, the authors claim that the empirical EDIP potential fails to predict experimentally observed sp^3/sp^2 ratios. However, according to my knowledge and the findings of Zhang et al. (Sci. Adv., 11, eadx5007, 2025), EDIP performs reasonably well and even comparable to machine-learned potentials in describing the structural characteristics of amorphous carbon. The authors should revisit this statement and provide a more balanced discussion supported by up-to-date references.*

Response: We thank the reviewer for pointing out the inappropriate description in our manuscript. We acknowledge that the work by Zhang et al.¹ demonstrated good agreement between the EDIP and the NEP machine learning potential in terms of the predicted sp^3 content in amorphous carbon structures. As shown in their comparison (particularly at densities between 2.3 and 3.2 g·cm⁻³), the sp^3 fractions predicted by EDIP and NEP are indeed consistent, which is also confirmed in our own simulation results (see Fig. 1e of the revised manuscript).

However, it is worth noting that the NEP potential used in Zhang et al.’s study was originally developed by Song et al.¹⁶ for a 16-element metallic alloy system (Ag, Al, Au, Cr, Cu, Mg, Mo, Ni, Pb, Pd, Pt, Ta, Ti, V, W, Zr). This potential is primarily trained for metallic alloys and their compounds, and does not include carbon in its fitting set. This raises some uncertainty about whether the referenced NEP model is appropriate for direct comparison with EDIP potential. It is possible that the authors referred to a different NEP potential, though we are currently unable to determine which specific version was used.

Our original claim that EDIP fails to reproduce the experimentally observed sp^3/sp^2 ratios was primarily based on the findings from two prior studies by Miguel A. Caro and co-authors^{17, 18}. In those works, the authors investigated carbon film growth under high-energy deposition conditions, and found that EDIP failed to capture the pressure-induced

densification mechanism responsible for high sp^3 content. The sp^3 fractions predicted by EDIP in those simulations rarely exceeded 60%, while experimental measurements often report values above 85% for tetrahedral amorphous carbon¹⁸.

We fully recognize that EDIP remains one of the most robust and well-tested empirical potentials for carbon systems. In many regimes, especially at moderate to high densities, it produces reasonable structural predictions, including relatively good estimates of sp^3 content. However, its limitations must also be acknowledged:

1. Lack of long-range Van der Waals (vdW) interactions: EDIP does not include an explicit vdW attractive term between graphene layers^{3,4}. Its long-range interaction extends only to ~ 3.2 Å due to a π -repulsion term. In annealing simulations of low-density amorphous carbon, this results in abnormally large interlayer spacings driven solely by volume constraints. For instance, at $1.5 \text{ g}\cdot\text{cm}^{-3}$, the predicted 002 diffraction peak occurs at $s = 0.22 \text{ Å}^{-1}$ (corresponding to a d-spacing of ~ 4.5 Å), which is significantly larger than the experimental graphite value of 3.35 Å^2 .

2. Lack of energy penalty for isolated sp^2 bonds: The bond-order formulation in EDIP is atom-centered and does not penalize energetically unfavorable, isolated sp^2 hybridizations (such as non-conjugated double bonds)². This can affect the local bonding network, especially in defect-rich or edge regions.

Therefore, we believe that even if EDIP can accurately predict the ratio of sp^3/sp^2 , it is still inaccurate in describing the carbon structure at low densities. We have revised the manuscript accordingly to reflect this more balanced view.

“Despite its ability to reproduce sp^3/sp^2 ratios under certain conditions, EDIP fails to accurately predict low-density structures due to missing long-range van der Waals (vdW) interactions and insufficient penalization of isolated sp^2 bonds.” (Page 3, Line 61-63)

Comment 3.4: *Minor corrections and typos: 1) A redundant full stop appears in line 61 of the Introduction and should be removed. 2) In Fig. 2, panel (i), the term "Nano-polycrystalline (NPD)" is misspelled and needs correction. 3) The reference to Fig. 4C in line 268 appears to be incorrect and should likely refer to Fig. 4b. Please check and correct this reference.*

Response: We thank the reviewer for carefully identifying these minor errors. We have

made the following corrections accordingly: 1) The redundant full stop in **line 59** has been removed. 2) The term “Nano-polycrystalline (NPD)” in Fig. 2(i) has been corrected to “**Nano-polycrystalline diamond (NPD)**”. 3) The incorrect reference to Fig. 4c in line 268 has been revised to **Fig. 4b**. In addition, we checked the entire text to avoid such spelling errors.

Reference

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