Finite-temperature stability of hydrocarbons: fullerenes versus flakes

Ariel Francis Perez-Mellor,1,a) Pascal Parneix,1 Florent Calvo,2 and Cyril Falvo1,2,b)  
1) Institut des Sciences Moléculaires d’Orsay (ISMO), CNRS, Université Paris Saclay, 91405 Orsay, France  
2) Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France

The effects of a finite temperature on the equilibrium structures of hydrocarbon molecules are computationally explored as a function of size and relative chemical composition in hydrogen and carbon. Using parallel tempering Monte Carlo simulations employing a reactive force field, we find that in addition to the phases already known for pure carbon, namely cages, flakes, rings and branched structures, strong effects due to temperature and the addition of little amounts of hydrogen are reported. Both entropy and the addition of moderate amounts of hydrogen favor planar structures such as nanoribbons over fullerenes. Accurate phase diagrams are proposed, highlighting the possible presence of multiple phase changes at finite size and composition. Astrophysical implications are also discussed.

I. INTRODUCTION

Carbon systems from small clusters to bulk matter exhibit a large variety of structures and properties due to the ability of carbon to form single, double and triple bonds. In the solid state, carbon is present as graphite and diamond, but can also be amorphous or even porous, making it useful for separation or energy conversion purposes. Carbon also drives a huge interest as the key to advanced low-dimensional materials such as nanotubes or graphene. Despite being the focus of extensive research for many decades,2–6 many properties of carbon systems remain poorly understood. This is particularly true for carbon systems under extreme conditions such as clusters in the gas phase,7 or liquid carbon.8

In the dilute limit, carbon clusters and hydrocarbon molecules play an important role in astrochemistry. For example, the presence of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM) was suggested nearly forty years ago through the observation of the so-called aromatic infrared bands (AIB).9,10 In addition, a variety of pure carbon clusters have now been conclusively observed in the ISM, ranging from small carbon chains,11–13 up to C60 and C70 fullerenes.14,15 However, a much larger variety of hydrocarbon systems is expected to be present under astrophysical conditions, and contribute to different spectral features of the ISM, such as the diffuse interstellar bands (DIB) and the ultraviolet (UV) bump, as well as the AIBs themselves.16–18

The allotropy of carbon conveys to the nanoscale, as pure carbon clusters display a large variety of structures and can be found as chains, rings, flakes (mostly planar, aromatic structures) and cages (which include fullerenes)2,12,13 Quite a number of theoretical studies using different potential energy surfaces have focused on low-energy structures, typically explored as a function of the number of carbon and hydrogen atoms.2,24 While these studies generally highlighted the dependence of the results on the specific energy model, they all concluded that for small pure carbon clusters ($N_C \lesssim 8$) the lowest isomers are linear chains, followed by rings ($8 \lesssim N_C \lesssim 16$), flakes ($16 \lesssim N_C \lesssim 24$), and fullerenes ($N \gtrsim 24$). Additional hydrogen atoms strongly alter the stability of these structures.25 In particular, it is expected that fullerenes, which are the most stable structures for large clusters, become less stable as hydrogen atoms are added. Conversely, flakes structures (which includes the PAH family) should become edge stabilized by hydrogenation much more conveniently than fullerenes.

Besides structural investigations, only a few studies were aimed at including the effects of a finite temperature or excess energy on isolated hydrocarbon compounds.39–41 In their seminal computational study, Kim and Tománek42 showed using a tight-binding model that fullerenes exhibit multiple phase transitions upon heating. After first losing their well-defined, highly symmetric structures forming the low-temperature solid state, a more floppy phase arises that still consists of cages but with increasing amounts of topological defects. Upon further increasing the temperature, the fullerenes undergo dramatic phase changes at 4000 K into a so-called pretzel phase corresponding to interconnected carbon rings, and eventually into multiple connected chains, until they finally dissociate at even higher temperatures. The pretzel phase transition was suggested as the equivalent of the melting phase transition in bulk carbon.43 While these temperatures are notably high for laboratory experiments, they can be reached rather easily under astrophysical conditions, even for small isolated molecules that undergo photonic excitation in the UV range: a single 10 eV photon absorbed by a 60-atom molecule is already equivalent to 700 K heating.

To a large extent, the phenomenology of fullerene melting explored by Kim and Tománek42 is consistent with the structural diversity in carbon clusters recently addressed more extensively through systematic sampling methods.43–45 However, while the importance of sp$^2$-dominated cages at low temperature or energy and sp$^3$-dominated pretzels and chains at higher temperatures could be confirmed, the phase of flakes, still sp$^2$ domi-
inatted but with a much more open character, has remained relatively overlooked. Yet flakes and graphene nanoribbons are important motifs of carbon at the nanoscale, not only for their use as building blocks for innovative materials, but also, in the astrochemical context, as possible intermediates in the formation of fullerenes themselves. Flakes and nanoribbons can be stabilized by the presence of hydrogen, acting to protect the unsaturated and peripheral carbon atoms that are specific to this rather open phase. In view of the abundance of hydrogen in the Universe, it is also essential to determine its effects on the thermodynamics of dilute carbon matter, and how the combined influences of temperature, cluster size, and relative amount of hydrogen affect the preferred structures. Our goal in this article is to bridge this gap with our current understanding that is mostly limited to pure carbon, by means of atomistic modeling that includes exhaustive sampling methods and a reactive potential relevant for hydrocarbon compounds. In particular, by designing appropriate order parameters, we are able to delineate the stability conditions of cages, pretzels and chains, but also of the elusive flakes, through entire finite size phase diagrams.

II. THEORETICAL METHODS

Carbon clusters are characterized by a highly rugged energy landscape whose exploration requires efficient computational approaches. In this work, we use the well-established parallel tempering Monte Carlo (PTMC) method in the canonical ensemble. To prevent irreversible dissociation that is likely to occur at high enough temperatures, we further impose a connectivity criterion to the structures sampled during the Monte Carlo process, rejecting disconnected configurations. Here, simple distance criteria were used to define connectivity, with $d_{CC} = 3 \, \text{Å}$ for carbon-carbon distances and $d_{CH} = d_{HH} = 2 \, \text{Å}$ for distances involving hydrogen atoms. These values were chosen significantly larger than typical chemical bond distances in such a way that bond breaking and formation are still allowed, while also avoiding irreversible dissociation. As a result, at high temperatures, the presence of dissociated structures is expected, but with fragments that remain close to each other. This also provides a means of quantifying the stability of the fully connected structures.

Following our earlier work, we use the second-generation reactive empirical bond order (REBO) potential to describe atomic interactions between carbon and hydrogen atoms in the clusters. This reactive force field was originally designed to describe the energetic properties of isolated hydrocarbon molecules as well as various carbon materials in condensed phases. In particular, it has been used to describe the lowest-energy structures of carbon clusters with good agreement with respect to other methods that explicitly account for electronic structure, such as the density-functional-based tight-binding (DFTB) method.

PTMC simulations were performed for 12 different pure carbon clusters with sizes in the range of 20–80 atoms. Hydrogenated clusters were also studied for specific amounts of carbon, namely 28 or 60 carbon atoms and 0–12 or 0–20 hydrogen atoms, respectively. For all systems, the PTMC simulations employed a total of 28 or 32 replicas with temperatures allocated according to a geometric progression, additional temperatures being inserted around the main melting phase change to further enhance sampling. The complete numerical details of the PTMC simulations are provided as Supplementary Information. The raw data from the PTMC simulations were then processed using a version of the weighted histogram analysis method based on an implementation from Poteau et al. to yield the various properties of interest as a continuous function of temperature.

To interpret the thermodynamical observables and connect their features to the underlying structural properties of the clusters, and also to merely assign the phases themselves, a number of order parameters were employed. Following previous works, the shape of the clusters is characterized using three rotationally invariant parameters derived from the successive moments of the gyration tensor, namely the gyration radius $R_g$, the asphericity $A_3$ and the prolateness $S$ of the atomic distribution. Altogether, these quantities, fully explicit in the Supplementary Information, measure the geometrical extension, the similarity to a sphere, a disk, or a chain. In addition to providing insight into the geometrical extension of the system for a given size, the gyration radius is also naturally expected to be particularly sensitive to size itself. In two-dimensional flakes, but also in hollow (single shell) cages, $R_g$ should scale with the number of carbon atoms $N_C$ as $\sqrt{N_C}$. A similar scaling is expected for branched structures according to polymers theory. To better compare $R_g$ across system sizes, we thus employ a scaled gyration radius $\tilde{R}_g = R_g/\sqrt{N_C}$. For hydrogen-containing systems, and since our interest lies in the effects of hydrogen on the carbon nanostructure, hydrogen atoms are neglected when calculated the gyration tensor and the same definition is used for $\tilde{R}_g$.

In addition to their geometrical features, clusters were also characterized in terms of their chemical bonding. Here we have used simple coordination parameters as measures of hybridization of the carbon atoms, defining the fractions $\tilde{N}_\alpha = N_\alpha/N_C$ of such atoms having a fixed coordination number $\alpha = 2$ or 3. We use the definition of the atomic coordination introduced in the REBO potential itself, which for any carbon atom $i$ yields a number $N_i^C$ of nearest neighbors as

$$N_i^C = \sum_{j \neq i} f^\text{REBO}_{CC}(r_{ij}),$$

where $f^\text{REBO}_{CC}(r_{ij})$ is a smooth cutoff function acting between 1.7 Å and 2.0 Å (see Ref. 19).
FIG. 1. Temperature dependence of various properties of pure carbon clusters: (a) normalized specific heat at its maximum; (b) average scaled gyration radius; (c) average fraction of triply-coordinated carbon atoms. The specific heats curves have been shifted vertically to improve readability.

III. RESULTS

A. Pure carbon clusters

First-order finite-size phase changes are conveniently identified by sudden variations in the system energy upon increasing temperature. With increasing size, these energy variations become sharper until an abrupt discontinuity (the latent heat) is recovered in the bulk limit of the proper first-order phase transition. As a result, the specific heat, which corresponds to the derivative of the internal energy with respect to temperature, may exhibit one or several prominent peaks at the corresponding transition temperatures in finite size systems as well. Fig. 1(a) shows the specific heat as a function of temperature for the various carbon clusters, normalized at their maxima for a better comparison across sizes.

For the larger clusters $C_{60}$, $C_{70}$ and $C_{80}$ only a single peak is found at $T = 3390$ K, $T = 3580$ K and $T = 3740$ K, respectively, suggesting that these clusters experience only a single phase change. This phase change corresponds to melting, as already analyzed in Ref. 39. In $C_{60}$, the peak appears slightly asymmetric with a clear shoulder on the low-temperature side. In the smaller clusters containing 30–50 atoms, an additional peak is found in the specific heat, which becomes increasingly separated from the main peak as size decreases. Moreover, the two features shift to lower temperatures as size decreases. In $C_{34}$ and below, a third feature can be perceived at temperatures higher than the main peak, in the 3000–4000 K range, which furthermore becomes increasingly well defined as the clusters become smaller.

To assist in the interpretation of these thermal features, Figs. 1(b) and 1(c) show the temperature dependence of the average scaled radius of gyration $\tilde{R}_g$ and the proportion $\tilde{N}_3$ of triply-coordinated atoms. The three phase changes identified in the specific heat are clearly seen with these parameters. For $N_C \geq 28$, the scaled radius of gyration at low temperature is around 0.47 Å and all carbon atoms are triply coordinated. This corre-

FIG. 2. Most representative structures for various pure carbon clusters at different temperatures, as defined from distances based on the minimal set of descriptors.
sponds to cages and is consistent with the known geometry of fullerenes. For instance, buckminsterfullerene has a radius of 3.60 Å with the REBO potential, corresponding to a value of the scaled radius of gyration of 0.465 Å, a zero-temperature value that is fully consistent with the data in Fig. 1b).

From the PTMC simulations, structures were characterized based on their values of the different order parameters $R_g$, $A_3$, $S$, $N_2$ and $N_3$, which form a minimal set of descriptors for the clusters. At a given temperature, a specific structure can be retrieved from the sample as the one closest to the configuration with average values of these descriptors. Here, a simple Euclidean metric was used to define distances in descriptor space (see Supplementary Information). Several of these most representative structures are depicted in Fig. 2 for different relevant temperatures.

At low temperature, the most representative structures of C$_{28}$ and C$_{60}$, as shown in Figs. 2a and 2e), are clearly those of cages with little or no topological defect. As temperature increases and reaches the 3000–4000 K range, clusters with up to 60 carbon atoms lose their aromaticity with sharp decreases in the numbers of triply-coordinated atoms and increases in the radii of gyration. The statistical distributions of these parameters (see Fig. S2, in Supplementary Information) remain very narrow around the average at low temperature but, above the transition temperature, become much broader, particularly for the scaled radius of gyration, showing an increased structural diversity. The configurational population in this higher temperature range corresponds to branched and dissociated structures, see Figs. 2d and 2h). According to our rather loose criterion for disconnected structures (carbon-carbon distances above 3 Å), dissociated structures only become significant at temperatures above the melting range. However, at 4000 K, their proportion remains rather small, although it steadily increases above this temperature, reaching 20% and 47% at 5500 K for C$_{28}$ and C$_{60}$, respectively (see Fig. S3 in Supplementary Information). The continuous progression between branched and dissociated structures above the melting temperature indicates that, from a purely thermodynamical point of view, they can be considered to form a single broad family.

Smaller pure carbon clusters exhibit a different phenomenology, which can be inferred from the variations in the descriptors. While cages are still favored at low temperature, the substantial increase of $R_g$ towards 0.64 Å and the decrease of $N_3$ towards 0.6 indicate the predominance of flakes, which is confirmed by looking at the most representative structures such as the one obtained for C$_{28}$ at 1500 K in Fig. 2b). Returning to C$_{60}$, a closer inspection of the structural features indicates that flakes are also found as the main phase but in a rather narrow temperature range, just below the melting point (see Fig. 2g) for the most representative structure at 3390 K). This very narrow range of stability, together with different sampling methods, explain why this phase was not seen in the earlier work by Kim and Tománek especially for fullerenes larger than C$_{60}$. Yet a fourth population of structures is also visible on the variations of the scaled radius of gyration, which exhibits values between $R_g \approx 0.9$ Å and $R_g \approx 1.1$ Å for clusters containing 40 atoms or less. This population cannot be seen with the triply-coordinated atoms as they are buried within the family of branched structures. However, a direct analysis shows that this population corresponds to rings, as illustrated in Fig. 2c) for C$_{28}$ at 2500 K.

B. Effect of hydrogenation

The above results indicate that the thermodynamics of carbon clusters depends qualitatively on their size, with up to four possible phases at finite temperature. We now show that the addition of hydrogen atoms also strongly affects this thermal behavior. Fig. 3a) depicts the temperature dependence of the normalized specific heat for C$_{28}$H$_n$ clusters with $0 \leq n \leq 12$. As the hydrogen content increases, the main peak in the specific heat progressively increases from 1960 K in the pure cluster to 3450 K in C$_{28}$H$_{12}$. Conversely, the lower temperature peak marking the structural transition from cages to flakes further shifts to even lower values as more hydrogen is introduced into the system, becoming no longer discernable above $n = 3$. The broad high-temperature peak found for C$_{28}$ near 3400 K is also very sensitive to the presence of hydrogen, as it is no longer visible already for $n = 1$.

Strong effects of hydrogen on the phases and phase changes are also found for C$_{60}$, the specific heats being illustrated in Fig. 3d) for hydrogen atoms increasing in numbers from 0 to 16. The single asymmetric peak in the specific heat found for C$_{60}$ smoothly evolves with increasing hydrogen loadings, the low-temperature shoulder becoming a distinct peak that shifts from 3390 K towards lower and lower temperature, reaching 1590 K in C$_{60}$H$_{10}$, while the main melting peak slightly shifts from 3390 K in the pure carbon cluster to 3780 K in C$_{60}$H$_{16}$.

The structural features associated with the clusters underlying the thermodynamical phases are again inferred by considering the scaled radius of gyration and the fraction of triply-coordinated carbon atoms, whose variations with temperature are shown in Figs. 3b), 3c), 3e) and 3f), respectively.

Upon inspection of these quantities, both the cage and ring structures for C$_{28}$H$_n$ are found to be strongly destabilized by the addition of hydrogen, and for $n \geq 4$ only the flake and branched/dissociated structures remain, as illustrated on their most representative structures in Fig. 3. In C$_{60}$H$_n$, increasing the hydrogen loading also leads to the stabilization of the flakes to the expense of cage structures, which are even no longer found for $n \geq 12$, leaving again flakes and branched or dissociated structures as the only relevant phases. While the addition of hydrogen generally simplifies the phenomenology
FIG. 3. Temperature dependence of various properties of hydrocarbon clusters, containing 28 (left panels) or 60 (right panels) carbon atoms: (a) and (d) normalized specific heat at its maximum; (b) and (e) scaled gyration radius; (c) and (f) fraction of triply-coordinated carbon atoms. The specific heats curves have been shifted vertically to improve readability.

of melting in hydrocarbon clusters at low temperatures, it also affects the high-temperature behavior by producing greater amounts of fragments (see Fig. S3 in Supplementary Information), also with a greater chemical diversity that notably includes acetylene.

C. Phase diagrams

The results obtained from our simulations can be further processed and interpreted in terms of finite temperature phase diagrams. More precisely, and as supported by the sets of representative structures depicted in Figs. 2 and 4, we distinguish cages, flakes, branched/dissociated structures, as well as rings. The gyration radius and fraction of triply-coordinated carbon atoms suffice to assign structures from the three first families unambiguously (see Fig. S4 in Supplementary Information), but for the rings it is the fraction $\tilde{N}_2 = N_2/N_C$ of doubly-coordinated atoms that is needed in the absence of atoms with any greater coordination:

- cages: $\tilde{R}_g < 0.56$
- flakes: $\tilde{R}_g \geq 0.56, \tilde{N}_3 \geq 0.32$
- branched/dissociated: $\tilde{R}_g \geq 0.56, \tilde{N}_3 < 0.32$
- rings: $\tilde{N}_2 = 1$

The phase diagrams resulting from these definitions are represented in Fig. 5 as a double function of temperature and numbers of carbon or hydrogen atoms. Apart from minor size effects, the boundaries between the various phases are relatively smooth throughout the entire phase.
To summarize, the present computational study provided a fairly complete statistical survey of the structures of hydrocarbon clusters at various sizes, compositions, and temperatures in the broad range of 500–5500 K covering the solid-liquid-vapor phases. In large pure carbon clusters, the results from Kim and Tománek were recovered, with melting proceeding through the main phase change from cages to branched and dissociated structures. However, far more details could be unravelled here by scrutinizing descriptors aimed at probing separately the shape and the extent of sp2 hybridization. In particular, the importance of graphene flakes, which was overlooked in earlier studies, was confirmed and found to have a thermodynamical signature also in C\textsubscript{60} as a melting precursor.

In smaller clusters, but also in hydrogenated compounds, the flake structures become increasingly stable to the expense of cages and the benefit of (possibly unsaturated) polycyclic aromatic hydrocarbons, already with few hydrogen atoms. Ring structures also appear to be stabilized by entropy, contributing to rather rich phase diagrams exhibiting up to three possible phase changes driven by temperature, at fixed size and composition. The structural complexity is consistent with earlier ion mobility experiments and our results provide the typical ranges of excitation energies needed to access the various specific structures.

Beyond laboratory experiments, our results also have important implications in astrochemistry, where organic compounds can be heated quite significantly by absorption of single photons in the UV/visible range. This in itself would suffice to enable isomerization into a large diversity of structures, especially graphene flakes, thus contributing to different absorption and emission bands, and more generally to spectroscopic features that are much broader than the highly resolved and so specific fullerene signatures.

Another important result of the present work is the relatively easy stabilization of polycyclic aromatic hydrocarbons upon hydrogenation of pure carbon clusters, even by relatively small amounts of hydrogen. The connection between fullerene structures and planar flakes, which has been the subject of earlier works, is found here to be further favored by the astrophysical environment.

The present simulations at finite temperature extend the very recent survey of stable hydrocarbon structures at zero temperature (Ref. [38], and emphasize the key role of entropy in medium size clusters. However, kinetic considerations were ignored and we expect the observation time scale to play an important role on the possible characterization of the various species identified in the phase diagrams. The branched/dissociated family is particularly prone to kinetic effects, as cluster fragmentation could be irreversible depending on the experimental conditions of density and temperature. Larger scale re-

**IV. CONCLUSIONS**

In the following, we provide as Supplementary Information (Fig. S5) the 1D Landau free energies of C\textsubscript{60}H\textsubscript{n} with n = 0–10 associated with the scaled radius of gyration and the proportion of triply-coordinated carbon atoms, at various temperatures near the phase change between cages and flakes. Near its melting temperature of 3390 K, C\textsubscript{60} exhibits two free energy minima of comparable depth, confirming that the corresponding transition is first-order-like, rounded by size effects. Another more extended minimum can also be found for the branched and dissociated structures at large gyration radii or low N\textsubscript{3} numbers. The energy barrier separating cages and flakes from each other is about 1.7 eV, somewhat lower than Stones-Wales rearrangement energies and remains rather stable upon moderate hydrogenation for up to n = 8 hydrogen atoms.

Deeper insight into the specific phase changes can also be obtained by considering the (Landau) free energy and its variations with appropriate order parameters. As an example, we provide as Supplementary Information (Fig. S5) the 1D Landau free energies of C\textsubscript{60}H\textsubscript{n} with n = 0–10 associated with the scaled radius of gyration and the proportion of triply-coordinated carbon atoms, at various temperatures near the phase change between cages and flakes. Near its melting temperature of 3390 K, C\textsubscript{60} exhibits two free energy minima of comparable depth, confirming that the corresponding transition is first-order-like, rounded by size effects. Another more extended minimum can also be found for the branched and dissociated structures at large gyration radii or low N\textsubscript{3} numbers. The energy barrier separating cages and flakes from each other is about 1.7 eV, somewhat lower than Stones-Wales rearrangement energies and remains rather stable upon moderate hydrogenation for up to n = 8 hydrogen atoms.

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FIG. 5. (Temperature, size) stability diagram of (a) pure carbon clusters, (b) C_{28}H_n; (c) C_{60}H_n hydrocarbon clusters.

arrangements between cages and flakes, in the context of fullerene formation, would also be worth scrutinizing further, possibly through transition path sampling approaches but also using tools from graph theory.

In the astrochemical context, the internal energy of individual clusters could be transferred to other degrees of freedom through various photophysical processes, such as internal conversion but also radiation in the infrared or even optical range through the so-called Poincaré sphere.

SUPPLEMENTARY MATERIAL

A detailed description of the computational methods and structural parameters; Temperature evolution of the distribution of structural parameters as well as dissociation probability; Landau free energies along selected order parameters.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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