Chemistry-Mediated Ostwald Ripening in Carbon-Rich C/O Systems at Extreme Conditions

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Abstract

There is significant interest in establishing a capability for tailored synthesis of next-generation carbon-based nanomaterials due to their broad range of applications and high degree of tunability. High pressure (e.g. shockwave-driven) synthesis holds promise as an effective discovery method, but experimental challenges preclude elucidating the processes governing nanocarbon production from carbon-rich precursors that could otherwise guide efforts through the prohibitively expansive design space. Here we report findings from large scale atomistically-resolved simulations of carbon condensation from C/O mixtures subjected to extreme pressures and temperatures, made possible by machine-learned reactive interatomic potentials. We find that liquid nanocarbon formation follows classical growth kinetics driven by Ostwald ripening (i.e. growth of large clusters at the expense of shrinking small ones) and obeys dynamical scaling in a process mediated by carbon chemistry in the surrounding reactive fluid. The results provide direct insight into carbon condensation in a representative system and pave the way for its exploration in higher complexity organic materials. They also suggest that simulations using machine-learned interatomic potentials could eventually be employed as *in-silico* design tools for new nanomaterials.

1 Introduction

Carbon exhibits a remarkable propensity for forming nanomaterials with unusual physical and chemical properties arising from its ability to engage in different covalent bonding states.¹⁻⁴ Many of these “next-generation” nanomaterials, which include nanodiamonds, nanographite, amorphous nanocarbon, nano-onions etc., are currently being studied for possible applications spanning quantum computing to bio-imaging,¹ and ongoing research suggests that high-pressure synthesis could lead to the discovery and possibly the tailored design of many more. Both laser-driven shock^{5,6} and detonation experiments^{3,7,8} can be used to drive carbon-rich materials to the 1000s of K and 10s of GPa conditions under which complex processes lead to the formation of 2-10 nm nanocarbons within 100s of nanoseconds. However, the precise chemical and physical phenomena governing nanocarbon formation under elevated pressure and temperature largely remain *terra incognita*, due in part to the formidable challenges associated with studying systems at such extreme states. Recent experiments on nanodiamond production from hydrocarbons subjected to conditions similar with those of planetary interiors⁵ offer some clues on possible carbon condensation mechanisms, but the landscape of systems and conditions under which intense compression could yield interesting nanomaterials is too vast to be explored using experiments alone.

Atomistic simulations can be leveraged to provide insight into the fundamental processes controlling formation of nanocarbon materials, and could also serve as a design tool to help guide experimental efforts. However, the associated temporal and spatial scales are inaccessible to highly-predictive first-principles based approaches, e.g. Kohn-Sham Density Functional Theory (DFT), while molecular mechanics models applicable to materials exposed to extreme temperatures and pressures are quite scarce. Recently, we proposed a new machine-learned force-field and modeling paradigm, the Chebyshev Interaction Model for Efficient Simulations (ChIMES),⁹⁻¹⁵ which is capable of

retaining “quantum accuracy” while maintaining the computational efficiency of a molecular mechanics approach.

Here, we employ the ChIMES modeling framework for an in-depth investigation of carbon condensation (precipitation) in oxygen deficient C/O mixtures at high pressures and temperatures. C/O systems are often employed in practical applications and are excellent candidates for uncovering the essential features of this complex process due to their relative simplicity. For example, carbon monoxide (CO) has been used for carbon nanotube production under ambient to slightly elevated pressures, and explored as a precursor for other nanocarbon materials,¹⁶⁻¹⁸ while shock compression of liquid CO to 10s of GPa has yielded convincing evidence of nanocarbon formation.^{6,19} Furthermore, C/O systems serve as a logical stepping stone to the CNO (and CHNO) organic compounds traditionally employed for high-pressure nanodiamond synthesis (e.g. benzotrifuroxan, C₆N₆O₆),⁸ or those recently shown to yield carbon nano-onions (e.g. bis(nitrofurazano)furazan, C₆N₈O₈).⁷

Carbon condensation in organic systems subject to high temperatures and pressures is clearly a non-equilibrium process akin to phase separation in mixtures quenched from a homogeneous phase into a two-phase region,^{20,21} yet this connection has only been partially explored;²²⁻²⁴ it is worth noting that phase separation concepts remain very relevant for nanoparticle synthesis.²⁵ Chemical bonding adds a new dimension to the classical problem of segregation kinetics and can generate interesting and consequential features, e.g., by introducing length scales that determine system morphology.²⁶ Atomistic modeling could help elucidate such problems but the research remains in its infancy, with applications to carbon precipitation nearly nonexistent. Herein we leverage the machine-learned ChIMES reactive interatomic potential framework to simulate carbon-rich C/O mixtures and address open questions surrounding formation of nanocarbon from highly compressed organic materials, e.g.:

- What is the role of chemistry during

carbon condensation?

- How do carbon clusters evolve, both structurally and chemically, and what is their growth mechanism?
- How does overall system composition influence carbon cluster formation?

Our results provide the first atomistically-resolved view of carbon clustering in a condensed phase reactive system and open new investigative avenues that could lead to *in-silico* design of next-generation nanomaterials.

2 Methods

Unless otherwise stated, simulations were performed in the *NVT* ensemble at 6500 K and 2.5 g/cm³. These conditions approximately correspond to the Hugoniot state point achieved by a 7 km/s shock into cryogenic liquid CO, thereby mimicking the classic experiments of Nellis and coworkers¹⁹ that first suggested carbon precipitation from a shocked organic liquid. Simulations were initialized as an equilibrated fluid of CO and CO₂ molecules at a ratio yielding the target C/O composition, at $\simeq 100$ K; velocities were then rescaled yielding a system temperature of 6500 K. We note that system initialization protocols have a negligible influence on simulation predictions for this work due to the rapid dynamics occurring under such elevated temperatures. For example, results from exploratory simulations initialized as a system of randomly packed C and O atoms and those from exploratory simulations initialized from equilibrated DFT-MD simulations at 6500 K and 2.5 g/cm³ were statistically indistinguishable. All simulations were run using the LAMMPS²⁷ software suite, and interatomic interactions were evaluated using the ChIMES interatomic potential.¹² These models, which are machine-learned to Kohn–Sham density functional theory²⁸ (DFT), are capable of yielding “quantum accurate” predictions for structure, dynamics, and speciation, provide several-orders-of-magnitude increases in efficiency over first

principles methods, and exhibit computational efficiency that scales linearly with system size. A detailed description and validation of the ChIMES model for this system is available in Ref. 12, and further details on simulation protocols are available in the Supporting Information. We note that the ChIMES model utilized herein, a library for computing ChIMES interactions, and source code necessary for its use within LAMMPS is available in Ref. 29.

In this work, carbon condensates are defined as any set of carbon atoms containing at least 10 members, instantaneously separated by no more than $r_{CC} = 1.9$ Å from their nearest neighbor within a candidate cluster (with r_{CC} corresponding to the location of the first minimum of the C—C radial pair distribution function, RDF). For clusters containing both atom types, oxygen atoms within $r_{CO} = 1.8$ Å of a cluster carbon were also counted, with r_{CO} taken as the location of the first minimum of the corresponding RDF. While the choice of clustering criteria may have some effect on predictions, e.g. on cluster radii, we note that our overall analysis and conclusions remain unchanged.

3 Results

Carbon condensation predictions from atomistic simulations are vulnerable to finite size effects,^{12,30} since precipitation progresses through formation and evolution of a well-defined nano-sized carbon cluster population. As shown in Figure 1, simulations for 5 systems sizes spanning 4 orders of magnitude (i.e. $\approx 1.25 \times 10^2$ to 1.25×10^6 atoms) were investigated to quantify the extent of such effects. We summarize salient findings here, noting that further discussion is available in the Supporting Information. All systems containing more than $\approx 1.25 \times 10^2$ atoms yielded at least one cluster, though clusters did not become morphologically and compositionally indistinguishable until system sizes reached at least 1.25×10^4 atoms. This is notable within the context of recent studies of this system; ultra-fast laser-driven shock experiments, which

Figure 1: Top: snapshots for systems containing $\approx 1.25 \times 10^2$, 1.25×10^3 , 1.25×10^4 , 1.25×10^5 , and 1.25×10^6 atoms at 0.25 ns. Images are to scale, and for clarity, only show atoms participating in cluster formation. Bottom: representative cluster growth timeline.

probe a target system on similar scales (i.e. $1 \mu\text{m}$ and 10s to 100s of ps) have confirmed growth of nano-sized carbon condensates within 50 ps.⁶ Conversely, recent DFT-MD simulations found only small covalent species of $C_{2n}O_n$ stoi-

chiometry,³⁰ with $n \approx 21$. The discrepancy between the DFT-MD result and those from the present simulations (and available experiments) ultimately stems from the high computational expense associated with DFT, which

limits system scales to $\mathcal{O}$ 100 atoms and 10s of ps. Increasing system size in the current simulations has the primary effect of increasing the range of observed cluster dimensions. As expected, late time cluster growth is significantly impacted by system size; nevertheless, the average cluster radii and qualitative behavior are consistent across all systems with $\geq 1.25 \times 10^4$ atoms.

To determine how system composition impacts condensate formation, systems with eight C:O ratios were investigated in addition to the 1:1 C:O system described above. The initial compositions of these systems ranged from 95/5, to 25/75% CO/CO₂ and, as discussed in the Supporting Information, carbon clusters were found to form within 25 ps in each of them. We focus here on the 100% CO and 80/20% CO/CO₂ systems, which we henceforth distinguish by their respective C:O ratios, i.e. 1:1 and 5:6. We note that, in contrast to the 1:1 case, cluster morphology, composition, and formation kinetics for the 5:6 C:O system were largely unaffected by system size, provided $\geq 1.25 \times 10^4$ atoms were used. For the remainder of this work, simulation results for the 1:1 system will correspond to a single 500 ps simulation of 1.25×10^6 atoms, whereas results for the 5:6 system are an average over 4 independent 250 ps simulations of 1.25×10^5 atoms; when results are being compared between the 1:1 and 5:6 cases, data for both concentrations correspond to the latter simulation protocol, unless otherwise stated. We note that 5:6 C:O simulations were run at 6500 K and 2.46 g/cm³, yielding the same initial pressure as the 1:1 C:O simulation at 6500 K and 2.5 g/cm³.

3.1 Cluster Evolution

Figure 1 provides snapshots of representative carbon clusters during a typical growth progression, suggesting a few notable features of their evolution. At early time (Figure 1.i), small extended polymeric fragments are observed, typically showing C_{2n}O_n stoichiometry, consistent with previous, small-scale DFT studies.³⁰ As time passes (Figures 1.ii and 1.iii), the clus-

ters become more compact, begin to densify and expel interior oxygen, leading to the formation of large spherical liquid carbon droplets, with oxygen atoms located primarily on their surface (Figure 1.iv). Final snapshots for cluster-containing systems (i.e Figure 1), suggest that smaller clusters are morphologically distinct from their larger counterparts, and increasing system size leads to a broader cluster size distribution.

A quantitative picture of cluster evolution is provided in Figure 2, which shows reduced average radial density profiles, $\rho(r/R_g)$, for the 1:1 system cluster population, along with time resolved average cluster radii of gyration R_g (i.e. the average distance between cluster carbon atoms and cluster carbon center of mass). Note that plotted radii and density profiles correspond to hyperbolic tangent fits to each histogrammed $\rho(r/R_g)$ of the form: $\rho = 0.5\rho_0 \left\{ 1 - \tanh \left[w_0^{-1} (r/R_g - d_0) \right] \right\}$, with $w_0 = w/R_g$ and $d_0 = d/R_g$, where ρ_0 is the density in the center of the cluster, w is the interfacial width, and d is the distance from the cluster centroid to the interface.

For clarity, the present analysis considers only carbon atoms within a cluster; since oxygen is located almost exclusively at the exterior in mature clusters, this choice has minimal influence on late time results. These profiles indicate a transition from extended, low-density clusters at early time to clusters with an interior density of approximately 3 g/cm³. At the same time, the cluster interface steepens considerably, with the interfacial width, w , decreasing from approximately 2.50 to a stable value of $\simeq 1.25$ Å over 50 ps. Early time density profile curves correspond to clusters such as those in Figures 1.i, which exhibit approximately C_{2n}O_n stoichiometry and appear to be of covalent nature (note that our models do not explicitly treat bonding as is common in molecular mechanics formalisms), whereas late clusters (Figures 1.iv) are best described as liquid carbon droplets. As shown in Fig. 2 (inset) the average cluster radius R_g increases with time, with the largest clusters reaching sizes of a few nanometers. Additional radial

Figure 2: Top: Reduced radial density profiles, $\rho(r/R_g)$, and time-resolved average radius of gyration (inset), $\langle R_g \rangle$, for the 1:1 C:O system. Plotted radii and density profiles correspond to hyperbolic tangent fits to each histogrammed $\rho(r/R_g)$. The black dashed curve gives the profile at 500 ps and the shaded region in the $\langle R_g \rangle$ inset figures gives the maximum and minimum observed R_g at each time block, while the orange line gives the average value. Bottom: Radial atomic fraction of carbon (f_C , solid lines) and oxygen enhancement (f_O/f_C , dashed lines) emanating from cluster centroids. The color bars provide the corresponding time range for each line, in ps, unless otherwise specified.

density profiles and average radii of gyration for different C:O ratios are available in the Supporting Information. In general, we find that cluster structural evolution is mostly uncoupled from system composition.

Cluster chemical composition evolution is a crucial aspect of the carbon precipitation and growth kinetics. Time resolved, radial atomic

fractions emanating from cluster centroids are given in Figure 2. Note that these curves are obtained by considering all atoms in the system within r/R_g of a given cluster centroid. We find that at early times cluster interiors (i.e $r/R_g < 1$) have a sizable oxygen content, with values as large as 20%. As time progresses, oxygen migrates to the exterior, resulting in essentially pure liquid carbon droplets, surrounded by carbon depletion and oxygen enrichment layers (see Figure 2) with approximate CO_2 stoichiometry. The amount of oxygen within the growing clusters appears to decay exponentially in time, with a relaxation time constant of $\simeq 5$ ps (see Supporting Information). A similar analysis of the 5:6 C:O system (see Supporting Information) shows that the overall C:O ratio has little qualitative effect on the cluster evolution, indicating that under these conditions the densification and oxygen elimination processes are not very sensitive to system stoichiometry. As the average cluster composition stabilizes, so does the makeup of the reactive fluid that the clusters are immersed in; time-resolved molecular speciation, shows that this is chiefly comprised of CO_2 , CO, and free oxygen atoms at late times (see Supporting Information).

The total cluster volume fraction, $\langle f_{v,\text{clu}} \rangle$, calculated from individual cluster radii of gyration, exhibits behavior characteristic of precipitation from a supersaturated solution, with an initial delay followed by step-like growth and rapid leveling off to a value dependent on the system composition. As expected, the delay is slightly longer in the 5:6 system relative to the 1:1 case due to the lower initial carbon “supersaturation”, while the final condensed carbon volume fraction is smaller. A recent experimental study of CO at thermodynamic conditions similar to these simulations has indicated that carbon clusters occupy a volume fraction of $\simeq 10\%$ (which is significant enough to disrupt sample light absorbance) within the first ≈ 50 ps.⁶ The experimentally inferred volume fraction is in good agreement with the present results for our largest system ($\simeq 8\%$),

where clusters are found to already occupy $\approx 90\%$ of their maximum $\langle f_{v,clu} \rangle$ by 50 ps, and with chemical equilibrium calculations,⁶ which predict the end state of the system. As shown in Figure 3, the transition to near constant total cluster volume fraction coincides with a maximum in the number of clusters present in the system, suggesting that the later time evolution is dominated by coarsening kinetics.

Figure 3: Natural log of the average number of clusters, $\ln(\langle n_{clu} \rangle)$, and average cluster volume fraction, $\langle f_{v,clu} \rangle$ in the 1:1 and 5:6 CO systems.

3.2 Growth kinetics

We quantify cluster growth kinetics through analysis of the average cluster radius $\langle R_g \rangle$ as a function of time. Figure 5 shows that at late times both systems (i.e. 1:1 and 5:6 C:O) exhibit linear growth in the average cluster volume, $\langle R_g \rangle^3$ vs t , i.e. $\langle R_g \rangle \propto t^{\frac{1}{3}}$. This behavior is consistent with coarsening via Ostwald ripening (i.e. evaporation - condensation or dissolution - re-deposition mechanism), described by Lifshitz, Slyozov and Wagner (LSW),^{31–33} in which diffusional mass transfer occurs between the clusters, with clusters smaller than the average size shrinking and the larger ones growing. The present results thus establish the relevance of LSW phenomenology for carbon condensation in a high pressure - high temperature chemically reactive environment¹. Hydrodynamic effects are

¹An important feature of the LSW mechanism is that the average cluster size is the current critical nucleus size

known to determine fluid phase separations at large, ≈ 0.5 volume fractions of the minority phase (here carbon);³⁴ for intermediate values, direct cluster coagulation (Brownian aggregation) is expected to yield volume fraction-dependent growth,^{34,35} which is believed to be dominant in detonation-driven carbon condensation on long ($\mathcal{O} 100$ s ns) time scales.^{22,23,36} Such scales are beyond the practical reach of our atomistic simulations. Nevertheless, we note that the LSW mechanism identified here plays a crucial role in cluster coagulation by inducing composition correlations between neighbouring clusters which drive their direct aggregation;³⁷ a possible example is in Ref. 36.

Coarsening in phase separating systems is known to exhibit dynamical scaling, characterized by a time-invariant cluster population when scaled by the average cluster size.^{20,21} We find that the carbon cluster size distribution in the current simulations is largely self-similar, and compares well with the original LSW distribution³¹ (see Figure 4). Note that differences are likely due to volume fraction effects.³³ This further suggests that cluster growth through atomic diffusive flux is indeed the leading coarsening mechanism. However, we note that in the present system the mass transfer process is more complex than in classical fluid or solid solutions, in which minority phase atoms “evaporate” from smaller clusters, diffuse through the surrounding solvent matrix and “condense” on larger clusters. In particular, the carbon clusters are immersed in a reactive fluid primarily composed of CO_2 , CO, and O with virtually no free C atoms. Given the properties of the oxygen-rich cluster surface layer (see Fig. 2) and the make-up of the reactive fluid, carbon transfer between the clusters appears to principally involve the reactions $\text{C}_n + \text{CO}_2 \leftrightarrow \text{C}_{n-1} + 2\text{CO}$ and $\text{C}_n + \text{O} \leftrightarrow \text{C}_{n-1} + \text{CO}$, proceeding predominantly forward for small clusters and backward for larger ones, with CO and CO_2 being the main carbon carriers between the clusters. We illustrate this atomic-level “hitchhiking” process in Figure 5, which

for the system. This interpretation is likely valid for the present case as well; the idea was employed in Ref. 24

Figure 4: Left: Cubed average radius of gyration, $\langle R_g \rangle^3$, as a function of time, for the 1:1 and 5:6 C:O systems. Right: Cluster size distributions in terms of reduced cluster radii of gyration, $R_g/\langle R_g \rangle$, for $t = 300$ to 500 ps in the 1.25×10^6 atom 1:1 C:O system. The cluster size distribution predicted by LSW theory is given by the solid black line.

shows the chemical bonding environments of a single carbon atom as it travels from one cluster to another. This chemical picture likely becomes much more complex for organic systems that also contain nitrogen and/or hydrogen. Subsequent system quenching to lower pressures and temperatures (e.g. occurring in the wake of a shockwave) will have significant impact on the carbon condensation process, both through the phase transformation of the carbon nanodroplets to other carbon nanoallotropes, e.g. nanodiamond, and possible inhibition of chemical reactions between the clusters and the surrounding reactive fluid. These effects will play an important role in determining the properties of clusters that are ultimately recovered from experiments. Simulation studies of this quenching process will be the subject of future investigations.

4 Discussion

We have presented first-of-their-kind atomistic simulations of chemistry-coupled carbon condensation, addressing long standing questions

related to high pressure nanocarbon synthesis in organic systems. We find that this process can be suppressed by small system sizes, e.g. hundreds of atoms typically accessible to DFT-based methods, and that much larger simulations are needed to capture its physicochemical features. Our simulations have yielded a comprehensive picture of carbon cluster evolution in carbon-rich C:O systems at extreme conditions, which is surprisingly similar with canonical phase separation in fluid mixtures, but also exhibits unique features typical of reactive systems. At early times extended, polymeric seed clusters of approximate $C_{2n}O_n$ composition form rapidly as excess carbon precipitates out of the “supersaturated” solution. At the next stage, these clusters densify by expelling interior oxygen and become spherical, ultimately exhibiting purely molten-carbon interiors and oxygen-decorated exteriors. Clusters occupy $\simeq 8\%$ of system volume in the 1:1 C:O system, and possess interior densities of 3 g/cm^3 , typical of liquid carbon.

Their growth on hundreds of picoseconds time-scales occurs mainly through Ostwald

Figure 5: Reactive transport trajectory of a single carbon atom (black) from a small (lower left) to a relatively larger cluster (upper right). Large transparent blobs provide the approximate cluster carbon isosurface in a single frame, and oxygen atoms bonded to the carbon atom during transport are colored in red. For visual clarity, only a handful of frames showing the tracked carbon atom (and oxygen atoms bonded to it) have been rendered opaquely. A movie of this process is available in the Supporting Information.

ripening and generates cluster populations that obey dynamical scaling. However, in contrast to the classical picture prevailing in simple solid or fluid mixtures, inter-cluster carbon diffusive transport is chemistry-mediated and may perhaps be described as *atomic “hitchhiking” via chemical bonding*. These features are likely to play an important role in predicting and possibly controlling the condensation process and properties of resulting nanocarbon particles. The present simulation approach can be extended to CNO¹⁵ and CHNO systems, and could eventually be leveraged as an *in-silico* material design tool, substantially lowering experimental barriers associated with creating and refining carbon nanoallotrope synthesis protocols.

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Supporting Information Available

- SI.pdf: Supporting information for this article
- Ripening.gif: Simulation trajectory movie corresponding to Fig 5

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