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# A theoretical approach to the nanoporous phase diagram of carbon

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ABSTRACT

Nanoporous carbon has been extensively used in a wide range of applications from water treatment to electrochemical applications, such as in energy storage devices. However, an attempt to relate structural and thermodynamical properties has not been explored from an atomistic approach. In this work we present a methodology to produce nanoporous carbon structures, using molecular dynamics simulations and a many-body potential. We designed a heating-quenching procedure in a thermodynamic region limited between the critical and triple point densities of carbon to study a sample of 1750 atomic arrangements produced at different densities, quench rates, and using graphite and diamond unit cells as precursor structures. All these samples were numerically characterized through the calculation of the free volumes, surface areas, radial distribution functions, and structure factors. We found particularly useful the potential energy dependence with $sp^3$ hybridization content, to compute structural phases through clustering methods. Three phases were found that comprise graphite-like, sponge-like, and unstable states. From our results we can conclude that our methodology, based on Tersoff potential, is compatible with available experimental data and different theoretical findings. In such case, our methodology is a reliable choice to produce nanoporous structures with low computational cost.



## 1. Introduction

Triple point of carbon, where graphite, liquid and vapor coexist, is known to occur at temperatures located between 4800 *K* and 4900 *K* and pressures around 108 *bar* [1]. Therefore, in Earth's surface, where temperatures and pressures are around 300 *K* and 1 *bar* respectively, many disordered atomic structures of carbon may exist in glassy-like metastable states. Nanoporous carbons are part of these states, and can be understood as amorphous solid structures containing hollow spaces with characteristic lengths below 100 *nm*, large enough to allow diffusion of other atoms or molecules through them.

Amorphous carbons are experimentally characterized in terms of the $sp^2$ and $sp^3$ ratio, with $sp^3$ hybridization as high as 12% [2]. The properties of amorphous carbons are highly dependent on their nanoporosity due to their ability to adsorb atoms and their electronic properties [3–6], which are useful for many applications, such as in air and water filters, and electrodes for supercapacitors and batteries [7].

Improvement of these energy storage devices, faces the challenges of understanding electrochemical processes, like ion intercalation [8,9] in lithium batteries and electric double layer formation [6,10] in supercapacitors. In these problems the use of numerical simulations play an essential role, due to experimental difficulties that arise while measuring the atomic environment in nanopores.

The first challenge on the study of theoretical methods to predict nanoporous carbons, resides in finding a proper method to build up a set of atomic arrangements with structural properties that are close to real geometries. For this purpose the appropriate choice of the interaction potential, the simulation methodology, and the possibility to include quantum effects, must be essential.

Reverse Monte Carlo (RMC) technique [11,12] has been used to obtain amorphous structures of carbon from the experimental radial distribution functions (RDF). The numerical procedure involves placing atoms at random positions in a compatible manner according to the RDF, then relax through a Tight Binding Molecular Dynamics (TBMD) simulation. RMC methods can be used to build

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structures of several thousand of atoms but always restricted to use the experimental RDF or structure factor as input.

The *ab initio* Molecular Dynamics (AIMD) [13,14] simulation techniques are promising for the generation and study of amorphous samples. However they are computationally expensive, since only systems of a few hundred of atoms can be generated in a reasonable calculation time. The search of an amorphous phase at this scale, is a demanding task.

Classical Molecular Dynamics (CMD) with the aid of many body potentials such as Brenner and Tersoff [15,16] is a reliable choice. With the recent introduction of Reactive Force Fields [17,18], some quantum effects may be considered. CMD techniques are still being a source of new results concerning nanoporous carbon [19]. In previous works the numerical strategy to obtain the amorphous carbon has been usually based on melt-quenching methods. For instance, Peng et al. [20] generated a set of amorphous carbon structures by variations of density and quenching rate to study the Hydrogen adsorption over them. The samples were built with densities ranging from 0.6 to 2.4 g/cm$^3$ using TBMD molecular dynamics. They found that the samples agree in some extent to the experimental radial distribution function (RDF) obtained by Gallego et al. [21]. Li et al. [22] found amorphous samples by quenching from the melt technique in the common allotropic carbon densities, i. e., densities ranging from 2.0 to 3.2 g/cm$^3$ and using a variety of empirical potentials such as REBO, ReaxFF and Tersoff [16,17,23]. It was reported that Tersoff potential is a suitable choice for carbon structures with density around diamond, that is close to 3.5 g/cm$^3$. Very recently Raganthan et al. [19] also employed this melt-quenching method within a CMD simulations using Reactive potentials, finding that at low densities the structures are predominantly anisotropic. At densities higher than 1 g/cm$^3$ the differences are due to hybridization changes.

The aim of this work is to generate computationally nanoporous structures of carbon, proposing a simple and systematic numerical strategy that allows to obtain an ensemble of hundreds of structures that may probably exists in nature. Our purpose is to search clues to define a structural phase diagram of nanoporous carbon. We sustain that the ensemble may bring new insights into the geometrical disposition of these structures, and their probable physical origins. Such properties may be the foundation for the creation of descriptors to design materials for carbon electrodes that are useful for energy storage applications.

We based our numerical study on some strategies taken from the phenomenon of bubble nucleation in liquids [24]. This has been studied through Lennard-Jones fluids, using CMD or Monte Carlo (MC) simulations in superheated conditions [25–27]. One strategy to form such bubbles is to place the system in an unstable condition at densities and temperatures between the critical and triple points. In real systems such states lead to a liquid-gas coexistence phase, and in numerical simulations tend to create void formations in the liquid, assumed as the nucleation of nano-bubbles. Considering this process, our main hypothesis considers that by using CMD simulation of particles interacting with a suitable forcefield for carbon, computed at densities between the critical and triple point and with temperatures below the triple point, a spontaneous nucleation of bubbles takes place in a solid-gas phase, analogous to that obtained in liquid-gas coexistence. After quenching is performed, pores are formed. The critical and triple point densities have been determined at around $0.64\,g/cm^3$ [28] and $1.37\,g/cm^3$ [29], respectively, and the triple point temperature at around $4800\,K$.

We expect two major contributions of our work: 1) evaluation of the Tersoff potential reliability for massive production of atomic structures containing thousands of atoms, and 2) a systematical exploration of the statistical mechanical properties on the set of atomic arrangements obtained with low computational cost. This may aid in the understanding and *in silico* design of nanoporous carbon based materials.

There is experimental evidence in the literature of nanoporous carbon at extremely low densities to compare with, for example Zani et al. [30] produced carbon foam layers with densities in the range 0.001–1.0 g/cm$^3$. It was reported via a Raman study interpretation that the samples they produced are nearly pure sp$^2$ network which contains topologically disordered graphite-like regions, as the resolution given as allowed by the Pulsed Laser Deposition technique used in that work. Our objective is also to evaluate the predictive characteristics of Tersoff potential in the low density regime, by comparing structural properties of the samples such as surface area, volume fraction, RDF with experimental available data. As far as we know, no systematic process based on the density and quench rates has been proposed or developed within the range of densities between the critical and triple points of carbon.

First we will show the numerical techniques to perform simulations in order to obtain the ensemble of nonporous structures; followed by the discussion of the results; then the prediction capability of the methodology will be evaluated comparing obtained structures with experimental results. Finally we will present the conclusions and contribution of our work to the state of the art within this field.

## 2. Simulation strategy

The generation of a statistically representative ensemble of nanoporous carbons in a systematic way, requires the computation of hundreds of numerical simulations on a reasonable time. It is very important to achieve a balance between the details of the simulation model and the physical meaning of the results. In a recent work, Raganthan et al. [19] simulated a set of structures by using Molecular Dynamics with a ReaxFF [31] reactive potential, demonstrating the capability of modeling amorphous carbons with melt-quench methods in a wide range of densities ($0.5 - 3.2\ g/cm^3$). It was concluded that the atomic arrangements and quench rate (QR) play an important role simulation box size effects, and some of the obtained results are compatible with experiments.

To design a full numerical strategy to go further, by evaluating hundred of cases obtaining a large variety of possible different densities and quench rates, three choices have to be taken into account: 1) a reliable interaction potential efficient in CMD simulations, 2) a set of initial conditions defined as precursor structures, and 3) a thermal melt-quench process able to obtain a wide variety of possible structures. The first choice was to use Tersoff potential instead of reactive force fields, the reasons are: to perform the simulations faster, increasing the number of sampled structures, and to answer an unexamined question: how this potential reproduce the real nanoporous structures?

### 2.1. Heating-quenching process

Looking for the bubble formation mentioned in earlier section, we propose to examine densities between the critical a triple points. The critical point density and temperature are found at $\rho_c = 0.64\,g/cm^3$ and at $T_c = 6800\,K$ [28], respectively, while the triple point density and temperature are found at $\rho_t = 1.37\,g/cm^3$ and $T_t = 4300\,K$ [29], respectively. If we perform simulations from $T_a = 300\,K$ to temperatures below $T_t$, we guarantee the system does not melt and therefore we expect all samples to form bubbles, that after quenching lead to porous structures. As in glass production, and by the precursor initial configuration, as it is subsequently presented.