Atomistic and Coarse-grained Simulations of Hexabenzocoronene Crystals

O G Ziogos, G Megariotis and D N Theodorou

1 School of Chemical Engineering, National Technical University of Athens, Athens, Greece
E-mail: oziogos@mail.ntua.gr

Abstract. This study concerns atomistic and coarse-grained Molecular Dynamics simulations of pristine hexabenzocoronene (HBC) molecular crystals. HBC is a symmetric graphene flake of nanometric size that falls in the category of polyaromatic hydrocarbons, finding numerous applications in the field of organic electronics. The HBC molecule is simulated in its crystalline phase initially by means of an all-atom representation, where the molecules self-organize into well aligned molecular stacks, which in turn create a perfect monoclinic molecular crystal. The atomistic model reproduces fairly well the structural experimental properties and thus can be used as a reliable starting point for the development of a coarse-grained model following a bottom-up approach. The coarse-grained model is developed by applying Iterative Boltzmann Inversion, a systematic coarse-graining method which reproduces a set of target atomistic radial distribution functions and intramolecular distributions at the coarser level of description. This model allows the simulation of HBC crystals over longer time and length scales. The crystalline phase is analyzed in terms of the Saupe tensor and thermomechanical properties are probed at the atomistic level.

1. Introduction
One of the most influential and groundbreaking milestones of the past decade regarding materials science and engineering was undoubtedly the advent of graphene [1]. Graphene is a planar, two dimensional (2D) periodic arrangement of sp2 hybridized carbon atoms residing on the sites of a honeycomb lattice – practically an isolated graphite sheet – with extraordinary electronic [2], mechanical [3] and chemical properties [4]. Besides its pristine 2D geometric state, graphene can exist in other allotropic forms, such as one dimensional graphene nanoribbons [5] and aperiodic nanoflakes [6]. Graphene flakes of nanometric dimensions and variable geometries have been placed in the epicenter of organic electronic research as candidate material to be used as active media for organic light emitting diodes, photovoltaics, and field effect transistors [7]. In such devices, nanographene flakes self-organize into well structured supramolecular assemblies, with the polyaromatic cores in close proximity, thus enabling the interaction of their delocalized pi-pi orbitals. Electronic conductivity in the aforementioned molecular arrays is not based on coplanar to the graphene flake ballistic transport but on transplanar hopping transport mechanisms [8].

The current flagship of nanographenes is hexa-peri-hexabenzocoronene (HBC), either in its pristine state [9] or in its functionalized state, where a series of flexible side chains decorate the periphery of the molecule, altering profoundly the properties of the molecular crystals [10]. Pristine HBC is a
planar molecule consisting of 42 carbon atoms and 18 peripheral hydrogen atoms in a perfectly hexagonal symmetric arrangement that crystallizes at monoclinic P2_1/a molecular crystals [9].

In our studies, we employ empirical Molecular Dynamics (MD) simulations in order to equilibrate the molecular crystals and derive structural, thermodynamic and dynamical properties at equilibrium. It is a fact that atomistic MD calculations that consider explicitly all atoms in a molecular system and factor in all sorts of time consuming energy and force calculations, e.g. reciprocal-space electrostatic interactions, are typically limited to a few tenths of nanometers and a few thousands of nanoseconds, as far as the spatial and temporal domains are concerned. Bearing in mind these limitations and using as input information from detailed atomistic MD calculations, a bottom-up coarse-graining approach is adopted and utilized, allowing the examination of the systems under study at augmented spatial and temporal regimes, ranging up to the micrometric scale.

2. Computational Details

2.1. Initial Configurations

The fact that HBC crystallizes into a monoclinic lattice would normally force all calculation to be carried out by employing simulation boxes of general triclinic geometry. In order to facilitate coarse grained calculations, initial configurations with orthogonal simulation boxes are created, with a minuscule compromise regarding the crystallography of the system. To be more precise, HBC crystals are described by a monoclinic primitive unit cell with parameters \( a_0 = 18.431 \text{Å}, \ b_0 = 5.119 \text{Å}, \ c_0 = 12.929 \text{Å} \) and \( \beta_0 = 112.6^\circ \) [9]. Upon careful geometric inspection, the molecular crystals can be also described by an alternative unit cell with parameters \( a = 34.06 \text{Å}, b = 5.119 \text{Å}, c = 38.79 \text{Å} \) and \( \beta = 92.1^\circ \). In order to alter the unit cell vectors aiming to obtain an orthogonal cell, one would have to shift the end of vector \( a \) by approximately 1.248Å along the direction of \( c \). Defining four periodic molecular arrays along the direction of \( c \), the orthogonal unit cell is achieved by en masse translations of each array by 0.312Å, 0.624Å, 0.936Å and 1.248Å respectively. All the aforementioned geometric elements and unit cells are depicted in Figure 1.

![Figure 1. Top view of the \( a, c \) unit cell for a HBC molecular crystal viewed along the direction of vector \( b \). Imbedded in this unit cell, the primitive \( a_0, c_0 \) unit cell is also drawn. The four short arrows over the unit cell highlight the four molecular arrays that are accordingly shifted along the \( c \) direction in order to transform the monoclinic unit cell to an orthogonal one. Peripheral hydrogen atoms are omitted for clarity.](image_url)

Apart from the orthogonal initial configurations, monoclinic P2_1/a molecular crystals are also created using the primitive unit cell in order to be used as input to MD calculations with triclinic simulation boxes.

2.2. Atomistic Molecular Dynamics Simulations

Empirical atomistic MD simulations are carried out in the isostress-isothermal statistical ensemble using the LAMMPS package [11]. The integration of the equation of motion is accomplished through the Martyna-Tobias-Klein numerical scheme [12] with a time step of 1fs, using a time constant of 100fs for temperate control and 2500fs for pressure control. Typical periodic boundary conditions are applied in each direction, allowing this way the examination of the systems in their bulk phase. For the
quantification of the bonded interactions, the force field parameterization is taken from earlier work on substituted HBC molecules [13].

2.3. Coarse-grained Simulations

The coarse-grained representation of HBC molecule consists of six superatoms forming a regular hexagon, as seen in Figure 2.

![Figure 2. Atomistic and coarse-grained representations of HBC molecule.](image)

In particular, all superatoms are of the same type (AR1) and are placed at the geometric center of the six outermost aromatic rings of the HBC polyaromatic core (see also Figure 1). As far as the interactions between the superatoms are concerned, they are categorized as intermolecular and intramolecular ones. The coarse-grained model is developed by applying the well-known Iterative Boltzmann Inversion (IBI) method which falls in the category of systematic coarse-graining techniques [14]. Due to the representation of HBC molecule by one superatom type, only one radial distribution function (RDF) should be reproduced at this level of description. All coarse-grained simulations were conducted with GROMACS package [15] in the canonical ensemble. Upon coarse-graining, the integration time step of the equations of motion increases from 1fs to 12fs, while the number of interaction sites per molecule is reduced from 60 to 6.

2.4. Structural characterization

The Saupe ordering tensor $Q$, which is widely used in the study of liquid-crystalline phases, is employed for the analysis of the HBC crystalline phase at the atomistic and coarse-grained level. The tensor in question is defined by the following equation

$$Q = \frac{1}{N} \sum_{i=1}^{N} \left\{ \frac{3}{2} \hat{u}_i \hat{u}_i - 1 \right\}$$

where $\hat{u}_i$ is a unit vector normal to the mesoscopic hexagonal ring (coarse-grained level) or the polyaromatic core (atomistic level). The sum in Equation 1 is taken over all molecules $N$ of the system. For the special geometry of the crystal system under consideration, the eigenvalues of $Q$ tensor are computed analytically by the next set of equations [16]:

$$
\begin{align*}
\lambda_1 &= -1/2 \\
\lambda_2 &= \left(3\sin^2\theta - 1\right)/2 \\
\lambda_3 &= \left(3\cos^2\theta - 1\right)/2
\end{align*}
$$

where $\theta$ is the tilt angle which is formed by the normal unit vector and the columnar direction.
2.5. Mechanical characterization

The simulation of the molecular crystals using general triclinic simulation boxes prompts us with the capability of estimating the elastic moduli of the material using typical strain fluctuation methodologies [17]. The isothermal compliance tensor $S^T$ is described by Equation 3:

$$S^T_{ijkl} = \frac{V_0}{k_B T} \left( \langle \eta_{ij} \eta_{kl} \rangle - \langle \eta_{ij} \rangle \langle \eta_{kl} \rangle \right)$$  \hspace{1cm} (3)

where $V_0$ is the average system volume at zero stress conditions, $\eta_{ij}$ the strain matrix element with respect to a zero stress average cell shape and the angular brackets correspond to time averages. The strain matrix is expressed as

$$\eta = \frac{1}{2} \left( h^{-1} \tilde{h} h h^{-1} - I \right)$$  \hspace{1cm} (4)

where $h_0$ is the reference cell shape matrix at zero stress and $h$ the instantaneous cell shape matrix, with the tilde corresponding to the transpose matrix. The singular 9×9 compliance matrix calculated this way is transformed to a non-singular 6×6 matrix by applying the Voigt convention [18]. From this new matrix, the isothermal bulk modulus $B$ and shear modulus $G_R$ are derived in a straight-forward fashion via the following two equations [18,19]:

$$B = S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{31})$$  \hspace{1cm} (5)

$$G_R = 15 \times \left[ 4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{23} + S_{31}) + 3(S_{44} + S_{55} + S_{66}) \right]^{-1}$$  \hspace{1cm} (6)

3. Results

The implementation of the IBI method entails the reproduction of a set of RDFs and intramolecular (or non-bonded) distributions at the coarse-grained level. As already detailed in the previous section, only one RDF (AR1-AR1) is considered for the HBC molecule. The fact that the system under consideration is found in the crystalline phase has as a consequence the existence of many peaks in the RDF AR1-AR1 which is a severe handicap for the full convergence of the IBI method. However, a partial convergence can be achieved as seen in Figure 3, in which the target and coarse-grained RDFs are depicted in black and red color respectively.

![Figure 3. Comparison of atomistic and coarse-grained RDFs for the pair AR1-AR1.](image-url)
The crystal phase predicted with the coarse-grained model is compared to the crystalline phase of the underlying atomistic model in terms of $Q$ tensor eigenvalues and $\theta$ tilt angle with the latter being experimentally observable. These properties are presented in Table 1, from which the consistency between the atomistic and coarse-grained model is evident. More specifically, in Table 1, the $\theta$ angles are compared for the two models while the eigenvalues from the simulations are compared with the corresponding analytical estimates computed by Equation 2.

| Simulation | Theory |
|------------|--------|
| $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\theta$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ |
| Atomistic model | -0.499 | 0.356 | 0.129 | 49.65° | -0.5 | 0.370 | 0.130 |
| Coarse-grained model | -0.498 | 0.340 | 0.159 | 48.52° | -0.5 | 0.342 | 0.158 |

As far as the elastic response of HBC in its crystalline state is concerned, the molecular crystal exhibits a rather stiff behavior, since the calculated elastic moduli vary in the region of tenths of GPa. Since the molecules are in their pristine form without any peripheral flexible substituents, the rise in temperature – always below the melting point – is expected to have a rather small effect in the elastic moduli. This is indeed the case, as it is demonstrated in Figure 4, where the evolution of the bulk and shear moduli is depicted upon material heating.

![Figure 4](image.png)

**Figure 4.** Temperature variation of bulk modulus $B$ and shear modulus $G_R$ of the HBC crystal. Values for the soluble HBC-C12 system are shown for comparison.

In order to emphasize the effect of the lack of peripheral side chains, the relevant elastic moduli for a grafted system [13] are also shown.

### 4. Conclusions

In this current work, we report the successful description of a molecular crystal of HBC molecules by means of detailed, fully atomistic and reduced, coarse-grained MD simulations. The two different levels of description are in fine agreement with each other, as well as with available experimental data. An analytical formulation for the eigenvalues of the Saupe orientation tensor for discotic materials is
proposed and validated against simulation results. Finally, state-of-the-art atomistic simulations are applied in order to quantify the elastic response of this material. Judging by our findings, pristine HBC crystals exhibit a stiff behaviour, ranging between their soft soluble grafted counterparts and typical covalent crystals.

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