

1 **Molecular dynamics simulations of nanosheets of polymeric carbon nitride and**  
2 **comparison with experimental observations**

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15 **Abstract**

16 A computational study of the properties of polymeric carbon nitride using molecular  
17 dynamics is presented. The analysis of ideal infinite-extent sheets permits to evaluate the  
18 effect of temperature on the network of hydrogen bonds responsible for the linkage of the  
19 material. The weakening of this binding mechanism at sufficiently high temperatures,  
20 together with the inter-layer interactions characteristic of this type of 2D materials, is  
21 shown to determine the conformation properties of polymeric carbon nitride at the  
22 nanoscale. The results obtained from the simulation of finite samples in the canonical  
23 ensemble at varying temperatures are consistent with those from the characterization of  
24 our experimentally synthesized samples. Hydrogen bonding between adjacent polymer

25 ribbons leads this process and is the cause of the typical crumpled structure of this  
26 material.

27 **Keywords:** carbon nitride; conformation; molecular dynamics; MOPAC; nanosheets

## 28 **1. INTRODUCTION**

29 Polymeric carbon nitride has attracted large interest as a precursor for the synthesis of  
30 super-hard carbon nitride phases (1-10). This material finds many applications in the wide  
31 field of sensors due to the combination of its chemical sensitivity with its optical and  
32 semiconductor properties (11-13). Also, monolayer polymeric carbon nitride forms a new  
33 family of wide-gap semiconducting materials, in which the gap can be tuned by small  
34 variations in the stress applied to the layers or by the presence of adatoms (14).

35 The various existing synthesis routes provide predominantly amorphous samples  
36 structured at the nanoscale level as graphite-like (15), nanosheets (16-19), nanotubes (20),  
37 or nanopillars (21-22). They can also be structured in mesoporous conformations that lead  
38 to new applications, like the generation of nanostructured metal nitrides (23).  
39 Conformation as single sheets that can be exfoliated from graphitic carbon nitride samples  
40 (24) or directly grown (25) permits to increase its efficiency as a catalyst. The detailed  
41 arrangement of this material is of most relevance for the specific applications and strongly  
42 depends on the ambient conditions of the synthesis (16-19) and on other parameters, such  
43 as the precursor type (25). Understanding of the detailed supramolecular mechanisms that  
44 rule the conformation of this material is thus essential for the optimization of the synthesis  
45 procedures and the development of new related materials and applications.

46 In this work, we perform a study of the conformation properties of polymeric carbon  
47 nitride sheets under different ambient conditions using atomistic molecular dynamics  
48 (MD) simulations. The analyses address both the general intrinsic properties of ideal  
49 infinite-extent 2D polymeric carbon nitride sheets and the evolution in the structural

50 organization of finite size samples; specifically, the routes towards the formation of  
51 crumpled nanosheets.

52 MD (26) is a useful tool in the study of the conformational transitions of very large  
53 molecular and supramolecular systems like, for instance, protein folding (27). It provides  
54 not only the final minimum energy structures, but the MD trajectories also afford the  
55 detailed pathways and a valuable insight into the underlying mechanisms determining the  
56 evolution. Molecular dynamics simulations have been extensively used in the study of the  
57 intrinsic properties of 2D materials, particularly graphene (28-31) and related materials  
58 like graphane (32) or multilayer graphene (33). These systems are especially interesting  
59 from a theoretical point of view since, according to the Mermin-Wagner theorem (34),  
60 long-wavelength fluctuations destroy any crystalline order in pure 2D systems.  
61 Nevertheless, 2D membranes can exist in a 3D space, where the displacements are not  
62 constrained in two dimensions.

63 Graphene-like materials can be modelled as polymerized or tethered membranes,  
64 which have been subject of intense theoretical investigations (35-37) and which are  
65 characterized by the fact that bonds linking the membrane sites are unbreakable. Even  
66 within the physical constraint of self-avoidance, these 2D membranes typically undergo a  
67 transition to a crumpled state (or a tubular state in the presence of anisotropy (38)),  
68 whereas a flat state, with strong height fluctuations, is also possible due to the coupling  
69 between bending and stretching modes. On the other hand, polymeric carbon nitride sheets  
70 are characterized by their binding through a network of relatively weak hydrogen bonds,  
71 far from the ideal unbreakable condition, that links the melon linear arrays of the basic  
72 heptazine building blocks. Using MD simulations, we find that the morphological  
73 properties of the material under study are predominantly determined by the behaviour of  
74 the hydrogen bonds under the varying ambient conditions and the inter-planar interactions

75 between the heptazine units. In spite of the limited size of our simulation cells when  
76 compared with the actual spatial extent of the investigated features, the results of the  
77 computations are consistent with the experimental results.

## 78 **2. METHODS**

### 79 **2.1. Experimental**

#### 80 2.1.1. *X-ray diffraction measurements*

81 X-ray diffraction patterns were obtained by means of a powder diffractometer ENRAF-  
82 NONIUS FR590, detector INEL CPS 120 (BRUKER AXS, The Netherlands), with  
83 monochromator-quartz discriminator, Debye-Scherrer geometry, using Cu K $\alpha$  radiation,  
84 and glass capillaries for sample mounting. The samples were ground in an agate mortar  
85 and sifted. The measurements always lasted for 1 hour, and crystalline silicon was used  
86 as a standard.

#### 87 2.1.2. *TEM and SEM characterization*

88 Transmission electron microscopy (TEM) and scanning electron microscopy (SEM)  
89 analyses were performed with a JEOL JEM-FS2200 HRP and a JEOL JSM-820 SEM  
90 microscope (JEOL, Japan), respectively.

### 91 **2.2. Computational**

92 The MD simulations were performed using the large-scale atomic molecular massively  
93 parallel simulator (LAMMPS) (39) using the DREIDING force field (40). This generic  
94 model includes parameters for H and the non-metallic main-group elements, plus a few  
95 metals. It specifically takes into account the effect of hydrogen bonds, which are  
96 particularly relevant for the material under analysis.

97 The data used for the MD simulations were built from the 2D ground state geometry of  
98 the PM6 Hamiltonian (41), calculated using MOPAC (42). The DREIDING force field  
99 polymer layers used as initial conditions for the MD computations were relaxed using

100 LAMMPS, both as finite size and periodic infinite-extent sheets. The minimized  
101 geometries yielded  $a=19.240 \text{ \AA}$ ,  $b=13.365 \text{ \AA}$  and  $\gamma=90.000^\circ$ . The values of  $b$  and  $\gamma$  were  
102 in excellent agreement with those derived from semi-empirical quantum chemistry  
103 calculations and previously reported in (19), with a somewhat larger deviation in the value  
104 of  $a$ . MD optimized geometries displayed very good planarity, very similar to that of the  
105 semi-empirical computations. Two nearly square sheets were generated with 7776 and  
106 31104 atoms and spanning  $13 \times 9$  and  $24 \times 18$  unit cells of the 2D polymer, respectively.  
107 Their approximate sizes were  $159.8 \text{ \AA} \times 159.5 \text{ \AA}$  and  $319.7 \text{ \AA} \times 319.0 \text{ \AA}$ , respectively.

108 The MD simulations of infinite 2D sheets were performed in the isothermal-isobaric  
109 (NPT) ensemble with periodic boundary conditions. The calculations for finite size  
110 systems, were started with well-formed one, three or six nearly square polymer sheets,  
111 and were performed in the NVT ensemble. The equations of motion used in LAMMPS  
112 were those of Shinoda, Shiga, and Mikami (43) and the time integration schemes closely  
113 followed those derived in (44). Thermostating and barostating were implemented using  
114 Nosé-Hoover algorithm.

### 115 **3. RESULTS AND DISCUSSION**

#### 116 **3.1. MD Simulations**

117 The properties of single sheets of polymeric carbon nitride are first analysed. These are  
118 the basic building blocks of three-dimensional arrangements (15, 19) and also the desired  
119 final products for many applications. These arrangements can potentially be obtained by  
120 exfoliation of more complex materials or by direct growth. The study of the response of  
121 infinite sheets to changes in temperature and pressure permit to quantify, in particular, the  
122 behaviour of the hydrogen bond network as the temperature grows. The results obtained  
123 are consistent with subsequent studies on the processes responsible for the morphological  
124 organization of the material under treatment at high temperatures.

### 125 3.1.1. *Infinite sheets*

126 The intrinsic properties of ideal, infinite extent, 2D arrangements were addressed using  
127 periodic boundary conditions in the NPT ensemble. Final trajectory equilibrium states for  
128 simulations at zero pressure and  $T=100$  K and  $T=700$  K are displayed in Fig. 3. The results  
129 show how a finite temperature induced height fluctuations in the sheet, similarly to the  
130 case of graphene (32-33). The average absolute deviations from the surface level  $h$  are  
131 shown in Fig. 2(a) for the range between 100 K and 1000 K. The results for the two sheets  
132 of different size were very similar, with the same approximate linear dependence of  $h$  in  
133 that range. As opposed to graphene, these height fluctuations have an important effect on  
134 the structural integrity of the layer through their impact on the hydrogen bonds network,  
135 as it can be appreciated by comparing subplots (a) and (b) with (c) and (d), respectively,  
136 in Fig. 1. This can be clearly appraised in the dependence of the energy contributed by  
137 hydrogen bonds normalized with the total number of heptazine units in the simulation  
138 domain shown in Fig. 2(b). These results show some dependence with the size of the  
139 sample under study. The contribution of the hydrogen bond network to lower the energy  
140 of the system decreases as temperature is increased and part of these bonds are broken.  
141 Further, the rate of change of this energy with  $T$  saturates at higher temperatures due to  
142 the finite number of total hydrogen bonds.

143 The structural integrity of other non-hydrogen-bonded 2D materials is preserved under  
144 very large in-plane uniaxial or biaxial stress, resulting in a net change of the potential  
145 energy in the membrane (32). In the polymeric carbon nitride presented herein,  
146 simulations conducted even at low temperature show that increasing the applied finite  
147 uniaxial or biaxial in-plane stress eventually results in the collapse of the 2D polymer at a  
148 finite time that depends on the applied pressure. The atom displacements in the onset of  
149 the instabilities resemble those associated to the low frequency lattice modes of the 2D

150 polymer (19), which may play a key role in the nascent growth of the instabilities.

### 151 3.1.2. *Finite size samples*

152 The simulations performed on finite size samples show that, in general, the dynamic  
153 trajectories leading to their final conformations are driven by two main effects: the  
154 previously described weakening of the hydrogen bonds network as temperature increases,  
155 plus the plane-to-plane interactions that take place after polymer sections are loosened or  
156 released from their hydrogen bond restraints. These two combined effects produce the  
157 folding and piling of the material layers in different manners, determining the final  
158 arrangement of the material. The detailed evolution depends not only on the ambient  
159 conditions, but also on the amount and the characteristics of the initially interacting  
160 material.

161 The conformation dynamics of a finite single sheet of polymeric carbon nitride were  
162 analysed from computations performed in the canonical ensemble. The final states of the  
163 calculations of 500 psec evolutions of a layer with  $13 \times 9$  unit cells in a volume of  
164  $200 \times 200 \times 200 \text{ \AA}^3$  at different temperatures are shown in Fig. 3. In all cases, equilibration  
165 of the structures took place within the first 100 psec.

166 For the lowest temperatures in the sequence, 500 K and 600 K, the sheet essentially  
167 kept its integrity. At 500 K only a very small defect in the 2D structure was found,  
168 localized in one of the corners of the sheet, and corresponded to the disordered two-layer  
169 piling of a section spanning very few heptazine units. At 600 K, a defect (a bilayer stripe)  
170 could be identified. The dynamics of its formation, starting with the folding of one of the  
171 corners and the sliding of the feature along the 2D structure, revealed a very interesting  
172 balance between the inter-heptazine interaction and its hindrance by the hydrogen bonds  
173 at this temperature.

174 At 700 K, the repetition of the folding and propagation of defect stripes produced the  
175 packing of several layers. This disordered and non-homogeneous piling, in turn, induced  
176 some curvature in the formed multilayer structures. As the temperature was increased, the  
177 folding of the structure and the packing of multiple layers was facilitated by the  
178 debilitation of the network of hydrogen bonds. The route to the layer piling then included  
179 the break-up of stripes of material and their layer-to-layer interaction. As the hydrogen  
180 bond network weakened with the temperature growth, the prominence of inter-planar  
181 interaction increased and pilings with larger numbers of layers were produced.

182 When similar computations were performed on a planar system spanning  $26 \times 18$  unit  
183 cells, this larger sheet seemed to be more robust against the folding process at 700 K, with  
184 morphological modifications that were limited to a somewhat smaller fraction of the total  
185 sheet surface than in the previous case. This can be explained by the fact that the initiation  
186 of the dynamical evolution eventually leading to the stacking and crumpling of the sheet  
187 would be facilitated by the irregularities in the system and the processes would become  
188 less likely in the more homogeneous system. At higher temperatures (900 K), the initial  
189 breakup of the hydrogen links between 1D chains and their inter-planar interaction led to  
190 the formation of a thread of 1D chains stacked in the direction perpendicular to the  
191 heptazine planes.

192 Fig. 4 shows the results obtained from the equilibration in the NVT ensemble of three  
193  $26 \times 18$  sheets, which were initially widely separated and with a random disposition. The  
194 computations were performed at different temperatures and, in all cases, the duration of  
195 the simulation is 500 psec. Equilibrium was reached within the first 200 psec. At the lower  
196 temperatures, 500 K and 700 K, the evolution was dominated by the interaction between  
197 the well-formed layers, which resulted in their piling in an essentially three-layer system.  
198 When the temperature was increased to 900 K, the thermally-driven sheet undulations



199 broke parts of the hydrogen-bond networks, loosening portions of the initial sheets. The  
200 subsequent plane-to-plane interactions of the fragmented material resulted in the  
201 formation of an irregular flake with a curved profile. The number of layers at some  
202 locations of this disordered cell was larger than three.

203 The results derived from the evolution in the canonical ensemble were very similar  
204 when the initial conditions consisted of six identical, well separated and placed at random  
205 sheets. The time required to reach an equilibrium state in this case was significantly larger.  
206 As in the previous case of three sheets in the starting conditions, the evolution at the lower  
207 temperatures produced the piling of the initially well-formed layers. The system  
208 dynamics, in this regime, were dominated by the layer-to-layer interactions. At 900 K, the  
209 thermally induced shaking and break-up of the initial sheets and the following layer-to-  
210 layer interaction of the resulting fragments finally produced a curved and disordered flake  
211 with a number of stacked layers that, at some places, was larger than the initial figure of  
212 six. Fig. 5 shows the resulting flake after being annealed by cooling it at low temperature.  
213 The top view in Fig. 5(a) displays a turbostratic arrangement of the layers of material  
214 within the flake, consistent with the experimental observations. The side view of Fig. 5(b)  
215 shows the curvature of the flake and the existence of stacked layers that can clearly exceed  
216 the number of six even at the edge of the flake. There are portions of the flake interior that  
217 display a larger numbers of layers.

218 Fig. 6 shows the radial distribution function (RDF) of the atoms in the flake processed  
219 at 900 K. The RDF of a single sheet of material at very low temperature is also plotted for  
220 comparison purposes. This second curve has been arbitrarily scaled to facilitate its  
221 contrast. The main peaks due to the in-layer interatomic distances in the single sheet of  
222 material are also clearly distinguishable in the sample that has been processed at high  
223 temperature. Nevertheless, the disorder in the flake is evident from the broadening of these

224 peaks. In the figure, the peak at 3.21 Å in the signal corresponding to the sample heated  
225 to 900 K has been highlighted. Even though there are nearby contributions from in-layer  
226 distances, the height of this peak relative to that of the low temperature single-sheet curve  
227 is much higher than in the neighbouring peaks. Therefore, this feature can be  
228 predominantly attributed to the interlayer stacking. The separation obtained from the  
229 calculations was in excellent agreement with the measured values at the corresponding  
230 processing temperature.

### 231 **3.2. X-ray diffractometry (XRD), scanning (SEM), and transmission electron** 232 **microscopy (TEM) observations**

233 A marked corrugation of the polymeric carbon sheets, synthesized from melamine  
234 cyanurate (discussed in (19)), was confirmed at temperatures above 600 K. Particles with  
235 tubular shape, formed by crumpling of flake particles, were observed at synthesis  
236 temperatures around 700 K (Fig. 7).

237 In fact, at 900 K, the crumpled particles, formed not only tubular particles but also  
238 globular ones, as tubules were further shrunk up to form globules with holes (Fig. 7).

239 This characteristic should be linked to H-bonding, and -as simulations showed- borders  
240 would be more instable and tend to crumple, transforming the flakes in either tubular or  
241 globular particles.

242 It is noteworthy to point out that this folding effect is coupled to a tighter interlayer  
243 distance upon synthesis temperature increase, indicating that -concomitant to the borders'  
244 folding- the stacking order increases, as shown in Fig. 8.

245 Therefore, the increase in the number of stacked sheets and the larger interlayer  
246 interactions would be linked to the folding effect that produces crumpled particles. In a  
247 previous research, it was found that the layers behaved as independent ones (i.e., as a 2D  
248 material) below a synthesis temperature of 800 K (around 650 °C). Above this

249 temperature, the folding effect increased the number of stacked layers as well as the order  
250 along the *c* direction. In summary, the diminution of the interaction on the layer plane  
251 implicates a stronger interplanar H-bond interaction.

252 This corrugation effect could be conveniently used to produce globular, spherical or  
253 tubular particles. Moreover, this effect of folding seemed to affect THz absorption in a  
254 considerable way (19), so that it could be used as a sensor of pressure in special  
255 environments. Hydrogen bond in carbon nitride (obtained from urea) was experimentally  
256 investigated by Hu et al. (X) and they concluded that melem oligomers were formed and  
257 arranged in layers. In spite of that study we suggest that the polymeric structure is  
258 compatible with the crumpled morphology. Hydrogen bonding weakening between  
259 adjacent polymer ribbons is the main cause of the typical crumpled structure of this  
260 material, especially observed at high synthesis temperatures (*ca.* 900 K). This process  
261 makes the material more sensitive to the external environment through the possibility of  
262 interacting by hydrogen bonding with molecules such as CO<sub>2</sub>, etc.

#### 263 **4. CONCLUSION**

264 A computational study of the morphological properties of a carbon nitride polymer was  
265 performed at the nanoscale using molecular dynamics. In spite of the fact that this survey  
266 was restrained by the limited size of the simulation domains, a good agreement with the  
267 experimental results was found. The synthesized samples consisted of crumpled  
268 nanosheets formed by a turbostratic arrangement of polymer layers, which is consistent  
269 with the small-size molecular dynamics simulations at the corresponding processing  
270 temperatures.

271 The analysis of the computer simulations results have provided a clear picture of the  
272 mechanisms that would lead to such arrangement. One determining factor is the weakness  
273 of the hydrogen bonding network that keeps together the 2D polymer and that determines

274 many of its physical and chemical properties(45). This fact had been previously noted, for  
275 instance, in relation with the calculation of the electronic band-gap of this material. Due  
276 to the very small interactions between heptazine units, the calculated band-gap for the 2D  
277 system is very similar to that of the monomer (19). At sufficiently high temperatures,  
278 molecular agitation can partly release this relatively weak bonding network and permit the  
279 conformational change in the material. The second element is the effect of the layer-to-  
280 layer interaction, typical of 2D carbon materials, that drives such change. Hydrogen  
281 bonding weakening between adjacent polymer ribbons is the main cause of the typical  
282 crumpled structure of this material, especially observed at synthesis temperatures above  
283 ca. 900 K. However, this property makes this material more sensitive to the external  
284 environment, and thus more suitable to be used as a catalyst and a sensor.

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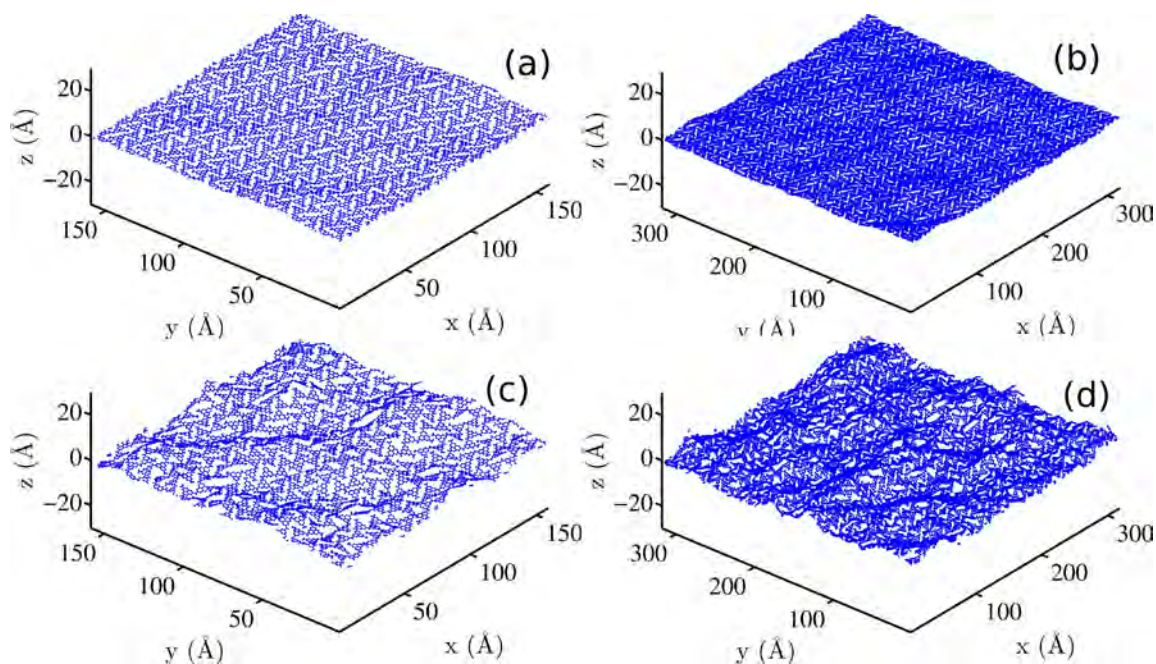
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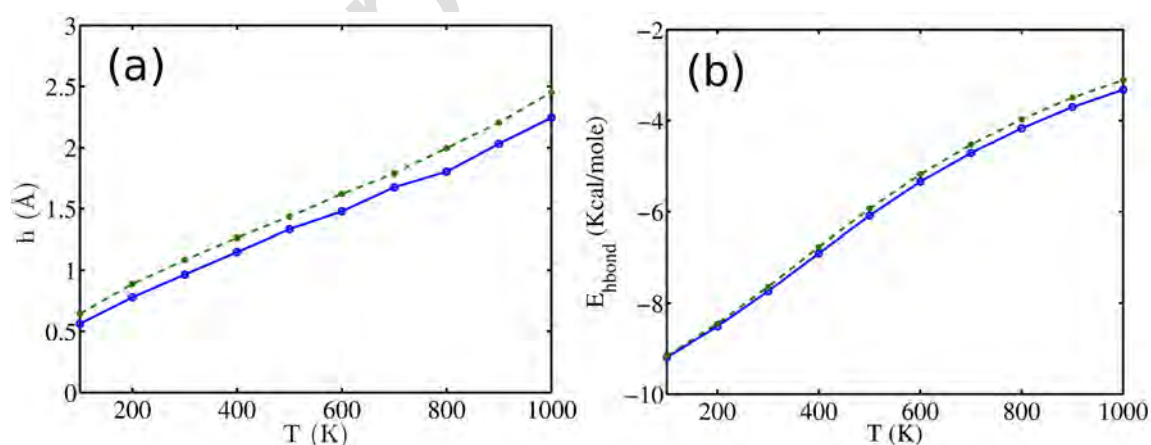
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418 Fig. 1. Equilibrium polymer sheets at zero pressure obtained using periodic boundary  
 419 conditions. Left column results ((a) and (c)) correspond to a period of  $13 \times 9$  unit cells;  
 420 right column ones ((b) and (d)) correspond to a period of  $26 \times 18$  unit cells. Top row results  
 421 ((a) and (b)) are for a temperature of  $T=100$  K and lower row ones ((c) and (d)) for  $T=700$   
 422 K.

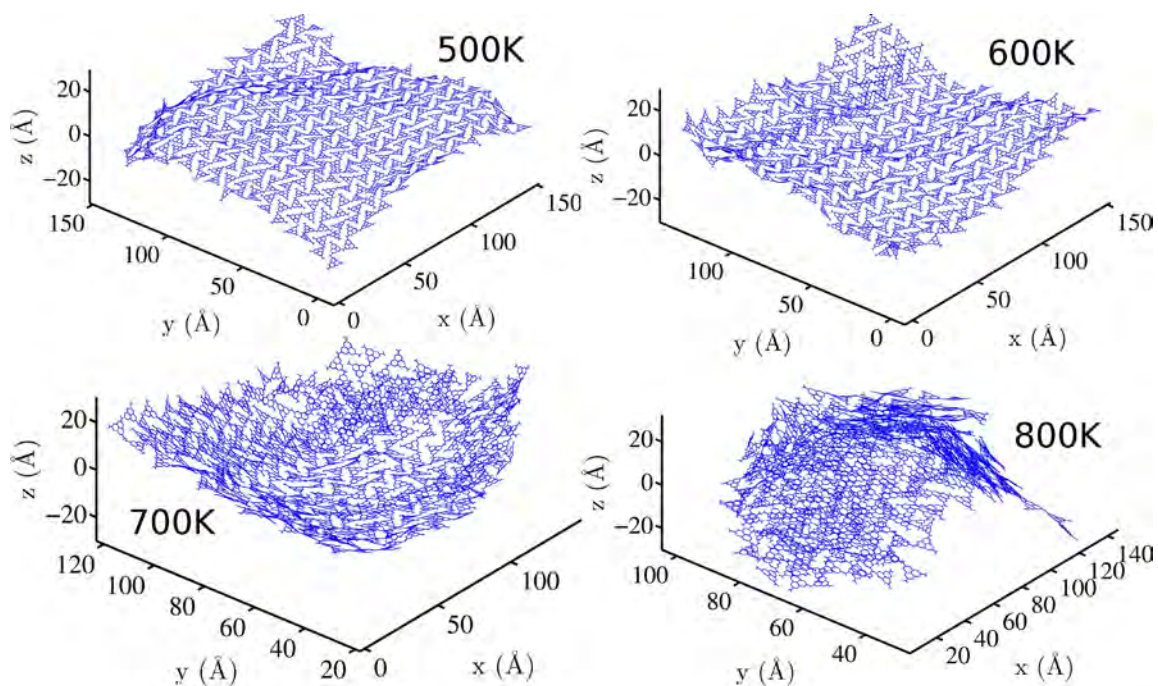
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425 Fig. 2. (a) Average height fluctuations and (b) hydrogen bond contribution to the system  
 426 energy per heptazine unit averaged over a simulation run after equilibration.

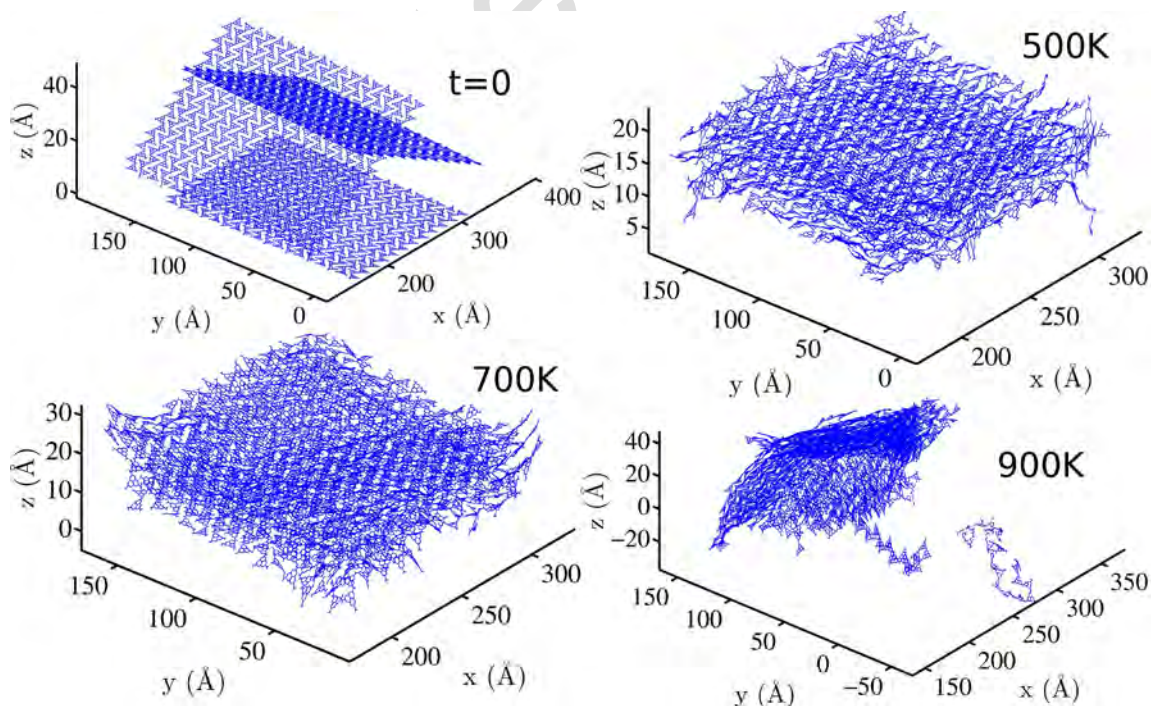
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429 Fig. 3. Final trajectory states after 500 psec evolution in the NVT ensemble at different  
 430 temperatures. The initial condition in all cases is a ground state, approximately square,  
 431 sheet spanning over  $13 \times 9$  unit cells of the 2D polymer.

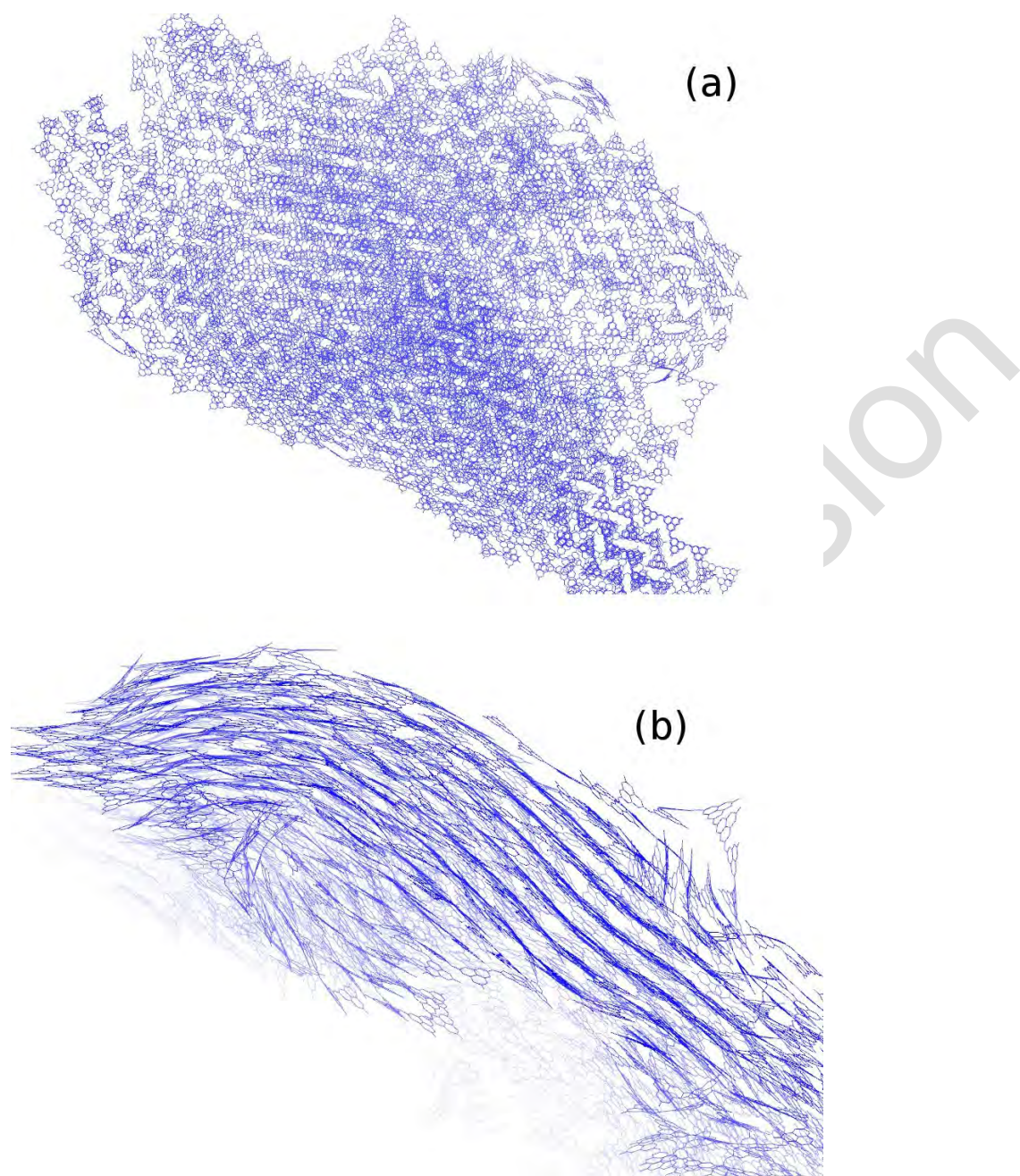
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434 Fig. 4. Initial ( $t=0$ ) and equilibrium final trajectory states at different temperatures after  
 435 the evolution of three sheets in the canonical ensemble.

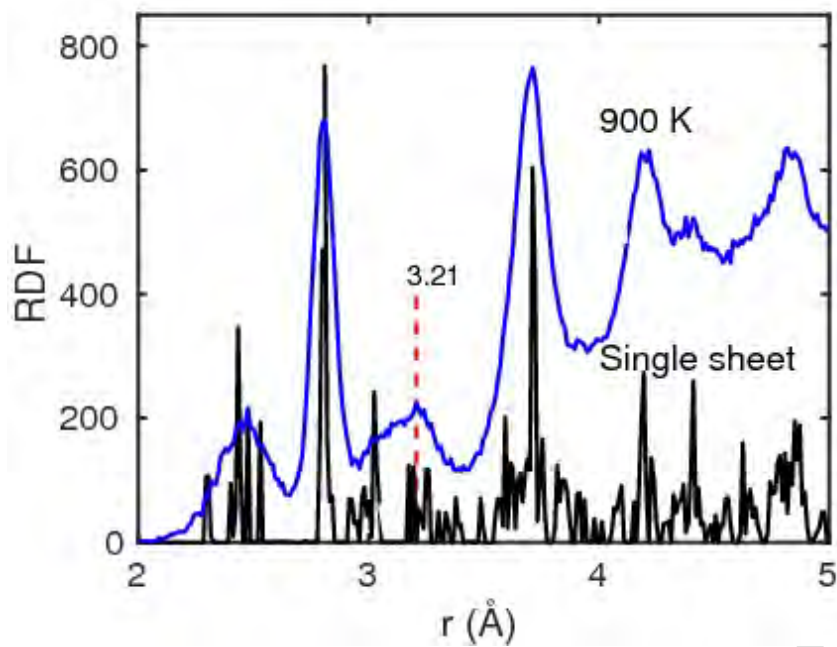




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438 Fig. 5. A flake obtained by annealing the final equilibrium geometry after evolution in the  
439 canonical ensemble at 900 K starting from six sheets of polymeric carbon nitride. (a) top  
440 view, (b) side view of the flake edge. Plots have been produced using VMD software (46).

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443 Fig. 6. Radial distribution function computed for flake depicted in Fig. 5 and for a single  
444 sheet of material at low temperature.

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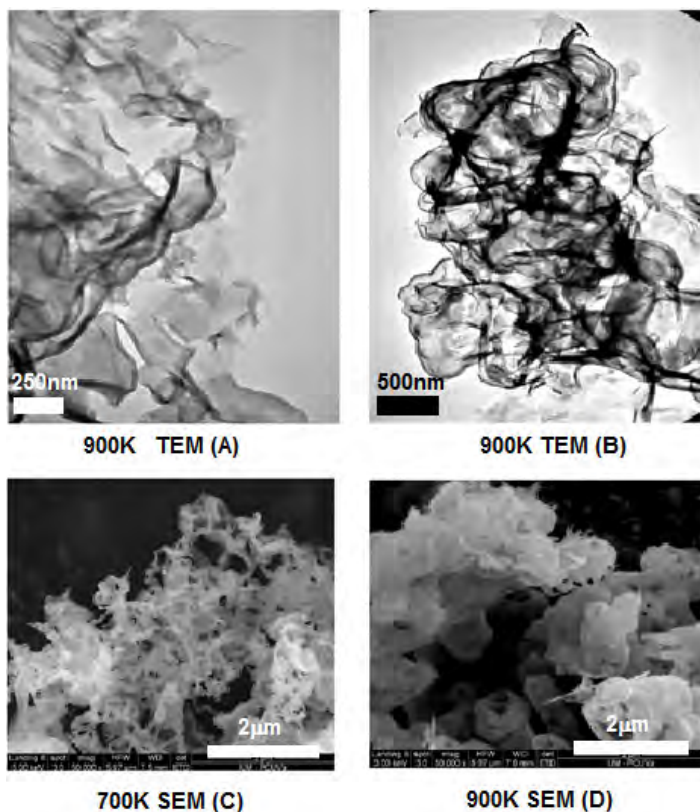
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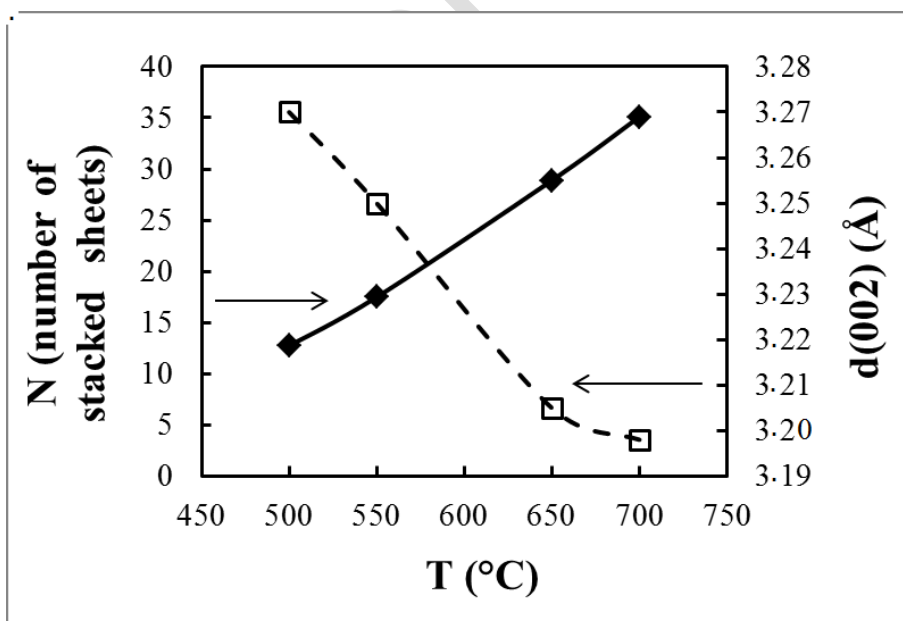
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458 Fig. 7. TEM and SEM images of polymeric carbon nitride obtained at 700 and 900 K from  
 459 melamine cyanurate pyrolysis.

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462 Fig. 8. Variation of the interlayer distance and stacked sheets as a function of the synthesis  
 463 temperature (19).