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MD CALCULATION MECHANICAL PROPERTIES OF FLUOROGRAPHENE

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We present the results for the elastic properties of a single layered carbon monofluoride or fluorographen (FG). The calculations were performed by molecular dynamics (MD) simulation using a force field with both bonded and non-bonded interatomic contributions, and the periodic boundary conditions in two dimensions, representing an infinite "nanoplate". Simulations were fulfilled both for three basic conformations of FG [1] and for the FG with number counts of structural defects. The elastic modulus was calculated from the curves of force versus displacement obtained at slow rates of deformation. Bending stiffness was estimated independently from the nonlinear deformation under compression. The atomistic results are explained in terms of a continuum model for the thin plates.

Keywords: fluorographene.

1. Introduction

In the last years the great attention is paid to the investigations of properties of one layered membranes of graphen and similar materials. It is connected with their unique electric and heart-conducting properties. The last time the special interest to FG appears after the experimental and theoretical investigation of its electronic properties [2–5], which show that FG is very perspective material for using in microelectronic. In details the investigations of partial cases of FG was fulfilled in the work [2], were it was shown experimentally that FG has the relatively large Young's modulus $\backsim 100\ N/m$ and the essential bending stiffness $\backsim 15\ N/m.$ The way of the graphen membrane producing is studied in the work [6].

The quantum chemical calculation for two plane crystallic structures of FG was firstly fulfilled in 1993 in the work [7], where it was shown that the "Chair" configuration is energetically more favorable than the "Boat" configuration. Then by using the more occurred algorithm this calculations were fulfilled also in the works [1], [8–10]. In the work [9] the structure and electronic properties of graphen in derivatives involving Group IA or Group VIIA elements [9] is studied. The detailed computational study of structure of FG in three-dimensional stacked arrangements were fulfilled [1]. The structural and electronic properties of four crystallic structures of graphane and of graphene fluoride is investigated in [8]. In this work the Young's modulus and the Poisson's ratios are found, and the theoretical estimations of the membrane stiffness's occurs 2.5 times larger than the experimental ones.

The MD simulation in contrary to the quantum chemical calculation allows us to study the membranes FG with large dimensions and to calculated all their mechanical characteristics and also to study the influence of temperature and the structural defect properties. It is essential that in the frame of the molecular-dynamic experiments it is possible to analyze the more complex systems, for example the systems containing FG structures or composite materials, but for the molecular simulation it is necessary to know reliable potentials (force field). Earlier to simulation the perfluoroalkanes from gas-phase and liquids. Some systems of force parameters are presented [11–13], but it is not clear that is it possible to use them for the MD simulation. In the work [1] Artyukhov and Chernozatonskii it was firstly derived the molecular mechanics force field for FG $(CF)_n$ that performs exceptionally well at reproducing our quantum chemical results and fits into a very general OPLS/AA molecular mechanics framework.

To verify the presented potentials and also to estimate the mechanical properties of various plane crystallic and defective structures of FG were fulfilled the MD experiments with the FG membranes by using the various potentials. In this work the potential OPLS-AA [11] is used. The unstressed membranes FG with temperatures $1, 100, 300$ and 500 K are studied and the results of their one-dimension deformations of temperature 300 K are analyzed.

2. FG Structures and force field

We consider three basic conformations of single-layered monofluoride crystals (Fig. 1. a, b, c) and the FG with the number random structural defects (adatoms (F) are positioned above or down the center of FG membrane).

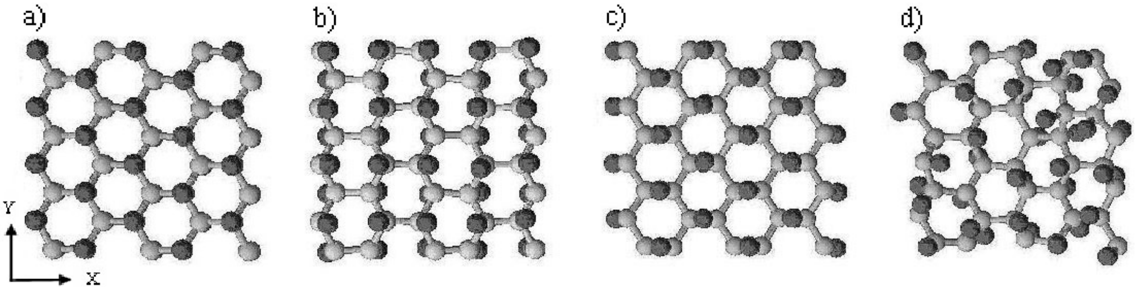

Fig. 1. Different structures of FG. a) “Chair”, b) “Boat”, c) “Zigzag”, d) structure “Chair” with many random defects; the different colors represent respectively C atoms - gray, F atoms - black

The total potential energy of in-plane lattice FG comprises the bond stretching, the angle bending, the torsion energy, the electrostatic, and the Van-der-Waals potential energy

$$\begin{cases} E^{bond}(r_{ij}) = \dfrac{1}{2}k_{ij}^{bond}(r_{ij} - r_{ij}^0)^2, \\ E^{angle}(\varphi_{ijk}) = \dfrac{1}{2}k_{ijk}^{angle}(\varphi_{ijk} - \varphi_{ijk}^0)^2, \\ E^{torsion}(\theta_{ijkl}) = \dfrac{1}{2}[F_1(1+\cos\theta_{ijkl}) + F_2(1-\cos 2\theta_{ijkl}) + \\ \qquad +F_3(1+\cos 3\theta_{ijkl}) + F_4(1-\cos 4\theta_{ijkl})], \\ E^{nonbonded}(\mathbf{r}) = \sum\limits_{ij} E^q(r_{ij}) + \sum\limits_{ij} E^{vdW}(r_{ij}), \end{cases} \tag{1}$$

$$E^q(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}, \qquad E^{vdW}(r_{ij}) = \varepsilon_{ij}\left[\left(\frac{R_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{ij}}{r_{ij}}\right)^{6}\right], \tag{2}$$

where the potentials (1)-(2) parameters are taken from [11] with corrections [1].

For the numerical solution of the Newtonian equations of motion, the fast Verlet algorithm [14] with an integration step of 1 fs is used. The temperature in the system is maintained by a "collision" thermostat [15, 16] with the parameters $\lambda = 5.1\ ps^{-1}$ and $m_0 = 1\ a.m.$ The pressure is set and maintained by a Berendsen barostat [17].

3. Results and discussion

3.1. Analysis of the energy

We calculate the contribution all of this potential energies and total potential energy of the crystals structures "Chair", "Boat" and "Zigzag". The "Chair" configuration is energetically more favourable. In Tables 1, 2 we present the relative energies with respect to "Chair" of temperature $0\ K$. In Table 1 through E^{bond}, E^{angle}, $E^{torsion}$, E^q, E^{vdW}, E_{pot} the bond stretching, the angle bending, the torsion energy, the electrostatic, the Van-der-Waals energy, and the total potential energy are denoted respectively.

In Table 2 we compare the presented energy with the energies obtained by the previous authors. We can see that for the "Boat" structure our energy is close to the quantum chemical approach. But for the "Zigzag" structure our energy is mach larger.

Table 1. Calculated relative energies $(kcal/mol)$

	ΔE("Boat"-"Chair")	ΔE("Zigzag"-"Chair")
E^{bond}	0.4253	0.0369
E^{angle}	0.6683	1.0605
$E^{torsion}$	-0.5681	0.3317
E^q	0.0879	0.195
E^{vdW}	0.8983	0.0724
E_{pot}	1.5118	1.6965

Table 2. Analysis of the relative energies E_{pot} $(kcal/mol)$

	ΔE("B"-"C")	ΔE("Z"-"C")
Presented study	1.512	1.697
O. Leenaerts, quantum chemical calculation	1.73	0.83
V. Artyukhov, quantum chemical calculation	1.71	0.82
V. Artyukhov, GROMACS	1.691	0.855

3.2. Equilibrium structure

The geometrical parameters in isolated layers for three configurations are presented in Tables 3–5. The crystal structure parameters $a,\ b$ and the distances between the atoms (in $\AA$) and angles (in deg) are given.

3.3. Deformation and Temperature extension

We design the FG membrane as an orthotropic material with the various stiffness coefficients in directions X and Y. For calculation of these stiffness and of the corresponding

Table 3. “Chair”, $0\ K$

	a	b	$a/(b\sqrt{3})$	d_{CC}	d_{CF}	φ_{CCC}	φ_{CCF}	θ_{CCCF}
Presented study	4.579	2.644	1.000	1.590	1.393	112.5	106.2	64.2
V. Artyukhov	4.521	2.611	1.000	1.584	1.382	110.9	108.0	61.9
O. Leenaerts	4.503	2.600	1.000	1.579	1.371	110.8	108.1	-

Table 4. “Boat”, $0\ K$

	a	b	$a/(b\sqrt{3})$	d_{CC}	d_{CF}	φ_{CCC}	φ_{CCF}	θ_{CCCF}
Presented study	4.642	2.629	1.019	1.592 1.635	1.392	111.3 115.5	104.2 104.4	-113.3 67.2
V. Artyukhov	4.617	2.585	1.031	1.574 1.667	1.377	114.0	104.0 107.4	-115.9 66.9
O. Leenaerts	4.603	2.574	1.032	-	-	-	-	-

Table 5. “Zigzag”, $0\ K$

	a	b	$a/(b\sqrt{3})$	d_{CC}	d_{CF}	φ_{CCC}	φ_{CCF}	θ_{CCCF}
Presented study	4.257	2.668	0.921	1.594 1.588	1.393	113.6 115.7	103.8 101.8	-68.1 158.0
V. Artyukhov	4.200	2.635	0.920	1.567 1.602	1.382	115.6	103.6 106.2	-65.8 156.6
O. Leenaerts	4.183	2.625	0.920	-	-	-	-	-

Poisson’s ratios we use the relations [18]

$$\begin{aligned}
e_{11} &= \frac{1}{E_1}\sigma_{11} - \frac{\nu_{12}}{E_2}\sigma_{22} - \frac{\nu_{13}}{E_3}\sigma_{33}, &\qquad e_{13} &= \frac{1}{G_{13}}\sigma_{13},\\
e_{22} &= -\frac{\nu_{21}}{E_1}\sigma_{11} + \frac{1}{E_2}\sigma_{22} - \frac{\nu_{23}}{E_3}\sigma_{33}, &\qquad e_{23} &= \frac{1}{G_{23}}\sigma_{23},\\
e_{33} &= -\frac{\nu_{31}}{E_1}\sigma_{11} - \frac{\nu_{32}}{E_2}\sigma_{22} + \frac{1}{E_3}\sigma_{33}, &\qquad e_{12} &= \frac{1}{G_{12}}\sigma_{12}.
\end{aligned} \tag{3}$$

Here E_i, G_{ij}, and ν_{ij} are the Young modules, the shear modules and Poisson’s ratios respectively, and the following restrictions are valid

$$E_1\,\nu_{12} = E_2\,\nu_{21}, \qquad E_1\,\nu_{13} = E_3\,\nu_{31}, \qquad E_2\,\nu_{23} = E_3\,\nu_{32}. \tag{4}$$

For estimation of the FG stiffness we fulfill the extension-compression simulation of FG membranes. The velocities of deformation are equal to 0.002 and $0.005\ \mathring{A}/ps$ (or 0.2 and $0.5\ m/s$). Two problems are solved, namely the problem of extension-compression with 1D stress state in the direction X and in the direction Y. As in all 2D plate theories we put $\sigma_{33} = 0$. Under there assumptions we get

$$e_{11} = \frac{\sigma_{11}}{E_1}, \qquad e_{22} = -\,\nu_{21}\,\frac{\sigma_{11}}{E_1}, \qquad (\sigma_{22} = 0); \tag{5}$$

$$e_{22} = \frac{\sigma_{22}}{E_2}, \qquad e_{11} = -\,\nu_{12}\,\frac{\sigma_{22}}{E_2}, \qquad (\sigma_{11} = 0). \tag{6}$$

Our algorithm allow us to measure and calculate only 2D stiffness's, and like this [8], [19] we introduce the "2D Young's modules" $\widetilde{E}$ by relations

$$\widetilde{E}_1 = E_1 \cdot h_{E1}\,, \qquad \widetilde{E}_2 = E_2 \cdot h_{E2}\,, \tag{7}$$

where $h_{E1},\ h_{E2}$ are the effective thickness's of the extension-compression simulation of FG membranes.

The extension-compression simulation is fulfilled for three studied crystal configurations of FG. We compare our results with the published early theoretical results. Our results concerning the Young's modules are correlated very accurately with the quantum chemical calculation [8] (see Table 6). But there is the essential disagreement of the Poisson's ratios. Also we mark the essential influence the structural defects to the Young's modules.

It occurs that the experimental values [2] of the Young's modulus $\widetilde{E} = 100 \pm 30\ N/m$ are 2—2.5 times lower than the theoretical ones. To explain this difference we investigate the membrane with the large number of defects.

From 400 pairs of atoms of a crystal lattice $(CF)_m$ structure "Chair" we choose by a random way N_i pairs of atoms and for them we change the position of fluorine atoms into opposite ones with respect to the plane of membrane. The calculations are fulfilled for $N_i = 8,\ 20,\ 40$ and 100 defects. The obtained elastic modules for structures with defects better agree with the experimental results.

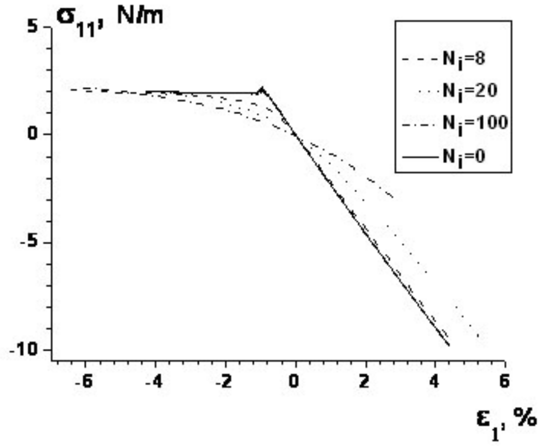

Fig. 2. The dependence between stress and extension for structures with defects

Our results shows (see Fig. 2) that the crystallic material is linearly elastic for the comparatively large deformations (until 2%), but for structures with defects are linear only for deformation $0.1 - 0.2\%$.

Also we fulfill the simulation of FG membranes with the beam stress state and calculate the bending stiffness of membranes. The magnitudes of bending constants for FG membranes are estimated by using the Euler's formula of the critical compressive load for a thin beam. For the periodic boundary conditions the plate loses its stability at the second bending mode and the Euler formula in the X direction gives

$$F_x^{cr} = D_1\, l_y\, \frac{4\pi^2}{l_x^2}\,, \qquad D_1 = E_1\, \frac{h_{D1}^3}{12}\,, \tag{8}$$

where D_1 is the bending stiffness, and h_{D1} is the effective membrane thickness at the cylindrical bending, E_1 is the Young's modulus and $l_x,\ l_y$ are the cell dimensions in the X and Y directions.

The compression simulation gives us the critical force F_x^{cr}, and by first equation of (8) we get $D_1 = D_1(F_x^{cr})$.

We assume that

$$h_{D1} = h_{E1} = h_1\,, \qquad h_{D2} = h_{E2} = h_2, \tag{9}$$

and calculate the membrane effective thickness $h_1,\ h_2$ from (7), (8)

$$h_1 = \sqrt{\frac{12\, D_1}{\widetilde{E}_1}}. \tag{10}$$

By such way we estimate the bending stiffness's $D_1\,,\ D_2$ and effective thicknesses $h_1\,,\ h_2$, but in the case with the large number of defects ($N_i = 20\,,\ 40\,,\ 100$) this way is unacceptable because the critical point is not definite. In these case we suppose that h_i are done and equal to the previous values of $h_1\,,\ h_2 = 2.6,\ 2.7$ $\mathring{A}$, and estimate values of $D_1\,,\ D_2$ by relation (10).

To estimate the numerical error we fulfill calculations for various values $l_x,\ l_y$.

Also we fulfill calculations for various temperatures $1,\ 100,\ 300$ and 500 K and calculate the coefficient of temperature extension (see Table 7). Calculations with the temperature 1 K are used for the comparison with the quantum chemical calculation at the temperature 0 K.

Table 6. Modulus $\widetilde{E}\,(N/m)$, Poisson's ratios ν, bending stiffness $D\,(N \cdot m)$ and effective thickness $h\,(\mathring{A})$ of FG membrane for temperatures 1 K or 1 K / 300 K

Structure	direction	$\widetilde{E}$	$\widetilde{E}$ [8]	ν	ν [8]	$D \times 10^{20}$	h
"Chair"	X	231 / 236	243	0.22 / 0.22	0.07	100	2.3
	Y	236 / 237	243	0.22 / 0.22	0.07	120	2.5
"Boat"	X	342 / 336	230	0.12 / 0.12	-0.01	185	2.5
	Y	234 / 236	262	0.08 / 0.08	-0.01	260	3.7
"Zigzag"	X	167 / 171	117	0.11 / 0.12	0.05	185	3.6
	Y	251 / 252	271	0.17 / 0.17	0.11	210	3.2
random	X	200 / 213	-	0.17 / 0.15	-	114	2.6
$N_i = 8$	Y	220 / 222	-	0.18 / 0.18	-	134	2.7
$N_i = 20$	X	118 / 119	-	0.08 / 0.10	-	66*	2.6*
	Y	177 / 178	-	0.13 / 0.15	-	108*	2.7*
$N_i = 40$	X	120 / 117	-	0.09 / 0.09	-	68*	2.6*
	Y	177 / 176	-	0.14 / 0.13	-	108*	2.7*
$N_i = 100$	X	76 / 80	-	0.11 / 0.10	-	43*	2.6*
	Y	141 / 137	-	0.20 / 0.22	-	86*	2.7*

Table 7. The coefficients of temperature extension

	"Chair"	"Boat"	"Zigzag"	random defects
$\alpha_x \times 10^6$	4.3	3.0	7.6	1.9 - 6.5
$\alpha_y \times 10^6$	4.5	5.0	4.7	4.3 - 5.2

In addition we get a number of calculations with the various parameters in the equations (1), (2). Our results show that the better coincidence with the quantum chemical results gives the force field OPLS/AA with correction [1], but the further corrections are desirable.

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References

[1] Artyukhov V. I., Chernozatonskii L. A. // J. Phys. Chem. A, 2010. V. 114. No. 16. P. 5389–5396.
[2] Nair R. R., Ren W. et al. // Small, 2010. V. 6, No. 24. P. 2877–2884.
[3] Robinson J. T. et al. // Nano Lett., 2010, V. 10, P. 3001.
[4] Withers F., Dubois M., Savchenko A.K. // Phys. Rev. B, 2010, V. 82, 073403.
[5] Cheng S.-H. et al. // Phys. Rev. B, 2010, V. 81, 205435.
[6] Osuna S. et al. // J. Phys. Chem. C, 2010. V. 114. P. 3340–3345.
[7] Charlier J.-C., Gonze X., Michenaud J.-P. // Phys. Rev. B, 1993. V. 47. No. 24. P. 16162–16168.
[8] Leenaerts O., Peelaers H. et al. // Phys. Rev. B, 2010. V. 82, No. 19, 195436.
[9] Klintenberg M., Lebegue S., Katsnelson M. I., Eriksson O. // Phys. Rev. B, 2010. V. 81. 085433.
[10] Samarakoon et al. // Small, 2011. V. 7. No. 7, P. 965–969.
[11] Watkins E. K., Jorgensen W. L. // J. Phys. Chem. A, 2001, V. 105, No. 16, P. 4118.
[12] Borodin O., Smith G. D., Bedrov D. // J. Phys. Chem. B, 2002. V. 106. No. 38. P. 9912–9922.
[13] Jang S. S., Blanco M., Goddard W. A., Caldwell G., Ross R. B. // Macromol., 2003. V. 36. No. 14. P. 5331-5341.
[14] Allen M. P., Tildesley D. J. Computer Simulation of Liquids. — Oxford: Clarendon Press, 1987.
[15] Lemak A. S., Balabaev N. K. // Mol. Simul. 1995. V. 15. No. 4. P. 223.
[16] Lemak A. S., Balabaev N. K. // J. Comput. Chem. 1996. V. 17. No. 15. P. 1685.
[17] Berendsen H. J. C., Postma J. P. M., Gunsteren W. F., Nola A., Haak J. R. // J. Chem. Phys. 1984. V. 81. No. 8. P. 3684.
[18] Rodionova V. A., Titaev B. F., Chernykh K. F. Applied theory of anisotropic plates and shells. — SPb.: SPbGU, 1996. — 278 p.
[19] Zhou J., Huang R. // J. Mech. and Phys. of Solids, 2008. V. 56. P. 1609–1623.