

# Nanoscale Prediction of Graphite Surface Erosion by Highly Energetic Gas - Molecular Dynamics Simulation -

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**Abstract** In order to understand the fundamental essence in the erosion of graphite by hot gas molecules, in this study we investigate the mechanical properties of a single layer of graphite (e.g. graphene) and the bombardment of CO<sub>2</sub> and H<sub>2</sub>O on graphene at high temperature by using extensive molecular dynamics (MD) simulations. The Reactive Empirical Bond Order (REBO) potential is employed to model the C-C bonds. The stress-strain curve shows that the stiffness of graphene decreases with increase in temperature. The strength of graphene at 2400 K is 60% less than the strength of graphene at 300 K. Also, we observe that the collision with CO<sub>2</sub> and H<sub>2</sub>O provokes the bond breaking of C-C bonds in graphene at high temperature. The bombardment of gas molecules is carried out for different temperatures ranging between 300 K and 3000 K. Until 2400 K, both H<sub>2</sub>O and CO<sub>2</sub> molecules are reflected back from the surface. However, at a critical temperature *i.e.*, 2700 K and beyond, the bombardment of gas molecules breaks the C-C bond in the graphene. As the temperature increases, the graphene is destroyed quickly. This study shows that even the real gas molecules can induce the fracture of graphene at high temperature.

**Keywords:** Surface Erosion, Rocket Nozzle, Highly Energetic Gas, Molecular Dynamic Simulation

## 1. Introduction

Graphene is a one-atom thick planar sheet of sp<sup>2</sup>-bonded carbon atoms, which has attracted the attentions of many researchers for its novel electrical and mechanical properties. For example, its stiffness is as high as 1 TPa and the fracture strength is 100 times greater than a hypothetical steel film of same thickness.

Recently many experimental and theoretical studies have been conducted to quantify the extensive mechanical properties of graphene for diverse conditions. The early experimental measurements (Blakslee et al., 1970) reported the Young's modulus of bulk graphite to be 1.06±0.02 TPa. Liu et al., (2007) computed the Young's modulus of graphene to be 1.050 TPa. The Young's modulus from MD simulations has been reported as 1.272 TPa with the modified Brenner potential (Gupta et al., 2005) and 1.026 TPa with reactive empirical bond order

(REBO) potential (Bao et al, 2004). The ultimate stress of graphene in armchair and zig-zag direction to be 97.3 GPa and 113.6 GPa at 1 K, respectively (Dewapriya et al., 2013). Zhao et al., (2009) computed the Young's modulus of graphene to be 1.01±0.03 by MD simulations and 0.91 TPa by Tight Bonding simulation. They have calculated the fracture stress of graphene in armchair and zig-zag direction as 90 GPa and 107 GPa at room temperature and the corresponding fracture strain is 0.13 and 2.0 respectively. They have also shown that the Young's modulus exhibits minor variation until 1200 K and decreases beyond 1200 K.

Previous studies of erosion phenomena on graphite surface have been performed at macroscopic level (Kuo et al., 1985; Keswani et al., 1986). The sputtering mechanism on the graphene surface by the collision of light gas molecules like hydrogen atom has been simulated by Ito et al., 2008. The collision resistance of graphene against hydrogen

bombardment has also been investigated by Ito et al., (2005). The collision between hydrogen and graphite is classified into three regimes of adsorption, reflection and penetration through the graphene layer. They have also stated that the adsorption rate is dependent on the incident energy and not on the temperature of graphene. As per our knowledge this is a pioneer study to simulate the erosion of graphene structures by ordinary gas molecules such as H<sub>2</sub>O and CO<sub>2</sub>, using molecular level simulations.

In this paper, the extensive molecular dynamics (MD) simulations are performed using LAMMPS (Plimpton, 1995). In order to investigate the strength of the graphene at high temperatures, the MD simulations are performed for a wide range of temperatures between 300 K and 3000 K. At each temperature, the uniaxial tension test is performed to calculate the values of Young's modulus, fracture stress, and fracture strain. The stress-strain relations are plotted for these temperatures and they are compared with the previous studies (Zhao et al., 2010). Then, the energetic combustion gas molecules (like CO<sub>2</sub> and H<sub>2</sub>O) are bombarded on the graphene at diverse temperatures.

This paper is organized as follows. In Sec. 2, we describe the present MD simulations along with the supplementary relations. In Sec. 3, strength and stiffness of the graphene sheet are discussed based on the results from uniaxial tension test. In Sec. 4, the effects of temperature on the Young's modulus of graphene are addressed. The results and discussions of bombardment of gas molecules on the graphene sheet are presented in Sec. 5 and finally concluded with some remarks and ideas for future work in Sec. 6.

## 2. MD simulations

In this paper, MD simulations are performed with reactive empirical bond order (REBO) potential. The 2<sup>nd</sup> generation REBO potential is well-suited for capturing the C-C bond interaction as well as for describing the

bond forming and bond breaking phenomena.

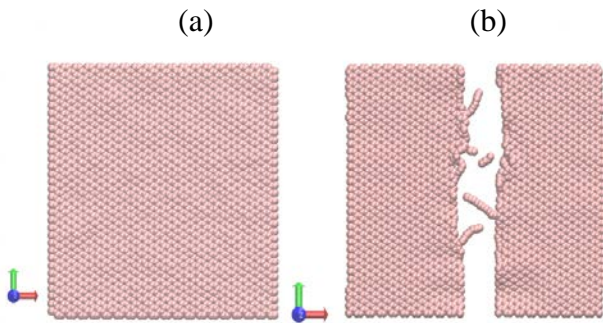
In order to eliminate the effect of strain hardening, the cutoff parameter is set to 2.0 Å (Dewapriya et al., 2013). Periodic boundary conditions (PBC) are used in all directions. All the simulations are performed in a single layer graphene sheet of size 79.53×79.95 Å with 2508 atoms. We perform Isothermal-Isobaric (NPT) simulations at the specified temperatures for 30 ps to let the system attain its equilibrium configuration. The NPT ensemble uses the Nose-Hoover thermostat and barostat to control the temperature and pressure respectively. The thermostat and barostat are applied at every 100 and 1000 time steps, respectively. The velocity-verlet time integration algorithm is used with a time step of 0.5 fs. For tension test, simulations are performed for time steps 0.1 fs, 0.2 fs and 0.5 fs. It is found that the results obtained from all the time steps are same. In order to save computation time and to get a fine resolution of the results, the time steps 0.5 fs and 0.2 fs are used for tension test simulation and bombardment simulations, respectively. The total time taken for the equilibration process for 30 ps is only 15 minutes on 32 CPU's.

## 3. Uniaxial tension test

To investigate the mechanical properties of graphene, we perform a deformation controlled uniaxial tension test with a constant strain rate of 0.001 /ps. The strain increment is applied in the armchair direction of the structure at every one time step with a step size of 0.5 fs. In this work, armchair direction is loaded in x-direction and zigzag direction is loaded in the y-direction. The engineering (nominal) strain, engineering (nominal) stress and Young's modulus are calculated from the following formula as (Zhao et al., 2009; Mehl., 1993; Karakasidis et al., 2007)

$$\varepsilon_x = \frac{l_x - l_x^0}{l_x^0}, \quad \varepsilon_y = \frac{l_y - l_y^0}{l_y^0}, \quad \sigma_x = \frac{1}{V^0} \frac{\partial U}{\partial \varepsilon_x},$$

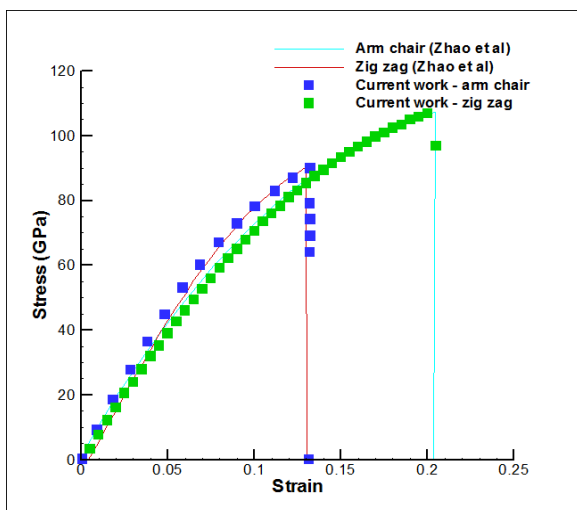
$$E = \frac{1}{V^0} \left. \frac{\partial^2 U}{\partial \varepsilon_x^2} \right|_{\varepsilon_x=0},$$



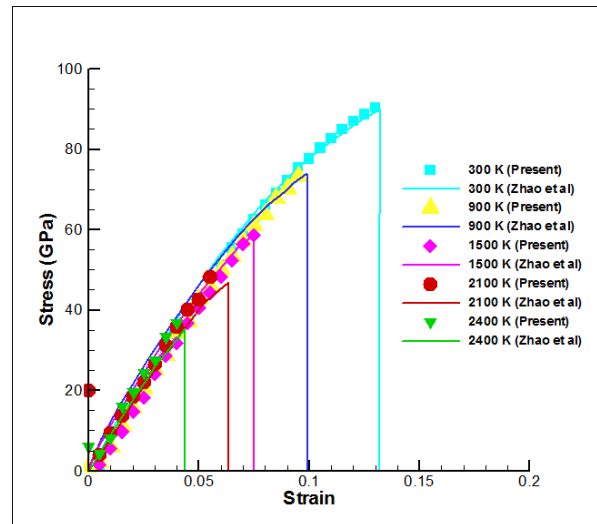
**Fig. 1.** (a) Equilibrium configuration of graphene  
 (b) Fracture due to uniaxial tension test

where  $l_x^0$  and  $l_y^0$  are the initial lengths of the nanoribbon in x and y directions respectively,  $l_x$  and  $l_y$  are the strained lengths of the nanoribbon, U is the strain energy,  $V^0 = l_x^0 l_y^0 t$  is the initial volume of the structure, E is the Young's modulus and  $t = 3.35 \text{ \AA}$  is assumed as the thickness of the graphene (Lee et al., 2008). Simple 2<sup>nd</sup> order forward difference scheme (Hoffmann et al., 2000) is used for calculating the stress and Young's modulus.

Initially, tension test is performed at room temperature in order to validate the simulation methods in the current study. Fig. 1 shows the stress-strain relation of graphene in armchair and zigzag direction. The fracture strength of graphene, at room temperature, in armchair



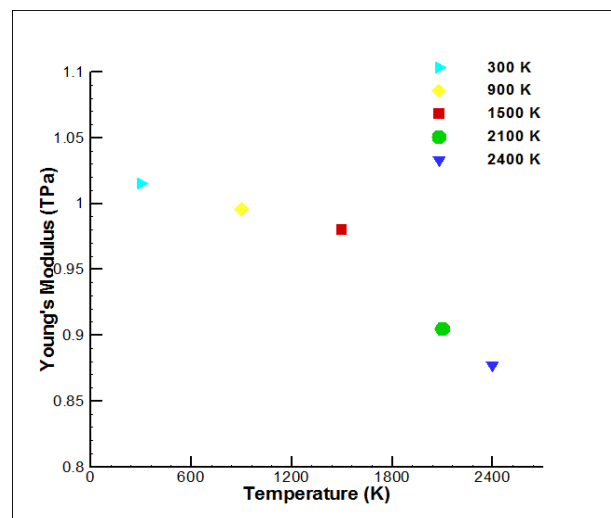
**Fig. 2.** Stress-strain curve in arm chair and zig-zag direction at 300 K



**Fig. 3.** Stress vs strain curve under the influence of uniaxial tension test at various temperatures

and zig-zag direction is 90 GPa and 107 GPa respectively, and the corresponding fracture strains are 0.13 and 2.0 respectively. Consequently, the same procedure is followed for temperature until 2400 K at an interval of 600 K. Fig. 2 shows the dependence of fracture strength on temperature in the armchair direction. The initial fluctuation in the stress-strain curve is due to noise in the molecular dynamics simulation.

The fracture strength and fracture strain decreases with increase in temperature. The fracture strength of graphene at 2400 K is



**Fig. 4.** Young's modulus at various temperature values

**Table 1**

Comparison of Young's modulus of present work with the previous studies at 300 K

	Young's modulus (TPa)	
	Armchair	Zigzag
Present	1.015	0.987
Zhao et al.	1.01	-
Grantab et al.	0.8	-

approximately 60% lower than the fracture strength at room temperature. Following the previous work of Zhao et al., (2010), we considered the tension test simulation until 2400 K. For temperature above 2400 K, the stress-strain curve appears to be unstable. And it is found that the results are in good agreement with the previous studies. The time taken to perform tension test is only 15 minutes on 32 CPU's.

The out-of-plane fluctuation  $\bar{h}$  is measured to be 0.608 Å, during the equilibrium stage. Also, the fluctuation satisfies a common relation of  $\bar{h} \propto L^\zeta$  (L is characteristic length) for a membrane by setting  $\zeta = 0.6-0.8$ . The ratio of  $\bar{h}/L^\zeta$  is calculated to be 0.0439 and this is in good agreement with the reference value 0.044 of Fasoline et al., (2007).

#### 4. Effect of temperature on Young's modulus

Young's modulus of graphene at room temperature is approximately around 1 TPa both in armchair and zigzag direction. It is found that the Young's modulus of graphene at 2400 K is only 10% less than that graphene at room temperature. Table 1 shows the value of Young's modulus in the armchair direction and zigzag direction at room temperature. The effect of temperature on Young's modulus can be clearly predicted from Fig. 3, that the Young's modulus shows minor variation initially and decreases with increase in temperature above 900 K. This shows that

**Table 2**

Lennard-Jones parameters for CO<sub>2</sub>, H<sub>2</sub>O and Graphene

Site	Charge	$\sigma$ (Å)	$\epsilon / k_B$	
CO <sub>2</sub>	O	-0.3256	3.033	80.507
	C	0.6512	2.757	28.129
H <sub>2</sub> O	O	-0.8476	3.182	78.2
	H	0.4238	0.0	0.0
Graphene	C	-	3.469	33.24

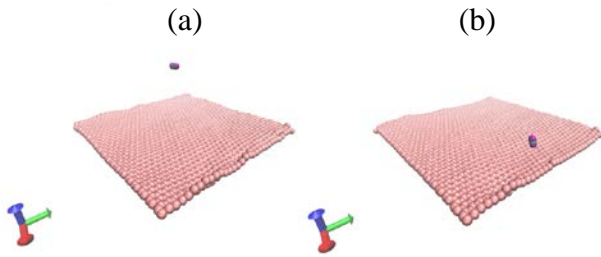
graphene is one of the strongest materials ever known even at high temperatures. This is also in good agreement with the previous studies.

#### 5. Gas Molecule Bombardment

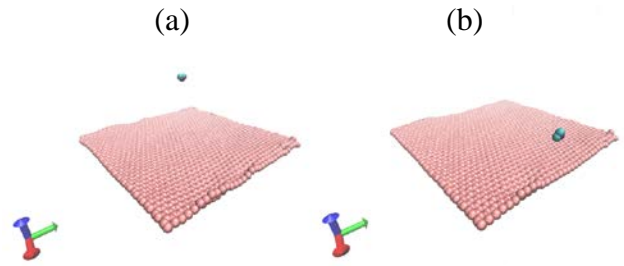
The main objective of bombarding the gas molecules like H<sub>2</sub>O and CO<sub>2</sub>, is to mimic the molecular level process taking place in the rocket nozzle, in which highly energetic hot combustion gaseous products strikes the surface of the nozzle, coated with graphene.

Water is modeled by SPC/E model (Berendsen et al., 1987). The equilibrium O-H bond length is fixed to 1 Å, with an HOH angle of 109.47 degrees. For Carbon dioxide we used EPM model of Harris and Yung (1995). This model is selected due to its simplicity and computational efficiency. The C-O bond length is fixed to 1.149 Å, with O-C-O angle of 180 degrees.

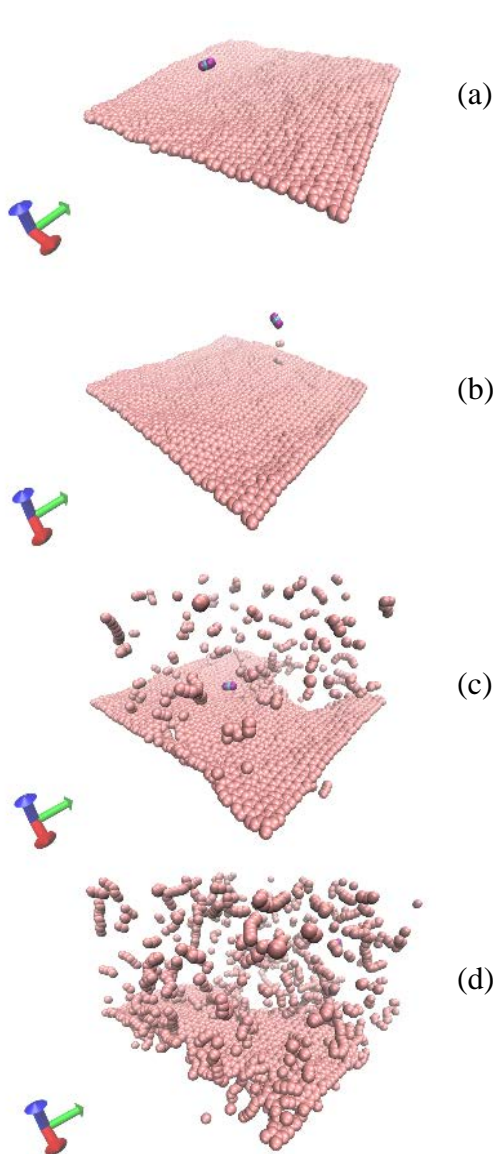
To investigate the response of the graphene sheet at low and high temperatures, collision process is carried for 300 K, 2700 K and 3000 K. The box dimension in the z-direction is set to 60 Å. The graphene sheet and the gas molecules are placed initially at a distance of 20 Å and 50 Å respectively, in the transverse direction. To conserve energy more efficiently at higher temperatures like 2700 K and 3000 K the time step is reduced to 0.2 fs. For temperatures above 2700 K, Langevin thermostat (NVT) is used to maintain the bath at its corresponding temperature. To clearly understand the bombarding phenomena two set of incident velocity is used *i.e.*, 1500 m/s



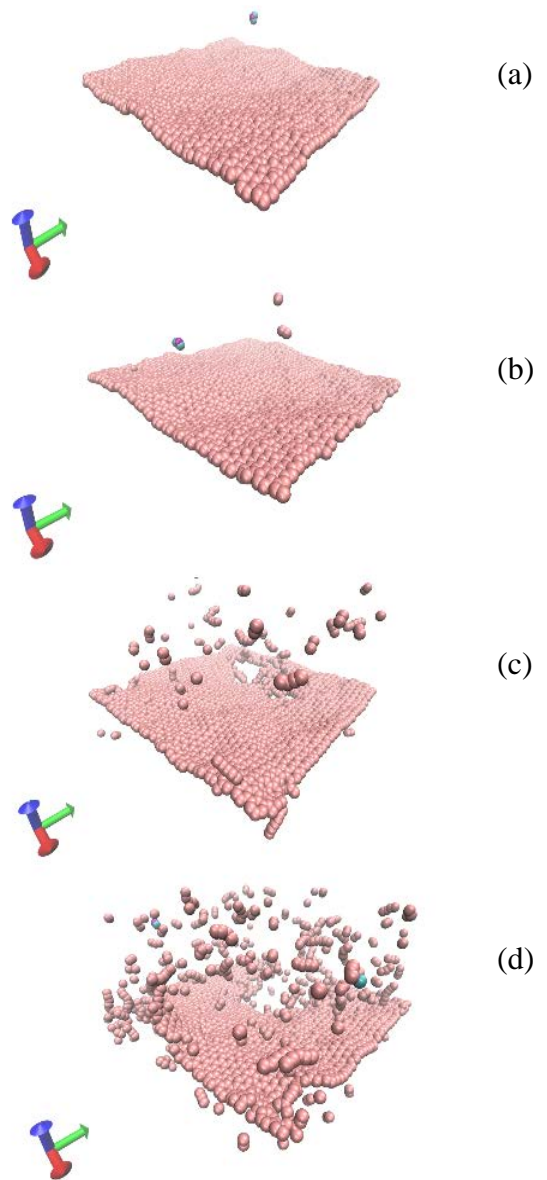
**Fig. 5.** Bombardment of graphene with CO<sub>2</sub> at 300 K (a) initial (0 ps) and (b) final configuration (200ps)



**Fig. 6.** Bombardment of graphene with H<sub>2</sub>O at 300 K (a) initial (0 ps) and (b) final configuration (200ps)



**Fig. 7.** Bombardment of graphene with CO<sub>2</sub> at 2700 K at 1500 m/s (a) 70 ps, (b) 84ps (c) 120ps (d) 140ps.



**Fig. 8.** Bombardment of graphene with H<sub>2</sub>O at 2700 K at 1500 m/s (a) 50 ps, (b) 66ps (c) 120ps (d) 140ps.

and 3000 m/s.

In our bombardment simulations, many-

body potential REBO is used to describe the C-C interaction and the Lennard Jones (LJ)

parameters are adjusted for C-H (H<sub>2</sub>O) interactions, C-O (H<sub>2</sub>O) interactions, C-C (CO<sub>2</sub>) interactions and C-O (CO<sub>2</sub>) interactions. LJ parameters are listed in Table 1 for CO<sub>2</sub>, H<sub>2</sub>O and graphene. The 2<sup>nd</sup> generation REBO and Lennard-Jones non-bonding potential are combined by using “hybrid” pair style in LAMMPS.

We inject the gas molecules like H<sub>2</sub>O and CO<sub>2</sub> onto the hot graphene sheet at a given temperature. Figs. 5-8, illustrate the bombardment processes of H<sub>2</sub>O and CO<sub>2</sub> for different temperatures. When the highly-energetic gas molecule hits the graphene sheet, wave-like motion is observed in the graphene sheet due to the sudden impact.

Until 2400 K, there is no fracture or bond-breaking happens due to the bombardment of H<sub>2</sub>O and CO<sub>2</sub> for both the incident energies. However, at 2700 K breaking happens due to the collision between graphene and H<sub>2</sub>O at 66 ps, and collision between graphene and CO<sub>2</sub> at 84 ps for incident velocity of 1500 m/s.

As the temperature increases the bombardment of gas molecules breaks the bond very quickly. Table 3 clearly shows that the molecules at high velocity and graphene at high temperature breaks the graphene sheet easily. Comparing the higher and lower velocity bombardment of H<sub>2</sub>O and CO<sub>2</sub> on graphene at 2700 K, the bond breakage happens faster for CO<sub>2</sub> at 3000 m/s than H<sub>2</sub>O but the case is reverse for 1500 m/s. This is because, CO<sub>2</sub> is heavier compared to H<sub>2</sub>O. Therefore the acceleration will be higher when the velocity is doubled. Consequently it loses momentum when it strikes the graphene causing breakage. On the other hand, H<sub>2</sub>O being lighter than CO<sub>2</sub> produces low acceleration even if the velocity is doubled. Hence the breakage happens later for H<sub>2</sub>O.

## 5. Conclusions

In summary, we have performed extensive MD simulations to understand the mechanical properties of graphene and collision process between gas and graphene. The mechanical properties like fracture stress, fracture strain and Young’s modulus of a graphene sheet was

**Table 3**

Comparison of time (ps) at which bond breaking happens for the bombardment of CO<sub>2</sub> and H<sub>2</sub>O

Temperature (K)	Velocity (m/s)	Onset of Bond Breakage (ps)	
		CO <sub>2</sub>	H <sub>2</sub> O
300	3000	No	No
2400	3000	No	No
2700	1500	84	66
	3000	20	30
3000	1500	38	7

studied using deformation controlled tension test. The fracture strength of graphene decreases with increase in temperature. This study shows that the fracture strength of graphene at 2400 K is 60 % less than that of room temperature. Collision process shows that the gas molecules at low temperatures are reflected back and causes no damage to the surface. With increase in temperatures the gas molecules destroys the graphene slowly with respect to time and at very high temperatures the graphene was destroyed quickly. Even though the bond breaks faster for the bombardment of H<sub>2</sub>O on graphene at 2700 K than CO<sub>2</sub> (Fig. 7 & 8), the no. of bonds broken at 140 ps is more for CO<sub>2</sub> than H<sub>2</sub>O. This is because H<sub>2</sub>O is lighter than CO<sub>2</sub> and therefore the force acting on the H<sub>2</sub>O will be less than CO<sub>2</sub>.

For the future study, the bombardment process can be repeated by increasing the number of layers of graphene (e.g. graphite). Also, the density of incident gas molecule can be increased to investigate the criteria for the bond-breaking.

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