Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Negative Poisson's ratio in graphene-based carbon foams

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1. Supplementary video

Movie 1: Structures of CFs when they are compressed in the *x* direction.

Movie 2: Structures of CFs when they are compressed in the *y* direction.

2. Supplementary figure

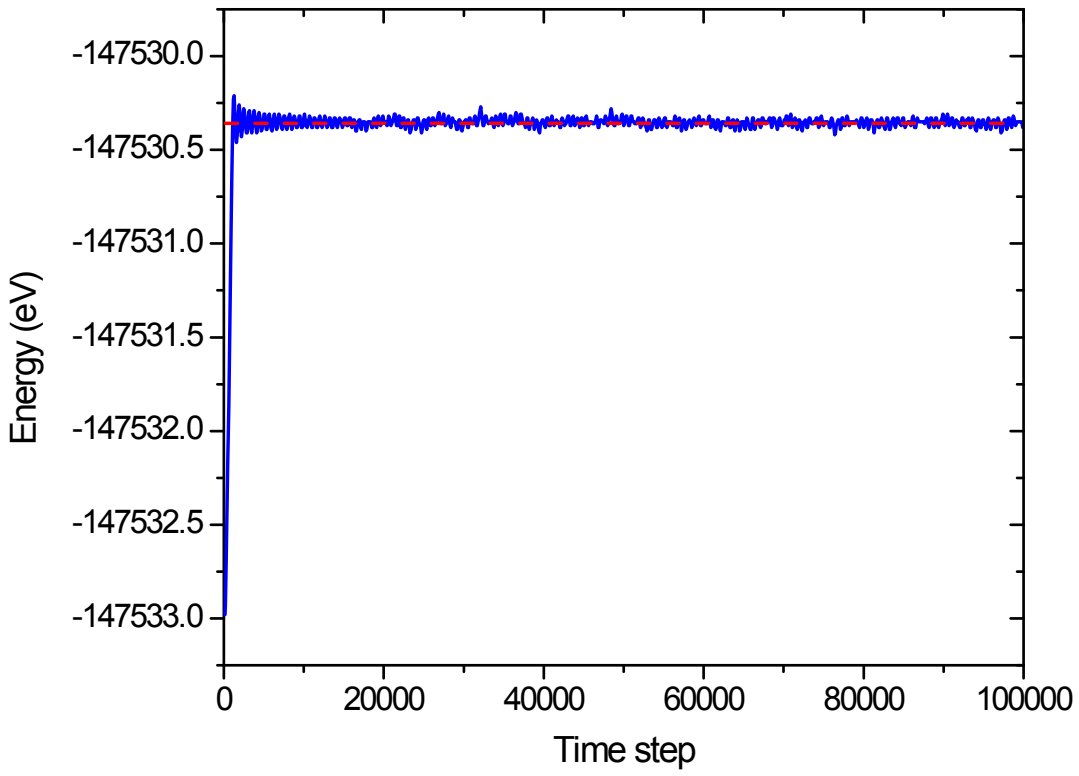

Fig. S1. Internal energy evolution for CFs during the initial structural relaxation process

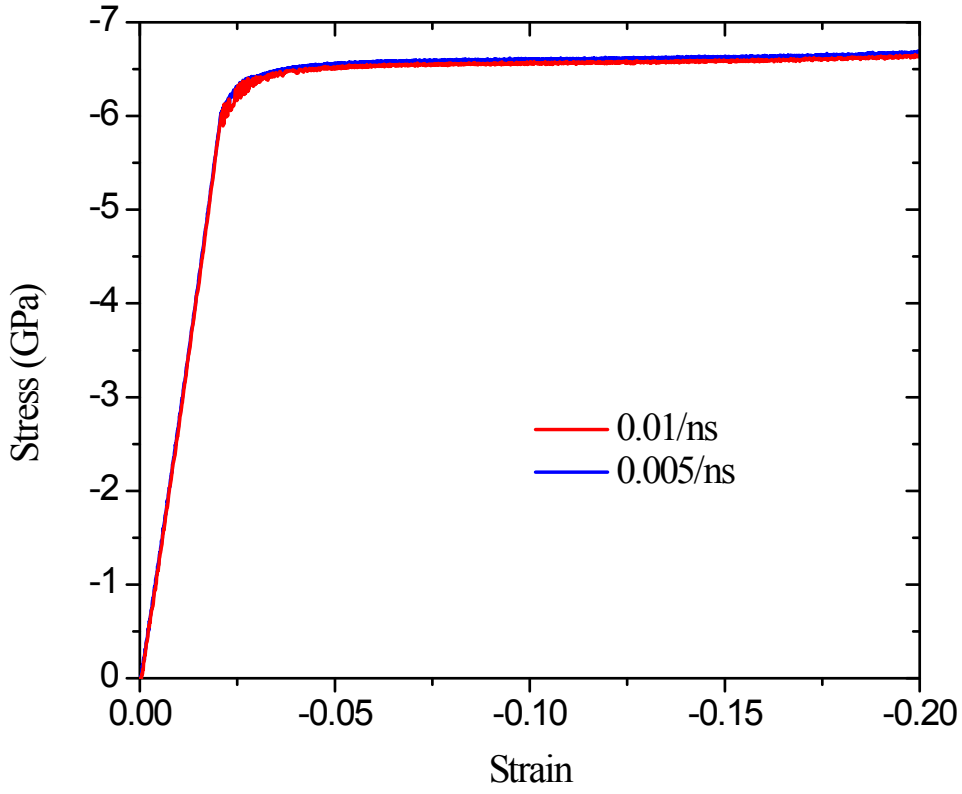

Fig. S2. Stress-strain response of CFs subjected to the uniaxial compression, respectively, with a strain rate of 0.005 ns^{-1} and 0.01 ns^{-1}. Here the cell length is 1.3 nm

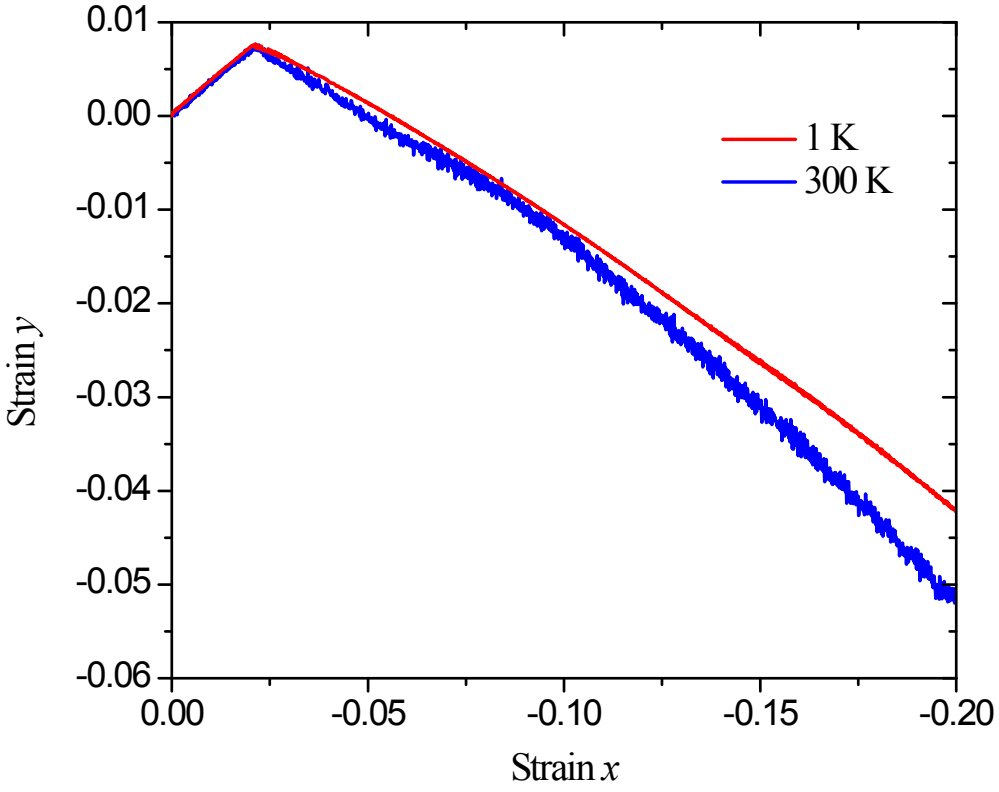

Fig. S3. The transverse strain versus the applied axial strain when CFs are uniaxially compressed within 1 K and 300 K. Here the cell length is 1.3 nm

3. Continuum models of CFs

3.1 Density

The density ρ of the unit cell of CFs shown in Fig. S4 can be defined as

$$\rho = \frac{M}{S}, \tag{S1}$$

where M and S are the mass and area of the unit cell, respectively.

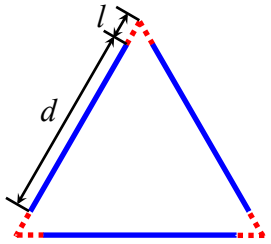

Fig. S4. A unit cell of CFs

Considering the fact that each component graphene sheet in CFs is shared by two neighbouring unit cells, the mass of each unit cell is thus

$$M = \frac{3Pd}{2}, \tag{S2}$$

where P is the areal mass density of graphene and d is the length of the component graphene element, i.e., the cell length.

Meanwhile, the area of the unit cell shown in Fig. S4 can be expressed as

$$S = \frac{\sqrt{3}}{4}(d + 2l)^2, \tag{S3}$$

where l is the side length of the hexagon carbon ring in CFs. Substituting Eqs. S2 and S3 in Eq. S1 we obtain the density of CFs as

$$\rho = 2\sqrt{3}\frac{P}{d}\frac{1}{(1+2l/d)^2}, \tag{S4}$$

Usually, l is significantly smaller than d. Under this circumstance, the density of CFs can be approximately expressed as

$$\rho \approx 2\sqrt{3}\frac{P}{d}. \tag{S5}$$

3.2 Stress distribution

We consider two different cases, where CFs are compressed along x and y directions as shown in Fig. S5. The stresses induced in the cell walls are shown as T_1 and T_2 in Fig. S5. Since the two different compressive loading cases induce different stresses within the cell walls, we will analyse these two cases individually.

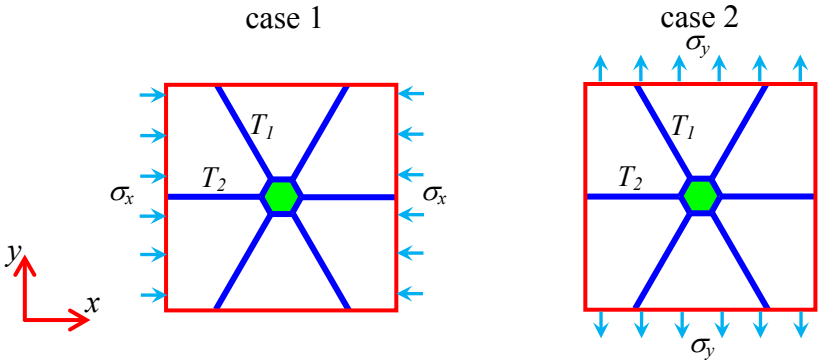

Fig. S5. CFs under two cases of compressive loading

Considering the fact that the deformation of the hexagon carbon ring in CFs is extremely small, it thus can be ideally assumed as a rigid body. Under this circumstance, when a compressive stress σ_x is applied along the x direction, i.e., case 1 shown in Fig. S5, the equilibrium equations can be written as

$$T_2 + 2T_1\cos(\pi/3) = \sigma_x(d+2l)\sin(\pi/3), \tag{S6.1}$$

$$2T_1\sin(\pi/3) = 0. \tag{S6.2}$$

From Eq. S6 we see that when CFs are compressed along the x direction, the stresses in their component graphene sheets can be expressed as

$$T_1 = 0\,,\;\; T_2 = \frac{\sqrt{3}}{2}\sigma_x d\left(1+\frac{2l}{d}\right) \approx \frac{\sqrt{3}}{2}\sigma_x d\,. \tag{S7}$$

When a compressive stress σ_y is applied along the y direction, i.e., case 2 shown in Fig. S5, the equilibrium equations can be written as

$$T_2 + T_1\cos(\pi/3) = 0\,, \tag{S8.1}$$

$$2T_1\sin(\pi/3) = \sigma_y(d+2l)\,. \tag{S8.2}$$

From the above equation we see that when CFs are compressed along the y direction, the stresses in their component graphene sheets can be expressed as

$$T_1 = \frac{1}{\sqrt{3}}\sigma_y d\left(1+\frac{2l}{d}\right) \approx \frac{1}{\sqrt{3}}\sigma_y d\,,\;\; T_2 = -\frac{1}{2\sqrt{3}}\sigma_y d\left(1+\frac{2l}{d}\right) \approx \frac{1}{2\sqrt{3}}\sigma_y d\,. \tag{S9}$$

3.3 Young's modulus and Poisson's ratio of CFs prior to buckling

Here we will consider a unit cell of CFs as shown in Fig. S6, where the initial length of the inclined and horizontal cell walls is d_1 and d_2, respectively. Considering the fact that the side length of the hexagon carbon ring in CFs is l, two sides of unit cell shown in Fig. S6 can be thus expressed as $L_1 = d_1+2l$, while the base length is $L_2 = d_2+2l$. If the cell walls of the unit cell deform by small amounts of Δd_1 and Δd_2, the inclined cell walls then have length $d_1+\Delta d_1$, and the length of the horizontal cell walls becomes $d_2+\Delta d_2$. As a result, the length of the sides of the deformed unit cell shown in Fig. S6 becomes $L_1+\Delta d_1$, while the base length becomes $L_2+\Delta d_2$. Meanwhile, the height of the unit cell becomes $h+\Delta h$ after the deformation. By using Pythagoras' theorem we obtain:

$$\left(\frac{L_2+\Delta d_2}{2}\right)^2+\left(h+\Delta h\right)^2=\left(L_1+\Delta d_1\right)^2, \tag{S10}$$

Ignoring terms of second order for small extensions in Eq. S10, and using the results $L_1 = L_2/[2\cos(\pi/3)]$ and $h = L_2\tan(\pi/3)/2$ we get:

$$\frac{\Delta h}{h}=\frac{4}{3}\left(\frac{\Delta d_1}{L_1}\right)-\frac{1}{3}\left(\frac{\Delta d_2}{L_2}\right). \tag{S11}$$

The quantities $\Delta d_1/L_1$ and $\Delta d_2/L_2$ in Eq. S11 are simply the strains of the cell walls under stress T_1 and T_2 (see Fig. S5) given by T_1/Y and T_2/Y, respectively, where Y is the tensile rigidity of component graphene.

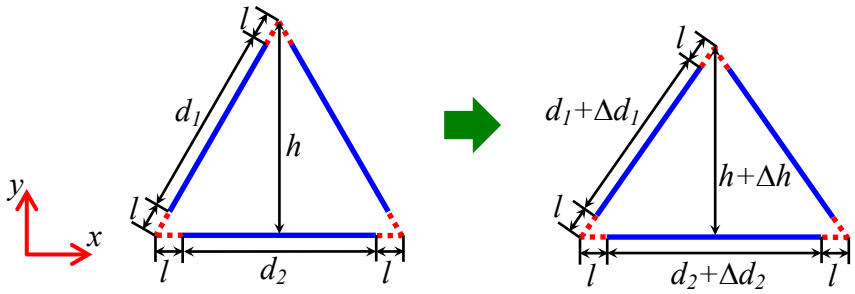

Fig. S6. Deformed unit cell of CFs for calculating Young's modulus and Poisson's ratio

When CFs are compressed along the x direction, i.e., $T_1 = 0$ and $T_2 = \sqrt{3}\sigma_x d(1+2l/d)/2$, the strains in x and y directions are, respectively,

$$\varepsilon_x=\frac{\Delta d_2}{L_2}=\frac{\sqrt{3}}{2}\frac{\sigma_x d}{Y}, \tag{S12.a}$$

$$\varepsilon_y=\frac{\Delta h}{h}=-\frac{1}{3}\left(\frac{\Delta d_2}{L_2}\right)=-\frac{\sqrt{3}}{6}\frac{\sigma_x d}{Y}. \tag{S12.b}$$

From Eq. S12 the Young modulus E_x and Poisson's ratio ν_{xy} of CFs in the x direction can be expressed as

$$E_x = \frac{\sigma_x}{\varepsilon_x} = \frac{2}{\sqrt{3}}\frac{Y}{d},\ \ \nu_{xy} = -\frac{\varepsilon_y}{\varepsilon_x} = \frac{1}{3}. \tag{S13}$$

When CFs are compressed along the y direction, i.e., $T_1 = \sqrt{3}\sigma_y d(1+2l/d)/\sqrt{3}$ and $T_2 = \sigma_x d(1+2l/d)/(2\sqrt{3})$, the strains in x and y directions are, respectively,

$$\varepsilon_x = \frac{\Delta d_2}{L_2} = -\frac{1}{2\sqrt{3}}\frac{\sigma_y d}{Y}, \tag{S14.a}$$

$$\varepsilon_y = \frac{\Delta h}{h} = \frac{4}{3}\left(\frac{\Delta d_1}{L_1}\right) - \frac{1}{3}\left(\frac{\Delta d_2}{L_2}\right) = \frac{\sqrt{3}}{2}\frac{\sigma_y d}{Y}. \tag{S14.b}$$

From Eq. S14 the Young modulus E_y and Poisson's ratio ν_{yx} of CFs in the y direction can be expressed as

$$E_y = \frac{\sigma_y}{\varepsilon_y} = \frac{2}{\sqrt{3}}\frac{Y}{d},\ \ \nu_{yx} = -\frac{\varepsilon_x}{\varepsilon_y} = \frac{1}{3}. \tag{S15}$$

3.4 Geometrical predictions of Poisson's ratio of CFs after buckling

When a unit cell of CFs shown in Fig. S7 is compressed along the y direction with a strain of 100%, according to our MD observations the midpoints in the inclined cell walls become in contact with midpoints of the horizontal cell walls. Therefore, when a compressive strain of 100% is applied the central hexagon ring rotates 60^o in the plane. Thus, based on the geometrical estimation technique [S1], the horizontal cell walls initially with length d will bend such that their final length in horizontal direction becomes 0.8d (see Fig. S7). Under this circumstance, the transverse strain ε_x can be expressed as

$$\varepsilon_x = \frac{0.8(3d) + 3a - (3d + 6a)}{3d + 6a} = -0.2 \cdot \left(\frac{1 + 5l/d}{1 + 2l/d}\right). \tag{S16}$$

Thus, the Poisson's ratio ν_{yx} can be calculated as

$$\nu_{yx} = -\frac{\varepsilon_x}{\varepsilon_y} = -\frac{-0.2\cdot\left(\dfrac{1+5l/d}{1+2l/d}\right)}{-1} = -0.2\cdot\left(\frac{1+5l/d}{1+2l/d}\right). \tag{S17}$$

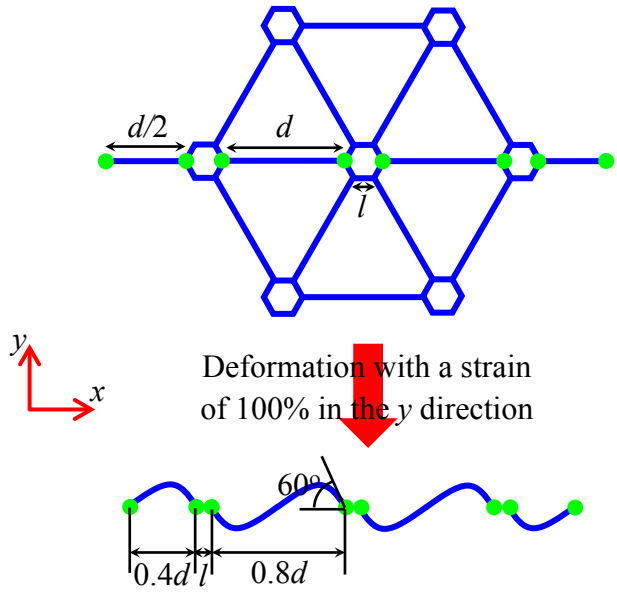

Fig. S7. The schematic of undeformed unit cell of CFs and predicted configuration of deformed unit cell at 100% compressive strain

4. FE simulations for the buckling analysis of foam structures

In the FE calculations we considered a foam structure structurally analogous to the CFs considered in our study. Here, the ratio between the cell wall length d and the side length l of the hexagon ring is set as 5. In Fig. S8 we show the FE model of the foam structure, where BEAM3 element was selected to describe the elastic cell wall of the foam structure. The buckling analysis was performed by initially applying a reference level of force to the foam structure. Then, a standard linear static analysis was carried out for the foam structure to obtain its geometric stiffness matrix. Thus, the lowest eigenvalue and the corresponding buckling mode of the foam

structure can be obtained by using the block Lanczos algorithm in the commercial code ANSYS. The readers can refer to Re. [S2] for more details.

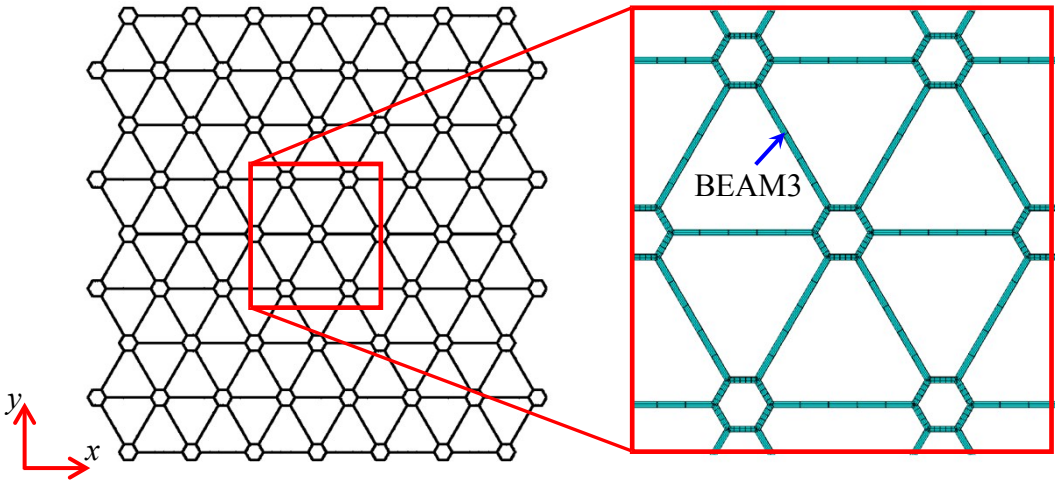

Fig. S8. The FE model of a foam structure

References

[S1]. D. Mousanezhad, H. Ebrahimi, B. Haghpanah, R. Ghosh, A. Ajdari, A. M. S. Hamouda and A. Vaziri, Int. J. Solids Struct., 2015, 66, 218-227.

[S2]. D. L. Logan, A First Course in the Finite Element Method, Thomson, Toronto, 2007.