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Tianjiao Shao,[1,2] Bin Wen,[1,a)] Roderick Melnik,[3,4] Shan Yao,[2] Yoshiyuki Kawazoe,[5] and Yongjun Tian[1]

[1]*State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China*
[2]*School of Materials Science and Engineering, Dalian University of Technology, Dalian 116023, China*
[3]*M²NeT Lab, Wilfrid Laurier University, 75 University Ave. West, Waterloo, Ontario N2L 3C5, Canada*
[4]*Ikerbasque, Basque Foundation for Science and BCAM, Bilbao 48011, Spain*
[5]*Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

Based on the first principles calculation combined with quasi-harmonic approximation in this work, we focus on the analysis of temperature dependent lattice geometries, thermal expansion coefficients, elastic constants, and ultimate strength of graphene and graphyne. For the linear thermal expansion coefficient, both graphene and graphyne show a negative region in the low temperature regime. This coefficient increases up to be positive at high temperatures. Graphene has superior mechanical properties with Young's modulus E = 350.01 N/m and ultimate tensile strength of 119.2 GPa at room temperature. Based on our analysis, it is found that graphene's mechanical properties have strong resistance against temperature increase up to 1000 K. Graphyne also shows good mechanical properties with Young's modulus E = 250.9 N/m and ultimate tensile strength of 81.2 GPa at room temperature, but graphyne's mechanical properties have a weaker resistance with respect to the increase of temperature than that of graphene. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4766203]

I. INTRODUCTION

Graphene only contains the sp^2-hybridized C–C bond, the corresponding bond energy[1] is larger than that of diamond sp^3-hybridized bond[2] and, therefore, it is expected to own super mechanical properties.[3–5] Graphyne can be constructed by altering one-third carbon-carbon bonds in graphene by triple-bonded carbon linkages and it can be seen as the simplest member in the graphdiyne material, the acetylene group results in a large difference in the properties of graphene and graphyne. Owing to their novel structures, as well as exceptional optical, electrical, and mechanical properties of these materials, graphene[5–9] and graphyne[10–15] have generated substantial interest in recent years for many experimental and theoretical researchers.

Two-dimensional materials are important for future applications in nano-electromechanical system and semiconductors, thus, it is essential to clarify mechanical properties of graphene and graphyne and their resistance against temperature. Recently, several works have been performed to calculate and measure the mechanical properties of single layer graphene.[16–26] Already in 2001, Kudin *et al.* predicted some mechanical properties of graphene by employing density functional theory (DFT),[19] in particular, it was found that the elastic moduli along both armchair [n, n] and zigzag [n, 0] directions are 345 N/m (corresponds to 1150.6 GPa by supposing the thickness of 0.335 nm). In 2007, Liu *et al.* determined the phonon-induced instability by using the first-principles method; they reported the Young's modulus of 1050 GPa, ultimate strength of 110 GPa along the [n, 0] direction, and 121 GPa along [n, n] direction, respectively.[20] In the same year, Khare *et al.* investigated theoretically the deformation of graphene with defects through combining several approaches including the first principle method, molecular dynamics, and a linear elastic continuum description.[21] In 2008, Lee *et al.* measured graphene first in the experiment and reported the Young's modulus of 340 N/m (1020 GPa) and ultimate strength of 130 GPa at room temperature.[7] In 2009, Wei *et al.* evaluated the high order elastic constant of graphene up to the fifth order elastic constants by using DFT. In particular, they reported $c_{11} = 358.1$ N/m and $3_{12} = 60.4$ N/m. Their work added important insight into the nonlinear elastic behavior of graphene.[23] In 2010, Shen and Zhang calculated the isotropic monolayer graphene's temperature dependent elastic constants (TDEC) at 300 K, 500 K, and 700 K by employing classical molecular dynamics (MD) methodology, and both temperature and sample size effects on graphene were presented.[25] In the same year, Zhao and Aluru predicted the graphene's temperature dependent ultimate strength (TDUS) from 0 K to 2500 K by using both classical MD and quantized fracture mechanics methods.[26] In 2011, Cranford and Buehler investigated the mechanical properties of graphyne on the basis of first-principles-based ReaxFF field by MD.[27] Although mechanical properties of graphene have been measured and calculated, divergence in the actual values still exists, as shown in Table I.

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a)Author to whom correspondence should be addressed. Electronic mail: wenbin@ysu.edu.cn. Tel.: 086-335-8568761.

TABLE I. Reported mechanical properties of graphene at different temperatures from calculations and experimental measurements.

Temperature (K)	Method	c_{11} (N/m)	c_{12} (N/m)	Young's modulus	Ultimate strength (GPa)	Year	References
0	DFT			345 N/m	110 [n, 0]	2001	15
					121 [n, n]		
0	DFT			1050 GPa		2007	17
300	Expt.			340 N/m	130	2008	3
0	DFT	358.1	60.4			2009	19
300	MD	306	21			2010	21
500	MD	304	18			2010	21
700	MD	300	17			2010	21
300	MD				93	2010	22
600	MD				85	2010	22
900	MD				76	2010	22
1200	MD				66	2010	22

Temperature influences on the mechanical properties of materials was shown in many carbon materials, such as carbon nanowire,[28–30] carbon nanotube,[31] and so on. Graphene and graphyne, being two kinds of carbon materials, temperature may have a great influence on their properties. Therefore, it is important to clarify their temperature dependent mechanical properties to pave the way for their potential applications. In addition, mechanical properties of graphyne dependence on temperature have never been investigated to date, while the temperature influence on graphene's mechanical properties has only been evaluated by the classical MD.

Quasi-harmonic approximation (QHA) treats phonons as phonon "gas," as if they did not interact and the system becomes equivalent to a collection of independent harmonic oscillators. If the phonon frequencies are known, the energy levels of the system are well defined, and the partition function and Helmholtz free energy can be determined, and further the other thermodynamic properties can be calculated. High temperature and high pressure properties of crystals have been predicted successfully by combining DFT with QHA method (DFT-QHA).[32] Very recently, a new methodology has been developed by our group for implementing lattice geometry optimization and calculating TDEC within a given temperature range by using this method.[33] This work extends this methodology to address the problem of temperature dependent lattice geometry optimization and mechanical properties of two-dimensional lattices. Based on this extension, in this work, temperature dependent lattice geometries, in-plane linear thermal expansion coefficients, temperature dependent elastic constants, Young's modulus, and ultimate strength of graphene and graphyne are analyzed and discussed in detail.

II. METHODOLOGY

This work extends the methodology of temperature dependent geometry optimization and elastic constants calculation for three-dimensional crystals in Ref. 33 to address the temperature dependent lattice geometry optimization and mechanical properties of two-dimensional lattices. The detailed computation methodology used in this work is given in the supplementary material.[34]

Figure 1 shows the structure of the graphene and graphyne. Figure 1(a) shows graphene and its conventional graphene lattice containing 4 atoms and circled with a red
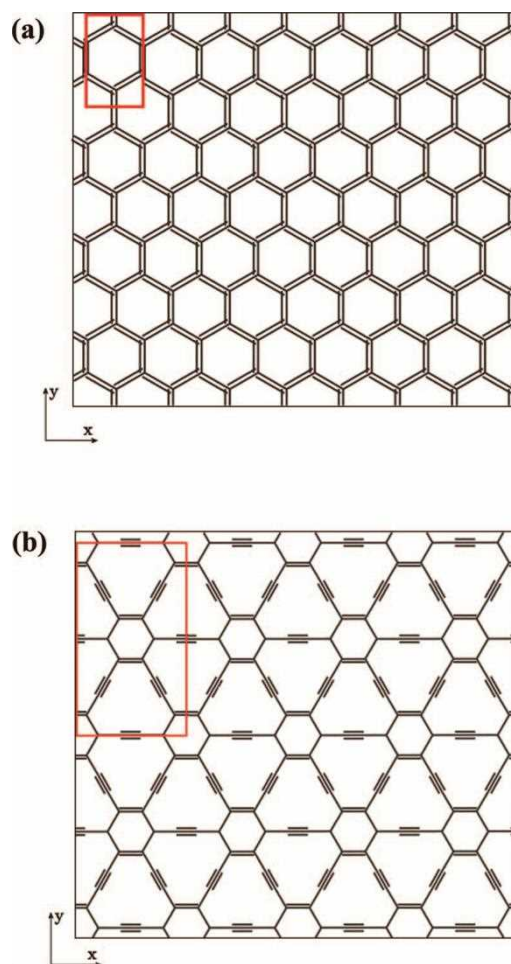

FIG. 1. (a) Graphene and its four-atom conventional cell for calculation (circled with red line); (b) graphyne and its 24-atom conventional cell for calculation (circled with red line).

solid line on this picture. The structure in Figure 1(b) is the graphyne super-cell structure and its conventional lattice containing 24 atoms which is circled with red solid line. To avoid the interaction between adjacent atomic sheets, the conventional lattice height Z for graphene and graphyne is set to be 15 Å.

The calculations are implemented in the Vienna *ab initio* simulation package (VASP) developed by the Hafner research group.[35] We perform our first-principle calculation by using the plane-wave basis soft VASP projector augmented wave (PAW) method[36] within the local density approximation (LDA).[37,38] To determine the Helmholtz free energy of the configuration, we calculate the phonon spectra by using the displacement method[39] under the quasi-harmonic model.[40,41] A plane-wave energy cutoff of 375 eV has been used and the Brillouin zone of the conventional graphene lattice, which has been sampled by $6 \times 4 \times 1$ **k**-point mesh for graphene conventional cell, including four atoms, $4 \times 2 \times 1$ **k**-point mesh for the graphyne conventional cell. Supercells of 2×2 times the graphene conventional cell including 16 atoms, 1×1 times the graphyne conventional cell including 24 atoms were used in computing the force constants. Phonon calculations were performed by using the PHONOPY code.[40,41] In the phonon frequency calculation, a set of supercells is built with different displacements of the inner atoms. Then, in the supercells, after one atom is displaced, the forces on the atoms are calculated. According to the collected sets of forces, phonon frequencies are obtained.

III. MECHANICAL PROPERTIES OF GRAPHENE

A. Temperature dependent lattice geometry optimization of graphene

In order to pave the way for graphene's applications in graphene based devices where temperature changes in working surroundings, it is important to know the thermal expansion coefficient (TEC) for graphene. Recently, several research works have been carried out to determine the TEC of graphene by theoretical and experimental approaches.[42–47] In this work, we employ our methodology to calculate the thermal expansion behavior of graphene from 0 K to 1000 K. As shown in Figure 2(a), below 430 K, there is a negative TEC region for graphene. Above 430 K, the TEC for

graphene is positive and increases slowly, reaching a small value of 4.27×10^{-6} K^{-1} at 1000 K. The TEC values of graphene measured by Bao *et al.*[44] and Yoon *et al.*[45] by different experimental approaches are with the same minimum value of -1×10^{-5} K^{-1}. The negative minimum of the TEC of graphene measured by experiments is larger than our theoretical prediction and it might be contributed to two reasons. The first one is the ripples effect in the real two-dimensional films[48,49] and the second one might be contributed to the substrate effect. It is pointed by Conley *et al.*[50] that every atom in graphene can be significantly affected by the local environment. Thus, the substrate can largely affect the mechanical property of graphene. For experimental processing, substrate is inevitable. But for our computational work, it can be considered as an "ideal experimental processing." Therefore, the calculated TEC of graphene is different from the experimentally measured ones.

Next, we plotted graphene's lattice parameter *a* by integrating the TEC versus graphene's lattice parameter *a* at 0 K as shown in Figure 2(b). The lattice parameter $a = 2.4630$ Å at 0 K, then graphene shows a thermal contraction and achieves its minimum of lattice parameter of $a = 2.4626$ Å at 430 K, as shown by our first principle calculation. By increasing the temperature further, graphene has a positive thermal expansion trend and its lattice parameter *a* achieves the values of 2.4643 Å at 1000 K. Comparison is also made with the lattice parameter *a* calculated as well as results calculated by Monte Carlo (MC),[46] and *ab initio* molecular dynamics (AIMD).[47] The lattice parameter *a* predicted in this work qualitatively agrees with the results by AIMD and MC.

Nuclear quantum effect (NQE) such as zero-point energy is important in condensed-matter system and it can cause computational deviation by considering and not considering it. To evaluate its magnitude, DFT-QHA calculations by both with and without NQE have been performed and the comparison is listed in Table II. It is shown that the lattices of graphene by considering NQE at 0 K and 300 K increased by 0.345% and 0.347% than not, respectively. However, as shown in Figure 2(a), the thermal expansion behavior is less influenced by NQE. Under conditions of QHA, phonon frequencies are dependent on the structural parameters, with increase of lattice parameters, the interaction of atoms decreases and the phonon frequencies decrease. Furthermore, the
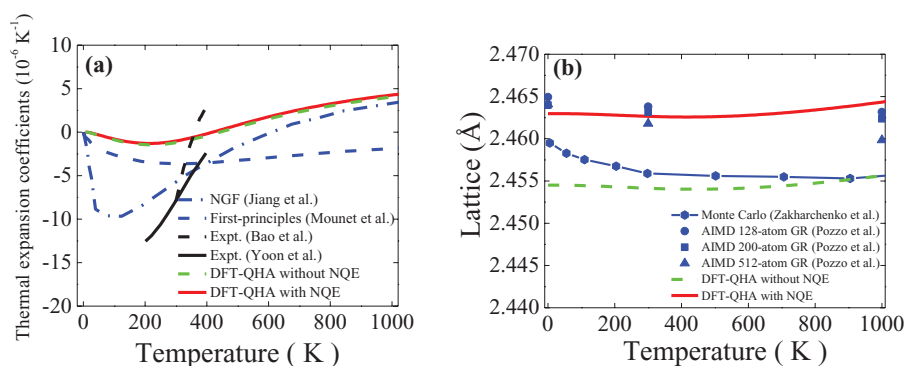

FIG. 2. (a) Calculated thermal expansion coefficients of graphene by both with and without NQE compared with other theoretical and experimental results.[41–44] (b) Calculated temperature dependent lattice of graphene compared with other theoretical results.[45,46]

TABLE II. Thermal and mechanical properties of graphene. DFT-QHA calculation by both with and without NQE compared with experimental results.

Temperature	Properties	DFT-QHA with NQE	DFT-QHA without NQE	Expt.
0		0.0	0.0	
300	TEC	-1.01×10^{-6} K^{-1}	-1.20×10^{-6} K^{-1}	
1000		4.27×10^{-6} K^{-1}	4.04×10^{-6} K^{-1}	
0		2.46298 Å	2.45451 Å	
300	Lattice parameters	2.46265 Å	2.45414 Å	
1000		2.46434 Å	2.45562 Å	
0		360.84 N/m	370.36 N/m	
300	c_{11}	359.93 N/m	369.99 N/m	
1000		351.78 N/m	363.22 N/m	
0		66.33 N/m	70.45 N/m	
300	c_{12}	61.36 N/m	70.51 N/m	
1000		57.54 N/m	70.07 N/m	
0		350.07 N/m	358.77 N/m	
300	Young's modulus	350.01 N/m	358.41 N/m	340 N/m [7]
1000		342.37 N/m	352.20 N/m	
0		120.23 GPa	124.28 GPa	
300	Ultimate strength	119.23 GPa	123.39 GPa	130 GPa [7]
1000		115.38 GPa	119.15 GPa	

zero-point energy, integrate of phonon frequencies, should decrease with increase of lattice parameters. Therefore, the minimum position of free energy will shift to right after the zero-point energy is considered. This means that the lattices by considering NQE increased than not. The increased magnitude is about 0.3% in our calculation of graphene's lattices and it is the same as Mounet's results,[42] and it is comparable to the discrepancy between AIMD and MC methods. For the thermal expansion behavior, the TEC is the ratio of lattice parameters under given temperature with the lattice parameters under temperature of 0 K. Both the lattice parameters under given temperature and 0 K have been increased by considering NQE and the increased magnitude is about 0.3%, therefore, the thermal expansion behavior is less influenced by NQE. Therefore, NQE effect can be neglected for lattice optimization and thermal expansion calculations.

B. Temperature dependent elastic constants of graphene

The Debye temperature of graphene is measured as 1045 K and calculated to be 1287 K by Politano *et al.*[51] The QHA provides an effective and accurate tool for determining thermal characteristics below the Debye temperature. In the following, we report the elastic constants and ultimate strengths of graphene and graphyne versus temperature ranging from 0 K to 1000 K by DFT-QHA. Experimental data and results obtained by other theoretical method are also taken as a comparison and they are shown in Figure 3. In this work, the elastic constants are calculated by both considering and not considering NQE. If NQE is not considered, as in Figure 3(a), it is shown that c_{11}, which is obtained by deforming the hexagonal graphene lattice along the [n, 0] direction, is 360.83 N/m at 0 K (corresponds to 1208.78 GPa by sup-

posing the thickness of 0.335 nm) and 359.93 N/m at 300 K (1205.76 GPa). $c_{12} = 62.33$ N/m at 0 K (208.81 GPa) and 61.36 N/m at 300 K (205.56 GPa). Elastic constants c_{11} and c_{12} in this work are close to $c_{11} = 358.1$ N/m and $c_{12} = 60.4$ N/m at 0 K calculated by the *ab initio* method from the work of Kudin *et al.*[19] By considering NQE, c_{11} of graphene at temperature of 300 K decreased by 2.72% than not considering NQE. Since the elastic constants represent the second derivatives of the energy density with respect to strain, the effect of NQE on elastic constants can be estimated by the second derivatives of the zero-point energy with respect to strain. Although the first derivative of zero-point energy with respect to strain is negative, positive or negative of the second derivative of the zero-point energy with respect to strain is not determined. Therefore, positive or negative effect of NQE on elastic constants is not determined. For graphene, c_{11} of graphene at temperature 300 K decreased by 2.72% than when not considering NQE and it is comparable to the discrepancy of increasing of temperature from 0 K to 1000 K. Therefore, the NQE effect cannot be neglected for temperature dependent elastic constants calculations.

As shown in Figure 3(b), if NQE is not considered, we obtain Young's modulus E = 350.07 N/m (1172.73 GPa) at 0 K and 350.01 N/m (1170.72 GPa) at 300 K. Moreover, the calculated Young's modulus in this work is slightly larger than measured 340 N/m (1020 GPa) by Lee *et al.*[7] This might be attributed to the LDA potential employed in this work which has a tendency to overestimate the elastic modulus.[39] By using the MD approach, Shen *et al.* calculated c_{11} softening slope $\Delta c_{11}/T = 0.0275$ N/m and the c_{12} softening slope $\Delta c_{12}/T = 0.0425$ N/m from 300 K to 700 K;[21] while in our work $\Delta c_{11}/T = 0.0128$ N/m and $\Delta c_{12}/T = 0.0143$ N/m in the corresponding temperature range. The relationship of this elastic constant versus temperature is in qualitative agreement with
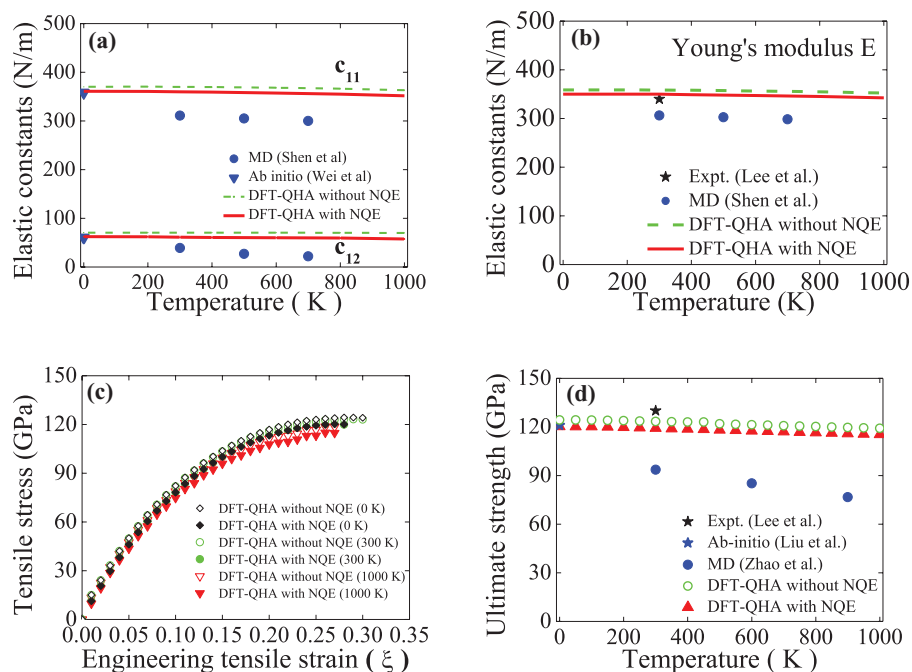
FIG. 3. (a) Calculated temperature dependent elastic constant compared with other theoretical results[25, 31] for graphene. (b) Calculated temperature dependent Young's modulus compared with other theoretical[25] and experimental results[7] for graphene. (c) Tensile stress versus equivalent engineering strain for graphene along the [n, 0] direction at 0 K, 300 K, and 1000 K. (d) Temperature dependent ultimate strength for graphene along the [n, 0] direction compared with other theoretical[20, 26] and experimental results.[7]

their work. With the increase of temperature from 0 K to 1000 K, c_{11} softened from 360.83 N/m to 351.78 N/m, by 2.51%; Young's modulus E decreases from 350.1 N/m to 342.4 N/m, by 2.2%. It indicates that graphene retains its superior mechanical properties even at high temperatures. By considering NQE, Young's modulus of graphene at temperature 300 K decreased by 2.34% than when not considering NQE. The effect of NQE on Young's modulus is the same as elastic constants, positive or negative effect of NQE on Young's modulus is not determined, also the NQE effect cannot be neglected for temperature dependent Young's modulus calculations.

C. Temperature dependent ultimate strength of graphene

Graphene's temperature dependent stress-strain relations at 0 K, 300 K, and 1000 K are plotted in Figure 3(c). If NQE is not considered, beyond the deformation strain of 0.10, the stress depends linearly on the deformation strain, when the deformation strain surpasses the 0.10, a nonlinear mechanical behavior of the graphene was clearly shown. The calculated ultimate strength and strain for graphene at 0 K are 120.2 GPa and 27% in arm chair direction, respectively. These values agree well with Liu's first-principle calculation results (ultimate strength and strain are 121 GPa and 26.6%, respectively).[20] The calculated values at 300 K also accord with experimental results with ultimate strength of 130 GPa and ultimate strain of 25%. These results further confirmed that our computational method is reasonable. Figure 3(d) presents graphene's TDUS against temperature. In the temperature ranges from 0 to 1000 K, the ultimate strength de-

creases with the increase of temperature monotonously. The ultimate strength decreases by 4.03% from 120.23 GPa at 0 K to 115.38 GPa at 1000 K. This softening tendency in the ultimate strength is caused by weaker interactions between the atoms due to stronger vibrations with the increase of temperature. By considering NQE, ultimate strength of graphene at temperature of 300 K decreased by 3.37% than when not considering NQE and it is comparable to the discrepancy by increasing of temperature from 0 K to 1000 K. Therefore, the NQE effect cannot be neglected for temperature dependent ultimate strength calculations.

Our calculated ultimate strength decreases with the increase of temperature monotonously in this work, which agrees with the calculated results of the work of Zhao *et al.* by using the classical MD,[26] but our calculated results are qualitatively larger than those in the work of Zhao *et al.* It is found that the larger the strain-rate the smaller the ultimate strength.[26, 27, 29] For first principle calculation of this work, the strain-rate is treated as static which is expected to cause a larger ultimate strength compared with the results from MD simulations calculated by stretching graphene dynamically.[25] In addition, the difference is also due to the different atomistic potential and approaches used by Zhao *et al.* and us.

IV. MECHANICAL PROPERTIES OF GRAPHYNE

A. Temperature dependent lattice geometry optimization of graphyne

Here, for the first time we present the temperature dependent lattice geometry and TEC for graphyne. In this work, the geometry optimization is performed by both considering and not considering NQE. If NQE is not considered, the TEC of
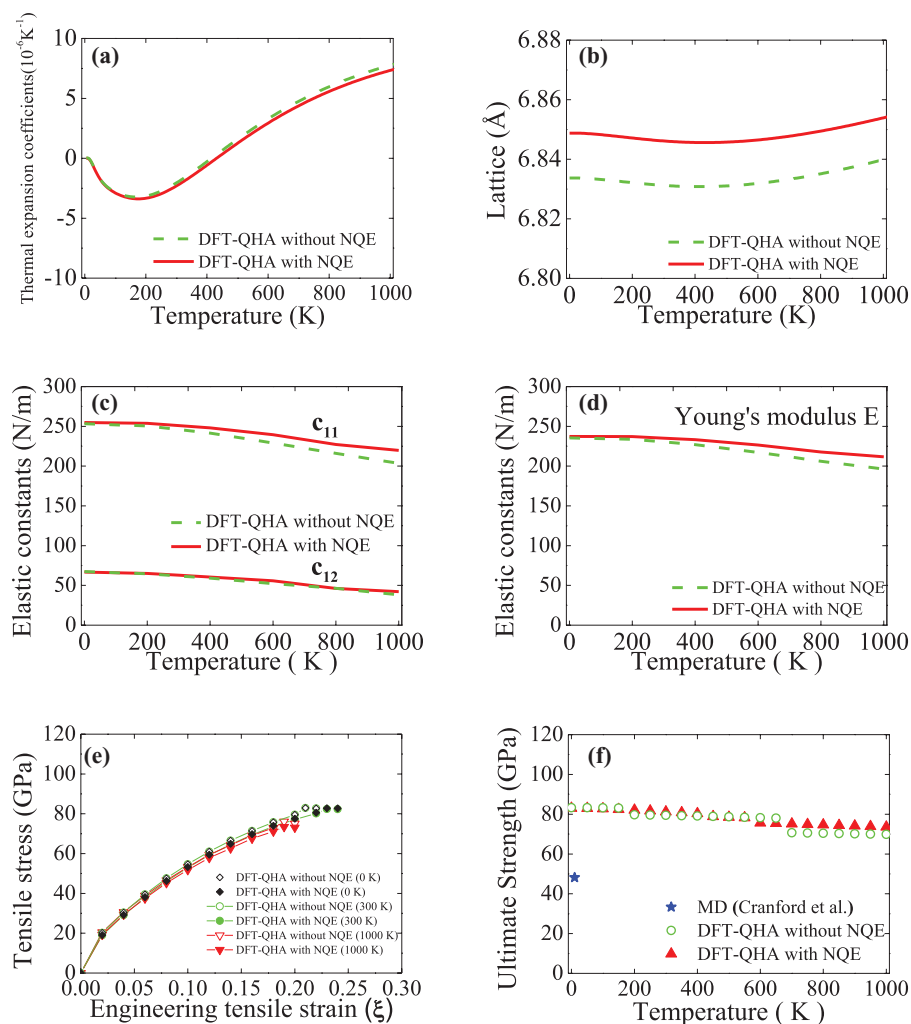
FIG. 4. (a) Calculated in-plane linear thermal expansion coefficient of hexagonal graphyne. (b) Calculated temperature dependent lattice of graphyne. (c) Calculated temperature-dependent elastic constants c_{11}, c_{12} for graphyne. (d) Calculated temperature-dependent Young's modulus E for graphyne. (e) Tensile stress versus equivalent engineering strain for graphyne along the x-axis direction at 0 K, 300 K, and 1000 K. (f) Calculated temperature-dependent ultimate strength for graphyne along the x-axis compared with others theoretical results.[27]

graphyne is given in Figure 4(a), the graphyne is contracted with the increase of temperature, it shows a negative TEC region between 0 K to 435 K and achieves its minimum negative value of -3.39×10^{-6} K^{-1} at 175 K. From 175 K, the TEC of graphyne shows a positive slope versus the temperature and begins to expand with the increase of temperature, achieves the value of -2.31×10^{-6} K^{-1} at 300 K and 7.33×10^{-6} K^{-1} at 1000 K. The initial negative region for the TEC and then a positive thermal expansion with the increase of temperature is very similar to graphene's. In Figure 4(b), in the temperature ranges from 0 K to 1000 K, the lattice parameter of graphyne is plotted. From 0 K to 300 K, the lattice of graphyne decreases from 6.8488 Å to 6.8461 Å, reaches the minimum of 6.8456 Å at 435 K, and then increases with the temperature and expands to 6.8539 Å at 1000 K. This calculated initial negative TEC region for graphyne is also due to its intrinsic two-dimensional configuration property.[48,49] By considering NQE, the results are the same as graphene, the lattices increased when not considering NQE. The increased magnitude is about 0.3%, as well as the thermal expansion behavior is less influenced by NQE. Therefore, the NQE also can be

neglected for lattice optimization and thermal expansion calculations for graphyne.

B. Temperature dependent elastic constants of graphyne

Next, we use our first principle calculation to predict the TDEC for hexagonal graphyne. Graphyne, which can be seen as the simplest material, belongs to the group of graphdiyne materials and also has superior mechanical properties as shown in our calculations. In this calculation, the mechanical properties are calculated by both considering and not considering NQE. If NQE is not considered, as shown in Figures 4(c) and 4(d), at temperature of 0 K, $c_{11} = 254.78$ N/m (corresponds to 853.51 GPa by supposing the thickness of 0.335 nm), $c_{12} = 66.75$ N/m (223.61 GPa), and Young's modulus E = 237.29 N/m (794.93 GPa). The $c_{11} = 239.0$ N/m and Young's modulus E = 221.6 N/m are smaller than their graphene counterparts, e.g., $c_{11} = 360.83$ N/m and Young's modulus E = 350.07 N/m for grapheme at 0 K. From the optimized conventional cell at 0 K, we suppose a thickness of

h = 0.335 nm, graphyne's volume per carbon atom is given as 11.52 A^3/ per carbon atom, while graphene's volume per carbon atom is given by 8.79 A^3/ per carbon atom. Due to the lower density of graphyne, the bond density of graphyne is expected to be lower than graphene, which leads to the poorer mechanical properties of graphyne, such as its elastic modulus and ultimate strength.[52] As can be seen from Figures 4(c) and 4(d), when temperature increases, the elastic constants of graphyne decrease. At 1000 K, c_{11} = 219.74 N/m (736.13 GPa), c_{12} = 42.10 N/m (141.03 GPa), and Young's modulus E = 211.68 N/m (709.13 GPa) at 1000 K. From 0 K to 1000 K, c_{11} and Young's modulus E decrease by 13.75% and 10.79%, respectively. These results suggest that mechanical properties of graphyne have weaker resistance with respect to the increase of temperature compared with graphene. If NQE is considered, as shown in Figures 4(c) and 4(d), trends of the elastic constants with temperature are same as that without considering NQE, but the values of elastic constants are increased when not considering NQE, and the increased magnitude is different for different temperatures and types of elastic constants. The maximum increased magnitude is about 3%. But for graphene, the elastic constants are decreasing by considering NQE. This further confirmed that positive or negative effect of NQE on elastic constants is not determined and that NQE is an important factor and cannot be neglected for temperature dependent elastic constants calculations.

C. Temperature dependent ultimate strength of graphyne

For hexagonal graphyne, we stretched the lattice along the x-axis as plotted in Figure 1(b); the stress-strain relationship at 0 K, 300 K, and 1000 K are shown in Figure 4(e). In this calculation, the TDUS are calculated by both considering and not considering NQE. If NQE is not considered, the results for graphyne are the same as graphene, as shown in Figure 4(e), beyond the deformation strain of 0.10 the stress depends linearly on the deformation strain, when the deformation strain surpasses the 0.10, a nonlinear mechanical behavior of the graphene was clearly shown. Figure 4(f) shows the TDUS for graphyne from 0 K to 1000 K. The tensile TDUS along the x-axis decreases monotonously with the increase of temperature. By comparing TDUS of graphyne with TDUS of graphene (in Figure 3(d)), the ultimate strength for graphyne is clearly lower than graphene at the same given temperature. The same reason might be behind the low value of Young's modulus E of graphyne due to weaker interactions between atoms that originated from its lower bond density.[52] By increasing the temperature from 0 K to 1000 K, the ultimate strength of graphyne decreases from 83.73 GPa to 73.60 GPa by 12.10%. For comparison, Cranford *et al.*'s MD results are also plotted in Figure 4(e). Cranford *et al.* calculated that the ultimate strength of graphyne at a temperature of 10 K is 48.2 GPa, but our calculated ultimate strength of graphyne at the temperature of 10 K is about 82 GPa. The reason for the difference between this work and Cranford *et al.*'s work might also contribute to the high strain-rate for MD simulations' reduced lower ultimate strength.[25–27,29] If NQE is considered,

as shown in Figure 4(f), at low temperature range, the TDUS is less than that without considering NQE, but at high temperature range, the TDUS is larger than that without considering NQE.

V. SUMMARY AND CONCLUSIONS

This work has been motivated by the importance of two-dimensional nano-films in a wide range of current and potential developments in nano-electromechanical system and semiconductor technologies. Recently, a new promising methodology for calculating temperature dependent lattice geometries and TDEC of three-dimensional crystals has been proposed. Here, we have addressed temperature dependent lattice geometry optimization, determining thermal extension coefficients, TDEC, and TDUS of the two-dimensional graphene and graphyne by extending this methodology. First, we found that the thermal expansion coefficient for both graphene and graphyne has a negative region at low temperatures and increases up to positive values at high temperatures.

Graphene is shown to have exceptional mechanical properties with Young's modulus E = 350.01 N/m and ultimate tensile strength of 119.2 GPa at room temperature. These results agree well with the recent experimental data of Young's modulus E = 340 N/m and the ultimate strength of 130 GPa reported by Lee *et al.*[3] Graphene keeps its superior mechanical property even at elevated temperatures. We have reported here that, from 0 K to 1000 K, graphene's Young's modulus E and ultimate tensile strength decrease by 2.2% and 4.03%, respectively.

For graphyne, we reported a Young's modulus E = 250.91 N/m and ultimate tensile strength of 81.2 GPa at room temperature. This indicates that graphyne, as the simplest member in the group of graphdiyne materials, has also strong mechanical properties, but is inferior to graphene. Graphyne's mechanical properties soften with the increase of temperature. From 0 K to 1000 K, Young's modulus E decreases by 10.79%, while the ultimate tensile strength decreases from 83.73 GPa to 73.60 GPa by 12.10%.

The effect of NQE on lattice optimization, TDEC, and TDUS has been discussed. It is concluded that the NQE can be neglected for lattice optimization and thermal expansion calculations, but it cannot be neglected for TDEC and TDUS calculations. This work demonstrates a methodology for calculating two-dimensional crystals TDEC and TDUS and paves the way for an accurate prediction of two-dimensional nano-films lattice temperature dependent thermal and mechanical properties.

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