Anomalous thermal response of silicene to uniaxial stretching

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Silicene-the silicon counterpart of graphene-has a two-dimensional structure that leads to a host of interesting physical and chemical properties of significant utility. We report here an investigation with nonequilibrium molecular dynamics simulations of thermal transport in a single-layer silicene sheet under uniaxial stretching. We discovered that, contrary to its counterpart of graphene and despite the similarity of their honeycomb lattice structure, silicene exhibits an anomalous thermal response to tensile strain: The thermal conductivity of silicene and silicene nanoribbons first increases significantly with applied tensile strain rather than decreasing and then fluctuates at an elevated plateau. By quantifying the relative contribution from different phonon polarizations, we show first that the phonon transport in silicene is dominated by the out-of-plane flexural modes, similar to graphene. We attribute subsequently the unexpected and markedly different behavior of silicene to the interplay between two competing mechanisms governing heat conduction in a stretched silicene sheet, namely, (1) uniaxial stretching modulation in the longitudinal direction significantly depressing the phonon group velocities of longitudinal and transverse modes (phonon softening) and hindering heat conduction, and (2) phonon stiffening in the flexural modes counteracting the phonon softening effect and facilitating thermal transport. The abnormal behavior of the silicene sheet is further correlated to the unique deformation characteristics of its hexagonal lattice. Our study offers perspectives of modulating the thermal properties of low-dimensional structures for applications such as thermoelectric, photovoltaic, and optoelectronic devices.

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I. INTRODUCTION

The understanding of the behavior and the determination of the properties of silicene, a silicon monolayer arranged in a honeycomb lattice similar to graphene, is rapidly attracting significant interest in the basic and engineering sciences.^{1–6} Analogous to graphene, it represents a conceptually new class of two-dimensional nanomaterial, and exhibits exceptionally high crystallinity^{7–9} accompanied by unusual electronic properties.^{10–13} Despite its short history, silicene appears to offer the possibility for new inroads into low-dimensional physics and related applications.

In the past few years, extensive research on heat transport in single-layer graphene (SLG) sheets both in the form of experiments^{14–16} and numerical simulations^{17,18} has demonstrated an ultrahigh thermal conductivity, which is crucially important to diverse applications, such as thermal management^{19–22} in electronics and thermal conductance enhancement for composite materials.²³ Nanoengineering enables the tailoring of the thermal conductivity with respect to application-specific requirements such as in thermoelectrics,^{24–28} electronics thermal management,^{29–33} and thermal rectification.^{34,35}

The thermal conductivity of graphene can be modified by defects, vacancies, impurities, edge functionalization, and tailored geometry shapes including size and asymmetry, strain, substrate, etc.^{17,18,36–40} Among these methods, applied strain could be one of the most worthwhile candidates to pursue, due to its continuous and robust tunability and its flexibility to realize even at the nanoscale. Recent molecular dynamics simulations have demonstrated that the thermal conductivity of graphene nanoribbons (GNRs) decreases remarkably under tensile strain,^{41–43} either in the form of uniaxial or biaxial tension. Up to 77% reduction in thermal conductivity of zigzag graphene nanoribbons was observed at a uniaxial strain of about 16%.⁴¹ The significant reduction was attributed to the phonon softening under tension.⁴² The same trend has also been found in bulk materials^{44–46} and other nanostructures.^{47,48} Existing works^{41–48} seem to support the notion of a universal phenomenon, that mechanical tension has a negative effect on the thermal transport of materials in terms of softening phonon modes, decreasing the phonon group velocity and/or decreasing the relaxation time.

In this paper we show that the above behavior does not hold for silicene, despite the similarity of its honeycomb lattice with graphene. By performing nonequilibrium molecular dynamics simulations (NEMD) we show an "abnormal" behavior of single-layer silicene, in that its thermal conductivity increases significantly with applied tensile strain. In spite of common features in phonon mode changes shared by both silicene and graphene, we identify a different mechanism in silicene attributed to the deformation nature of its honeycomb lattice that is responsible for its unexpected thermal response to the external stress.

II. MODEL SYSTEM AND METHODOLOGY

Our model system consists of $m \times n$ supercells with each supercell constructed by a honeycomb lattice and composed of eight Si atoms. The nearest Si-Si bond length at equilibrium of 2.309 Å is taken to construct the initial structure for the following simulations. For zigzag silicene, m = 10 and n =1000, i.e., the zigzag configuration is along the y direction,



FIG. 1. (Color online) Snapshot of a typical zigzag silicene sheet used as model system in the MD simulations. The x axis (transverse direction) is along the armchair edge; the y axis (longitudinal direction) is along the zigzag edge, and the uniaxial tension along the y direction is indicated by blue arrows; the z axis is the out-of-plane flexural direction. The total length of the silicene is 1000 unit cells. The two fixed ends served as "rigid walls" and are colored in red.

corresponding to an area of $6.87 \times 793.6 \text{ nm}^2$. For armchair silicene, m = 1000 and n = 10, i.e., the armchair configuration is along the x direction, corresponding to an area of $7.94 \times$ 687.3 nm². Shorter zigzag silicene was also considered with m = 10 and n = 200 and similar results were found (results not shown for brevity). A schematic of a zigzag silicene structure is illustrated in Fig. 1. For comparison purposes, a zigzag graphene monolayer with similar length was constructed by the same procedure, having a nearest C-C bond length of 1.438 Å and a different number of supercells (m = 10 and n = 1500, corresponding to an area of $4.31 \times 747.2 \text{ nm}^2$). In all molecular dynamics (MD) simulations performed here, the Tersoff potential⁴⁹ was used to describe the Si-Si interactions unless clearly stated otherwise. Separate simulations for a square silicene sheet using the Tersoff potential yields the nearest-neighbor distance, i.e., the Si-Si bond length, to be 2.309 Å, which is different by only 2.6% from the value of 2.25 Å of *ab initio* calculations.¹⁰ For graphene and graphene nanoribbons the optimized Tersoff potential in (Ref. 50) was employed.

All MD calculations herein were performed using the LAMMPS (Ref. 51) package with some source files modified as needed. The periodic boundary condition was switched on (off) to mimic the behavior of silicene [silicene nanoribbon (SNR)]. A time step of 0.5 and 1 fs was used for silicene and graphene, respectively, with low strains (less than 5%-8%) and this time step was reduced at least by half for large strains, in order to ensure energy conservation of the system. For silicene and graphene nanoribbons at large strains, the time step was even smaller (0.15 and 0.25 fs for SNR and GNR, respectively) compared to their counterparts of silicene and graphene monolayers. The two ends in the y direction (Fig. 1), each one unit cell (u.c.) long, served as "rigid walls" For each strain, we moved the walls outwards to the positions corresponding to the desired strain value in 1 ns and then relaxed the system at 300 K and 1 atm (only for silicene and graphene) for 3 ns with the walls fixed, using a Nosé-Hoover thermostat.^{52,53} Thereafter, we continued to relax the system with NVT (constant particles, volume, and temperature) and NVE (constant particles and volume without thermostat) ensembles, each for 0.5 ns.

Following equilibration, we computed the thermal conductivity of the system using NEMD. A heat source and a heat sink were placed at the left and right end of the system, respectively, to mimic typical experimental conditions. The constant heat flux method with the Muller-Plathe algorithm^{54,55} was adopted, in which the heat flux is determined by an input parameter and the resulting temperature gradient is calculated. Once steady state was reached, which typically took 2 and 10 ns for graphene and silicene, respectively, a constant heat flux $J_Q = (dQ/dt)/A$ in the longitudinal direction is established. Here, A = wd is the cross-sectional area where w is the width and d is the thickness of the layer. The thickness of graphene was taken as 3.4 Å, as standard in the literature, 40,43 and the thickness of silicene was chosen as 4.2 Å, equal to the van der Waals diameter of the Si atoms. It should be noted that the choice of the thickness of silicene does not affect the relative change in its thermal conductivity upon stretching, since the thickness is a constant factor in calculating the heat flux. After the system reaches steady state, a time averaging of the temperature profile is performed for an additional 20 ns. The nonlinear effects on the temperature gradient arisen from the heat source/sink ends are avoided by fitting only the middle region of the time-averaged temperature profile with a linear function to obtain the temperature gradient. Finally, the thermal conductivity is calculated with Fourier's law:

$$\kappa = -\frac{J_Q}{\partial T/\partial y},\tag{1}$$

where J_Q is the heat flux in the longitudinal direction and $\partial T/\partial y$ is the temperature gradient. It is worth mentioning that for all systems we stretched the monolayer step by step in a gradual manner, e.g., we first stretched the unstrained silicene monolayer by 2%, relaxed the system, and calculated the thermal conductivity; we then continued to stretch the silicene monolayer from 2% to 4%, relaxed the system, and calculated the thermal conductivity again, and so on.

III. RESULTS OF NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATION

A. Thermal response of silicene to uniaxial stretching

A comparison of the dependence of thermal conductivity on the uniaxial strain between silicene and graphene monolayers is shown in Fig. 2(a). Here the strain is defined as $\varepsilon \equiv \frac{L}{L_0} - 1$. All zigzag single-layer silicene (SLS) and SLG as well as SNR and GNR with different widths were considered. The reference values (κ_0) of unstrained systems are 40.1 W/mK for SLS (w = 10 u.c. corresponding to a width of 6.87 nm) and 31.4 W/mK, respectively, 35.0 W/mK for SNR with w = 5, respectively 10 u.c. For unstrained SLG with length of 747.2 nm and width of 4.31 nm, the calculated conductivity is $\kappa_0 = 2002.2$ W/mK. This value is in agreement with that reported in Ref. 56 using the same optimized Tersoff potential. For GNRs (w = 5 and 10 u.c.), the conductivity values are $\kappa_0 = 1323.3$ and 1531.9 W/mK, respectively.

In Fig. 2(a) we first notice that when the tensile strain is applied, the thermal conductivities of zigzag SLG and GNRs decrease remarkably with increase in tensile strain. These results are in good agreement with previous NEMD simulations on GNRs,^{41,42} despite the different interatomic potentials adopted. At the largest strain of 16% (beyond that the SLG and GNR break), the thermal conductivities of SLG and GNR are reduced by 64% and 62%, respectively, very close to the values of 77% and 60% reported in Refs. 41 and 42. Previous literature attributed this thermal conductivity reduction to the softening of phonon modes and the increase of lattice anharmonicity.^{41,42} In this paper we reexamined the underlying mechanism from a different angle, by quantifying the contribution of the dominant flexural phonon modes in SLS and SLG. The results will be presented later. It is also interesting to note that the relative changes in the thermal conductivity of SLG and GNR with larger width (w = 10 u.c.) are approximately similar, while the GNR with smaller width (w = 5 u.c.) shows an even lower relative change, meaning that narrower GNRs are more resistant to tensile strain. This can be attributed to the reduced boundary scattering of the flexural phonon modes dominating in the two-dimensional materials with single-atom thickness.

An important result in Fig. 2(a) is that an anomalous response of the thermal conductivity of single-layer silicene sheet and silicene nanoribbons to uniaxial strain is found compared to graphene and graphene nanoribbons, despite the similarity of their honeycomb lattices. The thermal conductivity of both SLSs and SNRs with different widths initially increases dramatically with tensile strain, then reaches a plateau and stabilizes for further strain increase until final breakup. More interestingly, this time the narrower SNR (w = 5 u.c. corresponding to a width of 3.44 nm) has higher relative change in thermal conductivity than the wider SNR and the silicene sheet, indicating that the narrower SNR is more sensitive to the uniaxial strain. This trend is exactly opposite to that for graphene and graphene nanoribbons and deserves careful scrutiny.

In order to exclude the possibility that the observed phenomenon is not an artifact from a specific interatomic potential employed, which is well known to play an important role in the outcome of MD simulations, we also used the



FIG. 2. (Color online) (a) Comparison of the relative thermal conductivities (κ/κ_0) of silicene monolayer (width = 10 unit cells), silicene nanoribbon (width = 5 and 10 unit cells), graphene monolayer (width = 10 unit cells), and graphene nanoribbon (width = 5 and 10 unit cells) as a function of uniaxial strain along the longitudinal direction. All silicene and graphene layers are zigzag and are 1000 and 1500 unit cells long, respectively. The reference values (κ_0) are 40.1, 31.4, and 35.0 W/mK for silicene monolayer (w = 10 u.c.) and silicene nanoribbons (w = 5 and 10 u.c.), respectively. $\kappa_0 = 2002.2$, 1323.3, and 1531.9 W/mK for graphene monolayer (w = 10 u.c.) and graphene nanoribbons (w =5 and 10 u.c.), respectively. For comparison, the results of the same silicene monolayer with EDIP interatomic potential (filled magenta squares) and silicon nanowire extended in [110] direction with Tersoff potential (filled black squares) are also shown, with κ_0 of 26.0 and 14.8 W/mK, respectively. (b) The mean total (kinetic plus potential) energy of atoms in the system as a function of strain. The symbols are the same as those in panel (a).

environment-dependent interatomic potential (EDIP) (Ref. 57) to model the silicene sheet behavior, and the result is included in Fig. 2. The EDIP model yields nearly the same trend as the Tersoff potential, which confirms the independency of the abnormal behavior on the interatomic potential adopted.

For further comparison, we ran additional simulations on a silicon nanowire (NW) with the same Tersoff potential and stretching procedure as with the silicene sheet. The Si nanowire was 76.6 nm long and extended in the [110] direction with a diameter of 4.18 nm. The result is also included in Fig. 2. Here, the thermal conductivity of the Si NW first stays practically constant for tensile strain up to 8%and then decreases rapidly to half of the original value for further strain increase. A comparison of Si NW and silicene underlines the unique thermal response of silicene to uniaxial stretching. We also point out that recently the same Tersoff potential was adopted to study the vacancy effect on thermal conductivity of silicene using equilibrium molecular dynamics simulations.⁵⁸ Moreover, we computed the mean total (kinetic plus potential) energy of all the systems simulated, as shown in Fig. 2(b). As expected, the atomic energy increases with strain, proving that all the layers are indeed in a tensile state.

We noticed that in the silicene literature there is a recent paper⁵⁹ which studied the thermoelectric properties of armchair and zigzag silicene nanoribbons with the nonequilibrium Green's function method and with nonequilibrium molecular dynamics simulations. The phonon thermal conductance of a zigzag silicene nanoribbon with width of 6.87 nm and length of 793.6 nm, the closest case we could find in our simulations for comparison purposes, was obtained to be around 0.115 nW/K. This value is in good agreement with the above study (they obtained a range of 0.10-0.13 nW/K for slightly narrower silicene nanoribbons; see Table 1 in Ref. 59). This means that if the same electrical conductivity values are used, we will obtain similar ZT results (\sim 0.3–1.2 at 300 K) for unstrained silicene nanoribbons, as shown in Ref. 59. On the other hand, and to put this statement into proper perspective, it is hard to tell how the ZT coefficient will change with external strain (upon stretching), since the electronic contribution to the thermal conductance is important and the stain will also affect the electrical transport properties. A detailed study of this effect requires dedicated ab initio calculations and experiments in future studies.

B. Mechanism: Phonon softening and stiffening in silicene

In order to elucidate the strain effect on the unexpected thermal transport properties of silicene sheet and nanoribbons, we first calculated the vibrational density of states (VDOS) of phonons of silicene at typical strains and compared with those of a graphene sheet. The VDOS are calculated by a Fourier transform of the autocorrelation function of atomic velocity and the result is shown in Fig. 3. For convenience, we show the VDOS contributed by the lattice vibrations in x, y, and z directions separately, corresponding to transverse acoustic/optical (TA/TO), longitudinal acoustic/optical (LA/LO), and flexural acoustic/optical (ZA/ZO) phonon modes, respectively. Note that TA/TO and LA/LO are in-plane modes and ZA/ZO are out-of-plane modes. For both SLS and SLG, phonon softening (redshift) of transverse and longitudinal modes was observed, as evidenced by experiments for graphene⁶⁰ and was also reported for GNRs by numerical simulation.⁴² However, the flexural phonons in SLG are also softened while the frequency of the flexural modes in SLS increases, i.e., a blueshifting occurs (phonon stiffening). We also computed the phonon dispersion curve and the phonon group velocity of SLS and SLG for the corresponding strains in Fig. 3. The results are reported in Figs. 4 and 5 for SLS and SLG, respectively, with all phonon branches explicitly labeled. The phonon dispersion curves were computed using the PHONOPY software⁶¹ and the group velocity was obtained from the relation $V_g = \frac{\partial \omega}{\partial a}$ where q is the wave vector. Our result of phonon dispersion curves of silicene using the Tersoff potential is in good agreement with previous studies with *ab initio* calculations.^{10,13} The common feature in Figs. 4 and 5 shared by SLS and SLG is that the longitudinal and transverse branches for both SLS and SLG are significantly depressed upon stretching, resulting in considerable reduction in phonon group velocities of these branches. But for the flexural branches the SLS and SLG behavior deviates. For SLG the flexural modes are depressed as well, while for SLS they move clearly upward, leading to large increase in frequency (blueshift) and enhancement in phonon group velocity. It is worth noting that the trends shown in Figs. 4 and 5 are in exact correspondence with those presented in Fig. 3.

Next we correlate the above found phonon softening and stiffening to the phonon transport. Usually the phonon softening has a negative effect on thermal transport. Using the single-mode relaxation time approximation of the Boltzmann equation, the contribution of each phonon mode (κ_i) to the total thermal conductivity can be expressed as

$$\kappa_i(\boldsymbol{q}) = C_i(\boldsymbol{q}) v_i^2(\boldsymbol{q}) \tau_i(\boldsymbol{q}), \qquad (2)$$

where C_i is the specific heat, v_i is the group velocity, and τ_i is the phonon relaxation time. As phonon frequency decreases (redshift) and phonon group velocity is significantly reduced, the thermal conductivity is anticipated to be low. Moreover, as phonons with fixed number of frequencies gather in a narrower frequency range, the chance for phonon scattering increases and the phonon relaxation time decreases, which is an additional negative effect on heat conduction in the two-dimensional sheets. In contrast, the phonon stiffening enhances thermal transport due to the higher-frequency modes carrying more energy and less phonon scattering in a broader frequency range.

The above phonon softening/stiffening mechanism can be used to explain the opposite trend in the thermal response of silicene and graphene due to the uniaxial stretching. For graphene, the tension causes phonon softening uniformly for all phonon modes thus drastically reducing the thermal conductivity. For silicene, however, there is an interplay between the longitudinal/transverse modes and the flexural modes. The uniaxial stretching induces two opposite effects on the thermal transport; namely, the phonon softening in the transverse and longitudinal modes hinders heat conduction but the phonon stiffening in the flexural modes facilitates thermal transport. Combining the above two opposite effects we can understand why the thermal conductivity of the silicene sheet initially increases with increasing strain, then reaches a plateau and stabilizes for further strains. It is worth noting that for silicene the phonon dispersion curve and group velocity of the flexural modes, especially the flexural acoustic branch, does not change noticeably for strains beyond 8%, which is



FIG. 3. (Color online) Comparison of vibrational density of states between single-layer (a) silicene and (b) graphene at typical strains of 0%, 3%, 8%, 12%, and 16%. For each column the top, middle, and bottom panel correspond to the density of states contributed by the lattice vibrations in *x* (transverse), *y* (longitudinal), and *z* (flexural) directions, respectively.

exactly the transition point for the thermal conductivity shown in Fig. 2(a). As we will see shortly, this is not coincident but intrinsically related.

C. Phonon transport in silicene: Dominated by flexural modes

An important question that must be addressed is whether the flexural modes contribute markedly to the thermal transport in silicene. If this is not the case, the phonon stiffening of the flexural modes may not be strong enough to compensate for the decrease in thermal conductivity due to the phonon softening of the transverse and longitudinal modes. To answer this question, we quantify the relative contributions of longitudinal, transverse, and flexural modes to the total phonon transport. To this end, we define an imaginary cross section normal to the longitudinal direction (y), set there the coordinate origin y = 0, and denote the atoms on the two sides of this origin as "left," respectively, "right." Then the contribution to the total heat flux in the monolayer due to the vibration in a specific direction can be expressed as

$$J_{\text{left}\to\text{right},\alpha} = -\frac{1}{2wd} \sum_{i \in \text{left}} \sum_{j \in \text{right}} F_{ij\alpha}(\upsilon_{i\alpha} + \upsilon_{j\alpha}), \quad (3)$$

where $J_{\text{left} \rightarrow \text{right},\alpha}$ is the heat flux across the imaginary interface contributed by the lattice vibrations in the α direction, α can be the *x*, *y*, or *z* direction, *w* is the width of the monolayer, *d* is the thickness, $F_{ij\alpha}$ is the α component of the force acting on atom *i* due to atom *j*, $v_{i\alpha}$ is the α component of the velocity of atom *i*, and the two sums are taken over atoms *i* and *j* belonging to the group of "left" and "right," respectively. Note that the above formula is based on two-body interactions, but the Tersoff potential used is a three-body potential. To calculate



FIG. 4. (Color online) (a) Phonon dispersion curves of silicene monolayer at some typical tensile strains. The six branches of longitudinal acoustic (LA)/optical (LO), transverse acoustic (TA)/optical (TO), and flexural acoustic (ZA)/optical (ZO) are labeled. The LO and TO branches after stretching are also indicated for clarification. (b) Corresponding phonon group velocity vs frequency. The same group lines and color code are used. Note that different lattice constant "a" should be used when calculating group velocity at different strains, which results in significantly different group velocity even if the phonon dispersion curves are visually the same.

the results of the equation above, we decompose the three-body forces into two-body components. For example, assume that atoms *i*, *j*, and *k* are the three bodies in interaction, then the force \vec{F}_i can be decomposed to be \vec{F}_{ij} and \vec{F}_{ik} , which can be considered as the forces acting on atom *i* due to atom *j* and atom *k*, respectively. Similar treatment can be applied to the forces of \vec{F}_j and \vec{F}_k . For all cases, we have verified that the sum of the three components of the heat fluxes calculated by Eq. (3) is technically equal to J_Q in Eq. (1) after long time averaging (typically longer than 250 ps).

Figure 6 shows the relative contribution to the total heat flux from the lattice vibrations in the x, y, and z directions, corresponding to the longitudinal, transverse, and flexural modes. Surprisingly, for SLS the out-of-plane flexural modes contribute the most to the total heat flux, especially for large strains, and the phonon transport in SLG is completely



FIG. 5. (Color online) (a) Phonon dispersion curves and (b) corresponding phonon group velocities of graphene monolayer. The same labels, group lines, and color codes are used as in Fig. 4.

dominated by the flexural modes. The calculated 60% of the flexural mode (acoustic plus optical) contribution to the total heat flux for unstrained SLG is close to the value of \sim 70% (read from graph) from the flexural acoustic (ZA) modes reported in Refs. 16,62, obtained by numerical solution of the phonon Boltzmann equation. It is worth emphasizing that such contribution percentage depends on the total length of the graphene simulated (the longer the graphene, the higher the contribution from the flexural modes). For strains beyond 14%, the flexural modes carry as much as 80% of the total

energy in SLG. We are aware that there is still a debate on the relative contributions of different phonon polarizations to the thermal conductivity of SLG (see Ref. 63 and references therein). Nevertheless, our method, simple yet powerful, quantitatively determines the relative contributions of the longitudinal, transverse, and flexural modes from the perspective of nonequilibrium molecular dynamics simulations.

These results provide direct evidence that the out-ofplane flexural modes dominate the thermal transport in the graphene/silicene two-dimensional structures. It should be



FIG. 6. (Color online) Relative contribution (percentage) to total heat flux from vibrations in x, y, and z directions as a function of uniaxial strain for single-layer silicene and graphene sheet. The x, y, and z correspond to transverse, longitudinal, and flexural directions, respectively.

pointed out that, so far in our method, we cannot distinguish the contribution between acoustic and optical modes, which shall be the direction of future research. More importantly, there are some evident differences in the trend of the relative contribution change with strain between SLS and SLG. For SLG, the contribution from ZA/ZO continuously increases with increasing strain and, at the same time, the contributions from TA/TO and LA/LO continuously decrease. For SLS, the contribution from ZA/ZO first increases up to the strain of 8% and then reaches a plateau and stabilizes above 8%. This trend is exactly the same as for the relative change of the thermal conductivity shown in Fig. 2(a). At larger strains, if the flexural modes, which are the only mechanism for enhancing thermal conductivity as discussed earlier, cannot carry more energy, the thermal conductivity will certainly not increase. From Figs. 4 and 5 we already know that the phonon group velocity of the flexural modes, especially the flexural acoustic branch, does not change noticeably for the strain beyond 8%. This implies that the flexural modes cannot sustain higher-energy transport for further strains, thus the thermal conductivity of SLS will stop increasing at the strain of 8%. Therefore, combining with Figs. 4 and 5, the trend of the relative contribution from the flexural modes underpins the governing mechanism stated above, i.e., that the interplay between the longitudinal/transverse and flexural modes determines the abnormal behavior of silicene shown in Fig. 2(a).

D. Correlation between structure and thermal conductivity behavior

To further explore the intrinsic relationship between the silicene structure and its thermal conductivity behavior, we characterized the deformation of the structure in the transverse direction, i.e., the *x* direction shown in Fig. 1. We then calculated Poisson's ratio by $v = -d\varepsilon_{\text{tran}}/d\varepsilon_{\text{long}}$, where $\varepsilon_{\text{tran}}$ and $\varepsilon_{\text{long}}$ are the transverse and longitudinal strains, respectively. The results for silicene and graphene are compared in Fig. 7. The



FIG. 7. (Color online) Comparison of Poisson's ratio (left axis) and transverse strain (right axis) as a function of uniaxial stretching strain between single-layer silicene and graphene sheet. The two horizontal lines denote the zero point of Poisson ratio and transverse strain.

trend of Poisson's ratio of SLG decreasing with longitudinal strain agrees well with a previous study by density functional perturbation theory.⁶⁴ In contrast, the transverse strain in SLS decreases more rapidly with longitudinal strain than SLG and thus causes Poisson's ratio of silicene to increase remarkably, indicating severe shrinkage of the silicene structure in the lateral direction upon pulling in the longitudinal direction. This means that compared to SLG, SLS is much more flexible for deformation in the transverse direction, which should benefit the blueshifting of the flexural modes mentioned before. The large shrinkage in the transverse direction can be further understood by analyzing the variation of the bond length and bond angle of the honeycomb structure, as presented in Fig. 8. The common feature shared by SLS and SLG resides in the transition from a single sharp peak to a broader peak and to a double peak. This is understandable as the uniaxial stretching along the zigzag direction largely elongates the inclined (with respect to stretching) bonds. As a result, their length undergoes a large right shift, while the perpendicular to the stretching bond length hardly changes; see the schematic in the inset of Fig. 8(a). Despite the above common characteristics, there are still some distinct differences in the distribution of bond length and bond angle between SLS and SLG. For the same strain, the bonds in SLG are prolonged more than those in SLS while the bond angles in SLS are split further than those in SLG. For example, at the largest strain of 16%, the majority of the bonds in SLG are extended by as large as 10.9% and for SLS this number is 8.5%, but the bond angles in SLS are pushed away to the two peak values of 113.4° and 133.5° while for SLG the corresponding two peaks are 115.3° and 128.9°, respectively. This is because the SLG has much lower Poisson's ratio than SLS; thus the deformation in SLG is mainly realized by the stretching of the C-C bonds with C-C-C bond angles slightly changed.

On the contrary, for SLS the Si-Si bonds are less stretched but the Si-Si-Si bond angles are significantly influenced; thus the deformation in SLS is mainly achieved by the



FIG. 8. (Color online) Comparison of (a), (c) bond length and (b), (d) bond angle at some typical stretching strains between single-layer silicene (top) and graphene (bottom). All occurrence probabilities are normalized by the total number of occurrences so that the integral across the entire range of the bond length or angle is equal to unity. For comparison, the bond length in (a) and (c) is normalized by the unstrained values, corresponding to 0% strain, of 2.309 and 1.438 Å for silicene and graphene, respectively. The same color codes are used for all figures. Inset in (a) shows the deformation of a hexagonal cell undergoing a uniaxial stretching along the zigzag direction. Filled circles with solid lines and open circles with dashed lines are structures before and after stretching, respectively.

change in Si-Si-Si angles. The large stretching of the C-C bonds induces lattice anharmonicity^{41,42} and lowers the bond strength thus reducing the thermal conductivity of SLG. On the other hand, less stretching of the Si-Si bonds and wider Si-Si-Si angles along the tension direction stiffen the flexural vibrations, reducing phonon scattering of the flexural modes, thus increasing the thermal conductivity of SLS. We believe that the anomalous behavior of the flexural modes upon stretching could originate from the unique feature that the atoms in silicene do not lie in the same plane. We further examined the energetically favored geometry of single-layer silicene at room temperature and found that, unlike the planar graphene structure, the Si atoms in silicene indeed do not maintain the planar structure but form a low-buckled stable structure. It is worth pointing out that our structure is exactly the same as that obtained by some other groups using the same Tersoff potential.⁵⁸ Such low-buckled structure of freestanding silicene sheets has been confirmed by theory^{10,65} and by recent experiments.⁶⁶ We believe that it is this lowbuckled structure that leads to the fundamentally different characteristics of the structure deformation upon stretching. The buckling structure allows the silicene to deform in the lateral direction more flexibly, aiding the blueshifting of the flexural modes, as discussed earlier, and resulting in the anomalous behavior of the thermal response of silicene to external uniaxial strain.

IV. SUMMARY

In conclusion, by performing nonequilibrium molecular dynamics simulations we show that a single-layer silicene sheet, a material with a two-dimenisonal honeycomb lattice, exhibits an anomalous thermal response to uniaxial tensile strain. Contrary to its counterpart graphene, the thermal conductivity of silicene and silicene nanoribbons first increases significantly with applied tensile strain and then fluctuates at an elevated plateau, despite the similarity in structure and some common features in phonon modes shared by silicene and graphene. By performing phonon mode analysis and quantifying the relative contribution from different phonon polarizations, we found that phonon transport in silicene is mainly taking place by the out-of-plane flexural modes. We also explained that the special property of silicene stems from the interplay between two competing mechanisms governing heat conduction in a stressed silicene sheet. These are uniaxial stretching modulation in the longitudinal direction significantly depressing the phonon group velocities of longitudinal and transverse modes (phonon softening) and hindering heat conduction, and phonon stiffening in the flexural modes counteracting the phonon softening effect and facilitating thermal transport. We further correlated the abnormal behavior of the silicene sheet to the unique deformation characteristics of its hexagonal lattice. The above findings provide an understanding and a guide of how to modulate the thermal properties of lowdimensional structures with strain engineering and may be of use in tuning their electronic and optical properties for electronic, thermoelectric, photovoltaic, and optoelectronic applications.

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