Coulomb excitations of monolayer germanene

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The feature-rich electronic excitations of monolayer germanene lie in the significant spin-orbit coupling and the buckled structure. The collective and single-particle excitations are diversified by the magnitude and direction of transferred momentum, the Fermi energy and the gate voltage. There are four kinds of plasmon modes, according to the unique frequency- and momentum-dependent phase diagrams. They behave as two-dimensional acoustic modes at long wavelength. However, for the larger momenta, they might change into another kind of undamped plasmons, become the seriously suppressed modes in the heavy interband e–h excitations, keep the same undamped plasmons, or decline and then vanish in the strong interband e–h excitations. Germanene, silicene and graphene are quite different from one another in the main features of the diverse plasmon modes.

The layered IV-group condensed-matter systems have stirred a lot of experimental1–15 and theoretical studies16–28, mainly owing to the nano-scaled thickness and hexagonal symmetry. They are very suitable for studying the unique two-dimensional (2D) physical phenomena, such as, the Dirac-cone band structure1–18, the acoustic plasmons3–5,19,20, the quantized Landau levels6,7,21,22, the ultrahigh carrier mobility8–10,23, the quantum spin Hall effect11,24–26, and the rich absorption spectra12,13,27,28. Furthermore, such systems are expected to have high potential for future technological applications14,15. Since the successful exfoliation of graphene in 200429, germanene and silicene have been synthesized on distinct substrate surfaces, e.g., Ge on Pt(111), Au(111) & Al(111) surfaces30–32 and Si on Ag(111), Ir(111) & ZrB2 surfaces33–36. Germanene and silicene possess the buckled structures, while graphene has a planar structure. The spin-orbit coupling (SOC) of the two formers is much stronger that of the latter. These two characteristics will play critical roles in the essential physical properties. This work is mainly focused on the low-frequency elementary excitations in extrinsic monolayer germanene. A detailed comparison is also made among these three systems.

The IV-group single-layer systems exhibit the unusual electronic properties. The low-lying electronic structures near the K and K' points (the first Brillouin zone in the inset of Fig. 1(b)) are dominated by the outermost $p_z$ orbitals16,17, although the buckled germanene and silicene are built from the weak mixing of $sp^3$ and $sp^2$ chemical bondings. They are characterized by the gap-less or separated Dirac-cone structures, depending on the existence of SOC. Graphene, without SOC, has two linear valence and conduction bands intersecting at the Dirac point1,18. The SOC's in germanene and silicene can separate the merged Dirac points; that is, the intrinsic systems are narrow-gap semiconductors ($E_g \sim 93$ meV for Ge & $\sim 7.9$ meV for Si)37. The application of gate voltage ($V_g$) further induces the splitting of spin-related energy bands38,39. Moreover, the band structures, with a strong wave-vector dependence, behave the anisotropic dispersions at sufficient high energy ($\sim 0.2$ eV for Ge & $\sim 0.4$ eV for Si)37. This is closely related to the hopping integral ($t$) of the nearest-neighbor atoms. However, the effects of (SOC, $V_g$, $t$) on energy bands are more obvious in germanene, compared with silicene. Such critical differences lie in the fact that the larger $4p_z$ orbitals lead to the bigger SOC and buckling, but the smaller $t$. The main characteristics of energy bands in germanene are expected to create the diverse Coulomb excitations.

Many theoretical predictions are made on few-layer graphenes16,40–49, but only some studies on mono-layer silicene and germanene. The low-frequency plasmons due to free carriers in conduction and/or valence bands can be generated by the temperature40–42, interlayer atomic interactions43–45, doping46–48, magnetic field49, and electric field50,51. As for layered graphenes, the frequency, number and intensity of plasmon modes are very sensitive to the changes in stacking configuration50,43 and layer number50,47. The single-layer graphene and silicene can exhibit an acoustic plasmon with a square-root dependence on the transferred momentum under the finite temperature51 and Fermi energy52–54. Furthermore, the excitation spectra of the buckled silicene are enriched by $V_g$51–54.

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In addition, the $\pi$ and $\pi + \sigma$ plasmons, which, respectively, come from the valence $\pi$ and $\pi + \sigma$ electrons are also investigated in detail. On the experimental side, the high-resolution electron-energy-loss spectroscopy (EELS) has been utilized to examine the electronic excitations in layered graphenes. The acoustic, $\pi$ and $\pi + \sigma$ plasmons are identified to be appeared at the low (~0.1–1 eV), middle (~5–7 eV) and high frequencies (~14–18 eV). It is also noticed that the inelastic light scattering spectroscopy is successful in the verifications of the lower-frequency Coulomb excitations in doped semiconductors, e.g., ~0.01–0.1 eV plasmons.

The tight-binding model, with the SOC, is used to calculate the energy bands of monolayer germanene, and the random-phase approximation (RPA) to study the $\pi$-electronic Coulomb excitations. The dependence on the magnitude ($q$) and direction ($\theta$) of transferred momentum, the Fermi energy ($E_F$) and the gate voltage is explored in detail. This work shows that there exist the diverse frequency-momentum phase diagrams, directly reflecting the significant SOC and buckled structure. The single-particle excitations (SPEs) are greatly enriched by ($q$, $\theta$, $E_F$, $V_z$), so that germanene is predicted to have four kinds of collective excitation modes. The main features of these plasmons are mainly determined by the strength of intraband and interband Landau dampings and the existence of extra modes. Germanene quite differs from silicene and graphene in excitation spectra. The theoretical predictions could be verified from the experimental measurements using the EELS and the inelastic light scattering spectroscopy.

**The tight-binding model**

Monolayer germanene has a low buckled structure with the weak mixing of $sp^2$ and $sp^3$ bondings; furthermore, the low-lying electronic structure is dominated by $4p_z$ orbitals. There are two equivalent sublattices of A and B atoms (Fig. 1(a)), being separated by a distance of $l = 0.66 \text{Å}$. Each sublattice has a hexagonal lattice with the Ge-Ge bond length of $b = 2.32 \text{Å}$. Moreover, the SOC plays an important role in the electronic properties. The Hamiltonian built from the sub-space spanned by the four spin-dependent tight-binding functions is expressed as

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**Figure 1.** Monolayer germanene has (a) a buckled structure, (b) a pair of valence and conduction bands along the high symmetry points, (c) the anisotropic energy contours measured from the K point, and (d) the $V_z$-induced splitting energy bands near the Fermi level. Also shown in the insets of (b) are the separated Dirac points and the first Brillouin zone.
The dynamical dielectric function, defined as the ratio between the bare and effective Coulomb potentials, under two charges is the sum of the external potential and the induced one arising from the screening charges. The effective potential and conduction electrons will screen this field and thus create the charge redistribution. The effective potential corresponding to the A (B) sites. The diverse relationship among the orbital bondings, the spin-orbit interactions, and the electric field can generate the unusual energy bands and thus enrich the Coulomb excitations.

When monolayer germanene is perturbed by an external time-dependent Coulomb potential, all the valence and conduction electrons will screen this field and thus create the charge redistribution. The effective potential between two charges is the sum of the external potential and the induced one arising from the screening charges. The dynamical dielectric function, defined as the ratio between the bare and effective Coulomb potentials, under the RPA is given by ref. 46.

$$\epsilon(q, \theta, \omega) = \epsilon_0 - V_q \sum_{\sigma, \sigma', \alpha, \beta, \gamma, \delta} \int_{1st BZ} \frac{dk_x dk_y}{(2\pi)^2} |[\sigma'; h'; \vec{k} + \vec{q}]^{\sigma'} [\sigma; h; \vec{k}]^{\sigma}|^2 \times \frac{f(E^{q\alpha}_{\sigma'; h'; \vec{k} + \vec{q}}) - f(E^{q\alpha}_{\sigma; h; \vec{k}})}{E^{q\alpha}_{\sigma'; h'; \vec{k} + \vec{q}} - E^{q\alpha}_{\sigma; h; \vec{k}} - (\omega + i\Gamma)}.$$  

$$q_x = q \cos \theta \quad \text{and} \quad q_y = q \sin \theta, \quad \text{where} \quad \theta = \text{the angle between} \quad \vec{q} \quad \text{and} \quad \hat{k}_z \quad \text{(along} \Gamma M \text{in the inset of Fig. 1(b)).}$$

### Results and Discussion

Germanene exhibits the feature-rich band structure which strongly depends on the spin-orbit coupling, the wave vector, and the gate voltage. The unoccupied conduction band is symmetric to the occupied valence one about the zero energy. Electronic states in the presence of SOC are doubly degenerate for the spin freedom (Fig. 1(b)). They make the same contribution to the Coulomb excitations. Moreover, the SOC can generate the separation of Dirac zero energy. Electronic states in the presence of SOC are doubly degenerate for the spin freedom (Fig. 1(b)). They correspond to the interband and intraband SPEs consistent with the Fermi-Dirac distribution, and the conservation of energy and momentum. $\epsilon_2$ exhibits an asymmetric square-root divergent peak at the threshold energy $\omega_{th} = 2\sqrt{\lambda_0 + \nu_F q^2/4}$ at $E_D = 0$ and $\theta = 0^\circ$ (the black dashed curve in Fig. 2(a); $\nu_F = 3tbq/2$ is the Fermi velocity). This structure comes from the interband excitations which are associated with the valence or the
conduction band-edge states (the separated Dirac points). From the Kramers-Kronig relations between the real and the imaginary parts of the dielectric function, $\frac{1}{\epsilon_1}$ exhibits a similar divergent peak at the left-hand side (Fig. 2(b)). It is always positive at the low-frequency range, implying that collective excitations hardly survive.

The competition between the interband and intraband excitations is created by the changes of the free carrier density. The former are gradually suppressed by the latter in the increase of the Fermi energy. The former and the latter could coexist at $E_F = 0.2$ eV; they, respectively, have a shoulder structure and a prominent square-root divergent peak in $\epsilon_2$ (red curve). These two structures, which are closely related to the electronic excitations of the Fermi-momentum states, are separated by an excitation gap due to the energy spacing of Dirac points. The strong asymmetric peak appears at $\omega_{\text{intra}} \approx v_F q$, directly reflecting the linear energy dispersion. This specific excitation energy is the upper boundary of the intraband SPEs (Fig. 4(a), discussed in detail later). Moreover, $\frac{1}{\epsilon_1}$ and $\frac{2}{\epsilon_2}$ have the peak structures, in which the second zero point of the former is located at where the latter is rather small. The intensity of intraband excitation peaks is getting stronger with the increasing $E_F$. However, the zero point of $\frac{1}{\epsilon_1}$ is revealed at the higher frequency, accompanied with the reduced $\frac{2}{\epsilon_2}$. That is, the further increment of $E_F$ will reduce the e-h Landau dampings and enhance the frequency of collective excitations.

The change in the direction of transferred momentum leads to the anisotropic SPEs. The constant-energy contours are vertically flipped between the K (Fig. 1(c)) and K’ points. The energy variation measured from them along the direction of $\theta = 30^\circ$ is, respectively, smaller and bigger, compared with the $\theta = 0^\circ$ case. In the vicinity of the K (K’) point, the highest intraband and the lowest interband excitation energies become lower (higher). As a result, each above-mentioned structure is changed into double structures at $E_F = 0.2$ eV and $q = 0.075$ Å$^{-1}$ (red curve versus green curve in Fig. 2(a)). Furthermore, the higher-frequency intraband peak might overlap with the first interband shoulder, instead of the excitation gap associated with the K point. The distinct excitations near

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**Figure 2.** (a) The imaginary part and (b) the real part of the dielectric function at $q = 0.075$ Å$^{-1}$ for the distinct $E_F$'s, $\theta$'s and $V_z$'s.
the two valleys are also reflected in $\epsilon_{ij}$, e.g., the change of special structures. With the increasing $\theta$, the widened frequency range of the e-h damping is expected to significantly affect the plasmon modes.

The gate voltage can split energy bands and thus diversify the channels of SPEs. There are eight kinds of excitation channels, in which two and six kinds, respectively, belong to the intraband and the interband excitations. Specially, the four interband excitation channels, $2^v \rightarrow 1^v$, $2^c \rightarrow 1^c$, $1^v \rightarrow 2^c$ and $1^c \rightarrow 2^v$ in the low-frequency

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**Figure 3.** The energy loss spectra (a) for ($\theta = 0^\circ$, $E_F = 0.2$ eV) at different $q$’s, (b) for ($q = 0.075 \AA^{-1}$, $E_F = 0.2$ eV) at different $\theta$’s, and (c) for ($q = 0.075 \AA^{-1}$, $\theta = 0^\circ$) at different $E_F$’s. The $V_z$-dependent spectra are shown for (d) ($q = 0.075 \AA^{-1}$, $\theta = 0^\circ$, $E_F = 0.2$ eV), (e) ($q = 0.075 \AA^{-1}$, $\theta = 30^\circ$, $E_F = 0.2$ eV), and (f) ($q = 0.075 \AA^{-1}$, $\theta = 0^\circ$, $E_F = 0.3$ eV).
excitation range are negligible, mainly owing to the almost vanishing Coulomb matrix elements (the square term in Eq. (2)). The $V_z$-dependent dominating e-h excitations come from the intraband excitations ($2^c \rightarrow 2^c, 1^c \rightarrow 1^c$) and the interband excitations ($1^v \rightarrow 1^c, 2^v \rightarrow 2^c$). They, respectively, cause $\omega_1$ to exhibit two square-root divergent peaks and two shoulder structures, as shown at $V_z = 2\lambda_{so}$, $E_F = 0.2$ eV, $\theta = 0^\circ$ and $q = 0.075$ Å$^{-1}$ (yellow curve). The second peak due to the $1^c \rightarrow 1^c$ channel has the excitation frequency almost independent of $V_z$. Moreover, the threshold excitation energies of the $1^v \rightarrow 1^c$ and $2^v \rightarrow 2^c$ interband excitations, which mainly come from the valence Dirac point and the Fermi-momentum state, are given by $\omega_{\text{th}}^{\text{inter}} = 2\sqrt{(\lambda_{\text{so}} \pm V_z)^2 + V_F^2 q^2/4}$ (Fig. 5). They will determine the enlarged boundaries of the interband SPEs (Fig. 5). The frequency of the former shoulder structure becomes lower as $V_z$ reduces from $2\lambda_{\text{so}}$ to $\lambda_{\text{so}}$ and then higher in the further decrease from $\lambda_{\text{so}}$ to 0. Differently, that of the latter is monotonically declining with the decrease of $V_z$. However, the zero-point frequency in $\epsilon_1$, corresponding to the $1^c \rightarrow 1^c$ e–h peak, hardly depends on $V_z$. This will induce the suppression of the interband Landau dampings on plasmon modes.

The loss function, defined as $\text{Im} \left[ -\frac{1}{\epsilon} \right]$, measures the screened excitation spectrum and is useful to characterize the collective excitations. It strongly depends on the magnitude and direction of transferred momentum. Therefore, one can investigate the collective excitation properties by studying the $	ext{Im} \left[ -\frac{1}{\epsilon} \right]$ at various momentum and frequency. This can be done by plotting the $(\mathbf{q}, \omega)$-phase diagrams, as depicted in Fig. 4. The intraband and interband SPE regions are, respectively, enclosed by the dashed and solid curves. The plasmon frequency dispersions are indicated by the bright curves. $k_F$ is the Fermi momentum along the $\Gamma M$ direction.

**Figure 4.** The $(\text{momentum}, \text{frequency})$-phase diagrams at (a) ($\theta = 0^\circ$, $E_F = 0.2$ eV, $V_z = 0$), (b) ($\theta = 30^\circ$, $E_F = 0.2$ eV, $V_z = 0$), and (c) ($\theta = 0^\circ$, $E_F = 0.1$ eV, $V_z = 0$). The intraband and interband SPE regions are, respectively, enclosed by the dashed and solid curves. The plasmon frequency dispersions are indicated by the bright curves.
exists a prominent peak at $q = 0.045 \text{ Å}^{-1}$, $\theta = 0^\circ$ and $E_F = 0.2$ eV, as indicated by a yellow dashed curve in Fig. 3(a). It corresponds to the collective excitations of free carriers in conduction bands. With the increase of momentum, the plasmon frequency ($\omega_p$) grows because of the higher-energy zero point in $\epsilon_p$, while its intensity is reduced by the stronger interband e-h damping. Moreover, a prominent peak is changed into a composite structure of a narrow sharp peak and a shoulder structure. The loss spectrum is enriched by the distinct directions of momentum transfer. An extra peak, marked by the triangle in Fig. 3(b) ($q = 0.075 \text{ Å}^{-1}$ and $E_F = 0.2$ eV), comes to exist with the increase of $\theta$. This arises from the free carriers in the K valley and it is damped by the SPEs due to the K$'$ valley.

Figure 5. Same plot as Fig. 4, but shown at $V_z = \lambda_{so}$ in (a–c) and at $V_z = 2\lambda_{so}$ in (d–f). I, II, III and IV, respectively, correspond to the $2\uparrow \rightarrow 2\downarrow$, $1\uparrow \rightarrow 1\downarrow$, $1\uparrow \rightarrow 1\uparrow$ and $2\uparrow \rightarrow 2\uparrow$ SPE channels.
The enlarged frequency range of the e-h dampings will cover the excitation gap at larger \( \theta \)'s. As a result, the sharp peak is seriously suppressed and only the shoulder structure due to the \( K' \) valley can survive.

The variation in free carrier density could modify the SPE channels and thus drastically change the plasmon peaks in the loss spectrum. Without free carriers, only a shoulder structure corresponding to the interband SPEs is revealed in the excitation spectrum at \( q = 0.075 \text{ Å}^{-1} \) and \( \theta = 0^\circ \) in Fig. 3(c) (green curve); that is, the plasmon peak is absent. When the free carrier density gradually grows, the loss spectrum exhibits a narrow sharp plasmon peak and a shoulder structure, being attributed to the strong interband e-h dampings. With the further increase of \( E_F \), those two structures are enhanced, and then only a prominent plasmon peak comes to exist. This is due to the fact that the interband excitations are progressively replaced by the intraband excitations.

The gate voltage can diversify the spin-dependent SPE channels and thus enrich the loss spectra (Fig. 3(d–f)). The sharp plasmon peak might change into the lower and broader one under the \( V_z \)-enlarged SPE range (Fig. 3(d)). This indicates the transformation between the different kinds of plasmon modes (Fig. 6(a)). There exist more low peak structures induced by the extra excitation channels, especially for the large-\( \theta \) case (Fig. 3(e)). With the increase of \( V_z \), the intensity of the prominent plasmon peak is greatly enhanced for the large \( E_F \) (Fig. 3(f)). However, the monotonous \( V_z \)-dependence is absent in the other cases. The variation of plasmon intensity is determined by whether the inter-band excitation energy is away from or close to the plasmon frequency.

Free carriers could induce the unique SPEs and plasmon modes, as clearly indicated in the \((w, q)\)-dependent phase diagrams. The boundaries of intraband and interband SPEs are mainly determined by the Fermi-momentum states and the Dirac points, as shown in Fig. 4(a–c). There exist three kinds of collective excitations with the relatively strong intensities, according to the Landau damping. First, the free-carrier induced plasmon is undamped at small \( q \) for \( E_F = 0.2 \text{ eV} \) and \( \theta = 0^\circ \). The excitation gap, which is formed between the intraband and the interband SPEs, is responsible for this behavior (the white dashed and solid curves). In addition, the \((q, \omega)\)-range of the excitation gap grows with the increment of Dirac-point spacing. With the increasing \( q \), this plasmon will enter the interband excitation region and experience the gradually enhanced damping. Specially, the partially undamped plasmon exhibits a sharp peak beyond a sufficiently large \( q \); that is, this mode could survive in the frequency gap between the interband and the intraband excitation boundaries. Secondly, at large \( \theta (\theta \sim 30^\circ) \) (Fig. 4(b)), the larger-\( q \) undamped plasmon is replaced by the seriously damped plasmon in the interband excitation region (the red curve). The weak plasmon intensity is due to the replacement of excitation gap by the extended and overlapped excitation regions. Moreover, for a sufficiently low Fermi energy (\( E_F = 0.1 \text{ eV} \) in Fig. 4(c)), the plasmon remains as an undamped mode even at large \( q \). This plasmon appears in the enlarged excitation gap determined by the comparable \( E_F \) and \( E_D \). The above-mentioned plasmon frequencies have the \( \sqrt{q} \)-dependence at long wavelength limit, a feature of acoustic plasmon modes. The similar mode has been observed in a 2D electron gas\(^5\).

Figure 6. The (voltage, frequency)-dependent phase diagrams for \((q = 0.075 \text{ Å}^{-1}, E_F = 0.2 \text{ eV})\) at (a) \( \theta = 0^\circ \), and (b) \( \theta = 30^\circ \).
The gate voltage leads to more complicated SPE boundaries because of the splitting energy bands, as revealed in Fig. 5(a–f). I, II, III and IV, respectively, represent the $2\rightarrow 2'$, $1'\rightarrow 1'$, $1'\rightarrow 1$ and $2\rightarrow 2'$ SPEs. Specially, $V_z$ can create the fourth kind of plasmon mode during the dramatic variation of energy gap. For $V_z = \lambda_{\omega} E_p = 0.2$ eV and $\theta = 0^\circ$, an undamped plasmon occurs at small $q$ (Fig. 5(a)). This plasmon is dominated by the first pair of the $V_z$-induced energy bands without energy spacing. At larger $q$, it will compete with the interband SPEs and gradually disappear. The damping behavior is closely related to the vanishing excitation gap and the enlarged SPE regions. Moreover, the main characteristics of the $(\omega, q)$-phase diagrams are insensitive to the changes in $E_p$ and $\theta$, as indicated in Fig. 5(b,c). A similar plasmon mode is also observed in an extrinsic graphene47,48,55,56, while germanene has the stronger intensity because of the weakened e-h damping. With the increase of $V_z$ (Fig. 5(d–f)), the main plasmon modes are similar to those of the zero-voltage ones (Fig. 4(a–c)). However, the SPE regions become more complicated, so that the extra plasmon modes could survive in phase diagrams, e.g., two weak plasmon modes are heavily damped by the intraband SPEs in Fig. 5(e).

The $V_z$-dependent excitation spectrum can provide more information on the collective and single-particle excitations. The plasmon modes and the e-h boundaries are dramatically altered during the variation of $V_z$. The undamped plasmon at larger $q$ will vanish within a certain range of $V_z$, e.g., $0.5 \lambda_{\omega} \leq V_z \leq 1.5 \lambda_{\omega}$ (Fig. 6(a)), being attributed to the serious suppression of $1'\rightarrow 1'$ SPEs. It is replaced by the fourth kind of plasmon which occurs in the absence of $1'\rightarrow 1'$ SPEs. With the further increase of $V_z$, the undamped plasmon will be recovered. The dependence of plasmon mode on $V_z$ is very sensitive to the change in the direction of transferred momentum (Fig. 6(b)). The undamped plasmon is absent at low and high voltages. However, the fourth kind of plasmon can survive in the middle $V_z$ range.

There are certain important differences among germanene, silicene and graphene, mainly owing to the strength of spin-orbit interaction and the buckled structure. In addition, the Hamiltonians of silicene and graphene are, respectively, given in refs 37 and 48. For the extrinsic systems, all of them can exhibit the similar 2D plasmon modes at long wavelength limit (Figs 5 and 7), in which the effects due to the SOI-induced energy spacing are fully suppressed. But at larger transferred momenta, the excitation gap can create an undamped plasmon mode in germanene. The first kind of plasmon is absent in silicene and graphene because of the rather small $E_p$'s ($<$ 0.8 meV), as shown in Figs 4(a) and 7(a,c). To observe the $\theta$-dependent plasmon modes, the required Fermi energies are, respectively, about 1.0 eV, 0.4 eV and 0.2 eV for graphene, silicene and germanene (Figs 4(b) and 7(b,d)). The third kind of plasmon is revealed in germanene and silicene, with the requirement of extremely low Fermi energy ($\sim 0.01$ eV in Fig. 7(e)) for the latter. Also, silicene can exhibit the fourth kind of plasmon at the lower gate voltage, e.g., $V_z$ equal to the effective SOC ($\lambda_{\omega} = 17.5$ meV/Å in Fig. 7(f)). In short, germanene possesses four kinds of plasmon modes only under the small variation in the Fermi energy.

The high-resolution EELS can be served as the most powerful experimental technique to explore the Coulomb excitations in 2D materials. The experimental measurements on single- and few-layer graphenes are utilized to comprehend the collective excitations due to the free carriers, the $\pi$ electrons, and the $\pi + \sigma$ electrons. They have identified the low-frequency acoustic plasmon ($\omega_p < 1$ eV), accompanied with the interband Landau damping at larger momentum34. The interband $\pi$ and $\pi + \sigma$ plasmons are, respectively, observed at $\omega_p \geq 4.8$ eV and $\omega_p \geq 14.5$ eV; furthermore, their frequencies are enhanced by the increase of layer number57. The feature-rich electronic excitations of monolayer germanene, the four kinds of plasmon modes, the $E_p$- and $E_p$-created excitation gaps, the interband and intraband SPEs, and the $V_z$-enriched excitation spectra, are worthy of further examinations by using EELS. The detailed measurements on the loss spectra can provide the full information on the diverse $(q, \omega)$-phase diagrams, especially for the strong $(q, \theta, E_p, V_z)$-dependence. Also, they are useful in distinguishing the critical differences of excitation spectra among germanene, silicene and graphene.

In addition, Silicene has been successfully synthesized on distinct substrates53,56. Its band structure will be affected by the atomic interactions between silicene and substrate. The theoretical calculations69 predict that the destruction of inversion symmetry leads to the significant changes in energy bands, such as an enlarged energy gap and energy dispersions. This will be directly reflected in band-dominated Coulomb excitations. The single- and many-particle excitations are expected to exhibit the dramatic transition, especially for the interband excitations. For example, the frequency- and momentum-dependent excitation spectra will present very different features, e.g., an obvious energy spacing between the intraband and the interband e-h excitations, and the stronger doping-induced intraband plasmons in the absence of interband e-h damped plasmons.

Conclusion

In this work, we have studied the low-frequency elementary excitations of monolayer germanene within the RPA. The calculated results show that the SPE regions are mainly determined by the Fermi–Dirac distribution, and the conservation of energy and momentum, and they are greatly enlarged by $V_z$. Four kinds of plasmon modes are predicted to reveal in the $(q, \theta, E_p, V_z)$-dependent loss spectra; furthermore, their main features are characterized by the undamped and damping behaviors. The differences and similarities among germanene, silicene and graphene lie in the existence of plasmon modes and excitation gaps. Similar studies could be further extended to the middle-frequency $\pi$-electronic excitations, the few-layer germanene, and the other IV-group systems (e.g., the single-layer Sn and Pb).

The excitation properties directly reflect the characteristics of the low-lying bands, the strong wave-vector dependence, the anisotropic behavior, the SOC-created separation of Dirac points, and the $V_z$-induced destruction of spin-configuration degeneracy. There exists a forbidden excitation region between the intraband and interband SPE boundaries, being attributed to the Fermi–momentum and band-edge states. The undamped plasmons could survive within this region with a prominent peak intensity. All the plasmons due to the free conduction electrons belong to 2D acoustic modes at small $q$'s, as observed in an electron gas. With the increasing $q$, they might experience the interband damping and become another kind of undamped plasmons, change into the
seriously suppressed modes in the heavy intraband damping, remain the same undamped plasmons, or gradually vanish during the enhanced interband damping. Specifically, the first kind of plasmon modes only appears in germanene with the stronger SOC. The fourth kind of plasmon modes in monolayer germanene are purely generated by $V_z$, while they are frequently revealed in few-layer extrinsic graphenes without external fields\(^47,48,55,56\). The detailed measurements using EELS could examine the diverse ($q, \omega$)-phase diagrams and verify the differences or similarities among the 2D group-IV systems.

Figure 7. The (momentum, frequency)-phase diagrams for graphene at (a) ($\theta = 0^\circ$, $E_F = 1.0$ eV, $V_z = 0$); (b) ($\theta = 30^\circ$, $E_F = 1.0$ eV, $V_z = 0$), and for silicene at (c) ($\theta = 0^\circ$, $E_F = 0.4$ eV, $V_z = 0$), (d) ($\theta = 30^\circ$, $E_F = 0.4$ eV, $V_z = 0$), (e) ($\theta = 0^\circ$, $E_F = 0.01$ eV, $V_z = 0$); (f) ($\theta = 0^\circ$, $E_F = 0.01$ eV, $V_z = \lambda_{so} = 17.5$ meV/Å).

The detailed measurements using EELS could examine the diverse ($q, \omega$)-phase diagrams and verify the differences or similarities among the 2D group-IV systems.
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Author Contributions
M.F.L. conceived this research. P.H.S. performed the major part of the calculations and the theoretical derivations. All authors discussed the results. P.H.S. and M.F.L. composed the manuscript.

Additional Information
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