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A method for distinguishing between propagons, diffusions, and locons

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The majority of intuition on phonon transport has been derived from studies of homogenous crystalline solids, where the atomic composition and structure are periodic. For this specific class of materials, the solutions to the equations of motions for the atoms (in the harmonic limit) result in plane wave modulated velocity fields for the normal modes of vibration. However, it has been known for several decades that whenever a system lacks periodicity, either compositional or structural, the normal modes of vibration can still be determined (in the harmonic limit), but the solutions take on different characteristics and many modes may not be plane wave modulated. Previous work has classified the types of vibrations into three primary categories, namely, propagons, diffusions, and locons. One can use the participation ratio to distinguish locons, from propagons and diffusons, which measures the extent to which a mode is localized. However, distinguishing between propagons and diffusons has remained a challenge, since both are spatially delocalized. Here, we present a new method that quantifies the extent to which a mode's character corresponds to a propagating mode, e.g., exhibits plane wave modulation. This then allows for clear and quantitative distinctions between propagons and diffusons. By resolving this issue quantitatively, one can now automate the classification of modes for any arbitrary material or structure, subject to a single constraint that the atoms must vibrate stably around their respective equilibrium sites. Several example test cases are studied including crystalline silicon and germanium, crystalline silicon with different defect concentrations, as well as amorphous silicon, germanium, and silica. *Published by AIP Publishing.*
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INTRODUCTION

The most widely used descriptions of phonon transport are all based on the phonon gas model (PGM), whereby the energy of phonons is treated like a gas of particles that scatter with each other and/or other obstructions in their path such as defects, boundaries, interfaces, or impurities.[1–3] The PGM, however, hinges on a very basic assumption, namely, that every mode/particle must have a velocity, which then sets the speed at which it can transport energy. This assumption is perfectly justified for a pure homogenous infinite crystal, where all atoms are perfectly arranged in a periodic structure. However, any degree of inhomogeneity in the composition or structure breaks the periodicity, and as a result, rigorously speaking, one can no longer properly define the phonon dispersion in terms of wave-vectors. As a secondary consequence, one can also no longer define the phonon velocities, and one must therefore resort to various levels of approximations to continue using the PGM for systems that are not infinitely periodic compositionally pure crystals. For many decades, applying such approximations has demonstrated excellent success for finite sized materials,[1–5] even nanostructured crystalline materials, and also arguably for alloys in some cases.[1–3] However, for strongly disordered systems, such as amorphous materials, adaptation of the PGM becomes exceedingly problematic and alternative methods such as that of Allen and Feldman (A-F),[6] or more recently the Green-Kubo modal analysis (GKMA) method by Lv and Henry,[7] must be used to more accurately calculate the modal contributions to thermal transport.

Arguably, one of the major reasons that the A-F and GKMA methods find better agreement with experimental data than adaptations of the PGM, such as the k_{min} model,[2,8] is because the fundamental foundation of the approach is not to assume that all modes have the same character. In 1993, A-F[6] reported the first lattice dynamics (LD) calculation of an entire supercell of atoms in an amorphous structure and remarkably found that the normal modes of vibration naturally segregated into three predominant types of modes. Here, the term "type" of mode is used to indicate that each classification has a different mode character, which here we take to be the spatial variations in the atomic motions, accounting for both magnitudes and directions. In the following, we refer to the eigen vectors that represent the solutions to the equations of motion in the harmonic limit, as a normal mode velocity field, due to its similarity to a fluid flow velocity field, which varies in magnitude and direction as a function of location. In this sense, the mode character is simply a way of terming the features of mode velocity field, i.e., if it is spatially periodic, randomized, or localized, and so on. A-F named these three mode types as propagons, diffusions, and locons. Propagons are delocalized modes with sinusoidally modulated velocity fields that exhibit a rather identifiable wavelength and corresponded to low frequencies that in concept must occur in the low frequency limit as one must eventually observe sound waves. Diffusons are delocalized modes that do not exhibit sinusoidally modulated velocity fields, but instead appear to exhibit random vibrations similar to the randomized amorphous structure itself. Lastly, locons correspond to localized vibrations that often center on atoms with significant deviations in local coordination than the rest of the structure, and A-F have already shown that they can be distinguished from diffusons and propagons by calculation of the participation ratio.

Considering the seminal work of A-F,[6] it has been known that any degree of compositional or structural disorder should give rise to a change in mode character, yet due to the lack of alternatives, the PGM is still applied to systems consisting of propagons, diffusons, and locons.[8–10] Conceptually, one might expect that each of the three classes of modes might contribute to thermal transport in a fundamentally different way. For example, one might expect that propagons can still be treated with the PGM, since they largely resemble the normal definition of a phonon as a sinusoidally modulated vibration (propagating modes), that can carry energy from one location to another a speed given by its group velocity. However, it is still not clear how diffusons or possibly locons contribute to thermal transport, although the A-F approach, as well as the GKMA method appear to offer useful means of quantifying their contributions. Nonetheless, an absolutely critical first step towards developing a revised framework for thermal transport that properly accounts for the role a mode's character plays in its contribution is to first develop a means of identifying each type of mode, in a quantitative/systematic way.

Distinguishing locons from propagons and diffusons is straightforward, by using the participation ratio[11]

$$PR_n = \frac{\left(\sum_i \vec{e}_{i,n}^{\,2}\right)^2}{N \sum_i \vec{e}_{i,n}^{\,4}}, \tag{1}$$

where $\vec{e}_{i,n}$ is the eigenvector, N is the number of atoms in the system, n is the mode index, and index i runs over all the atoms in the supercell. The above definition implies that spatially extended modes have a large value of PR_n, on the order of 1, whereas localized modes have small ratios that can reach a minimum value of $\frac{1}{N}$ for a mode completely localized on a single atom. In concept, locons are modes that involve a small minority of the system and typically have PR values below 0.1. However, here it is important to point out that the spectrum of PR values is continuous and there is in general no strict set of rules that would require any abrupt shift in mode character. Thus, even though any scheme for identifying modes will be somewhat arbitrary, it is no different than the distinctions between photons. For example, the border between visible and infrared (IR) photons is approximate/arbitrary, and it is well acknowledged that the regime of wavelengths between 699 and 701 nm is approximately the regime where the transition occurs. Thus, one cannot strictly claim that a photon with a wavelength of 701.5 nm is not in the visible spectrum, but rather that it lies near the border between visible and IR light as the exact boundary is arbitrary. Nonetheless, distinguishing photons by terms such as visible, IR, ultra-violet, and X-Rays is still quite useful, since each regime has rather unique and distinguishing types of interactions with matter, despite the fact that all photons are simply excitations of the electromagnetic field. Similarly, it is likely to be quite valuable to distinguish between different types of phonons, since each group may contribute to thermal transport in fundamentally different ways. With this potential utility established, the key question then becomes how to distinguish between propagons and diffusons.

Using structure factor based methods is an approach to distinguishing between propagons and diffusons by testing the plane-wave character of vibrational modes at a particular polarization and wave vector.[12,13] The primary problem, however, is that structure factor methods yield different magnitudes for different materials. Therefore, the magnitude of the structure factor alone cannot distinguish propagons or diffusons on a universal scale, and as a result, one must compare the relative magnitudes for different modes in the same structure. This approach is nonetheless useful, but it is preferable to have a universal scale by which a mode's character can be judged more generally, which would allow propagons and diffusons to be directly compared for different material systems. Recently, Larkin and Mcgaughy[14] estimated the transition cut-off frequency between propagons and diffusons in amorphous silicon and silica by calculating relaxation times for modes using molecular dynamics (MD) simulations. However, this only resulted in an estimated transition frequency and could not be used to distinguish an individual mode based on its character alone.

To distinguish between propagons and diffusons, one often manually looks for the frequency range where the mode character changes, which is usually quite narrow <1 THz. This is also generally regarded as the frequency regime where the relaxation times deviate from the well-known inverse frequency squared behavior, termed the Ioffe–Regel cut-off. For this reason, the distinction between propagons and diffusons is often described by a transition/cut-off frequency, above which the modes are all diffusons and locons and below which the modes are all propagons. However, it should be noted that rigorously there is no requirement that the mode character must change abruptly with respect to frequency. In essence, there are almost no rigid or strict rules for the mode character, other than the fact that in the low frequency limit one will likely always observe the existence of sound waves, which are propagons, for large systems (e.g., not small individual molecules with a finite extent). Thus, one cannot rule out the possibility of finding a system where very low frequency diffusons and locons and/or high frequency propagons exist, despite the fact that in practice one typically observes rather sharp transitions and segregations with respect to frequency. For example, if one were to make a bulk material that consisted of an crystalline matrix with amorphous nano particles embedded that are distributed throughout the structure randomly, it might be possible to observe localized modes in each nanoparticle at low frequencies. Thus, it would be particularly useful to develop an approach that can distinguish propagons from diffusons that is general and will measure the extent to which a mode is propagon-like or diffusion-like, on a universal scale that is material agnostic.

Inspired by the automated scheme for sorting modes in interfacial systems developed by Gordiz and Henry,[15] as well as the original work of A-F[12] here, we introduce a general method for classifying vibrational modes and specifically distinguishing propagons from diffusons. The method uses equilibrium atomic positions and eigenvectors of atoms in each vibrational mode and then calculates the degree of periodicity in the mode's velocity field—termed eigenvector periodicity (EP). It then compares the EP of a mode to another fictitious mode that has pure sinusoidal modulation. In this way, the method normalizes the EP so that every mode falls between zero and unity. The extremes of zero and unity then correspond to a 0% and 100% sinusoidal/propagating velocity field for a given mode. Herein, we demonstrate its application to several crystalline and amorphous solids, which for the first time allows us to clearly quantify what fraction of the modes in a given structure are propagons as a function of the degree of disorder. The key here is that calculation of the EP for a mode is well-defined for any normal mode of vibration and can be evaluated in its entirety for a single mode, without any reference or relative scaling to the values of other modes.

EIGENVECTOR PERIODICITY ANALYSIS

Starting with a harmonic or anharmonic lattice dynamics (LD) calculation (e.g., at the gamma point, since the wave vectors are not well-defined for non-periodic systems and the objective here is to remain general), the eigenvectors (e.g., the velocity field) are calculated for all atoms in a supercell. For N atoms that can move in 3 dimensions, one then obtains all 3N solutions to the equations of motion at one time, each of which consists of a list of eigenvectors that describe the direction and magnitude of each atom's motion (referred herein as its velocity field) and a frequency for each of the 3N solutions/normal modes.

We then seek to calculate the degree of spatial periodicity for the eigenvectors of each mode. Here, in essence, we are defining the key characteristic that makes a mode a propagon as motions of the atoms that repeat spatially, in some way. This trait is not observed for diffusons, as diffusons seem to exhibit almost random velocity fields, with no clear preferred direction or periodicity that is indicative of the underlying structure or composition that is disordered/nonsymmetric. Towards measuring the degree of spatial periodicity, we note that what periodicity implies is that two atoms separated by some distance in a particular direction will have eigenvectors pointing in the same or opposite directions, with similar magnitudes. For such pairs of atoms, the inner product of their eigenvectors $\vec{e}_i \cdot \vec{e}_j$ will be a larger number than a pair of atoms that have randomly pointed vectors. This distinction then becomes the basis of distinguishing propagons from diffusons.

By comparing the inner product of the eigenvectors for a pair of atoms to the corresponding value that would have been obtained if the eigenvectors followed a periodic function oriented along a particular direction denoted by $k = \frac{2\pi}{\lambda}$, where λ is the wavelength/period of spatial repetition, one can then assess the extent to which the functions match. This matching can be determined by simply taking the product of the two functions integrated over the entire super cell, via

$$\begin{aligned}\Psi_n(\vec{\mathbf{k}},\varphi) &= \sum_i \sum_{j\geq i} \left|[A_{ij,n}]\cdot[B_{ij,n}]\right| \\ &= \left|\sum_i \sum_{j\geq i} [\vec{e}_{i,n}\cdot\vec{e}_{j,n}]\,[f(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}_i+\varphi)f(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}_j+\varphi)]\right|,\end{aligned} \tag{2}$$

where the function f represents the periodic function chosen for comparison. Here, any spatially oscillatory function such as $\sin(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}})$, $\cos(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}})$, or $e^{i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}}$ can be used for f and each will yield the same final answer when properly normalized. The first product in brackets $\vec{e}_{i,n}\cdot\vec{e}_{j,n}$ measures whether the two atoms have the same direction and magnitude. If this is true for many pairs, then the sum of the products will be a large number. The second product in brackets $f(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}_i+\varphi)$ $f(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}_j+\varphi)$ yields the corresponding value that would be obtained if the velocity field corresponded to a periodic function with wavelength λ, phase φ, and direction $\vec{\mathbf{k}}$. The summation over all pairs then yields the equivalent of a spatial integral, which only becomes large when the values in each set of brackets match for many pairs of atoms. As a result, the function $\Psi_n(\vec{\mathbf{k}},\varphi)$ becomes large if the mode velocity field resembles that of the periodic function, and it provides a direct and quantitative measure of the degree of resemblance. The problem is then that one does not know for a given propagon, *a priori*, what direction and what wavelength will best resemble its motion. Thus, one can simply search over a wide range of values for $\vec{\mathbf{k}}$ and phase φ, to determine which values maximize $\Psi_n(\vec{\mathbf{k}},\varphi)$. In the ensuing description, the prime superscript and n subscript will be used to denote the values of $\vec{\mathbf{k}}$ and φ that maximize Ψ_n, for mode n.

The next issue then becomes the criterion used to determine the search space for $\vec{\mathbf{k}}$ and φ. To minimize computational expense, one would prefer to minimize the search space as much as possible. Therefore, for crystalline solids, including alloys, the k-space can be defined using reciprocal lattice vectors of the primitive cell. For strongly structurally disordered systems, such as an amorphous solid, since the wave vector cannot be defined, the search space for $\vec{\mathbf{k}}$ can be based on the maximum ($R_{\max}$) and minimum ($R_{\min}$) distance between any two atoms in the super cell, i.e., $\vec{k}_{\min} = \frac{2\pi}{R_{\max}}$, $\vec{k}_{\max} = \frac{2\pi}{R_{\min}}$. The spacing between adjacent points on the three-dimensional k point grid can then be calculated based on the maximum possible wavelength that can occur in that supercell, namely, $\Delta\vec{k} = \vec{k}_{\min}$. In addition, since the underlying function is periodic, one only needs to search through phase factors between $\left[0,\frac{\pi}{2}\right]$.

The next issue becomes the normalization, since we specifically seek to define a value that measures the degree of EP, which should be 100% for a perfectly periodic propagating mode and likely near zero for a non-propagating mode such as a diffuson. The normalization can then be done by comparing the value of Ψ_n for the actual mode, with Ψ_n for a fictitious mode that is based on the value of $\vec{\mathbf{k}}'$ and φ' that maximized Ψ_n for the mode in question. Thus, the appropriate fictitious mode for comparison is one that is oriented along the $\vec{\mathbf{k}}'$ vector with phase φ'. To do so, we construct a fictitious mode and assign a displacement vector proportional to $f(\vec{\mathbf{k}}' \cdot \vec{\mathbf{r}}_i + \varphi')$ for every atom i as follows:

$$\vec{d}_i(r_{i_0}) = \frac{\vec{e}_{i,n}}{|\vec{e}_{i,n}|} f\left(\vec{\mathbf{k}}' \cdot \vec{\mathbf{r}}_{io} + \varphi'\right), \tag{3}$$

where the subscript index o denotes the equilibrium position, and $\vec{d}_i$, $\vec{\mathbf{k}}'$, and φ' are the displacement vector of atom i in the fictitious mode, wave vector, and phase angle corresponding to maximum value of Ψ_n, respectively. Therefore, the polarization vector of each atom in the fictitious mode used for comparison can be written as

$$\vec{s}_{i,n} = \frac{\vec{d}_i(\vec{\mathbf{r}}_{io})}{\sqrt{\sum_i \vec{d}_i(\vec{\mathbf{r}}_{io}) \cdot \vec{d}_i^{\,*}(\vec{\mathbf{r}}_{io})}}, \tag{4}$$

where $\sqrt{\sum_i \vec{d}_i(\vec{\mathbf{r}}_{io}) \cdot \vec{d}_i^{\,*}(\vec{\mathbf{r}}_{io})}$ is the normalization factor for the eigenvectors, $\vec{s}_{i,n}$ is the eigenvector of the fictitious mode, and the superscript * indicates the complex conjugate. Therefore, the normalized Ψ_n can be calculated as

$$\gamma_n = \frac{\left|\sum_i \sum_{j \geq i} [\vec{e}_{i,n} \cdot \vec{e}_{j,n}] \left[f\left(\vec{\mathbf{k}}' \cdot \vec{\mathbf{r}}_i + \varphi'\right) f\left(\vec{\mathbf{k}}' \cdot \vec{\mathbf{r}}_j + \varphi'\right)\right]\right|}{\left|\sum_i \sum_{j \geq i} [\vec{s}_{i,n} \cdot \vec{s}_{j,n}] \left[f\left(\vec{\mathbf{k}}' \cdot \vec{\mathbf{r}}_{io} + \varphi'\right) f\left(\vec{\mathbf{k}}' \cdot \vec{\mathbf{r}}_{jo} + \varphi'\right)\right]\right|}. \tag{5}$$

The value of γ_n therefore represents the degree of EP on a normalized scale from zero to unity. For a mode with 100% propagating character $\gamma_n = 1$, while modes with γ_n values far from unity correspond to either localized or de-localized but non-propagating modes.

APPLICATION OF EP (γ_n) TO CRYSTALLINE AND AMORPHOUS SOLIDS

We now examine several example test cases, including crystalline and amorphous silicon and germanium, with different defect concentrations as well as amorphous SiO_2. First, we calculated the γ_n for crystalline (denoted by the "c-"prefix) and amorphous (denoted by the "a-"prefix) silicon and germanium supercells with 216 atoms and compared the results to visual, qualitative inspection to confirm that the method correctly distinguishes individual eigenmodes. Second, we consider larger systems of a-Si, a-Ge, and a-SiO_2 to study size effects and examine convergence to the infinite system size limit.

The frequencies and eigenvectors were computed using harmonic LD calculations in the General Utility Lattice Program (GULP),[16] employing the Tersoff potential for each material (Si,[17] Ge,[18] SiO_2[19]). For crystalline silicon (c-Si) and germanium (c-Ge), we used 216 atom supercells and the lattice constants were 5.431 Å and 5.658 Å, respectively. The amorphous structures have between 216 and 4100 atoms, and the densities of a-Si, a-Ge, and a-SiO_2 were 2.33 g/cm^3, 5.32 g/cm^3, and 2.35 g/cm^3, respectively. The amorphous structures were generated using the melt and quench method as discussed in the report by Larkin and McGaughey.[14] In order to avoid structural metastability, the initial structures were annealed at 1000 K for 10 ns (Ref. 14) using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[20] and subsequent energy relaxation performed in GULP.

Figures 1 and 2 illustrate the EP vs. frequency for c-Si and a-Si and c-Ge and a-Ge. It can be seen that in crystalline systems, all of the vibrational modes are periodic ($\gamma_n \approx 1$) and therefore correspond to propagons, as would be expected. However, in the amorphous materials, only some of the low frequency modes have a large value of γ_n, and the majority of the modes have less than 10% eigenvector periodicity. It is also particularly interesting to note that in the a-Si structure, there are several modes with high values of γ_n at significantly higher frequencies ~1 THz, higher than what would have been deemed the Ioffe–Regel cut-off, which is where the predominant shift in character occurs at 2 THz. This is particularly interesting and is the first direct evidence that even in a typical amorphous structure, the transition between propagon-like and diffusion-like behavior may not occur at a particular frequency. Instead, the new methodology employed here shows that propagons and diffusons can exist at different frequencies with a significant amount of overlap. Figure 3 shows illustrations of the eigenvectors associated with several example propagons, diffusons, and locons in the a-Si studied, as identified in Figure 1. In the top, middle, and bottom panels, the three propagons, labeled P_1, P_2, and P_3, three diffusons, labeled D_1, D_2 and D_3, and the three locons, labeled L_1, L_2 and L_3, were identified by their respective EP in Fig. 1. Video files illustrating the motions are also included in the supplementary material. The propagating modes (P_1, P_2, and P_3) from the top panel have some plane-wave-like character. These modes are representative of modes with large values of EP, where modes with $\gamma_n > 0.2$ show similar features to that shown in top panel. The high frequency modes (L_1, L_2, and L_3) corresponding to bottom panel are highly localized. The diffusons (D_1, D_2,

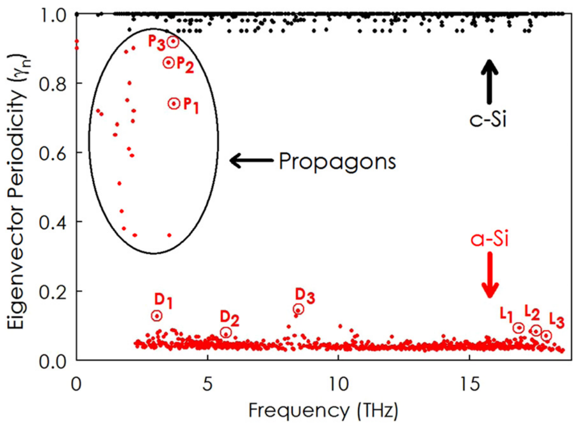

FIG. 1. Eigenvector periodicity for crystalline and amorphous silicon (c-Si, a-Si).

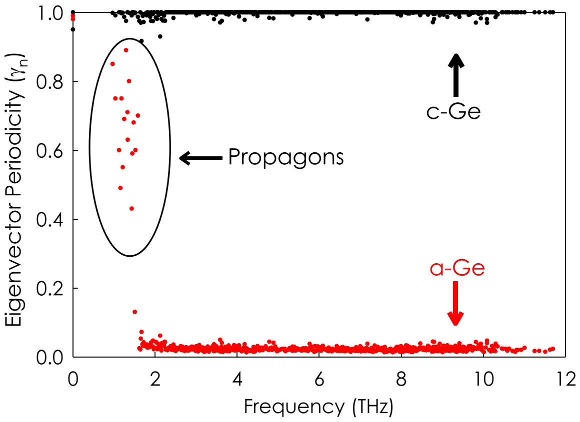

FIG. 2. Eigenvector periodicity for crystalline and amorphous germanium (c-Ge, a-Ge).

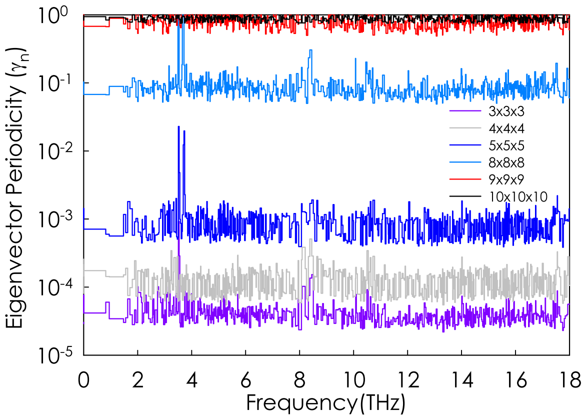

FIG. 4. Effect of reciprocal space resolution on the determination of EP in c-Si with 512 atoms.

and D_3) are neither plane-wave-like nor localized and appear to correspond to values of $\gamma_n < 0.2$.

In performing calculations of γ_n, it is important to ensure that the resolution of the k point grid is sufficiently high. This can make it challenging to evaluate γ_n for large systems due to significant increase in computational cost, but it can have a significant effect, particularly for propagating modes with high values of γ_n as shown in Figs. 4 and 5. As depicted, propagating modes are strongly sensitive to the k-space density while non-propagating modes are not and they can be calculated using a coarser k-space grid. This is due to the fact that the non-propagating modes are not well represented by any periodic function, and thus, their values of γ_n converge quickly with increasing k-point resolution, while propagating modes are described by a single unique $\vec{\mathbf{k}}$ vector, that may not exactly lie on the $[k_{\min}, k_{\max}]$ based grid. Therefore, in order to decrease the computational cost, one can use the baseline k-point density based on $[k_{\min}, k_{\max}]$ and for modes with low values of γ_n, and for modes with higher values of $\gamma_n > 0.25$, an increasingly finer grid can be used until convergence. Furthermore, one can center the refinement on $\vec{\mathbf{k}}'$ of each iteration, thereby reducing the size of the

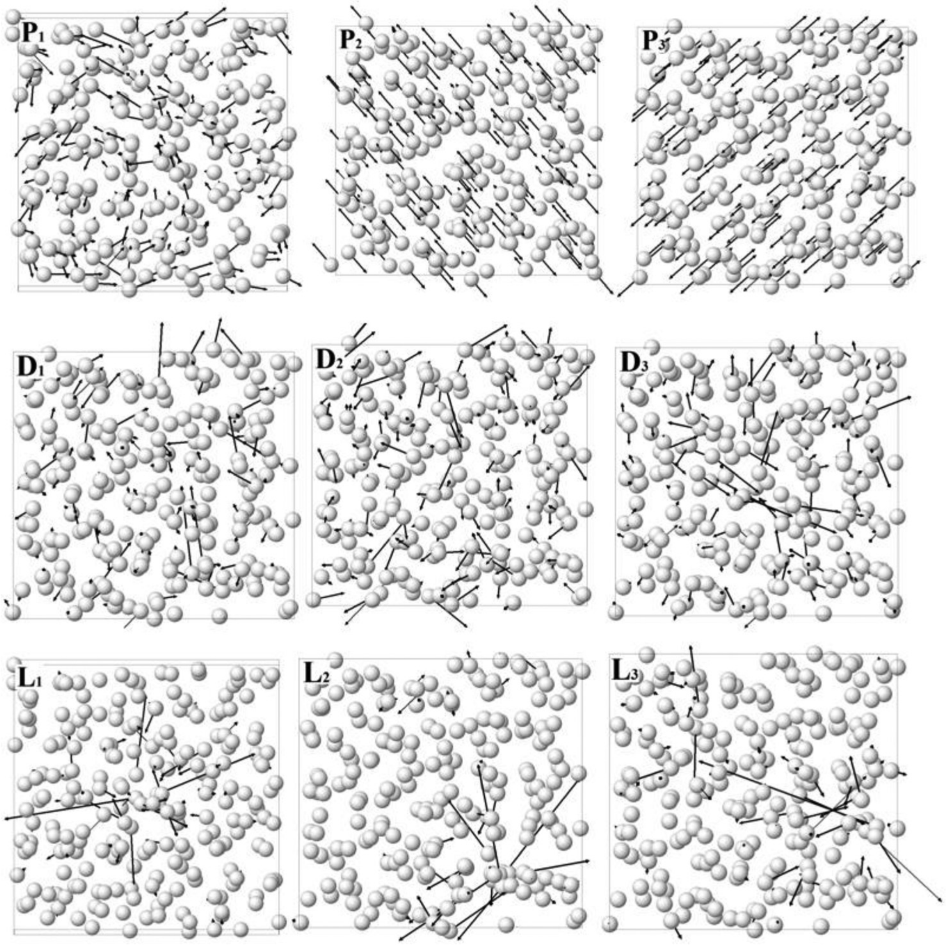

FIG. 3. Illustration of the velocity field for example, normal modes in a-Si System as identified by their EP in Fig. 1.

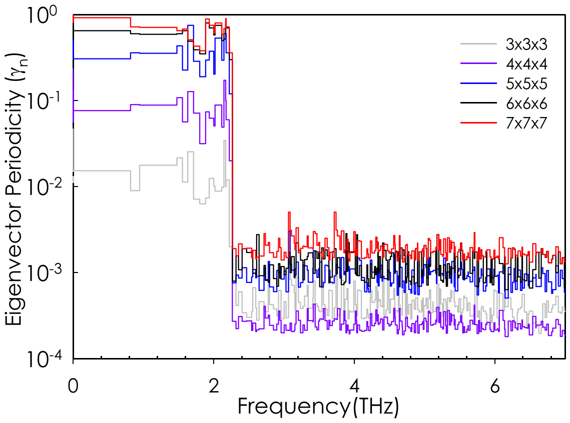

FIG. 5. Effect of reciprocal space resolution on the determination of EP in a-Si with 512 atoms.

search space and making the procedure efficient. As seen, there is a discernible *k*-space density dependence for resolutions smaller than $9 \times 9 \times 9$ for c-Si, while less k-space resolution is needed for the diffusons and locons in a-Si. It is also important to note that the phase φ has a significant effect on the value of γ_n for the modes with high values of γ_n, while locons and diffusons are quite insensitive to phase offsets.

The participation ratio and γ_n for large structures of a-Si, a-Ge, and a-SiO$_2$, consisting of 4096, 4096, and 4608 atoms, respectively, are shown in Figs. 6–8. For a-SiO$_2$, there are two regions of locons separated by diffusons. For a-Si and a-Ge, it can be seen that the PR dramatically drops at both low and high frequency ends of spectrum. In the high-phonon frequency regime, the modes involve a considerably reduced number of atoms corresponding to locons. This feature is independent of the sample size suggesting that truly localized states exist in this regime. Such localized vibrational states have also been observed in grain-boundary structures, a-Ge, a-Si, and so on. The drop at the low end of the frequency spectrum, however, is due to the presence of resonant or localized modes.[13] Resonant modes are not truly localized, because they are an artifact of the finite size of the supercell and diminish as the size of the system increases.[13]

With this new approach, we can now use a universal scale for judging whether a mode is a propagon or diffuson. In reality, just as the cut-off between different types of photons (visible vs. IR) is somewhat arbitrary, one cannot define a single value cut-off for γ_n that will determine whether a mode is a propagon or diffuson. However, with this now physically meaningful normalization embedded in the definition of γ_n, one can define a regime on the absolute scale between zero and unity where the transition between the two occurs, albeit heuristically. Based on the relative magnitudes of γ_n for different modes as well as visual inspections of the eigenvector periodicity for various cases, it appears that the transition regime between propagon- and diffusion-like character occurs between $\gamma_n = 0.15$ and 0.25.

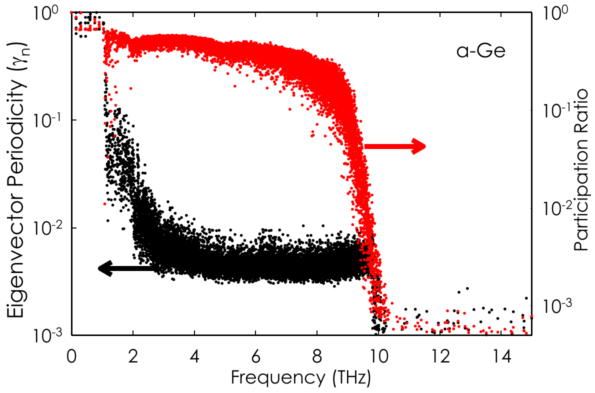

FIG. 7. Eigenvector periodicity and participation ratio for a-Ge.

Lastly, with an approximate transition region now defined, we can unambiguously evaluate what fraction of the modes fall above a certain value of γ_n and are therefore deemed propagons. In the following, we have deemed any mode with γ_n above 0.2 as a propagon, and with this fixed threshold, we can now systematically examine how the number of propagons changes with respect to increasing disorder. For example, we calculated γ_n for c-Si silicon with increasing amounts of Si vacancies. The results, shown in Fig. 9, show that when a vacancy is encountered in a crystal, it not only acts as a scattering site for other propagating phonons but also changes some of the mode characters converting them to non-propagating modes (diffusons and locons). Figure 9 shows how this effect occurs as a function of defect concentration. What is remarkable is that there is a major effect with only 5% defects (25% of the modes become non-propagating). Although 5% would be an extremely high

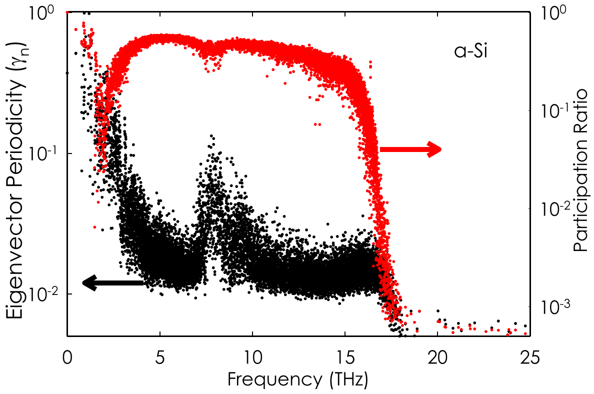

FIG. 6. Eigenvector periodicity and participation ratio for a-Si.

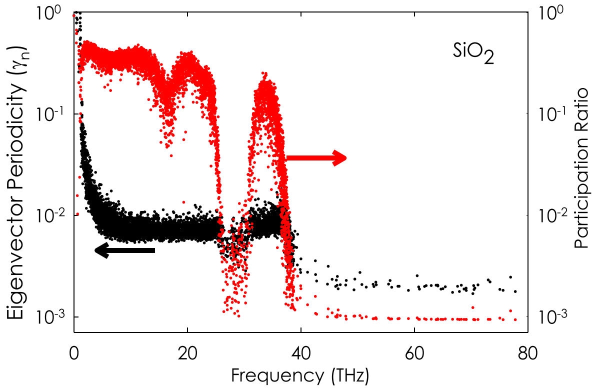

FIG. 8. Eigenvector periodicity parameter and participation ratio for a-SiO$_2$.

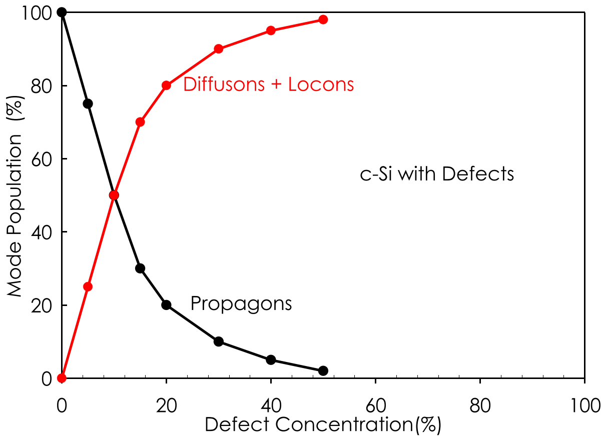

FIG. 9. Mode population for c-Si with different defect concentrations.

defect concentration for most materials, it still provides a strong indication that the mode character changes may be non-negligible even at the low defect concentrations typically encountered in rather pristine samples.

CONCLUSION

We have developed and tested a new method for classifying normal modes of vibrations that is general and based on their individual mode character. Previous classification methods have been restricted to structure factor based methods and qualitative relative sorting of the vibrational modes according to their frequencies, which may not be accurate in many instances. However, with the introduction of our definition for EP, one can classify the propagating vibrational modes based on their mode character, which is more general and provides a universal scale that can allow for comparisons between different materials. We confirmed that by using an EP based scheme for classifying the modes in c-Si and c-Ge, all modes are in fact propagons as expected. However, in a-Si, a-Ge, and a-SiO_2, the majority of the modes are non-propagating. Furthermore, the results for a-Si, a-Ge, and a-SiO_2 indicated that there is no sharp cut off frequency between propagating and non-propagating modes, as has been assumed in the literature. Instead, we find that there is no strict rule that requires such a transition, and it is possible for propagons to exist above the Ioffe–Regel crossover frequency and for diffusons to exist below it. Furthermore, by studying how the number of propagons decreases with respect to defect concentration, we found that even small defect concentrations may have a significant effect on the mode character, as the majority of the modes become non-propagating above a 10% defect concentration in c-Si. These results provide important guidance and assessment of the validity of the approximations associated with defect scattering mechanisms and on the importance of incorporating mode character into examinations of phonon interactions.

SUPPLEMENTARY MATERIAL

See supplementary material for video files illustrating the motions of atom in vibrational modes.

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