

## Characterizing phonon dynamics using stochastic sampling

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Predicting phonon relaxation time from molecular dynamics (MD) requires a long simulation time to compute the mode energy auto-correlation function. Here, we present an alternative approach to infer the phonon life-time from an approximate form of the energy auto-correlation function. The method requires as an input a set of sampled equilibrium configurations. A stochastic sampling method is used to generate the equilibrium configurations. We consider a truncated Taylor series expansion of the phonon energy auto-correlation function. The different terms in the truncated correlation function are obtained using the stochastic sampling approach. The expansion terms, thus, obtained are in good agreement with the corresponding values obtained using MD. We then use the approximate function to compute the phonon relaxation time. The relaxation time computed using this method is compared with that obtained from the exact correlation function. The two values are in agreement with each other. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4943590>]

### I. INTRODUCTION

Phonon dynamics play an important role in determining the different properties of condensed matter. The thermo-mechanical properties of a crystalline solid are governed by the phonon relaxation time. The relaxation time of a given phonon mode is the time it takes to return to equilibrium condition when perturbed. The coupling of the thermal phonons with the elastic strain field plays an important role in the damping of the sound waves.<sup>1,2</sup> The coupling results in the modulation of the phonon frequencies and disturbs the equilibrium distribution. These then tend to relax towards the equilibrium state and results in the absorption of energy from the mechanical deformation. Phonon relaxation time is used as an input in the computation of thermal conductivity<sup>3,4</sup> and intrinsic dissipation of a dielectric material.<sup>5-7</sup> The finite relaxation time of a phonon results from different scattering processes. For a perfectly crystalline structure, scattering takes place due to phonon-phonon interaction. Phonon-phonon interaction is an an-harmonic process and results from the third and higher order terms in the inter-atomic potential.<sup>8</sup> The resulting dynamics is complicated and is not amenable to a closed form solution for a generic inter-atomic potential.

A number of computational methods have been developed to extract the phonon relaxation time.<sup>9</sup> These methods can be broadly classified as the perturbation and the non-perturbation methods. In the perturbation based method,<sup>10,11</sup> one considers a Taylor series expansion of the inter-atomic potential. Using the third order expansion and the Fermi's golden rule,<sup>8</sup> the phonon relaxation time is determined. The perturbation based methods, therefore, only account for the three phonon scattering process. The order of a scattering process is related to the order of non-linear terms considered in the perturbed Hamiltonian. Accounting for terms higher

than order three is cumbersome and prohibitive for most cases. The higher order processes play an increasingly important role with the increase in temperature. The perturbation based methods can, therefore, become inaccurate at higher temperature.

The non-perturbation approach requires evolving the system in time and can be broadly classified as equilibrium or non-equilibrium based methods. In the equilibrium based method,<sup>12-14</sup> one computes the auto-correlation of the mode energy or the spectral energy density.<sup>15</sup> The phonon life-time is obtained from the decay rate of the energy auto-correlation function. Computation of the auto-correlation function often requires generating long trajectories, especially for the case of slow decaying modes. In the non-equilibrium based method, the mode of interest is excited using either the velocity or the displacement perturbation. Subsequent decay of the mode energy, then, gives the relaxation time. This method, however, requires independent simulation set for each of the modes and is useful only when one is interested in a selected few modes. Since the inter-modal interaction is computed from the exact inter-atomic potential, all the phonon scattering processes are accurately accounted for in the methods based on time evolution. However, generating the required time length of the atomic trajectories for estimating the decay rate can be computationally prohibitive for some cases.

In this work, we present an alternative approach to compute an approximate form of the mode energy auto-correlation function. The method takes the full Hamiltonian into account. Hence, all the higher order non-linear effects and that characterize the short time dynamics are taken into consideration. Further, the proposed methodology does not require to generate a time series data of the atomic trajectories. Instead, the correlation function is computed using a set of independently sampled equilibrium configurations. The decay rate is estimated from additional information of the mode force and its time derivative. Using the proposed

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method, any approach to efficiently sample the equilibrium configurations can be used. In this work, a stochastic sampling method is presented to sample the equilibrium configurations. The phonon relaxation time computed using the approximate correlation function is compared with that obtained from the exact function generated using molecular dynamics (MD). In this work, we have used an empirical potential to compute the inter-atomic forces. The method can also be easily extended for the *ab-initio* case. For the *ab-initio* case, one can use the density functional perturbation theory<sup>16</sup> to compute the mode shapes and the phonon frequencies. Further, using the Hellmann-Feynman theorem, the inter-atomic forces can be obtained and then used to compute the different variables. We shall, however, only consider the case of an empirical inter-atomic potential (EIP) in this work.

The manuscript is organized as follows. In Section II, we first derive the expressions for the approximate form of the energy auto-correlation function. We then establish the relation between the modal and the atomic variables. The stochastic sampling method, to compute the required ensemble averages, is presented in Subsection II C. The results and the conclusions then follow.

## II. METHOD

### A. Energy correlation function

In this section, we characterize the mode energy auto-correlation function using a Taylor series expansion. We also derive expressions that relate different terms in the expansion with the mode based quantities. The relation between the modal and the corresponding per-atom variables will be established in Section II B.

Under the linear approximation, the modes constitute a set of orthogonal directions in the configuration space such that motion along one of them is independent of the motion along any other mode. Let  $a_m$  denote the displacement and  $v_m$  be the velocity for mode  $m$ . The mode  $m$  is characterized by its eigen-vector  $\epsilon_m$  and angular frequency  $\omega_m$ . The eigen-vector,  $\epsilon_m$ , describes the relative motion of all the atoms in the system when the specific mode  $m$  is excited. The method to obtain these modal properties will be discussed later. The modal energy,  $E_m(t)$ , under the harmonic approximation is given as

$$E_m = \frac{1}{2} m_{at} \omega_m^2 a_m^2 + \frac{1}{2} m_{at} v_m^2. \quad (1)$$

Here,  $m_{at}$  is the atomic mass. For a structure in equilibrium,  $E_m(t)$  is a stationary random process in time with  $\langle E_m \rangle = k_b T$  and is characterized by the correlation function,  $C_m(t)$ , defined as

$$C_m(t) = \langle \Delta E_m(0) \Delta E_m(t) \rangle. \quad (2)$$

Here,  $\Delta E_m(t) = E_m(t) - \langle E_m \rangle$ , where the angle brackets refer to the ensemble average,  $k_b$  is the Boltzmann constant, and  $T$  is the temperature. For an ergodic system, one can consider time average instead of the ensemble average.

Computing the phonon relaxation time entails estimating the function  $C_m(t)$ . An exponential fit of  $C_m(t)$  gives the decay rate,  $\tau_m$ . For small time  $t$ , one can consider a Taylor series approximation of  $C_m(t)$  as

$$C_m(t) \simeq C_m(0) + \frac{1}{2} C_m''(0) t^2 + \frac{1}{24} C_m''''(0) t^4. \quad (3)$$

In considering the expansion, the odd derivative terms of  $C_m(t)$  have been set to zero. This follows from the theory of stationary random process.<sup>17</sup> A system in thermal equilibrium, indeed, satisfies the requirement for a stationary random process. Further, we also have the following relations<sup>17</sup>

$$C_m''(0) = -\langle (E_m')^2 \rangle \quad (4)$$

and

$$C_m''''(0) = \langle (E_m'')^2 \rangle. \quad (5)$$

Here,  $E_m'$  and  $E_m''$  refer to the first and second time derivatives of  $E_m$  with respect to time. Thus, estimating the function  $C_m(t)$  requires computing the variance of the first and second time derivative of the modal energy. We shall now develop relations for computing these derivative values. Taking the derivative of Eq. (1) with respect to time, we obtain

$$E_m' = m_{at} \omega_m^2 a_m v_m + v_m f_m. \quad (6)$$

Here,  $f_m$  is the modal force and can be obtained using the inter-atomic potential. The method to compute  $f_m$  will be discussed later. For a purely harmonic system, we have  $f_m = -m_{at} \omega_m^2 a_m$ . For such a case, the R.H.S of Eq. (6) will be zero. This effectively corresponds to an infinite relaxation time for the phonon. The finite relaxation time, therefore, results from the an-harmonic forces in the system.

The second derivative of Eq. (1), further, gives

$$E_m'' = m_{at} \omega_m^2 v_m^2 + \omega_m^2 a_m f_m + \frac{f_m^2}{m_{at}} + v_m \dot{f}_m. \quad (7)$$

Here,  $\dot{f}_m$  is the time derivative of the modal force. The expressions for  $E_m'$  and  $E_m''$  can be plugged in Eqs. (4) and (5) to obtain  $C_m''(0)$  and  $C_m''''(0)$ . We can, thus, obtain an approximate form of  $C_m(t)$ .

### B. Mode variables

In the method described above, we have made use of different mode variables such as the  $a_m$ ,  $v_m$ , and  $f_m$ . These modal variables can be obtained from the corresponding per atom quantities using a linear transformation. We consider a vector  $\alpha$  which is the set of per atom variable. For example,  $\alpha$  can be a set of the force vector of all the atoms that constitutes the system. Let  $\alpha_i^j$  refer to the component of a vector  $\alpha$  associated with an atom  $i$  and along the direction  $j$ . Also, let  $\alpha_m$  denote the corresponding modal value of  $\alpha$  for mode  $m$ . We then have the following linear relation:

$$\alpha_m = \sum_{i=1}^{n_{atom}} \sum_{j=1}^3 \epsilon_{im}^j \alpha_i^j. \quad (8)$$

Here,  $\epsilon_{im}^j$  is the component of the mode eigen-vector  $\epsilon_m$  associated with an atom  $i$  and along the direction  $j$ . Also,  $natom$  is the total number of atoms in the system. Using the linear transformation in Eq. (8) and considering different cases of  $\alpha$ , mode dependent quantities can be obtained. For example, the mode force  $f_m$  can be determined as

$$f_m = \sum_{i=1}^{natom} \sum_{j=1}^3 \epsilon_{im}^j f_i^j, \quad (9)$$

where  $f_i^j$  is the  $j$ th component of the force for the  $i$ th atom.

The RHS of Eq. (7) involves the time derivative of the modal force,  $\dot{f}_m$ . It can be obtained from the per atom force derivative using the linear transformation described in Eq. (8). Let  $\dot{\mathbf{f}}$  denote the vector of the time derivative of the per atom forces. Let  $f_i^\alpha$  denote the force on the atom  $i$  along the direction  $\alpha$ . For a Hamiltonian system, we have  $f_i^\alpha = -\frac{\partial U}{\partial x_i^\alpha}$ . Taking the derivative of the force expression with respect to time, we get

$$\dot{f}_i^\alpha = \sum_{j=1}^{natom} \sum_{\beta=1}^3 -\frac{\partial^2 U}{\partial x_i^\alpha \partial x_j^\beta} v_j^\beta. \quad (10)$$

This can be recasted in the condensed form as

$$\dot{\mathbf{f}} = -\mathbf{D}\mathbf{v}. \quad (11)$$

Here,  $\mathbf{D}$  is the force constant matrix and  $\mathbf{v}$  is the vector of atomic velocities. The components of  $\mathbf{D}$  are given as

$$D_{3i+\alpha, 3j+\beta} = \frac{\partial^2 U}{\partial x_i^\alpha \partial x_j^\beta}. \quad (12)$$

Here,  $U$  is the inter-atomic potential, and  $x_i^\alpha$  denotes the  $\alpha$  component of the displacement of the  $i$ th atom. Similarly,  $x_j^\beta$  denotes the  $\beta$  component of the displacement of the  $j$ th atom. The indices  $\alpha$  and  $\beta$  can take integer values from 1 to 3, while  $i$  and  $j$  can take values from 1 to  $natom$ . The eigenvalues and the eigen-vectors of  $\mathbf{D}$  give  $\omega_m$  and  $\epsilon_m$ , respectively.

Thus, with the knowledge of the atomic positions, velocities and the inter-atomic potential, the different terms in Eqs. (6) and (7) can be computed. It now remains to establish a method to obtain the ensemble averages of these quantities as required in Eqs. (4) and (5). For this purpose, any sampling approach can be used to sample the different atomic configurations of the crystalline structure. For example, one can consider computing the time average of these quantities using MD simulation. Here, we consider a more efficient approach based on the self-consistent lattice dynamics.<sup>18</sup>

### C. Stochastic sampling

In this section, we will discuss the algorithm to sample the phase space of a crystalline solid taking anharmonic effects into consideration. We first provide a brief overview of the algorithm. The outline describes the main steps without delving into the mathematical details. The details,

pertaining to each step, shall be discussed in the subsequent paragraphs.

We first generate the mean position of the atoms in the crystal. The underlying lattice structure along with the information of the unit cell dimension is used to generate the mean position of the atoms. Using the given inter-atomic potential and the mean position of the atoms, the quasi-harmonic (QHM) analysis is performed. The eigen-vector,  $\epsilon_k$ , and the harmonic mode frequency,  $\omega_k$ , for mode  $k$  are determined. Using  $\omega_k$ , the probability density function (PDF) for the mode co-ordinates at a finite temperature,  $T$ , is constructed. We use this PDF to generate different samples of the mode co-ordinates and, hence, the atomic configurations. For each of the sampled atomic configuration, per-atom forces are computed using the full inter-atomic potential. From the per-atom force, the mode force is determined. The mode forces are then used to construct the mode force correlation matrix,  $\mathbf{F}$ . The mathematical expression for the components of  $\mathbf{F}$  will be provided later. Using  $\mathbf{F}$ , the anharmonic stiffness matrix,  $\mathbf{K}$ , is determined. The matrix  $\mathbf{K}$ , thus, obtained is then used to compute the anharmonic mode frequencies,  $\omega_k^{anh}$ . A new PDF for the mode co-ordinates is constructed using  $\omega_k^{anh}$ . The anharmonic PDF is used to sample a new set of atomic configurations. For each of these configurations, different mode variables are determined. These are then used for the computation of different expansion terms in the mode energy auto-correlation function.

We shall now discuss in detail the different steps outlined in the previous paragraph. We perform the QHM analysis using the mean atomic position generated using the underlying lattice structure. The harmonic mode frequency,  $\omega_k$ , for a mode  $k$  is, thus, obtained. Using QHM approximation, the Hamiltonian,  $H_{harm}$ , of the system can be written as

$$H_{harm} = \sum_{k=1}^{nmodes} \left( \frac{1}{2} m_{at} \omega_k^2 a_k^2 + \frac{1}{2} m_{at} v_k^2 \right). \quad (13)$$

Here,  $a_k$  is the displacement,  $v_k$  is the velocity, and  $\omega_k$  is the frequency for mode  $k$  obtained using the quasi-harmonic approximation. Also,  $nmodes$  is the number of modes in the system and is related to the number of atoms,  $natom$ , as  $nmodes = 3 \times natom$ . In the above expression, we have neglected higher order terms of the inter-atomic potential.

For a system whose dynamics is governed by  $H_{harm}$ , the PDF for the canonical ensemble is given as

$$P_{eqb}(A, V) = \prod_{i=1}^{nmodes} \sqrt{\frac{\omega_i^2 m_{at}}{2\pi k_b T}} \exp\left(-\frac{m_{at} \omega_i^2 a_i^2}{2k_b T}\right) \sqrt{\frac{m_{at}}{2\pi k_b T}} \times \exp\left(-\frac{m_{at} v_i^2}{2k_b T}\right). \quad (14)$$

Here,  $A = [a_1, a_2, \dots, a_{nmodes}]$  denotes the set of all the modal displacements and  $V = [v_1, v_2, \dots, v_{nmodes}]$  denotes the set of all the mode velocities. We will use this PDF to sample the phase space. This entails generating different samples of  $A$  and  $V$ . We recognize from the PDF in Eq. (14) that each of the mode displacement and velocity is an independent

random variable with a Gaussian distribution. Given the values of  $\omega_i$ ,  $a_i$  can be easily sampled out using an algorithm to sample Gaussian random number. We use the Box-Muller algorithm, and as implemented in the GNU scientific library,<sup>19</sup> to sample the random variables with a Gaussian distribution. A set of mode displacements and velocities are, therefore, obtained. Further, using the set of mode displacements, one can get the atomic displacement as

$$u_i^j = \sum_m \epsilon_{im}^j a_m. \quad (15)$$

Here,  $u_i^j$  refers to the displacement of an atom  $i$  along the direction  $j$ . We, thus, obtain a set of atomic configuration sampled using the quasi-harmonic approximation. For each of the sampled set, per-atom forces are determined using the full inter-atomic potential. These are then used to compute the mode force,  $f_i$ , for a mode  $i$ . The mode forces will be used to compute the force correlation matrix as introduced below.

The next step in the algorithm involves the determination of the anharmonic stiffness matrix,  $\mathbf{K}$ , and the anharmonic mode frequency. For this purpose, we introduce the mode force correlation matrix,  $\mathbf{F}$ . The components of  $\mathbf{F}$  are given as

$$F_{ij} = \langle f_i f_j \rangle_{hm}. \quad (16)$$

Here,  $f_i$  is the force for mode  $i$  and as computed using the full inter-atomic potential. The angle brackets with the subscript  $hm$  refer to ensemble average for the ensemble generated using the QHM approximation. We obtained the values of  $f_i$  from the atomic configurations generated using the QHM approximation. These are used to compute  $\mathbf{F}$  using Eq. (16).

The objective is to seek  $\mathbf{K}$  such that the force correlation matrix constructed using the full inter-atomic potential (as defined in Eq. (16)) is equal to the one obtained using  $\mathbf{K}$ . For this purpose, we shall now derive an expression for the mode force correlation matrix in terms of  $\mathbf{K}$ .

Let  $K_{ij}$  denote the component of  $\mathbf{K}$  in the basis of the modal co-ordinates. The effective Hamiltonian,  $H$ , of the system can then be written as

$$H = \sum_{i=1}^{nmodes} \sum_{j=1}^{nmodes} \frac{1}{2} K_{ij} a_i a_j + \sum_{i=1}^{nmodes} \frac{1}{2} m_{at} v_i^2. \quad (17)$$

Let  $f_m^H$  denote the mode force value computed using  $H$ . It is obtained by taking the derivative of  $H$  with respect to  $a_m$  and is given as

$$f_m^H = - \sum_{n=1}^{nmodes} K_{mn} a_n. \quad (18)$$

We construct the mode force correlation matrix  $\mathbf{F}^H$  such that  $F_{ij}^H = \langle f_i^H f_j^H \rangle_{hm}$ . Here, the angle brackets refer to the ensemble average for the canonical ensemble generated using  $H_{harm}$ . From the PDF in Eq. (14), it can be established that  $\langle a_m a_n \rangle_{hm} = \frac{k_b T}{m_{at} \omega_m \omega_n}$ . Using this result along with Eq. (18) and the definition of  $F_{ij}^H$ , we obtain

$$F_{ij}^H = \sum_n \frac{k_b T}{m_{at}} K_{in} \frac{1}{\omega_n^2} K_{nj}. \quad (19)$$

Equating  $\mathbf{F}$  with  $\mathbf{F}^H$ , we get

$$F_{ij} = \sum_n \frac{k_b T}{m_{at}} K_{in} \frac{1}{\omega_n^2} K_{nj}. \quad (20)$$

We use Eq. (20) to determine the stiffness matrix,  $\mathbf{K}$ . The anharmonic mode frequency,  $\omega_m^{anh}$ , for a mode  $m$  is computed from the eigen-values of  $\mathbf{K}$ .

The  $\omega_m^{anh}$ , thus, obtained will be used to sample a new set of atomic configurations and compute the required ensemble averages. In-order to sample the phase space, we need the corresponding PDF. We shall write the effective Hamiltonian and construct the PDF in terms of  $\omega_k^{anh}$ .

$H$  can be written in terms of  $\omega_k^{anh}$  as

$$H = \sum_{k=1}^{nmodes} \left( \frac{1}{2} m_{at} (\omega_k^{anh})^2 a_k^2 + \frac{1}{2} m_{at} v_k^2 \right). \quad (21)$$

The representation of  $H$  in terms of  $\omega_k^{anh}$  rather than in terms of  $\mathbf{K}$  corresponds to that of uncoupled harmonic oscillators. The corresponding PDF for a canonical ensemble at temperature,  $T$ , is then given as

$$P_{eqb}(A, V) = \prod_{i=1}^{nmodes} \sqrt{\frac{(\omega_i^{anh})^2 m_{at}}{2\pi k_b T}} \exp\left(-\frac{m_{at} (\omega_i^{anh} a_i)^2}{2k_b T}\right) \times \sqrt{\frac{m_{at}}{2\pi k_b T}} \exp\left(-\frac{m_{at} v_i^2}{2k_b T}\right). \quad (22)$$

The different terms in the above equation have the same representation as introduced before.

The PDF in Eq. (22) is used to generate the different atomic configurations of the crystalline structure (i.e., generate different sets of  $A$  and  $V$ ). We recognize from the PDF in Eq. (22) that each of the mode displacement and velocity is an independent random variable with a Gaussian distribution. As for the quasi-harmonic case, we use the Box-Muller algorithm to sample  $a_k$  and  $v_k$ . From the atomic configuration, thus, obtained the atomic forces, and their time derivatives are determined. These quantities are then used to compute  $f_m$  and  $\dot{f}_m$ .

Different atomic configurations are generated in this manner. We generate a total of  $nensb$  configurations. For each of the ensemble, different mode variables are computed. We obtain  $a_m$ ,  $v_m$ ,  $f_m$ , and  $\dot{f}_m$  for an ensemble  $i$ . These are then used to compute  $C_m''(0)$  and  $C_m'''(0)$  as

$$C_m''(0) = -\frac{1}{nensb} \sum_{i=1}^{nensb} \left[ (m\omega_m^2 a_m v_m + v_m \dot{f}_m)^2 \right]_i \quad (23)$$

and

$$C_m'''(0) = \frac{1}{nensb} \sum_{i=1}^{nensb} \left[ \left( m_{at} \omega_m^2 v_m^2 + \omega_m^2 a_m \dot{f}_m + \frac{\dot{f}_m^2}{m_{at}} + v_m \dot{f}_m \right)^2 \right]_i. \quad (24)$$

Here, the variables within the brackets correspond to the  $i$ th sampled configuration, and  $nensb$  is the total number of ensembles. The expressions for  $C_m''(0)$  and  $C_m''''(0)$  used here were derived before and are obtained using Eqs. (4) and (5) along with Eqs. (6) and (7). The estimation of  $C_m''(0)$  and  $C_m''''(0)$ , thus, gives us an approximate form of  $C_m(t)$ . The algorithm to compute the approximate form of  $C_m(t)$  is summarized in Algorithm 1.

We also obtained the mode energy auto-correlation function and its time derivative from the trajectories generated using MD. This requires computing different mode based quantities. The per atom quantities, generated using the MD trajectories, were projected on to the mode shapes to get the different mode variables. These were then used to compute  $E_m(t)$  and its time derivative. For each mode, the auto-correlation function  $C_m(t)$  was determined using Eq. (2). Also, from the MD generated trajectories, we obtained the values of  $C_m''(0)$  and  $C_m''''(0)$  using Eqs. (4) and (5). In these equations, we invoke the ergodic hypothesis. The time average was used instead of the ensemble average.

#### ALGORITHM 1.

- 1: Generate the mean position of the atoms using the underlying lattice structure.
- 2: Perform quasi-harmonic analysis to determine  $\omega_k$ .
- 3: Construct the PDF for the mode co-ordinates using Eq. (14).
- 4: Generate different samples of the mode co-ordinates using this PDF.
- 5: For each of the sampled set, determine the mode force,  $f_i$ , using the inter-atomic potential.
- 6: Compute the mode force correlation matrix,  $\mathbf{F}$ , using Eq. (16).
- 7: Determine  $\mathbf{K}$  from  $\mathbf{F}$  using Eq. (20).
- 8: Determine  $\omega_k^{anh}$  using  $\mathbf{K}$ .
- 9: Construct the anharmonic PDF for the mode co-ordinates using Eq. (22).
- 10: Sample the mode co-ordinates using this PDF.
- 11: Determine the mode variables for the generated atomic configurations.
- 12: Compute  $C_k''(0)$  and  $C_k''''(0)$  using Eqs. (23) and (24).

### III. RESULTS

We consider the case of a bulk silicon crystal with the dimension of  $5\text{ }lc \times 5\text{ }lc \times 5\text{ }lc$ . Here,  $lc$  is the lattice unit and has a value of  $5.431\text{ \AA}$  for silicon. Tersoff<sup>20</sup> potential was used to model the inter-atomic forces. The MD simulations were performed using LAMMPS.<sup>21</sup> A time step of 1 fs was used.

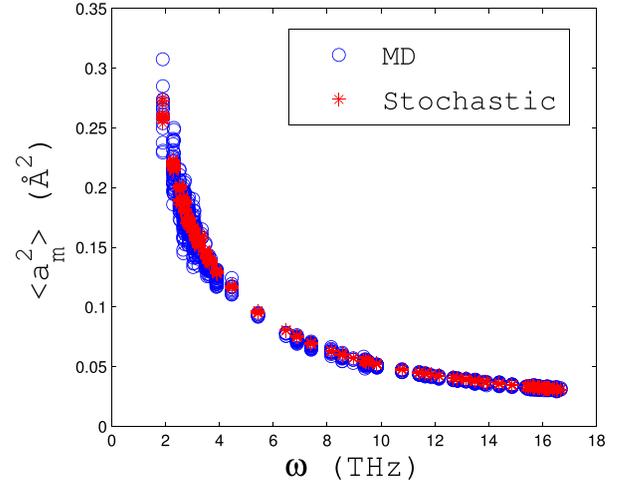


FIG. 1. The variance of the mode amplitude,  $\langle a_m^2 \rangle$ , as a function of the mode frequency. The figure shows the comparison of the results from the stochastic sampling approach and MD.

The structure was equilibrated at a temperature of 300 K using Nosé-Hoover thermostat and for 2 ns. A time constant of 1 ps was used for the thermostat. Subsequent to equilibration, the system was evolved as a micro-canonical ensemble for 5 ns. The mode energy correlation function,  $C_m(t)$ , was determined for different phonon modes. The exponential fit of  $C_m(t)$  gives the phonon life time  $\tau_m$ . These results will be discussed later and will be used to validate the corresponding values obtained using the stochastic sampling approach.

In order to sample the phase space using the stochastic approach, we first determine the values of the anharmonic mode frequencies,  $\omega_m^{anh}$ . The variance of the mode amplitude,  $\langle a_m^2 \rangle$ , is related to  $\omega_m^{anh}$  and the atomic mass  $m_{at}$  as

$$\langle a_m^2 \rangle = \frac{k_b T}{(m_{at} \omega_m^{anh})^2}. \quad (25)$$

Figure 1 shows the comparison of  $\langle a_m^2 \rangle$  values estimated using the stochastic method with the corresponding results obtained using MD. The results are in good agreement with each other. Hence, the phase space can be accurately sampled using these values of  $\langle a_m^2 \rangle$ .

The values of  $\omega_m^{anh}$  were used to sample the new set of atomic configurations. We generated 2000 ensembles for computing the approximate form of the energy auto-

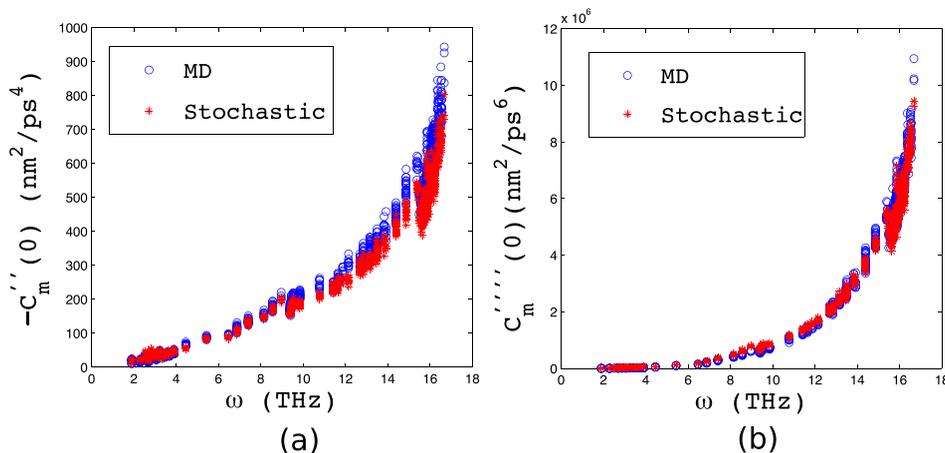


FIG. 2. (a) and (b) The second ( $C_m''(0)$ ) and the fourth ( $C_m''''(0)$ ) derivative of the mode energy auto-correlation function.

correlation function. Figures 2(a) and 2(b) show the value of  $C_m''(0)$  and  $C_m''''(0)$  obtained using the stochastic approach and from MD. The two values are in agreement with each other with small deviations. The time derivative of  $C_m(t)$  is, therefore, accurately computed using the stochastic sampling approach. The small deviation between the two is due to the small correlation between the mode amplitude which has been neglected in the stochastic sampling.

The approximate form of  $C_m(t)$  can now be used to determine the phonon relaxation time. The expansion of  $C_m(t)$  is valid only for a short time interval of time around  $t=0$ . We considered fitting the approximate form using a decaying exponential function for a time interval of 10 fs. From the time constant of the fitted exponential function, the phonon relaxation time was determined. The phonon relaxation time, obtained using the approximate form of  $C_m(t)$ , is termed as  $\tau_m^s$ . Figure 3 shows the value of  $\tau_m^s$  as a function of  $\omega_m$  and also the value of  $\tau_m$  obtained using MD. The phonon life-time obtained using the approximate function is in close agreement with those obtained using the exact one. Thus, the short time correlation function is able to accurately capture the phonon dynamics. There are deviations between the two values for some of the modes. For such modes, we expect that the long term dynamics governs the relaxation behavior.

It would be worthwhile to discuss the computational efficiency of the proposed algorithm. We generated 2000 ensembles using the stochastic sampling approach for the computation of  $C_m(t)$ . We consider generating an equivalent number of un-correlated ensembles using MD. For a correlation time of around 1 ps, this corresponds to a total simulation time of 2 ns. The time step for MD is limited by the highest phonon frequencies. We considered a time step of 1 fs for the MD simulation. Thus, we require a total of  $2e6$  integration time steps to generate 2000 un-correlated ensembles. Each time step of MD and each step of generating an atomic configuration using the stochastic approach requires roughly the same amount of resources. The total computational cost of the stochastic approach as compared to MD then corresponds to the ratio of the number of ensembles to

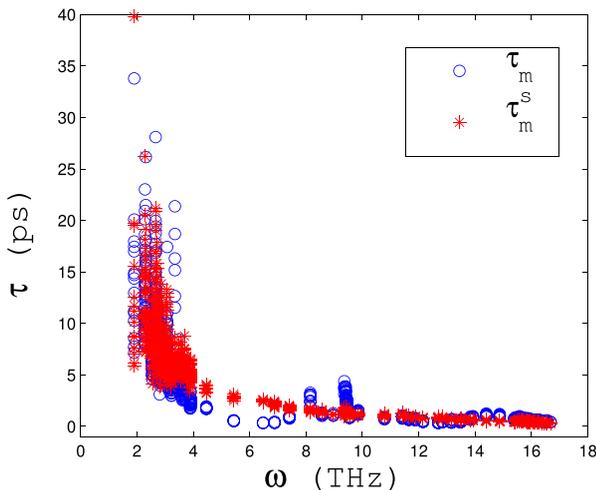


FIG. 3. Relaxation time as a function of the mode frequency obtained using the exact ( $\tau_m$ ) and the approximate ( $\tau_m^s$ ) mode energy correlation function.

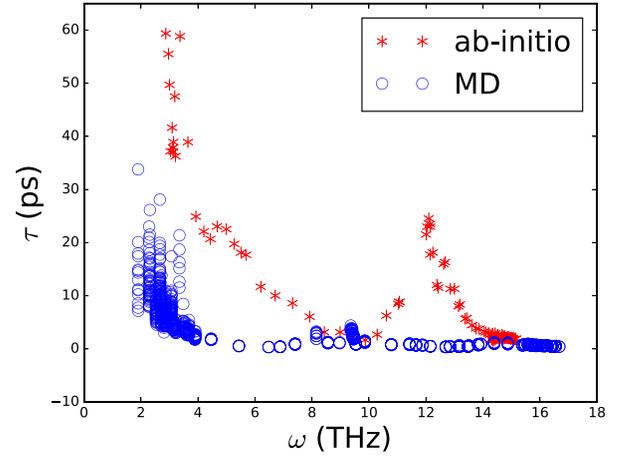


FIG. 4. Relaxation time as a function of the mode frequency obtained using MD and its comparison with the *ab-initio*.<sup>9</sup>

that of the number of MD steps (required for generating an equivalent number of un-correlated ensemble). The cost of the stochastic sampling is, therefore, estimated to be  $\frac{1}{1000}$  of that of MD for our case. It should be pointed out that we did not take into consideration the cost of the QHM analysis. This is because the QHM analysis is also required in the computation of the phonon relaxation time using MD. Also, the transformation between the modal and the per-atom basis is required in both the cases.

In this work, we have developed an algorithm to compute the relaxation time for a given EIP. It would be useful, here, to comment on the accuracy of an EIP in predicting the phonon properties. Figure 4 shows the comparison of the relaxation time for the Tersoff potential with the *ab-initio*.<sup>9</sup> We observe that the Tersoff potential shows deviations from the *ab-initio* values. Phonon relaxation time results from third and higher order effects. The EIPs are, often, developed to match the mechanical properties which is a second order effect. It is, therefore, expected that EIPs correctly predict the phonon velocity, density of states, etc. The EIPs can, however, fail to correctly describe the phonon dynamics which results from third and higher order terms.

#### IV. CONCLUSIONS

We considered Taylor series expansion to construct an approximate polynomial function for the mode energy auto-correlation function. We derived expressions for the different terms in the expansion in terms of the ensemble average of the mode variables. Mode force and its time derivative (along with displacement and velocity) were used in the computation of the approximate form of the function. We, next, considered a stochastic sampling approach to sample the phase space and compute the required ensemble average. The anharmonic mode frequencies were, first, estimated using the quasi-harmonic approximation. These were then used to sample different atomic configuration and evaluate the expansion terms of the mode energy auto-correlation function. We compared these terms with the corresponding values obtained using MD. The two values were in good agreement with each other. Phonon life time was computed

using the polynomial approximation and compared with that obtained using the exact correlation function generated from MD.

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