

# Phonon dispersion measured directly from molecular dynamics simulations<sup>☆</sup>

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## ABSTRACT

A method to measure the phonon dispersion of a crystal based on molecular dynamics simulation is proposed and implemented as an extension to an open source classical molecular dynamics simulation code LAMMPS. In the proposed method, the dynamical matrix is constructed by observing the displacements of atoms during molecular dynamics simulation, making use of the fluctuation–dissipation theory. The dynamical matrix can then be employed to compute the phonon spectra by evaluating its eigenvalues. It is found that the proposed method is capable of yielding the phonon dispersion accurately, while taking into account the anharmonic effect on phonons simultaneously. The implementation is done in the style of fix of LAMMPS, which is designed to run in parallel and to exploit the functions provided by LAMMPS; the measured dynamical matrices could be passed to an auxiliary postprocessing code to evaluate the phonons.

### Program summary

*Program title:* FixPhonon, version 1.0

*Catalogue identifier:* AEJB\_v1\_0

*Program summary URL:* [http://cpc.cs.qub.ac.uk/summaries/AEJB\\_v1\\_0.html](http://cpc.cs.qub.ac.uk/summaries/AEJB_v1_0.html)

*Program obtainable from:* CPC Program Library, Queen's University, Belfast, N. Ireland

*Licensing provisions:* GNU General Public license

*No. of lines in distributed program, including test data, etc.:* 105 393

*No. of bytes in distributed program, including test data, etc.:* 3 231 800

*Distribution format:* tar.gz

*Programming language:* C++

*Computer:* All

*Operating system:* Linux

*Has the code been vectorized or parallelized?:* Yes. 1 to  $N$  processors may be used

*RAM:* Depends on problem,  $\approx$  1 kB to several MB

*Classification:* 7.8

*External routines:* MPI, FFT, LAMMPS version 15, January 2010 (<http://lammps.sandia.gov/>)

*Nature of problem:* Atoms in solids make ceaseless vibrations about their equilibrium positions, and a collective vibration forms a wave of allowed wavelength and amplitude. The quantum of such lattice vibration is called the phonon, and the so-called “lattice dynamics” is the field of study to find the normal modes of these vibrations. In other words, lattice dynamics examines the relationship between the frequencies of phonons and the wave vectors, i.e., the phonon dispersion. The evaluation of the phonon dispersion requires the construction of the dynamical matrix. In atomic scale modeling, the dynamical matrices are usually constructed by deriving the derivatives of the force field employed, which cannot account for the effect of temperature on phonons, with an exception of the tedious “quasi-harmonic” procedure.

*Solution method:* We propose here a method to construct the dynamical matrix directly from molecular dynamics simulations, simply by observing the displacements of atoms in the system thus making the constructing of the dynamical matrix a straightforward task. Moreover, the anharmonic effect was taken into account in molecular dynamics simulations naturally, the resultant phonons therefore reflect the finite temperature effect simultaneously.

*Restrictions:* A well defined lattice is necessary to employ the proposed method as well as the implemented code to evaluate the phonon dispersion. In other words, the system under study should be

<sup>☆</sup> This paper and its associated computer program are available via the Computer Physics Communications homepage on ScienceDirect (<http://www.sciencedirect.com/journal/00104655>).

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in solid state where atoms vibrate about their equilibrium positions. Besides, no drifting of the lattice is expected. The method is best suited for periodic systems, although non-periodic system with a supercell approach is also possible, it will however become inefficient when the unit cell contains too many atoms. *Additional comments:* The readers are encouraged to visit <http://code.google.com/p/fix-phonon> for subsequent update of the code as well as the associated postprocessing code, so as to keep up with the latest version of LAMMPS.

*Running time:* Running time depends on the system size, the numbers of processors used, and the complexity of the force field, like a typical molecular dynamics simulation. For the third example shown in this paper, it took about 2.5 hours on an Intel Xeon X3220 architecture (2.4G, quadcore).

#### References:

- [1] C. Campa  a, M.H. M  ser, Phys. Rev. B 74 (2006) 075420.
- [2] L.T. Kong, G. Bartels, C. Campa  a, C. Denniston, M.H. M  ser, Comp. Phys. Commun. 180 (6) (2009) 1004–1010.

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## 1. Introduction

Atoms in solids have rather limited mobility comparing to those in liquids or gases; they are tethered to their respective equilibrium positions which can frequently be represented by a crystal lattice. The crystal lattice is however never rigid. Due to temperature, external field or pressure, the atoms vibrate around their equilibrium positions ceaselessly; even under the absolute zero temperature, the atoms are not stationary at all. The study of lattice vibrations – lattice dynamics – began with the understanding of thermal properties of solids, yet its role is not limited to thermal properties, instead it is of fundamental importance to many fields of study in the solid-state and mineral sciences [1–3].

It was however not until the last century that the lattice dynamics theory was established based on the quantum theory [1]. It revealed that the vibration of atoms in a crystal is correlated, and a collective vibration forms a wave of allowed wavelength and amplitude. The quantum of such lattice vibration is called the phonon, while the “phonon dispersion” gives the wave vector dependence of the phonon frequencies. Experimentally, the phonon dispersion can be determined indirectly via the interaction between lattice waves and other waves, such as neutron inelastic scattering or electron energy loss spectroscopy [2]. Alternatively, the phonon dispersion can also be determined by theoretical computation. In this regard, there are mainly two approaches based on the first principles calculations within density functional theory [3]: direct method (frozen-phonon) and the density functional perturbation theory (DFPT). The direct method imposes displacements of atoms, and constructs the dynamical matrix based on the Hellman–Feynman forces induced [4–6]. This method is relatively easy to implement and is therefore widely used. However, such calculations usually require a supercell that “should be comfortably larger than the longest-range interatomic force, and the phonon wavevector should be commensurate with the structure. With many atoms and electrons in a large supercell, however, the calculations can become unwisely, especially since the computation time often scales as the cube of the number of electrons” [3]. The DFPT approach makes use of the linear response theory to evaluate the dynamical matrix [7–9], which is found to be rather accurate and efficient. In spite of this, the methods based on first principles calculations are generally computationally demanding and frequently prohibitive, leaving the empirical or semi-empirical force field based methods more or less a practical choice. For the force field based methods, one usually constructs the dynamical matrix by evaluating the second derivatives of the force field with respect to the equilibrium positions [1,10,11], and then calculates the phonon frequencies by getting the eigenvalues of the dynamical matrix – the traditional lattice dynamics (LD). In general, the LD provides a straightforward scheme to investigate the phonon dispersion, provided that an accurate/reliable

force field is available. Nonetheless, there is also conditions where the formalism of the force field is too complicated to derive the Hessian, such as the charge transfer model where a self-consistent procedure is needed [12,13]. Most importantly, all the above mentioned computation methods suffer from the fact that the dynamical matrix can only be measured at zero temperature. That is to say, the effect of temperature on the phonons, or anharmonicity, could not be considered directly. Instead, they usually employ a “quasi-harmonic” procedure to account for the finite temperature effect, which is however tedious and sometimes unfeasible [14]. An alternative which could overcome such deficiency is to evaluate the phonons within molecular dynamics (MD) simulation, where the equations of motion are integrated to follow in time the positions and velocities of all atoms. Molecular dynamics is not restricted to harmonic forces, and large-amplitude displacements allow investigations of anharmonic behavior. Presently, the widely known method available to evaluate the phonon dispersion based on molecular dynamics simulation is to calculate the velocity–velocity autocorrelation function  $\langle v(t)v(0) \rangle$  from the trajectory of each atom in a molecular dynamics simulation, whose Fourier transformation gives the phonon density of states (PDOS) [2,15,16]:

$$g(\omega) = \int e^{i\omega t} \frac{\langle v(t)v(0) \rangle}{\langle v(0)v(0) \rangle} dt. \quad (1)$$

The dispersion relation could be obtained as well, but not as straightforward as the PDOS [16,17]. Despite of its advantage, an accurate evaluation of the velocity–velocity autocorrelation requires relatively large simulation cells, considerably long simulation time and rather complicated mathematical operations.

We propose here another approach based on molecular dynamics simulations. In our approach, the dynamical matrices are measured *directly* from molecular dynamics simulations, by observing the motion of atoms in the system and making use of the relations for harmonic/quasi-harmonic modes to construct the dynamical matrices [18,19]. The phonons can be measured at any finite temperature that is well below the melting point, as with the velocity–velocity autocorrelation approach, while both the phonon dispersion and the PDOS can be obtained straightforwardly.

We describe in this paper the physical background of our approach and present an implementation into a classic molecular dynamics simulation code LAMMPS [20–22], which is done in the style of fix. In LAMMPS, a “fix” is any operation that is computed during a time step which alters/measures some property of the system. Essentially everything that happens during a simulation besides potential force computation, neighbor list construction, and some forms of output, is a “fix” [22]. Our fix, FixPhonon, measures the elastic Green’s functions by making use of the fluctuation–dissipation theorem, from which the dynamical matrices are constructed. FixPhonon is called at the end of each  $N$ ’th time step ( $N$  to be specified by user) after equilibration has occurred. An

auxiliary postprocessing code, *phana*, is also provided to get the PDOS as well as phonon dispersion curves from the dynamical matrices produced by FixPhonon.

In the remaining part of this paper, the methodology and its implementation into LAMMPS are sketched. Some technical issues are discussed, followed by three applications which we used to test our theory and the implementation.

## 2. Theoretical backgrounds

### 2.1. Lattice dynamics

The basic theory of lattice dynamics will be reviewed in this section, while a thorough and detailed description of the lattice dynamics theory could be found in many solid state physics textbooks [23,24] as well as some monographs [1,2]. Phonon dispersion relations are calculated by looking for wavelike solutions to the classical equations of motion of atoms under a small displacement from their equilibrium sites.

We will consider a crystal composed of an infinite number of unit cells in three dimensions labeled  $l = (l_1, l_2, l_3)$  where  $l_i, i=1,2,3$  are integers. Each unit cell is defined by three linearly independent vectors  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  forming a parallelepiped. The origin of the  $l$ th unit cell can then be defined as:

$$\mathbf{r}_l = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3, \quad (2)$$

relative to the origin  $l = (0, 0, 0)$ . Each unit cell contains  $n$  basis atoms which are labeled by  $k = 1, \dots, n$ , and the  $k$ th basis atom lies at the position  $\Delta \mathbf{r}_k$  relative to the origin of its unit cell  $\mathbf{r}_l$ . Therefore the position of any atom  $lk$  is given by  $\mathbf{r}_{lk} = \mathbf{r}_l + \Delta \mathbf{r}_k$ .

Vibrations occur when the atoms are displaced from their equilibrium positions by an amount of  $\mathbf{u}_{lk} = (u_{lkx}, u_{lky}, u_{lkz})$ , the actual position of any atom under the influence of a vibration is then  $\mathbf{R}_{lk} = \mathbf{r}_{lk} + \mathbf{u}_{lk}$ .

Assuming the displacements are small compared to interatomic distances, which is generally true for stable crystals at a temperature well below its melting point, then the potential energy of the crystal can be expanded about the equilibrium positions:

$$U = U_0 + \sum_{lk\alpha} \Phi_{lk\alpha} u_{lk\alpha} + \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} \Phi_{lk\alpha, l'k'\beta} u_{lk\alpha} u_{l'k'\beta} + \dots, \quad (3)$$

where  $\alpha$  and  $\beta$  enumerate all  $x, y$ , and  $z$  coordinates and the coefficients  $\Phi_{lk\alpha}$  and  $\Phi_{lk\alpha, l'k'\beta}$  are given by

$$\Phi_{lk\alpha} = \left( \frac{\partial U}{\partial u_{lk\alpha}} \right)_0, \quad (4)$$

and

$$\Phi_{lk\alpha, l'k'\beta} = \left( \frac{\partial^2 U}{\partial u_{lk\alpha} \partial u_{l'k'\beta}} \right)_0, \quad (lk) \neq (l'k'), \quad (5)$$

respectively. The subscript 0 indicates that the derivatives are evaluated at the equilibrium positions,  $\mathbf{r}_{lk}$ .

The first term in Eq. (3) is independent of the displacements and can therefore be taken as zero. The second term will be zero since “equilibrium” suggests a minimum of the potential energy. In the harmonic approximation all terms in cubic or higher order are assumed negligible, therefore the potential can be expressed simply as the third term in Eq. (3).

That term is however not defined for self interactions, i.e., it allows only the  $(lk) \neq (l'k')$  terms. To define the self interaction term, consider a rigid translation of the entire crystal. This can be

defined by replacing the displacements of all atoms by a constant value  $v_\beta$ . The equation of motion of the atoms is then

$$m_k \ddot{u}_{lk\alpha} = -v_\beta \sum_{l'k'} \Phi_{lk\alpha, l'k'\beta}. \quad (6)$$

The left hand of Eq. (6) must be zero since such a rigid translation clearly cause the forces  $F_\alpha = m_k \ddot{u}_{lk\alpha}$  to vanish. But the  $v_\beta$  are arbitrary hence the sum over the coefficients  $\Phi_{lk\alpha, l'k'\beta}$  must be zero. Therefore, in addition to the definition of  $\Phi_{lk\alpha, l'k'\beta}$  given by Eq. (5), the diagonal terms must be given by

$$\Phi_{lk\alpha, lk\beta} = - \sum_{l'k' \neq lk} \Phi_{lk\alpha, l'k'\beta}. \quad (7)$$

This is known as the acoustic sum rule (ASR) [1].

Now that all the elastic constants  $\Phi_{lk\alpha, l'k'\beta}$  are well defined, it is possible to solve the equation of motion

$$m_k \ddot{u}_{lk\alpha} = - \sum_{l'k'\beta} \Phi_{lk\alpha, l'k'\beta} u_{l'k'\beta}, \quad (8)$$

by looking for the wavelike solutions

$$u_{lk\alpha} = \frac{1}{\sqrt{m_k}} \Lambda(\mathbf{q}) e_{k\alpha}(\mathbf{q}) \exp[i[\mathbf{q} \cdot \mathbf{r}_l - \omega(\mathbf{q})t]], \quad (9)$$

where  $\Lambda$  and  $e_{k\alpha}$  are amplitudes of the wave, and  $\mathbf{q}$  is the wavevector.

By substituting Eq. (9) into Eq. (8), the following dispersion relation is found

$$\omega^2(\mathbf{q}) e_{k\alpha} = \sum_{k', \beta} D_{k\alpha, k'\beta}(\mathbf{q}) e_{k'\beta}, \quad (10)$$

where  $\mathbf{D}$  is known as the dynamical matrix, whose element is given by

$$D_{k\alpha, k'\beta}(\mathbf{q}) = \frac{1}{\sqrt{m_k m_{k'}}} \sum_{l, l'} \Phi_{lk\alpha, l'k'\beta} \exp[i\mathbf{q} \cdot (\mathbf{r}_{l'} - \mathbf{r}_l)]. \quad (11)$$

The condition for Eq. (10) to have a non-trivial solution is that the determinant of the coefficients vanishes, that is to say

$$|D_{k\alpha, k'\beta}(\mathbf{q}) - \delta_{\alpha\beta} \delta_{kk'} \omega^2(\mathbf{q})| = 0. \quad (12)$$

Consequently the eigenvalues of the dynamical matrix give the allowed (squares of) phonon frequencies for a given  $\mathbf{q}$ . The dynamical matrix is Hermitian and the eigenvalues  $\omega^2(\mathbf{q})$  are therefore real; a negative eigenvalue usually suggests that the system under study is mechanically unstable.

### 2.2. Phonon dispersion from direct molecular dynamics simulations

We will outline in this section the theoretical background underlying our new approach; the basic idea is quite similar to our previously proposed Green's function molecular dynamics simulation method [25–27].

First consider a single particle with mass  $m$  that is connected to its equilibrium position by a massless spring with a force constant of  $k$ . Even that there is no other external field applied, the particle will not remain stationary. Instead, it will fluctuate about its equilibrium position; we might assume that it vibrates along the  $x$  direction only. Under equilibrium conditions, an equipartition of energy will be expected. We will therefore have

$$\frac{1}{2} k \langle \Delta x^2 \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} k_B T, \quad (13)$$

where  $\langle \dots \rangle$  denotes the “ensemble” average,  $\Delta x$  is the displacement of the particle,  $v$  is the velocity,  $k_B$  is the Boltzmann's constant, and  $T$  is the temperature, if we could define a temperature here for a single particle. Eq. (13) suggests that the force constant could be determined by

$$k = \frac{k_B T}{\langle \Delta x^2 \rangle}. \quad (14)$$

Such relationship remains valid for real crystal systems under harmonic vibrations; for detailed deduction, the readers are referred to our previous work on the Green's function molecular dynamics simulation method [27].

Accordingly, for the crystal we considered in Section 2.1, the lattice Green's function coefficient  $G_{lk\alpha, l'k'\beta}$  can be obtained by observing the second moment of the displacements [19,25,28]:

$$G_{lk\alpha, l'k'\beta} = \langle u_{lk\alpha} u_{l'k'\beta} \rangle, \quad (15)$$

which relates to the force constant via

$$\Phi_{lk\alpha, l'k'\beta} = k_B T [G^{-1}]_{lk\alpha, l'k'\beta}, \quad (16)$$

i.e.,

$$\Phi = k_B T \mathbf{G}^{-1}. \quad (17)$$

For crystal systems with Born-von Karman boundary condition [1,23], it would be more convenient to assess the Green's function coefficients and consequently the force constants in reciprocal space, since modes with different wave vectors do not couple with each other in periodic systems with harmonic degrees of freedom. The displacement in the reciprocal space is defined as the Fourier transformation of the real space ones:

$$\tilde{u}_{k\alpha}(\mathbf{q}) = \frac{1}{\sqrt{N}} \sum_l \mathbf{u}_{lk\alpha} \exp(-i\mathbf{q}\mathbf{r}_l). \quad (18)$$

Here  $N$  is the total number of unit cells in the crystal. The Green's function in reciprocal space is

$$\tilde{G}_{k\alpha, k'\beta}(\mathbf{q}) = \langle \tilde{u}_{k\alpha}(\mathbf{q}) \tilde{u}_{k'\beta}^*(\mathbf{q}) \rangle, \quad (19)$$

where  $*$  denotes the complex conjugate. The force constant is then given by

$$\tilde{\Phi}_{k\alpha, k'\beta}(\mathbf{q}) = k_B T [\tilde{G}^{-1}(\mathbf{q})]_{k\alpha, k'\beta}, \quad (20)$$

which is actually the Fourier transformation of the force constants in real space at  $\mathbf{q}$ :

$$\tilde{\Phi}_{k\alpha, k'\beta}(\mathbf{q}) = \sum_{l, l'} \Phi_{lk\alpha, l'k'\beta} \exp[i\mathbf{q}(\mathbf{r}_l - \mathbf{r}_{l'})]. \quad (21)$$

Combining Eqs. (11), (20) and (21), one sees that once  $\tilde{\Phi}$  is obtained by the Green's function method, the dynamical matrix is readily available:

$$D_{k\alpha, k'\beta}(\mathbf{q}) = \frac{1}{\sqrt{m_k m_{k'}}} \tilde{\Phi}_{k\alpha, k'\beta}(\mathbf{q}). \quad (22)$$

The theoretical deduction above therefore offers a unique routine to measure the dynamical matrix and the phonon dispersion directly from molecular dynamics simulations: one can simply observe the displacements of atoms during molecular dynamics simulations and then evaluate the Green's function coefficients in the reciprocal space. The force constant matrices and consequently the dynamical matrices can then be obtained by simple matrix inversion and multiplication operations.

### 3. Notes on implementation and technical issues

In this section, a few technical issues will be discussed, which related to the realization and implementation of our method into the open source package LAMMPS [20–22].

The measurement of the dynamical matrices based on the fluctuation-dissipation theorem was realized as a new fix to LAMMPS, which we name as FixPhonon. It takes the instantaneous positions of atoms in the equilibrated system, and transforms them into reciprocal space to get the Green's function coefficients. After a certain number of measurements, the “time” average of the Green's function coefficients is evaluated and for a long enough simulation, it can be seen as the “ensemble” average. The force constant matrices are then deduced, based on which the dynamical matrices are constructed. The results are written to both a log file and a binary data file, the latter can then be passed to an auxiliary postprocessing code *phana* to compute the phonon frequencies.

In practice, when evaluating the Green's function, it is easier to measure absolute atomic positions rather than displacements, Eq. (19) can then be replaced with the following equation [27]

$$\tilde{G}_{k\alpha, k'\beta}(\mathbf{q}) = \langle \tilde{R}_{k\alpha}(\mathbf{q}) \tilde{R}_{k'\beta}^*(\mathbf{q}) \rangle - \langle \tilde{R}_{k\alpha}(\mathbf{q}) \rangle \cdot \langle \tilde{R}_{k'\beta}^*(\mathbf{q}) \rangle, \quad (23)$$

where  $\langle \tilde{R}_{k\alpha}(\mathbf{q}) \rangle$  is the Fourier transformation of the mean positions  $\langle R_{lk\alpha} \rangle$  at  $\mathbf{q}$ . This way the instantaneous positions are evaluated rather than the displacements, which not only facilitates the measuring but also reduces statistical errors, aided by the fact that  $\langle \tilde{R}_{k\alpha}(\mathbf{q}) \rangle$  is expected to be zero in equilibrium for  $\mathbf{q} \neq 0$  [25].

Thus far, the theory seems to be complete, yet special attention needs to be paid to the force constants at the  $\Gamma$  point (denoted as  $\tilde{\Phi}_\Gamma$  hereafter), where  $\mathbf{q} = 0$ . From Eq. (9) one sees that a rigid translation of the crystal is possible for  $\mathbf{q} = 0$ , and therefore the “acoustic sum rule” should be satisfied for  $\tilde{\Phi}_\Gamma$ . Referring to Eqs. (7) and (21), in the reciprocal space the ASR requires that

$$\sum_{k'} \tilde{\Phi}_{k\alpha, k'\beta}(\Gamma) = 0. \quad (24)$$

In addition, since the partial differentiation is commutative, the force constant matrix should be symmetric/Hermitian as well [1,29]:

$$\tilde{\Phi}_{k\alpha, k'\beta}(\mathbf{q}) = \tilde{\Phi}_{k'\beta, k\alpha}^*(\mathbf{q}). \quad (25)$$

In the measuring procedure, the ASR is however not satisfied, mainly due to the finite size effect. It need therefore to be enforced afterwards. In real space calculations, one usually applies the ASR simply by ignoring the calculated values of  $\Phi_{lk\alpha, lk\beta}$  and replacing it with  $\Phi_{lk\alpha, lk\beta} = -\sum_{l'k' \neq lk} \Phi_{lk\alpha, l'k'\beta}$  [29]. In reciprocal space, it however cannot be achieved in such a straightforward manner. We therefore adopted an iterative procedure to enforce the ASR on  $\tilde{\Phi}_\Gamma$ : (1)  $\sum_{k'} \tilde{\Phi}_{k\alpha, k'\beta} = 0$  is enforced by subtracting each element involved by a constant term; this procedure removes the violation of ASR, while in turn, usually destroys the symmetry of the force constant matrix. (2) Symmetry is restored by replacing  $\tilde{\Phi}_{k\alpha, k'\beta}$  and  $\tilde{\Phi}_{k'\beta, k\alpha}$  with their average value; this will ensure the symmetry of the matrix, however, it will break the ASR slightly. (3) Steps (1) and (2) are repeated for several iterations, followed by a “symmetric ASR”: similar to step (1), the ASR is enforced by requiring  $\sum_{k'} \tilde{\Phi}_{k\alpha, k'\beta} = 0$ , while this time, only elements with  $k' \geq k$  are subtracted by a certain value, while setting  $\tilde{\Phi}_{k'\beta, k\alpha} = \tilde{\Phi}_{k\alpha, k'\beta}$ . By adopting this procedure, the eigenvalues of the resultant  $\tilde{\Phi}'_\Gamma$  corresponding to the acoustic modes are found to get closer to zero by several orders of magnitude, while those corresponding to the optical modes are hardly affected.



Once the dynamical matrices are available, the phonon dispersion can be obtained by getting their eigenvalues. This is done with an auxiliary postprocessing code, *phana*, which reads the binary file produced by FixPhonon and helps one to calculate the PDOS and phonon dispersion curves. In the simulations, the dynamical matrices are measured at  $\mathbf{q} = (\frac{h_1}{N_1}\mathbf{b}_1, \frac{h_2}{N_2}\mathbf{b}_2, \frac{h_3}{N_3}\mathbf{b}_3)$ , where  $h_i = 0, \dots, N_i - 1$ ;  $N_i$  is the number of unit cells along the  $i$ th dimension,  $\mathbf{b}_i$  is the basis vector of the corresponding reciprocal lattice. When evaluating the PDOS or the phonon dispersion curves, one frequently needs the information from the  $\mathbf{q}$  points that are not measured directly. Noticing that the force constant coefficients and consequently the dynamical matrix elements are continuous in the reciprocal space [25,27], an interpolation method could be employed to get the dynamical matrix at  $\mathbf{q}$  points that are not measured. Both a tricubic [30] and a trilinear interpolation method are implemented in the postprocessing code *phana*, while the tricubic interpolation is found to give smoother curves than the trilinear one, in general. Nonetheless, in order to capture the details of the phonon dispersion or the PDOS, a dense  $\mathbf{q}$ -mesh, i.e., a large supercell is recommended.

#### 4. Applications

In this section, three test runs will be presented to demonstrate the validity and usage of our method as well as the implemented fix.

Although the theory was deduced with a three-dimensional lattice, it works for lower-dimensional systems as well, such as one-dimension harmonic atomic chains, where the analytic solution of the phonon dispersion is available.

First, we take a one-dimensional monoatomic chain as an example to measure its phonon dispersion by FixPhonon. Such a system is a typical example to illustrate the lattice vibration theory. Assuming the chain has  $N$  particles with Born–von Karman boundary condition [1,23], the particles have a mass of  $m$  with equilibrium nearest neighbor distance of  $a$ . They interact with their nearest neighbors via a spring with a force constant of  $k$ . The phonon dispersion relation, i.e., the solution to Eq. (10) for such system is known analytically to be  $\omega = 2\sqrt{\frac{k}{m}}|\sin \frac{1}{2}aq|$ . Accordingly, a one-dimensional monoatomic chain with  $N = 16$  particles of  $m = 1$ ,  $a = 1$  and  $k = 1$  was setup, and molecular dynamics simulation in the NVT ensemble was carried out at  $T = 0.005$  with a timestep of  $dt = 0.005$  (in reduced units) for 1,500,000 time steps; the measurement was conducted in the last 1,000,000 time steps. Fig. 1 compares the phonon dispersion measured by the molecular dynamics simulations to the analytical results, where one sees a perfect agreement, suggesting the validity of the underlying theory as well as the implementation. For one-dimensional monoatomic chains, the element of the dynamical matrix is actually the same as its eigenvalue ( $\omega^2$ ), and one sees that the element of the dynamical matrix is indeed continuous in reciprocal space, thus making it possible to get the dynamical matrix at an unmeasured  $\mathbf{q}$ -point by certain interpolation method.

As our second example, we took a one-dimensional diatomic chain, which is another typical example in many solid state physics textbooks [23,24]. In the diatomic chain, particles of mass  $M$  and  $m$  sit alternatively along the chain with an equilibrium nearest neighbor distance of  $a$ ; Born–von Karman boundary condition is also assumed. The particles in the chain interact with their nearest neighbors via harmonic interactions with a force constant of  $k$ . The analytical solution of the phonon dispersion for such system is given by

$$\omega_{\pm}^2 = k \frac{M+m}{Mm} \left[ 1 \pm \sqrt{1 - \frac{4Mm}{(M+m)^2} \sin^2 aq} \right]. \quad (26)$$

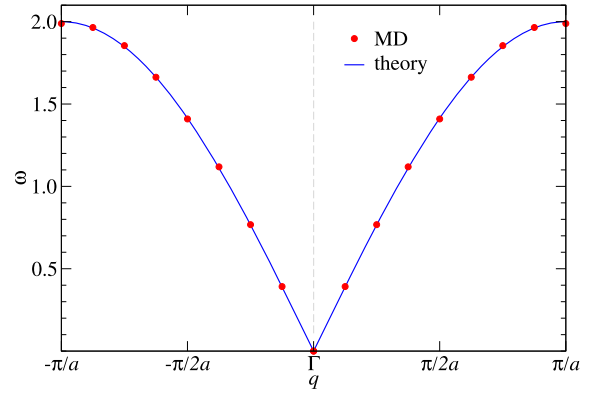


Fig. 1. Numerical (symbols) and analytical (lines) phonon dispersion curves in the first Brillouin zone of a monoatomic atomic chain with  $N = 16$ ,  $m = 1$ ,  $a = 1$ , and  $k = 1$ .

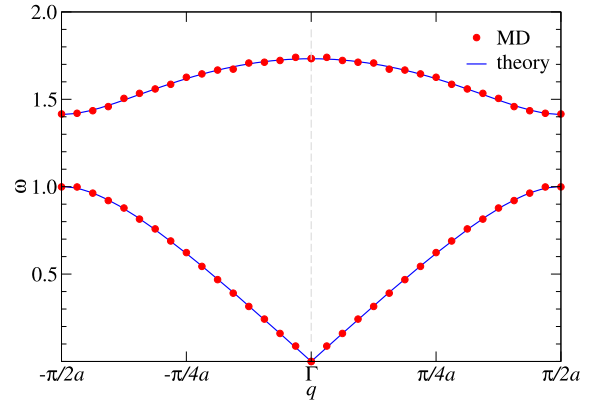
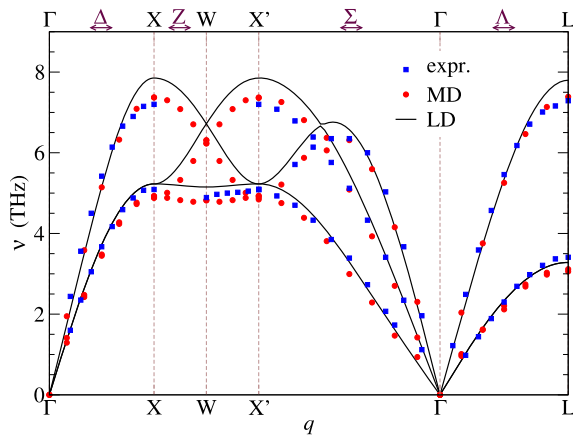


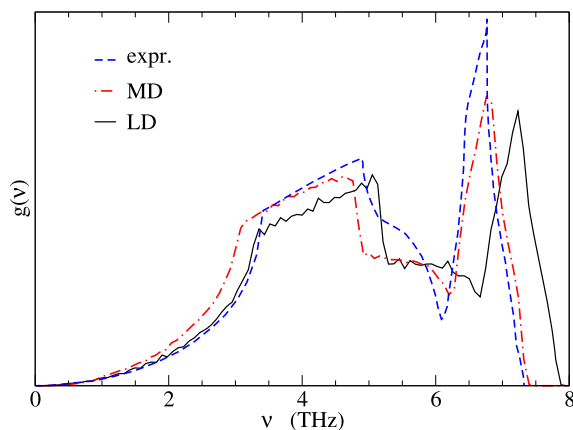
Fig. 2. Numerical (symbols) and analytical (lines) phonon dispersion curves in the first Brillouin zone of a diatomic atomic chain with  $N = 64$ ,  $M = 2$ ,  $m = 1$ ,  $a = 1$ , and  $k = 1$ .

Similar molecular dynamics simulations are performed to measure the phonon dispersion for a diatomic chain of 64 particles with  $M = 2$ ,  $m = 1$ ,  $a = 1$  and  $k = 1$ , respectively. All other MD settings are the same as in the monoatomic case. Fig. 2 shows the measured phonons together with the analytic results; again, one sees a perfect agreement, confirming the validity/reliability of the proposed method as well as the implementation.

The proposed method works with realistic crystalline systems as well. We now take FCC Cu as our third example to further exhibit its validity. Molecular dynamics simulations were performed with a triclinic box containing  $8 \times 8 \times 8$  primitive cells (512 atoms) of FCC Cu, with periodic boundary conditions applied in all directions. The interaction among atoms was described by a many body embedded-atom-method (EAM) potential [31], cutting off at a distance of 4.95 Å. The Nosé–Hoover style thermostat and barostat [32–36] were employed to maintain the system at 300 K and 1 atmosphere. A time step of 2 fs was used. The system was first equilibrated for 0.4 ns and the measurement was conducted every 20 MD steps in the following 12 ns; the whole simulation took about 2 and half hours on a PC with an intel Xeon 2.4G processor (quadcore). The resultant phonon dispersion curves along the major symmetry directions are shown in Fig. 3. The phonon dispersion curves were also calculated with the traditional lattice dynamics method by evaluating the second derivatives of the EAM potential [31], corresponding to the zero temperature. The LD results together with the experimental results [37] are also shown in Fig. 3. One sees that the frequencies measured by molecular dynamics simulations agree well with the experimental results. However, the frequencies by MD and experiment are generally lower



**Fig. 3.** The phonon dispersion curves for FCC Cu in the major symmetry directions. Here  $\nu = \omega/2\pi$ . The solid lines are obtained by getting the derivatives of the EAM potential [31], i.e., by traditional lattice dynamics method. The circles are measured by MD simulations at 300 K in this work, while the squares are experimental results from neutron inelastic-scattering measurements at 298 K [37].



**Fig. 4.** The phonon density of states for FCC Cu. The solid (black) line is obtained by the direct lattice dynamics method at 0 K, the dash-dot-dash (red) line is measured by MD simulations at 300 K in this work, while the dashed (blue) line was computed based on experimental measurements at 298 K [37]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

than those by LD; this is expected, as the LD results correspond to zero temperature, while the MD and experimental results are measured at 300 K/298 K. At high temperature, the metal was softened, thus leading to reduced phonon frequencies. One also sees from Fig. 3 that the frequencies measured by MD also agree very well with those determined by neutron inelastic-scattering measurements at 298 K [37]; this further confirms the validity/reliability of the proposed method as well as the reliability of the employed EAM potential [31].

The phonon density of states could also be easily obtained based on the dynamical matrices measured in the molecular dynamics simulations. In order to get a smooth curve, one usually needs to use a denser  $q$ -mesh than the one measured, which is determined by the simulation box size. Fig. 4 shows the PDOS calculated for FCC Cu by extending the measured  $8 \times 8 \times 8$   $q$ -mesh to  $50 \times 50 \times 50$ . The PDOS calculated by LD as well as that computed based on experimental measurements [37] are also shown in Fig. 4 for comparison. One sees again that at 300 K, the phonon frequencies shows a “red-shift”, referring to those at 0 K by LD. When compared to those computed based on experimental measurements, one sees that the presently measured PDOS gives a

relatively higher density at low frequencies and a lower density at high frequencies, yet in general the agreement is quite good.

## 5. Summary

In summary, we present in this paper a method to measure the phonon dispersion directly from molecular dynamics simulations, as well as its implementation as an extension to existing open-source classical molecular dynamics code LAMMPS. It is demonstrated that the implemented scheme is capable of measuring the phonon dispersion accurately, thus providing a promising tool to the study of lattice vibrations. It should be noted that the “correctness” of the measured phonons however depends on if the force field employed is realistic or not.

In principle, the measurement can be carried out at any temperature under the melting point, as well as different pressures. It is therefore superior to the traditional lattice dynamics method which needs a “quasi-harmonic” procedure to take into account the temperature effect. Besides, with the present method, one does not need to work out the Hessian at all. Comparing to the method based on velocity-velocity autocorrelation, the present method could yield directly the phonon dispersion besides the PDOS. Moreover, one does not need to store a long trajectory so as to evaluate the time autocorrelations. Yet the accuracy and efficiency over the autocorrelation based method need to be further investigated to conclude the superiority.

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## References

- [1] M. Born, K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford University Press, Oxford, 1956.
- [2] M.T. Dove, *Introduction to Lattice Dynamics*, Cambridge University Press, 1993.
- [3] B. Fultz, *Vibrational thermodynamics of materials*, *Prog. Mater. Sci.* 55 (4) (2010) 247–352, doi:10.1016/j.pmatsci.2009.05.002.
- [4] K. Kunc, P.G. Dacosta, Real-space convergence of the force series in the lattice dynamics of germanium, *Phys. Rev. B* 32 (4) (1985) 2010–2021, doi:10.1103/PhysRevB.32.2010.
- [5] G.P. Srivastava, K. Kunc, Phonon dispersion in the (110) direction: a testing ground for phenomenological models of germanium, *J. Phys. C: Solid State Phys.* 21 (29) (1988) 5087.
- [6] S. Wei, M.Y. Chou, Ab initio calculation of force constants and full phonon dispersions, *Phys. Rev. Lett.* 69 (19) (1992) 2799–2802, doi:10.1103/PhysRevLett.69.2799.
- [7] S. Baroni, P. Giannozzi, A. Testa, Green's-function approach to linear response in solids, *Phys. Rev. Lett.* 58 (18) (1987) 1861–1864, doi:10.1103/PhysRevLett.58.1861.
- [8] S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, *Rev. Mod. Phys.* 73 (2) (2001) 515–562, doi:10.1103/RevModPhys.73.515.
- [9] X. Gonze, First-principles responses of solids to atomic displacements and homogeneous electric fields: implementation of a conjugate-gradient algorithm, *Phys. Rev. B* 55 (16) (1997) 10337–10354, doi:10.1103/PhysRevB.55.10337.
- [10] L.T. Kong, L.J. Lewis, Transition state theory of the preexponential factors for self-diffusion on Cu, Ag, and Ni surfaces, *Phys. Rev. B: Condens. Matter Mater. Phys.* 74 (7) (2006) 073412.
- [11] L.T. Kong, L.J. Lewis, Surface diffusion coefficients: substrate dynamics matters, *Phys. Rev. B* 77 (16) (2008) 165422, doi:10.1103/PhysRevB.77.165422.

- [12] W.J. Mortier, K. Van Genechten, J. Gasteiger, Electronegativity equalization: application and parametrization, *J. Am. Chem. Soc.* 107 (4) (1985) 829–835, doi:10.1021/ja00290a017.
- [13] R.A. Nistor, M.H. Müser, Dielectric properties of solids in the regular and split-charge equilibration formalisms, *Phys. Rev. B* 79 (10) (2009) 104303, doi:10.1103/PhysRevB.79.104303.
- [14] G.C. Rutledge, D.J. Lacks, R. Martoňák, K. Binder, A comparison of quasi-harmonic lattice dynamics and Monte Carlo simulation of polymeric crystals using orthorhombic polyethylene, *J. Chem. Phys.* 108 (1998) 10274, doi:10.1063/1.476488.
- [15] J.M. Dickey, A. Paskin, Computer simulation of the lattice dynamics of solids, *Phys. Rev.* 188 (3) (1969) 1407–1418, doi:10.1103/PhysRev.188.1407.
- [16] P. Heino, Dispersion and thermal resistivity in silicon nanofilms by molecular dynamics, *Eur. Phys. J. B* 60 (2007) 171–179, doi:10.1140/epjb/e2007-00342-9.
- [17] J. Li, Simulations of inelastic neutron scattering spectra by molecular dynamics, *Phys. B: Condens. Matter* 263–264 (1999) 404–407, doi:10.1016/S0921-4526(98)01397-0.
- [18] B. Fraser, C. Denniston, M.H. Müser, Diffusion, elasticity, and shear flow in self-assembled block copolymers: a molecular dynamics study, *J. Polym. Sci. Part B: Polym. Phys.* 43 (2005) 970, doi:10.1002/polb.20387.
- [19] L.D. Landau, E.M. Lifshitz, *Physique Statistique*, 3rd edition, MIR, Moscow, 1984.
- [20] S.J. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J. Comp. Phys.* 117 (1995) 1–19.
- [21] S.J. Plimpton, R. Pollock, M. Stevens, Particle-mesh Ewald and rRESPA for parallel molecular dynamics simulation, in: *Proc. of the Eighth SIAM Conference on Parallel Processing for Scientific Computing*, Minneapolis, MN, 1997.
- [22] Large-scale Atomic/Molecular Massively Parallel Simulator, LAMMPS, <http://lammps.sandia.gov>.
- [23] N.W. Ashcroft, D.N. Mermin, *Solid State Physics*, 1st ed., Thomson Learning, Toronto, 1976.
- [24] C. Kittel, *Introduction to Solid State Physics*, 7th ed., Wiley, 1996.
- [25] C. Campañá, M.H. Müser, Practical Green's function approach to the simulation of elastic semi-infinite solids, *Phys. Rev. B: Condens. Matter Mater. Phys.* 74 (7) (2006) 075420.
- [26] C. Campañá, M.H. Müser, C. Denniston, Y. Qi, T.A. Perry, Elucidating the contact mechanics of aluminum silicon surfaces with Green's function molecular dynamics, *J. Appl. Phys.* 102 (11) (2007) 113511.
- [27] L.T. Kong, G. Bartels, C. Campañá, C. Denniston, M.H. Müser, Implementation of Green's function molecular dynamics: An extension to LAMMPS, *Comp. Phys. Commun.* 180 (6) (2009) 1004–1010, doi:10.1016/j.cpc.2008.12.035.
- [28] V.K. Tewary, Green-function method for lattice statics, *Adv. Phys.* 22 (6) (1973) 757–810.
- [29] G.J. Ackland, M.C. Warren, S.J. Clark, Practical methods in ab initio lattice dynamics, *J. Phys.: Condens. Matter* 9 (37) (1997) 7861.
- [30] F. Lekien, J. Marsden, Tricubic interpolation in three dimensions, *Int. J. Numer. Methods Engin.* 63 (3) (2005) 455–471, doi:10.1002/nme.1296.
- [31] S.M. Foiles, M.I. Baskes, M.S. Daw, Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys, *Phys. Rev. B* 33 (12) (1986) 7983–7991, doi:10.1103/PhysRevB.33.7983.
- [32] S. Nosé, A unified formulation of the constant temperature molecular dynamics methods, *J. Chem. Phys.* 81 (1984) 511, doi:10.1063/1.447334.
- [33] W.G. Hoover, Canonical dynamics: equilibrium phase-space distributions, *Phys. Rev. A* 31 (3) (1985) 1695–1697, doi:10.1103/PhysRevA.31.1695.
- [34] M.H. Müser, K. Binder, Molecular dynamics study of the  $\alpha$ - $\beta$  transition in quartz: elastic properties, finite size effects, and hysteresis in the local structure, *Phys. Chem. Minerals* 28 (10) (2001) 746–755.
- [35] W. Shinoda, M. Shiga, M. Mikami, Rapid estimation of elastic constants by molecular dynamics simulation under constant stress, *Phys. Rev. B* 69 (13) (2004) 134103, doi:10.1103/PhysRevB.69.134103.
- [36] G.J. Martyna, D.J. Tobias, M.L. Klein, Constant pressure molecular dynamics algorithms, *J. Chem. Phys.* 101 (1994) 4177, doi:10.1063/1.467468.
- [37] R.M. Nicklow, G. Gilat, H.G. Smith, L.J. Raubenheimer, M.K. Wilkinson, Phonon frequencies in copper at 49 and 298 K, *Phys. Rev.* 164 (3) (1967) 922–928, doi:10.1103/PhysRev.164.922.