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Testing the fourth moment approximation of vibrational mode lifetimes in fcc Lennard-Jonesium

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Abstract

A recently proposed method of approximating the vibrational mode lifetimes in insulators is based on ensemble averages of displacements and forces. In this report, the so-called ‘fourth-moment approximation’ is tested against the conventional ‘ensemble molecular dynamics’ method on vibrational modes in fcc ‘Lennard-Jonesium’. Cells of 4, 8, 16, and 32 atoms are used as a testbed for comparing the two methods. The results show that the moments method gives a quite reasonable accounting of the vibrational mode lifetimes in these cells at all temperatures and is orders of magnitude faster than the MD-based approach.

Keywords: vibrational mode lifetimes, Liouvillian, moment approximation

(Some figures may appear in colour only in the online journal)

1. Introduction

Vibrational modes constitute one of the fundamental excitations of solids, and knowledge of the energies and lifetimes of these modes is of fundamental interest to materials physicists, as is the ability to calculate such properties independent of measurements. The combination of mode frequencies (which are harmonic properties) and their lifetimes (which are determined by anharmonicity of the interactions) determines, for example, the lattice thermal conductivity of an insulator. Much work has been published on calculating vibrational frequencies, but the lifetimes represent a greater challenge, which is what this paper addresses.

In a series of three papers [1–3], Daw *et al* recently proposed an approximate method to calculate lifetimes of vibrational modes in insulating solids. The method is based on ensemble averages of powers of the Liouvillian, and can be carried out by conventional Monte Carlo in combination with a means of calculating forces, such as interatomic potentials or first-principles electronic structure codes. The approach was tested on a lattice model of non-linear

interactions, and it was shown that ensemble averages of the second power of the Liouvillian (that is, so-called ‘second-moment’ approximation) accounted for the mode lifetimes well at high temperatures but diverged at lower temperatures. The next level of approximation (‘fourth-moment’) was shown to account well for the vibrational mode lifetimes in the same model system over the full range of temperatures. It was also determined that the principle reason for the success of the fourth moment was that the density of states (DOS) for each mode was simple enough to be described as single broadened peak.

This paper reports a test of the fourth-moment approximation for a more realistic system: the vibrational modes of an fcc crystal with simple, Lennard-Jones interactions among the atoms. The test is made by comparing to the results of traditional ‘ensemble molecular dynamics’ (see, for example, Ladd, *et al* [10]) for cells of 4–32 atoms for temperatures ranging from the melting temperature down to 0.07 of that value. We find in this case that, as before in the simple lattice model, the vibrational mode lifetimes (as computed by MD) can be reasonably approximated by the fourth-moment method for these cells over the full range of temperatures. The MC-based moments method is also many orders of magnitude faster than the conventional MD approach.

It is important to recognize that the present aim is not to try to investigate the *specific* anharmonic dynamics of a rare gas solid, but instead to use these smallish cells of fcc-LJ as a *generic* testing ground for comparing the proposed MC-based moments method to the conventional, well-accepted MD-based method. The anharmonicities that are present in these cells, such as they are, will be calculated by both methods and the results compared. This is the sense in which it is possible for us to make conclusions from calculations on a cell of 32 atoms: not that it represents the full dynamics of a bulk solid, but that the anharmonic dynamics of this cell can be analyzed by two different methods and those results are related. In the scope of this work, we have been constrained by the limitations of the MD-based method, because the ensemble averaging requires tens of millions of trajectories which must be run for much longer than the longest mode lifetime of the cell. Also, because the lifetimes increase as an inverse power law of temperature at low temperatures, it is not practical to treat very low temperatures. Therefore, in this present work we are restricted to cells of up to 32 atoms and temperatures above about 0.07 of the melting point. The MC-based method do not have these limitations, and in fact can be used for much larger cells than demonstrated here and for an arbitrarily low temperature.

The strategy will be to sample the anharmonicity of the normal modes of various size cells at a variety of temperatures, and let the natural variation of the anharmonicities of these systems give us some range over which the two methods will be compared.

This paper is organized as follows. First, we recap briefly the approximation proposed by Dickel and Daw (‘DD’) and the evaluation at fourth moment by Gao *et al*. Then we describe how we carry out the test of the fourth-moment approximation for fcc Lennard-Jonesium. The results of the evaluation are presented, along with some analysis of the densities of states for typical modes. After a brief discussion, we draw our conclusions.

2. Brief review of proposed approximation scheme

The proposed approximation for the mode lifetimes [1–3] is based on an analysis of the amplitude auto-correlation function (AACF)

$$\chi_k(t) = \frac{\langle A_k(0)A_k(t) \rangle}{\langle A_k^2 \rangle},$$

where A_k is the amplitude in a normal mode indexed by k , and the angular brackets indicate phase-space averages over the canonical ensemble. In practice, the averaging can be accomplished by ‘ensemble MD’, which draws a set of initial starting conditions from an ensemble, evolves the system according to its natural dynamics, and then averages the amplitude(0)-amplitude(t) product over these initial conditions. Our simulations involve millions or tens of millions of samples. One avoids having to invoke the ergodic hypothesis by sampling over initial conditions in this fashion.

The auto-correlation can be studied in terms of the Liouvillian [8, 9], which governs the time evolution of any function $f(\{x\}, \{p\}, t)$ in phase space according to

$$\frac{\partial f}{\partial t} = -i\hat{L}f,$$

where the (Hermitian) Liouvillian operator is

$$\hat{L} = i\{H, \} = i \sum_l \left(\frac{\partial H}{\partial x_l} \frac{\partial}{\partial p_l} - \frac{\partial H}{\partial p_l} \frac{\partial}{\partial x_l} \right),$$

where H is the Hamiltonian. The dynamics are expressed primarily in terms of the positions and momenta of the atoms ($\{x_l, p_l\}$). The normal mode amplitudes ($\{A_k\}$) are related to the atomic coordinates via the normal mode transformation (as will be spelled out in section 3). The equation of motion can be integrated formally, so that

$$A_k(t) = e^{-it\hat{L}} A_k(0).$$

Thereby we can express the mode auto-correlation explicitly in terms of \hat{L} :

$$\chi_k(t) = \frac{\langle A_k e^{-it\hat{L}} A_k \rangle}{\langle A_k^2 \rangle}. \quad (1)$$

The Taylor Series of $\chi(t)$

$$\chi_k(t) = 1 - \mu_{k,2} \frac{t^2}{2!} + \mu_{k,4} \frac{t^4}{4!} - \mu_{k,6} \frac{t^6}{6!} + \dots$$

relates the derivatives of $\chi_k(t)$ at $t = 0$ to the moments of the Liouvillian acting on the mode amplitude:

$$\mu_{k,n} = \frac{\langle A_k \hat{L}^n A_k \rangle}{\langle A_k^2 \rangle}.$$

Specifically, the two lowest moments are related to averages involving forces:

$$\mu_{k,2} = \langle \dot{A}_k^2 \rangle / \langle A_k^2 \rangle = -\langle \ddot{A}_k A_k \rangle / \langle A_k^2 \rangle$$

(via the virial theorem) and

$$\mu_{k,4} = \langle \ddot{A}_k^2 \rangle / \langle A_k^2 \rangle,$$

where the \ddot{A}_k is the mode-resolved acceleration, which can be calculated via the normal mode transformation from the atomic accelerations.

The moments of the Liouvillian are also the moments of the density of states (DOS) derived from $\chi(t)$. That is, taking the Fourier transform of $\chi(t)$ to get $n(\omega)$, the moments are also

$$\mu_{k,m} = \int_{-\infty}^{+\infty} d\omega \omega^m n_k(\omega).$$

It is important in the following discussion for the reader to keep in mind that the analysis is done mode-by-mode. In particular, the DOS is that for a single normal mode, which is relatively simple, and is not the total DOS of all modes together, which is much more structured.

Auto-correlation functions corresponding to decaying modes typically have strong oscillations dampened by some sort of dying envelope. Gao *et al* [3] proposed to use the area under the square of the AACF as a measure of the lifetime

$$\tau_k = \int_{-\infty}^{+\infty} dt \chi_k(t)^2. \quad (2)$$

This ‘lifetime’ is not intended to correspond to any particular physical measurement that might be performed, but rather is suggested as a simple generic measure of the rate of the decay of the correlation. Such a measure also lends itself easily to analysis. Using Parseval’s Theorem, the lifetime is also given as the area under the $n(\omega)^2$ curve:

$$\tau = \int_{-\infty}^{\infty} dt \chi(t)^2 = \int_{-\infty}^{\infty} d\omega n(\omega)^2.$$

DD observed that the lifetime τ can be expressed as a function of the moments

$$\tau_k = F(\mu_{k,2}, \mu_{k,4}, \mu_{k,6}, \dots),$$

where a determination of the function F involves knowledge of the dynamics of the system. Using dimensional analysis, this form can be re-expressed as

$$\tau_k/\tau_{k,2} = G(\gamma_{k,4}, \gamma_{k,6}, \dots)$$

where $\tau_{k,2} = \mu_{k,2}^{-1/2}$, G is yet to be determined, and the γ ’s are dimensionless parameters

$$\gamma_{k,n} = \frac{\mu_{k,n}}{(\mu_{k,2})^{n/2}}.$$

(Note that $\gamma_n \geq 1$.) While it is not generally possible to know all of the moments, DD proposed that in certain circumstances the lifetime might be practically approximated from a knowledge of only the lowest moments. This suggests a series of approximations, starting with only the second moment

$$\tau = c\tau_2. \quad (3)$$

where c is some dimensionless constant to be determined by more knowledge of the dynamics of the system. The fourth-moment approximation would then be

$$\tau = \tau_2 \tilde{G}(\gamma_4), \quad (4)$$

where \tilde{G} is some function yet to be determined. The higher moments correspond to ensemble averages of higher powers of the Liouvillian, and so each higher moment involves higher time derivatives of the dynamical variables.

If some semblance of harmonic-like behavior holds, the second moment will generally reflect the quasiharmonic, temperature-dependent frequency (squared) of the mode. By contrast, γ_4 is a measure of the degree of anharmonicity of the mode *beyond quasiharmonic* as averaged over the ensemble. Specifically, γ_4 for a given mode k is related to specific ensemble averages involving displacements and forces:

$$\gamma_{4,k} = \frac{\langle A_k^2 \rangle \langle \ddot{A}_k^2 \rangle}{\langle A_k \ddot{A}_k \rangle^2}.$$

A harmonic system is, of course, defined where the force is proportional to the amplitude, so that $F \propto -A$. In the anharmonic ensemble, we could define an effective (that is, quasiharmonic) spring constant K by that which minimizes the deviation from harmonic. That is, we construct the function

$$\alpha = \langle (F + KA)^2 \rangle / \langle F^2 \rangle$$

and minimize that with respect to K to determine the effective force constant. The minimum value of α then measures the degree of anharmonicity of the system as effective for the ensemble. For a harmonic system, $\alpha_{\min} = 0$. In general, the quasiharmonic force constant $K_{\text{eff}} = -\langle AF \rangle / \langle A^2 \rangle = \mu_2$, and the measure of anharmonicity (beyond quasiharmonic) is

$$\alpha_{\min} = 1 - \gamma_4^{-1}$$

showing how the deviation $\gamma_4 - 1$ is directly related to the temperature-dependent anharmonicity of the system.

DD (in part 2) tested the second moment approximation on a simple model of non-linear lattice vibrations as a function of cell size and temperature. In this model, nearest-neighbors on a SC lattice experience a fourth-order coupling:

$$H = \sum_i \frac{1}{2} |\vec{p}_i|^2 + \sum_{\langle i,j \rangle} V(\vec{d}_i - \vec{d}_j)$$

where \vec{p}_i is the momentum of the particle at lattice site, i , and $V(\vec{d})$ is given by

$$V(\vec{d}) = \frac{1}{2} |\vec{d}|^2 + \frac{1}{24} |\vec{d}|^4. \quad (5)$$

The test consists of calculating using ‘ensemble MD’ the auto-correlation function for each normal mode in a periodic cell of a given size, and from the the AACF extracting the lifetime. Second, they calculated using standard Monte Carlo the second moment μ_2 (hence τ_2) for each mode. This second step in the demonstration, of course, requires much less computational time than the first. Then to test the second-moment supposition expressed in equation (3), they then scatter-plotted τ/τ_2 versus temperature for all modes, and found that at high temperatures the mode lifetimes were simply proportional to the respective $\tau_{k,2}$. Furthermore, at high temperature, the auto-correlation functions scaled in a simple way. That is, plotting all of the calculated $\chi_k(t)$ with a scaled time axis ($t/\tau_{k,2}$) exhibits a data collapse at high T , revealing that indeed the high-temperature dynamics of the mode decay could simply be described by a single parameter. Thus, the high temperature behavior was well approximated at the lowest level (second-moment).

The study by Gao *et al* [3] carried the approximation to the fourth moment, which was tested against the same fourth-order lattice model. To test the fourth-moment supposition expressed in equation (4), they arranged a scatterplot of the lifetimes and moments, by plotting τ/τ_2 (which would be a constant if the second moment were sufficient) against γ_4 , which is a direct measure of the anharmonicity. It was found that all of the modes for a variety of temperatures and sample sizes collapsed onto a single curve, which would then give knowledge of the function \tilde{G} in equation (4).

In addition, it was demonstrated that the mode-resolved DOS from the lattice model (as is true for most solids) is dominated by a single peak broadened and shifted by anharmonic interactions at elevated temperature. The second and fourth moments of the Liouvillian, being also the corresponding moments of the DOS, are the two most elemental parameters characterizing the DOS. In that way, μ_2 can be viewed as revealing the quasiharmonic frequency of the mode. Hence its relative value indicates the magnitude of the shift due to temperature. The ‘shape parameter’ γ_4 can be viewed as a dimensionless parameter indicative of the relative broadening. Higher-order parameters (γ_6 , etc)—which are not considered here—might later be used to give additional details as to the overall shape of the DOS. In the present case, however, those two trends (shifting and broadening) can be captured in principle by the two characteristic parameters (second and fourth moments), and thereby make possible a reasonable approximation to the mode lifetime.

3. Using fcc Lennard-Jonesium as a test of the fourth-moment approximation

Our goal in this paper is to determine the generic function \tilde{G} in equation (4), which is proposed to hold for all normal modes of vibrating solids. A particular normal mode of a system of given size at a given temperature will have only one value of τ , τ_2 and γ_4 , and would not by itself be enough to test the relation. However, if we were to vary the temperature of that system and examine how the lifetime τ of that particular mode changes, and then also examine the temperature dependence of τ_2 and γ_4 , that would establish a relation for that particular mode. Since the function \tilde{G} is proposed to be a universal function (at least for vibrating solids), doing this for *all* of the normal modes of a given cell over the same range of temperatures tests furthermore the universality of that function. Including in the set of calculations cells of different size also increases the scope of the test. This is the strategy of this paper.

For this test we have chosen as a generic example the vibrational modes of fcc-‘Lennard Jonesium’. We will conduct the test on all of the normal modes of periodic cells of various sizes and over a range of temperatures. The test consists of two parts. First, there is the calculation of the normal mode lifetimes through conventional, ‘ensemble MD’, which will be explained in more detail below. The second part consists of calculating the moments through Monte Carlo, which is orders of magnitude faster than the first part. The two approaches are then compared. The important part is that the scope of the test is restricted to what is feasible with the slower of the two methods, namely the conventional MD. This will limit us somewhat in terms of temperature but more so in terms of cell size.

For that reason, we will emphasize that our purpose here is not to investigate the size-dependence of periodic calculations of mode lifetimes. The cells given here are expected to have normal mode lifetimes that depend somewhat on the cell size, because the imposition of periodic boundary conditions limits the normal modes to those that are commensurate with the periodicity. This is expected to affect the lifetimes as calculated by *both methods*. That is, our argument is that the lifetimes as calculated by ensemble MD will be altered in the same way that the lifetimes as calculated by the moments. The point of the present work is to show how the moments calculations can reproduce the results of the ensemble MD in whatever cell is being investigated. The issue of size-dependence of the lifetimes could then be investigated (later) by the moments calculation, which has the potential of doing much larger cells and hence establishing the size-dependence more reliably than by ‘ensemble MD’.

So we determine the scaling (equation (4)) by calculating the lifetimes τ of normal modes of a cell using the conventional ‘ensemble dynamics’ and also the moments μ_2 and μ_4 for each mode by Monte Carlo, and then investigate their relation by doing a scatterplot of the data (τ/τ_2 versus $\gamma_4 - 1$). We include in the data set the calculations for cells of various sizes and at a range of temperatures. If the data do conform to that relation, we will have both determined the function for a range of its argument $\gamma_4 - 1$, as well as tested the universality (at least over some physical regime) of that generic function.

The testbed we have chosen for determining the function and for testing its universality is the vibrational dynamics of an fcc lattice of atoms interacting via a Lennard-Jones potential¹. We chose (as is done in LAMMPS) the length, energy, and mass scales to be the natural set of units for the LJ potential— $m = 1$, $\epsilon = 1$, and $\sigma = 1$.

$$\phi(r) = 4 \left(\frac{1}{r^{12}} - \frac{1}{r^6} \right).$$

¹ Specifically, we used the ‘lj/smooth/linear’ potential option in LAMMPS, which subtracts a small term, linear in r , to make the interatomic potential and its first derivative go to zero smoothly at the cutoff distance.

We chose a cutoff distance of 2.57, which is between 5th and 6th nearest neighbor shell at $T = 0$ (where $a_0 = 1.5565$). Periodic cells of various sizes were constructed.

The range of the argument $\gamma_4 - 1$ of the function will be explored by doing a variety of cell sizes and temperatures. The melting point for this potential is about 0.67 in these units [6]. The system is strongly anharmonic at temperatures just below the melting point, and we see values of γ_4 typically in the range 2–3. For temperatures in the range of 0.05, the system is only weakly anharmonic, and the parameter γ_4 approaches 1 like a power law.

Because these are mode-specific calculations, we must perform the normal mode decomposition. To this end, the force constant matrix [4] *specific to each cell* is constructed via

$$\Phi_{i\alpha,j\beta} = \left. \frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}} \right|_0, \quad (6)$$

where U is the total potential energy of the solid, i, j denote sites and α, β denote Cartesian coordinates, and the ‘0’ indicates that the second derivative is evaluated at equilibrium. The calculated normal mode transformation matrix X is constructed from the eigenvectors of the force constant matrix, so that

$$X_{i\alpha,k} = w_{i\alpha}^{(k)} \quad (7)$$

where the k -th eigenvalue, eigenvector pair satisfies

$$\sum_{j,\beta} \Phi_{i\alpha,j\beta} w_{j\beta}^{(k)} = m\omega_k^2 w_{i\alpha}^{(k)}. \quad (8)$$

The transformation matrix allows one to transform from atomic displacements ($u_{i\alpha}$ to normal mode amplitudes; for example, by

$$A_k = \sum_{i,\alpha} u_{i\alpha} X_{i\alpha,k}. \quad (9)$$

The same transformation is applied to obtain the mode accelerations from the atomic accelerations.

All calculations were performed using LAMMPS [5] and its Python interface, by writing a Python wrapper to drive the whole calculation. The wrapper we have written for LAMMPS is completely general, and can easily be modified to use *any* of the interatomic potentials contained in LAMMPS.

We did two sets of tests, at constant V and constant P , respectively. At constant V , for all temperatures the cell size was held at its $T = 0$ value. To do constant P calculations, we first calculated the lattice constant a at each simulation temperature by applying to a cubic cell of 256 atoms the isothermal–isobaric (‘NPT’) ensemble in LAMMPS. Having determined the lattice constant for a given temperature, the required MD calculations for the AACF were done at that fixed V . As shown in figure 1, the modes at constant V shift up in frequency with increasing temperature, while under constant P they shift down. The shifts in frequencies are consistent with earlier LJ calculations in the literature, for example Dickey and Paskin [7].

The test consists of two parts, both done according to normal modes: the first part determines the AACF and the second is strictly an MC calculation of the moments. For the first part—the ‘ensemble molecular dynamics’—we calculate the AACF by drawing initial conditions from the ensemble, which are then evolved using conventional molecular dynamics. For this, we used a velocity verlet algorithm with time step $dt = 0.02$ when temperature < 0.1 and $dt = 0.01$ when temperature ≥ 0.1 . The initial conditions were constrained to have fixed center-of-mass, so that the designation ‘canonical ensemble’ should be qualified as well to be in the CM frame. The AACF is then averaged over all samples from the ensemble, from a

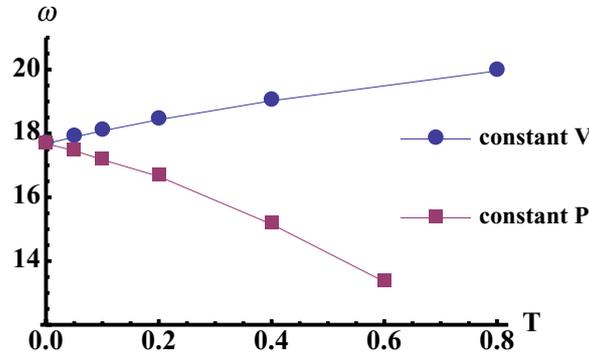


Figure 1. The frequency of the peak of the density of states for a typical mode in the 4-atom cell, as a function of temperature showing the up-shift of the mode frequency in constant V and the down-shift of the mode frequency in constant P.

minimum of 4×10^6 samples for the smallest cell to 25×10^6 for the largest. The simulated time of each MD run depends on the temperature (roughly inversely) and is determined such that the AACF for the longest-lived mode has decayed well enough that the calculated lifetime is converged to within 1%. From the AACF we extract the lifetime by equation (2). The second part of the test consists of calculating the second and fourth moments for each mode by MC sampling.

The first part is combined with the second by making a scatterplot of τ/τ_2 to $\gamma_4 - 1$. The test is done on systems of various sizes:

- 4 atoms in a cubic cell
- 8 atoms (doubled along one cube axis)
- 16 atoms (doubled along a second cube axis)
- 32 atoms in a cubic cell

under both constant V and constant P conditions, and at various temperatures (0.05, 0.1, 0.2, 0.4, 0.8 for constant V, 0.05, 0.1, 0.2, 0.4, 0.6 at constant P).

We present here the scatterplots resulting from the two-part test, where we see that the fourth moment does in fact account reasonably well for the mode lifetimes. We then present an analysis of the mode-resolved densities of states.

3.1. Scatterplots

The results for the 4-atom cell, the smallest cell considered here, are presented first (figure 2). We find that the mode lifetimes in this small cell can be represented by the same relation as found in the previous work on lattice models [1–3]), namely:

$$\frac{\tau}{\tau_2} = C \frac{1}{\sqrt{\gamma_4 - 1}}. \quad (10)$$

(A value of $C = 1.35$ fits the accumulated data for the modes in the 4-atom cell for both constant V and constant P.)

The results for the largest cell (32 atoms) under constant P condition are presented in figure 3. (The results for the 8-atom and 16-atom cells are very similar, as are the results for

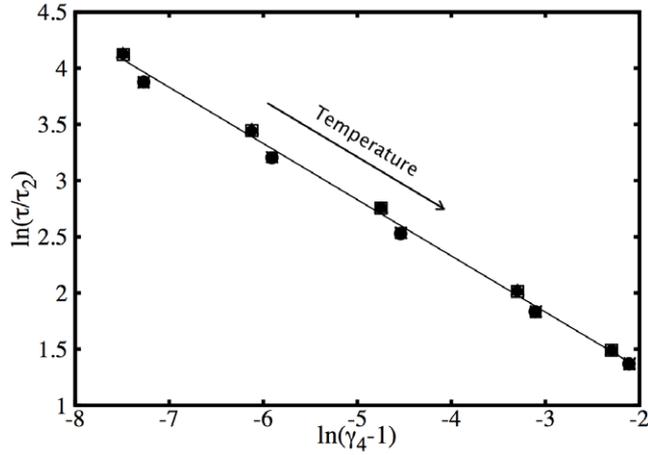


Figure 2. Scatter-plot of τ/τ_2 versus $\gamma_4 - 1$ for all nine non-sliding modes of the 4-atom cell, at constant P. The degeneracy of the results is in accordance with the symmetry of the cell but is not explicitly imposed in the calculation. The straight line is a fit to the results. The results for constant V condition are very similar.

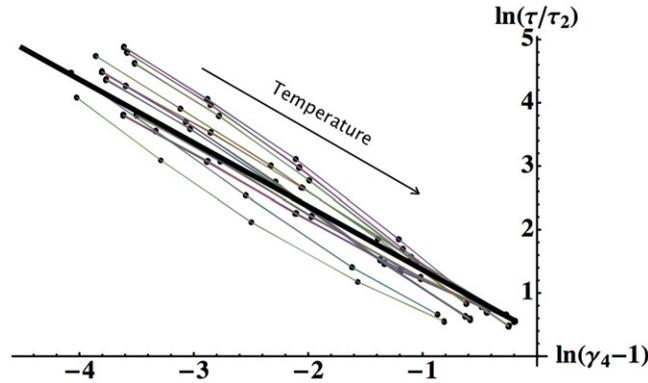


Figure 3. Scatter-plot of τ/τ_2 versus $\gamma_4 - 1$ for all non-sliding modes of the 32-atom cell, at constant P. The straight line is a fit to the collective results of all modes for 8, 16 and 32-atom cell. The results for constant V condition are very similar.

constant V for these cells.) The scatterplots in this figure show that the normal modes in these system follow a single trendline with a different power, namely equation (4):

$$\frac{\tau}{\tau_2} = C \frac{1}{\gamma_4 - 1}. \quad (11)$$

(A value of $C = 1.41$ fits the accumulated data for the modes in the 8-atom, 16-atom, and 32-atom cells at constant V. For constant P, the best value of $C = 1.55$.)

The difference in the two behaviors (equation (10) compared to equation (11)) can be understood in terms of the basic mode couplings present in the system. In the model potentials considered previously, such as equation (5), the coupling was chosen to be fourth order. This was true also in the simple, low-dimensional models. We find also that if the potential energy is expanded in terms of the normal modes, that the Hamiltonian for the 4-atom cell contains

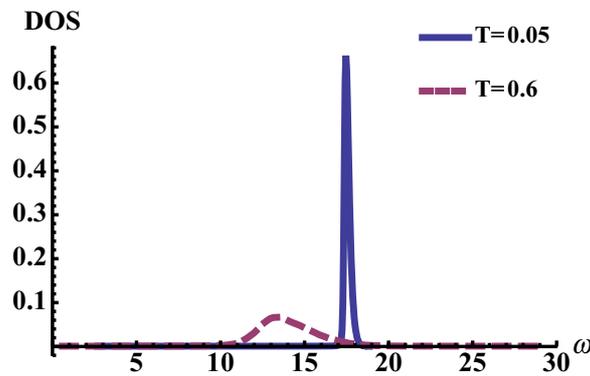


Figure 4. The density of states of a typical mode in the 4-atom cell at the lowest and highest temperatures we investigated, for constant P .

second- and fourth-order terms, but no third-order couplings (that is, couplings involving a product of three mode amplitudes, or two modes with one amplitude square, or the third power of a single mode amplitude). Thus, the basic mode coupling dynamics involves only fourth-order couplings in the 4-atom cell. However, the larger cells involve more degrees of freedom, and introduce third-order couplings, which are generally expected in solids. Expanding the potential energy for the 8-atom cell in terms of normal mode amplitudes, for example, shows the presence of third-order couplings. So, the primary difference between the larger cells (8, 16, and 32 atoms) of Lennard-Jonesium on the one hand, and the smallest cell (with 4 atoms) of Lennard-Jonesium along with the previously investigated lattice models, on the other hand, is precisely the difference between systems with and without third-order mode couplings.

The scatterplots obtained under condition of constant V are very similar to those obtained under constant P , so we do not display them here. So the fourth moment scaling captures the correct lifetime whether or not the frequency shifts up or down. The combination of tests for constant P and constant V calculations show that the scaling observed in figure 3 correctly captures the dependence of the mode lifetimes on various factors such as temperature and boundary conditions.

3.2. Density of states

Figures 4 and 5 show the densities of states of some typical modes from the smallest and largest cells we considered, at two different temperatures (the lowest and highest considered). These were obtained under constant P conditions. Typically, the DOS is dominated by single peak that broadens and shifts with increasing temperature².

4. Discussion

The ‘normal case’ of vibrating insulators, if one can use that term meaningfully, would be the situation where the DOS of a normal mode is relatively simple: a single peak that broadens and shifts with increasing temperature. The range of cells and temperatures tested here are enough to establish the argument that the fourth moment approximation (equation (4)) is reasonable

² The zone edge modes in our calculations show a small number of multiple frequencies even at low temperatures, but these are atypical modes. All of the other modes display the behavior shown here.

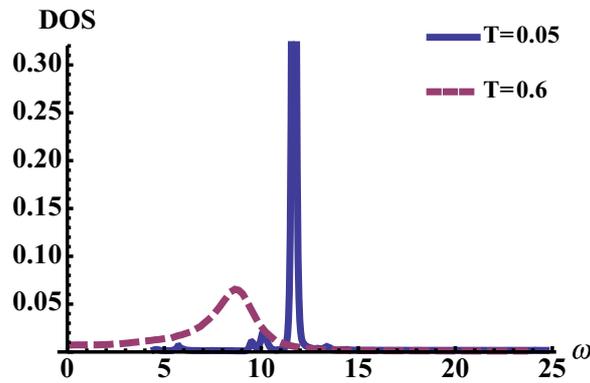


Figure 5. The density of states of a typical mode in the 32-atom cell at the lowest and highest temperatures we investigated, for constant P.

for that case. The DOS for the cells studied here are certainly ‘typical’ of that ‘normal case’. However, it would seem possible—for example, the case of ‘rattlers’ where small atoms visit multiple minima inside of open cages—for the DOS to be richer than what is studied here. The question about the utility of the moment approximations in those cases is left to another time.

An interesting parallel relationship has been obtained by Singh *et al* [13] for the lattice thermal conductivity of liquid Lennard-Jonesium. In that work, the auto-correlation of the heat current density J is related to what amount to moments (in that work the authors refer to ‘sum rules’ for the time-derivatives of the ACF). They find that the lattice thermal conductivity (λ) in the liquid phase follows well this simple relation (after some slight reformation of their expression into our notation):

$$\lambda \propto \frac{1}{\sqrt{M_2}} \sqrt{\Gamma_4 - 1},$$

where $M_2 = \langle \dot{J}^2 \rangle / \langle J^2 \rangle$, $M_4 = \langle \ddot{J}^2 \rangle / \langle J^2 \rangle$, and $\Gamma_4 = M_4 / M_2^2$. The motivation leading to their expression is different than in the present work, as certainly also is the physics of the liquid different than the solid, and even more importantly the primary quantity of interest is the thermal conductivity rather than the mode lifetime. However, we take the similarity of the two expressions as being another confirmation of the general possibility of extracting macroscopic properties from ensemble averages of appropriate microscopic quantities.

5. Conclusions

We have investigated the vibrational mode lifetimes in fcc Lennard-Jonesium at various temperatures up to the melting point, constant V and constant P conditions, and for cells ranging from 4 to 32 atoms. Based on previous work, we have tested whether the second and fourth-moments of the Liouvillian are sufficient to capture the behavior of the lifetimes. The second moment reflects basically the temperature-dependent, quasiharmonic mode frequency, and the fourth moment reflects the temperature-dependent anharmonicity (beyond quasiharmonic) of the mode. We conclude that the fourth-moment approximation captures the basic trends, though some scatter is observed that could be attributed to deviations at higher moment. Because the smallest cell has only fourth-order anharmonic couplings among the modes, the

fourth-moment scaling shown in equation (10) agrees with that reported in previous work on fourth-order lattice models. The other cells all have third-order anharmonic couplings, and as a result we see the fourth-moment scaling as shown in equation (11). This latter form should apply to the normal case of bulk insulators. The success of the fourth-moment scaling is understood to be due to the simple nature of the mode-resolved densities of states, which are single peaks that are shifted and broadened with increasing temperature.

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