



## Improved calculation of vibrational mode lifetimes in anharmonic solids—Part I: Theory

Doyle Dickel, Murray S. Daw<sup>\*</sup>

Dept. of Physics and Astronomy, Clemson University, Clemson, SC 29634, USA

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### ABSTRACT

We propose here a formal foundation for practical calculations of vibrational mode lifetimes in solids. The approach is based on a recursion method analysis of the Liouvillian. From this we derive the lifetime of a vibrational mode in terms of moments of the power spectrum of the Liouvillian as projected onto the relevant subspace of phase space. In practical terms, the moments are evaluated as ensemble averages of well-defined operators, meaning that the entire calculation is to be done with Monte Carlo. These insights should lead to significantly shorter calculations compared to current methods. A companion piece presents numerical results.

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### 1. Introduction

The state-of-the-art in calculating vibrational mode lifetimes in solids is surprisingly under-developed. While well-tested, reliable, and efficient means allow a determination of the electronic structure of newly discovered and hypothetical crystals—as least at the level of mean-field such as LDA—a comparable technique does not exist for determining mode lifetimes or its related property of the lattice thermal conductivity. The aim of this work is then to provide a fundamental approach that can be used to calculate in a practical way the intrinsic mode lifetimes of solids.

Two methods are used currently for calculating the intrinsic mode lifetimes: the first combines first-principles calculations of force constants with standard rate theory, the second utilizes molecular dynamics (MD) simulations based on inter-atomic potentials.

The very recent work of Broido et al. [1] combines Boltzmann rate formalism with LDA calculations of harmonic and third-order anharmonic force constants. Without fitting parameters, they ob-

tain excellent agreement with measurements of intrinsic lattice thermal conductivity in Si and Ge from 100 to 300 K. While mode lifetimes were not directly computed, they could have been by the same technique, with some additional expense. Quantitative estimates of the fourth-order rates showed them to be negligible compared to third-order. The agreement is indeed encouraging. However, the calculations are quite demanding, and the demands increase significantly with more complex unit cells. Time and memory bottlenecks preclude consideration of bulk materials with larger unit cells.

The second technique, based on molecular dynamics (MD) begins with the Green–Kubo relation [2], which expresses the lifetime  $\tau_k$  in terms of the mode auto-correlation function  $\chi_k(t)$

$$\tau_k = \int_{-\infty}^{+\infty} dt \chi_k(t) \quad (1)$$

where

$$\chi_k(t) = \frac{\langle \delta n_k(0) \delta n_k(t) \rangle}{\langle \delta n_k(0)^2 \rangle} \quad (2)$$

where  $k$  is the mode index (wave-vector),  $\delta n$  is the fluctuation of the occupancy factor, and the angular brackets indicate averages over

<sup>\*</sup> Corresponding author.

E-mail address: [daw@clemson.edu](mailto:daw@clemson.edu) (M.S. Daw).

the equilibrium distribution in phase-space.<sup>1</sup> First-principles MD simulations are possible, but the MD times must be long compared to the lifetimes, which is often impractical, especially because cell-size effects require the use of rather large simulation cells. Instead, the Green–Kubo relation is usually restricted to systems where there exists a reliable inter-atomic potential [3,4] such as Si and C. That constraint pretty much limits the studies to those materials which are already well-studied. Very few new materials are amenable to this approach.

More than twenty years ago, mode lifetimes were calculated by Ladd et al. [5] using MD for Lennard–Jones potentials for moderate-sized cells (864 atoms). This straightforward calculation gave surprising results for the lifetimes vs.  $k$  and temperature, which were not explained. To the present authors, this work seems fundamental and needs to be pursued further. With advances in computers it should be possible to do significantly larger cells today. It is also a surprise that—as far as we can determine—no further work has been done along these lines.

The analysis of vibrational mode lifetimes was encompassed as part of the general theory of energy dissipation in dynamical systems begun in the seminal work of Van Hove [6,7], and further developed by Prigogine and co-workers [8–14], and along similar lines by Zwanzig [15–17] and Mori [18]. The basic formalism considered the evolution of classical dynamical systems using the Liouvillian [19,20]. Zwanzig and Mori’s “projector–operator” approach was applied by Wilson and Kim specifically to the problem of mode lifetimes and lattice thermal conductivity [21]. While the formalism provided insights into the mechanism of equilibration of energy, there have been no quantitative predictions of mode lifetimes using this formalism (at least as far as we can find).

A recent breakthrough has been made in extracting the long-term dynamics within the Liouvillian formalism by applying the recursion method [22–24]. Haydock et al. [23] have recently proposed a practical scheme for calculating macroscopic rates from the resolvent of the Liouvillian. In this view, dissipation results from the flow of energy from large to small scale structures in phase space. By using the recursion method, along with careful considerations of the required analytical properties of the resolvent, Haydock and company investigated a way of extracting the long-time behavior from a finite amount of information about the resolvent. This new insight forms the inspiration and basis of the current work.

In this paper, we briefly review the formalism which relates the Liouvillian to mode lifetimes, and then demonstrate the application of the recursion method to this problem. On that basis, the problem becomes one of analyzing low moments of the power spectrum of the Liouvillian to extract the correct long-time dynamics. We show some results of the formalism.

These ideas are somewhat similar to the work of Tankeshwar et al. [25,26], who examined energy flow in a Lennard–Jones liquid using a continued fraction representation of the memory function. Unlike that work, in the present case we make explicit use of the Liouvillian formalism, so that the constants in the continued fraction are related directly to the moments of the Liouvillian. Also, we can take advantage of the recent work on the recursion relation in obtaining guidance for terminating the recursion. These two additions make it possible for us to flesh out a more complete formalism. And then, there is the obvious difference that we are dealing with solids here.

A companion piece [27] to this paper will lay out the results of applying the formalism to a simple model of vibrations in solids, in both 1 and 3 dimensions. In the context of the numerical simula-

tions, we will be able to address definitively the question of convergence which comes up in the recursion method.

## 2. Mode lifetimes and the Green–Kubo formula

In the Green–Kubo (GK) approach, the lifetime of an individual vibrational mode (labelled by wave-vector  $k$ ) is given by Eq. (1), where the mode auto-correlation function  $\chi_k(t)$  is given by Eq. (2). In  $\chi_k$ ,  $\delta n$  is the fluctuation of the occupancy factor

$$\delta n_k = n_k - \langle n_k \rangle$$

and where the angular brackets indicate averages over the equilibrium distribution in phase-space:

$$\langle A \rangle = Z^{-1} \int d\Gamma e^{-\beta H(\{p_i\}, \{q_i\})} A(\{p_i\}, \{q_i\}) \quad (3)$$

$$Z = \int d\Gamma e^{-\beta H(\{p_i\}, \{q_i\})} \quad (4)$$

with phase space differential volume

$$d\Gamma \equiv \prod_i dp_i dq_i$$

In the auto-correlation function, the appearance of time ( $t$ ) in the ensemble average can be given the following realization for the purposes of computation: a point in phase space is selected (for example, using Monte Carlo or “MC”) from the equilibrium distribution, and this point is then taken as the initial condition for dynamical evolution (using molecular dynamics or “MD”) for a time  $t$ . The product of the fluctuations at these two times is then averaged over the distribution. The resulting auto-correlation should decay with time as a result of anharmonicities in the interactions. The denominator of the auto-correlation is fixed so that the function goes to 1 as  $t \rightarrow 0$ . Then the area under the auto-correlation curve is the desired mode lifetime. In this way, the GK approach clearly mixes equilibrium and dynamical features.

The exact form of the time dependence of the auto-correlation is subject in some way to details of the interactions but some properties are general. For example, time-reversal symmetry means that the auto-correlation is symmetric in  $t$ , and also that

$$\dot{\chi}(0) = 0 \quad (5)$$

One might expect on general grounds [14] for  $\chi(t)$  to decay exponentially at very long times. However, the behavior observed at intermediate times in most applications is more complicated, and the lifetime in Eq. (1) is more strongly dependent on  $\chi(t)$  at intermediate times.

A property of the equilibrium averages which will be helpful is to know that the equilibrium averages are themselves independent of  $t$ :

$$\langle A(t) \rangle = \langle A(0) \rangle$$

from which it follows immediately that  $\langle \dot{A}(t) \rangle = 0$  for any function  $A$  of phase space. As a special case we see that

$$\dot{\chi}(0) = \langle \delta \dot{n}(0) \delta n(0) \rangle = 0 \quad (6)$$

consistent with our previous observation.

## 3. Canonical transformations

The expression of  $\delta n_k$  for vibrating solids in terms of particle coordinates and momenta ( $q_i, p_i$ ) is accomplished via a series of two canonical coordinate transformations: a transformation to normal modes is followed by the Hamilton–Jacobi transformation to action-angle variables.

<sup>1</sup> The time integral is long compared to the times involving energy transfer but is shorter than the Poincaré recurrence time.

It is revealing to recall the original arena in which the action-angle transformation and Hamilton–Jacobi [28] theory were developed, which was to study perturbations of planetary orbits by other planets. In that case, one has possibly strong effects of other planets, but there remains an underlying periodic nature to the motion. In the action-angle formalism, the various planets execute nearly periodic orbits while altering the action and relative phases of the other orbits. This coupled periodic orbital motion is clearly quite similar to the case of coupled anharmonic vibrations, where the underlying periodic motion of the normal modes is influenced by possibly strong coupling to other normal modes. So even in the presence of strong coupling, the action-angle transformation can be very helpful. Perhaps this was the insight that led to Prigogine’s interest [14]. At any rate, his work clearly shows the utility of the transformation.

The simple SHO hamiltonian involving coordinate and momentum variables ( $q, p$ )

$$H(p, q) = \frac{p^2}{2m} + \frac{kq^2}{2}$$

can be transformed to action-angle variables ( $S, \alpha$ ) by a transformation involving an arbitrary frequency  $\omega^X$

$$q = \sqrt{2S/(m\omega^X)} \sin \alpha \quad (7)$$

$$p = \sqrt{2Sm\omega^X} \cos \alpha \quad (8)$$

to

$$K(S, \alpha) = S(\omega^X \cos^2 \alpha + \frac{k}{m\omega^X} \sin^2 \alpha)$$

with the resulting equations of motion:

$$\dot{\alpha} = \omega^X \cos^2 \alpha + \frac{k}{m\omega^X} \sin^2 \alpha \quad (9)$$

$$\dot{S} = -2S(-\omega^X + \frac{k}{m\omega^X}) \sin \alpha \cos \alpha \quad (10)$$

The transformation is canonical for any value of  $\omega^X$ , but the equations of motion simplify greatly if the transformation frequency matches the harmonic frequency ( $\omega^X = \omega^H = \sqrt{k/m}$ ). In that case,  $S$  is a constant of the motion and  $K = \omega S$ , from which one sees the natural relationship  $n = S/\hbar$ .<sup>2</sup> Given that condition on  $\omega^X$ , the angle  $\alpha$  evolves uniformly in time ( $\alpha = \omega^H t$ ).

It is instructive to note that if the transformation frequency does *not* match the harmonic frequency, the resulting dynamical variables are still periodic, and their averages over a period of the motion are  $\bar{S} = 0$  and  $\bar{\alpha} \approx \omega^H$  if  $\omega^X$  is in the neighborhood of  $\omega^H$ .

The action-angle transformation is canonical regardless of the hamiltonian. It could also be applied to, for example, the anharmonic hamiltonian

$$H(p, q) = \frac{p^2}{2m} + \frac{kq^2}{2} + \lambda q^4$$

The motion of the this anharmonic system is yet periodic,<sup>3</sup> so that the angle  $\alpha$  will have an overall linear behavior in time with a periodic oscillation superimposed. Now the transformation frequency can be chosen to simplify the equations, but  $\alpha$  cannot be made simply linear in time. Instead, the overall slope of  $\alpha$  has the meaning of a quasi-harmonic frequency for the anharmonic

motion, so that, if we average over a period of the motion,  $\bar{\alpha} = \omega^Q$ . This observation will come in handy when we tackle the vibrating anharmonic lattice problem, where we will use a similar insight to find the quasi-harmonic frequency of a mode interacting with other modes in an ensemble. Even in this case, as we shall see, the transformation frequency  $\omega^X$  can be chosen to obtain some convenience.

The action-angle formalism can be applied easily to the normal modes of an anharmonic vibrating network. Consider, for example, a 1D anharmonic chain whose hamiltonian is

$$H = \frac{1}{2} \sum_n p_n^2 + \sum_n V(u_{n,n+1}) \quad (11)$$

where

$$V(d) = d^2/2 + d^4/24 \quad (12)$$

The transformation to normal mode variables  $q$  and  $\pi$

$$q_k = \frac{1}{N} \sum_n u_n e^{-ikn} \quad (13)$$

$$\pi_k = \frac{1}{N} \sum_n p_n e^{-ikn} \quad (14)$$

would decouple the modes in the harmonic case (drop the quartic term in  $V$ ).

Even in the anharmonic case, it is useful now to go from normal modes to action-angle variables, as was done previously.

$$S_k = \frac{N}{2\omega_k^X} |\pi_k + i\omega_k^X q_k|^2 = \hbar n_k \quad (15)$$

$$\alpha_k = \arg(\pi_k + i\omega_k^X q_k) \quad (16)$$

In the present case, the anharmonicity of  $V$  prevents  $S_k$  from being a constant of the motion for any  $\omega_k^X$ ; which is to say that the anharmonicity is responsible for fluctuations in the occupation of modes. We also find that the motion is quasi-periodic, with  $\alpha$  having an overall linear progression with superimposed oscillations. Now it makes sense to define the averages of quantities in terms of the ensemble, so that we can find the quasi-harmonic frequency (which depends on both temperature and wave-vector) from:

$$\langle \dot{\alpha}_k \rangle = \omega_k^Q(\beta)$$

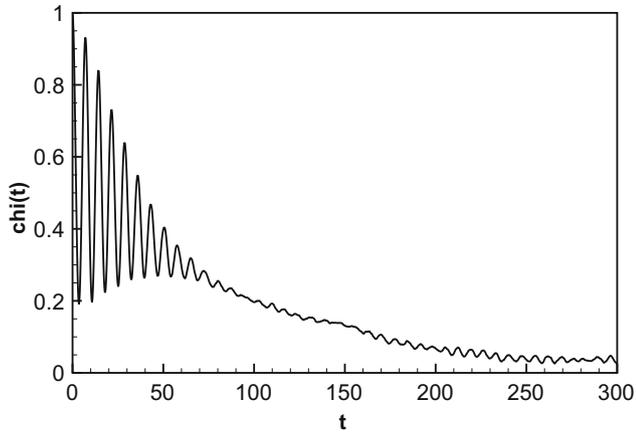
Generally it is expected that at low temperatures, the quasi-harmonic frequency will become the harmonic frequency of the lattice and deviate as the temperature increases.

At this point, the transformation frequency  $\omega_k^X$  is yet arbitrary. We will find in the following (departing from Prigogine’s approach) that the most convenient value of the transformation frequency will be  $\omega_k^X = \omega_k^Q(\beta)$  (an implicit equation for  $\omega^X$ ). This choice is made by considering the structure of the auto-correlation function and the resulting lifetime (area under the auto-correlation function). We show in Fig. 1 a plot of the auto-correlation function at elevated temperature. (The data are taken from calculations on a 1D anharmonic chain, but the behavior is generic). In this figure, the transformation frequency was arbitrarily chosen to be the harmonic (that is, low-temperature) frequency of the mode and kept at this value even for the analysis of the dynamics at higher temperature (note that the transformation does not affect the real dynamics—as expressed in the original coordinates—but only the interpretation in terms of the transformed coordinates). In this instance, we see that the auto-correlation function decays as expected but also has oscillations that complicate the analysis.

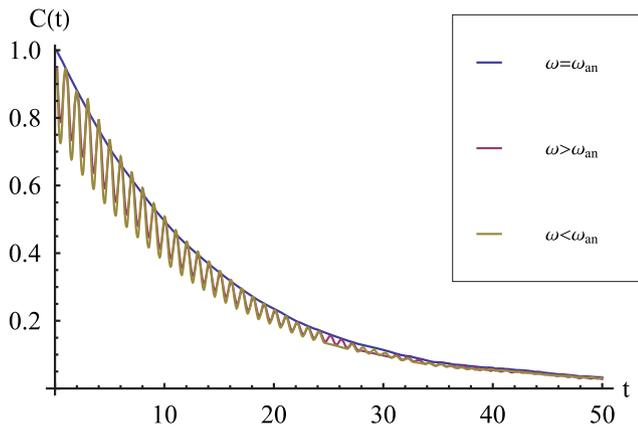
We can see how the choice of transformation frequency affects the auto-correlation function in Fig. 2, which shows the function for three values of  $\omega^X$ . We see that there exists one value,

<sup>2</sup> Planck’s constant appears unnaturally here because of the interpretation of  $n$  as a quantum number. We deal in this treatment only with behavior in the classical realm, but the use of occupation number in favor of action is overwhelmingly prevalent. Formally more consistent would be to define  $\chi_k(t)$  (Eq. (2)) in terms of  $S_k$  rather than  $n_k$ , but  $\chi_k$  is unaffected anyway.

<sup>3</sup> As long as  $\lambda \geq 0$ .



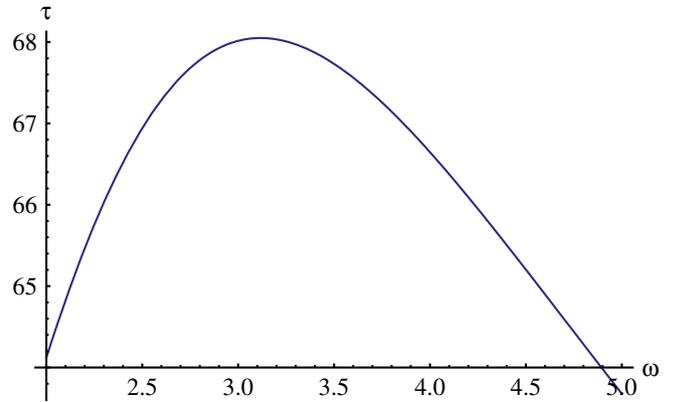
**Fig. 1.** A typical occupation auto-correlation (see Eq. (2)). This example was calculated for a simple anharmonic vibrating lattice model (discussed in more detail in Ref. [27]). The frequency of the transform  $\omega^x$  (see Eq. (8)) was fixed to match the harmonic frequency of a typical normal mode of the lattice at low temperatures. The temperature was then raised substantially for this calculation to illustrate the effect of not adjusting the transformation frequency to account for temperature shift of the mode frequency.



**Fig. 2.** The occupation auto-correlation at elevated temperature for three values of the transformation frequency  $\omega^x$ . For the top curve, the frequency has been matched to the temperature-dependent quasi-harmonic frequency of the mode. For the other two curves, the frequency is slightly above or below that of the quasi-harmonic frequency. With the frequency properly matched to the quasi-harmonic frequency, the auto-correlation is smooth. Going off-frequency introduces oscillations into the auto-correlation, with the on-frequency curve forming a maximum envelope for the oscillations. Clearly the area under the curve will be maximum for the frequency-matched case. Numerical results are displayed for a particular, simple model of anharmonic vibrating lattice [27], but illustrate a general behavior.

interpreted as the quasi-harmonic frequency for the mode, for which the oscillations in the auto-correlation function vanish, leaving a smoothly decaying function. Choosing the transformation frequency to be on either side of the quasi-harmonic frequency introduces oscillations into the auto-correlation. From this, we see that oscillations in the mode auto-correlation are artifacts of how we define the transform. If we set the transformation frequency to be the natural frequency of the system (which is the temperature-dependence quasi-harmonic frequency), then the auto-correlation is quite simple.

An alternative view gives a similar conclusion. Consider that the mode lifetime ( $\tau$ ) depends formally on the choice of  $\omega^x$  used to define the action-angle transformation. In Fig. 3, we see that  $\tau$  is a concave function of the transformation frequency. This is quite easily understood in relation to the previous observations about the auto-correlation function, noting that  $\tau$  is the area under the



**Fig. 3.** Mode lifetime as a function of the transformation frequency  $\omega^x$  (see Eq. (8)). As demonstrated in Fig. 2, the area under the curve (which is identified as the mode lifetime) is maximized by matching the transformation frequency to the temperature-dependent, quasi-harmonic frequency of the mode. Numerical results are displayed for a particular, simple model of anharmonic vibrating lattice, but should be general.

function. We note in Fig. 2 that the oscillations are always below the decaying envelope, so that zeroing out the oscillations will maximize the area. Thus, choosing the transformation frequency to match the quasi-harmonic frequency of the mode also maximizes the calculated lifetime. In the vicinity of the quasi-harmonic frequency, the lifetime is relatively insensitive to the transformation frequency. We see then that this definition of the transformation gives a natural definition for the (quasi-harmonic) frequency and lifetime. Fixing the transformation frequency in this manner, we see that *the occupation auto-correlation function is a monotonic, decaying function*. This property will greatly simplify the following analysis.

#### 4. The Liouvillian and mode lifetimes

The evolution of dynamical variables, such as the occupation  $\delta n_k$  as defined in the previous section, are governed by Hamilton's equations, which are, for anharmonic systems, naturally non-linear and correspondingly difficult to treat. However, the lifetime of the mode in a solid in equilibrium is expressed as an ensemble property, as defined in the auto-correlation Eq. (2). The lifetime is therefore an ensemble property, and reflects the dynamical behavior of different parts of the distribution function. The dynamics of distributions in phase space, even those systems with anharmonicity, is governed by the Liouvillian, which is a linear operator. That is, any function  $f$  on phase space evolves according to

$$\frac{df(p, q)}{dt} = -i\hat{L}f$$

where the (hermitian) Liouvillian operator

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

provides the time evolution, so that

$$f(p, q, t) = e^{-it\hat{L}}f(p, q, 0)$$

Note that any function  $g(H)$  is a constant of the motion, because  $\hat{L}g(H) = 0$ . The time-evolution of macroscopic variables can then be computed formally from the microscopic processes captured by the Hamiltonian, by considering the analytical properties of the Liouvillian. In particular, we can express the mode auto-correlation explicitly in terms of  $\hat{L}$ :

$$\chi_k(t) = \frac{\langle \delta n_k(0) e^{-i\hat{L}t} \delta n_k(0) \rangle}{\langle \delta n_k(0)^2 \rangle} \quad (17)$$

Extracting the mode-lifetime then becomes the challenge of understanding how the Liouvillian couples the phase-space function  $\delta n_k$  to other modes. One approach constructed by Prigogine and co-workers was to form a Taylor's series expansion in  $t$ , which can be captured in a corresponding set of Feynman diagrams. Other diagrammatic approaches have also been considered. These approaches must all come to grips with the basic structure of the auto-correlation. In Fig. 1, it is clear that the auto-correlation (once properly smoothed by a convenient choice of transformation) is somewhat exponential in appearance ( $\sim e^{-|t|/\tau}$ ). However,  $\chi(t)$  cannot be simply exponential. The requirement of time-reversal invariance would require that the auto-correlation have zero slope at  $t = 0$  (see Eq. (5)), but this is not consistent with purely exponential behavior. Furthermore, a log-linear plot shows clearly [27] that the behavior is not simply exponential, even at moderate times. It might be argued that the very long-time behavior should be exponential, but the mode lifetime (the area under the auto-correlation) is not strongly influenced by the very long-time tail of the auto-correlation, but by rather the moderate-time behavior, where the behavior is not simply exponential. These challenges have meant that the diagrammatic formalism has not been very useful as a computational tool, in the sense that (at least no our knowledge) no mode lifetimes for real systems have been calculated using this formalism. The diagrammatic expansions are instructive for general physical reasons, but we propose a different approach here, which we believe will yield a more directly computable form.

Another approach would be to consider the eigenfunctions, or some subset of the eigenfunctions, of the Liouvillian. Because  $\hat{L}$  is a linear (and also hermitian) operator, the properties of hermitian operators and their eigenfunctions can be applied to the present case. Related to that is the spectrum of  $\hat{L}$ . Generally speaking, that is a tall task, but it is helpful to recognize that we are considering only that part of phase space which is connected to  $\delta n_k$  by  $\hat{L}$ , and that simplifies the task. An efficient means for doing this is based on the recursion method, which captures the structure of the dynamics in an optimal way. We are therefore combining insights from the recursion method with those from the work on the Liouvillian in order to tackle the problem of the mode lifetime.

## 5. The recursion method applied to mode lifetimes

Consider the auto-correlation of fluctuations in the auto-correlation (see Eq. (2)), the area under which is the corresponding mode lifetime  $\tau$  (see Eq. (1)). The general approach here is to analyze  $\tau$  in terms of the recursion scheme, as discussed at length in the work of Haydock and co-workers [29,22–24]. In principle, the recursion scheme provides a relevant analysis of the dynamics of  $\delta n_k$ . In that sense, the method identifies the important sub-space of phase space, thereby focusing in on the relevant aspect to be dealt with. The fluctuation  $\delta n_k$  is a function on phase space, and so is its time derivative

$$\delta \dot{n}_k = i\hat{L}\delta n_k$$

and successive derivatives. The evolution in time can then be seen as a coupling via the operation of  $\hat{L}$  to other functions in phase space. This succession of states formally forms a linear sequence the nature of which has been well-studied.

Consider then the sequence of functions in phase space generated by acting on  $\delta n_k$  with higher powers of  $\hat{L}$ . The first in the sequence is  $\delta n_k$  itself:

$$v_0 = \delta n_k$$

and the next should reasonably be in the direction of  $\delta \dot{n}_k$ :

$$v_1 = \hat{L}v_0 = i\delta \dot{n}_k$$

Now we need a measure to determine to what extent the space has actually been expanded. This is naturally provided by the ensemble average (see Eq. (4)). Define the “dot product” of two phase space functions as

$$(A, B) = Q^{-1} \int d\Gamma e^{-\beta H} A^* B \quad (18)$$

Then we can see that  $v_1$  is orthogonal to  $v_0$ :

$$(v_0, v_1) = (v_0, \hat{L}v_0) = (1, v_0 \hat{L}v_0) = \frac{1}{2}(1, \hat{L}v_0^2) = \frac{1}{2}(\hat{L}1, v_0^2) = 0$$

where the second step is justified because  $v_0$  is real, the fourth by the hermiticity of  $\hat{L}$ , and the last because  $\hat{L}$  acting on any constant gives 0. (More generally, this can be seen as a consequence of the time-reversal symmetry, Eqs. (5) and (6).) Normalizing, we have

$$u_0 = \frac{\delta n_k}{\sqrt{\langle \delta n_k, \delta n_k \rangle}}$$

$$u_1 = \frac{\hat{L}\delta n_k}{\sqrt{\langle \hat{L}\delta n_k, \hat{L}\delta n_k \rangle}}$$

We note that  $u_0$  is a real function and  $u_1$  is pure imaginary.

The sequence of orthonormalized functions is continued by the three-term recursion (taking  $u_{-1} = 0$ )

$$b_{n+1}u_{n+1} = (a_n - \hat{L})u_n + b_n u_{n-1} \quad (19)$$

(along with the requirement that the  $u_n$  are orthonormal). In the first instance

$$b_1 u_1 = (a_1 - \hat{L})u_0 \quad (20)$$

along with  $(u_0, u_1) = 0$  gives  $a_1 = (u_0, \hat{L}u_0) = 0$  where the last result is from above. Taking the dot product of Eq. (20) with itself and requiring  $(u_1, u_1) = 1$  gives

$$b_1^2 = (\hat{L}u_0, \hat{L}u_0) = (u_0, \hat{L}^2 u_0)$$

The next instance gives,

$$b_2 u_2 = (a_1 - \hat{L})u_1 + b_1 u_0$$

We see that the choice above for  $b_1$  already ensures that  $(u_0, u_2) = 0$ . Requiring  $(u_1, u_2) = 0$  gives  $a_2 = (u_1, \hat{L}u_1)$ . We can repeat the argument that we used to show  $a_1 = 0$  to show also that  $a_2 = 0$ , except now we must remember that  $u_1$  is pure imaginary. Finally, requiring  $(u_2, u_2) = 1$  gives

$$b_2^2 = b_1^2 \left( \frac{(u_0, \hat{L}^4 u_0)}{b_1^4} - 1 \right)$$

Finally we see that  $u_2$  is pure real.

Continuing the sequence, we see that the functions  $u_n$  are alternately pure real and pure imaginary, that

$$a_n = (u_n, \hat{L}u_n) = 0$$

and that  $b_n$  involves moments up to  $(u_0, \hat{L}^{2n} u_0)$ .

The strength of this formalism is that this sequence of orthonormalized functions is optimally configured to represent the dynamics of  $\delta n_k(t)$ . Furthermore, in this basis the representation of the Liouvillian is a special tridiagonal form:

$$\underline{L} = \begin{bmatrix} 0 & b_1 & 0 & \dots & & & & 0 \\ b_1 & 0 & b_2 & 0 & \dots & & & \\ 0 & b_2 & 0 & b_3 & 0 & \dots & & \\ \cdot & \cdot \\ \cdot & \cdot \\ 0 & \cdot \end{bmatrix}$$

so that the coefficients  $b_n$  themselves provide the representation.

The response of the system is extracted most easily in terms of the resolvent of the Liouvillian

$$\widehat{R}(\omega) = (\omega - \widehat{L})^{-1}$$

defined on the frequency domain. The relevant behavior of the resolvent is captured by the coefficients  $b_n$ . That is, we examine the projection of  $R$  onto the initial basis function:

$$R_0(\omega) = (u_0, \widehat{R}(\omega)u_0) = (\delta n_k, (\omega - \widehat{L})^{-1} \delta n_k) / (\delta n_k, \delta n_k)$$

which can be expressed as the continued fraction

$$R_0(\omega) = 1 / \{ \omega - b_1^2 / [ \omega - \dots - b_n^2 / (\omega - \dots) ] \} \quad (21)$$

## 6. Partial Density of States

The Partial Density of States (PDoS)  $g_0(\omega)$  is given by the imaginary part of the resolvent [29]

$$g_0(\omega) = \frac{1}{\pi} |\Im\{R_0(\omega)\}|$$

and is related to the Fourier Transform (or power spectrum)  $\tilde{\chi}_k(\omega)$  of  $\chi_k(t)$  by

$$\tilde{\chi}(\omega) = \sqrt{2\pi} g_0(\omega)$$

The PDoS is even and normalized and its moments are related to the coefficients  $\{b_k\}$  of the recursion, by

$$\mu_m = \int_{-\infty}^{+\infty} d\omega \omega^m g_0(\omega) = (u_0, \widehat{L}^m u_0)$$

so that

$$b_1^2 = \mu_2$$

is related to the width of the distribution and the ratio

$$\left(\frac{b_2}{b_1}\right)^2 = \frac{\mu_4}{\mu_2^2} - 1$$

It is convenient to define

$$\gamma_4 \equiv \frac{\mu_4}{\mu_2^2}$$

which is a low-order measure of the shape of the power spectrum. A Gaussian distribution has  $\gamma_4 = 3$ , for example. In terms of  $\gamma_4$ , the angle  $\theta$  between  $\delta\ddot{n}$  and  $\delta n$  is given by

$$\cos \theta = \langle \delta\ddot{n} \delta n \rangle / \sqrt{\langle (\delta\ddot{n})^2 \rangle \langle \delta n^2 \rangle} = -\gamma_4^{-1/2}$$

To summarize, the recursion method provides an optimally efficient means of capturing all of the dynamical information relevant to the dissipation of fluctuations in the aspect under consideration (in this case, the occupation of a mode). The recursion maps the dynamics onto a sequence of states which are coupled by the Liouvillian to the first in the sequence, which is the occupation variable itself. The coupling is evaluated in terms of moments of the Liouvillian, from which one can reconstruct the resolvent and the auto-correlation function itself. The net result is then that the mode lifetime,  $\tau_k$  is a function of the complete set of moments:

$$\tau_k = F(\mu_2, \mu_4, \mu_6, \dots) \quad (22)$$

The function  $F$  can be determined, in principle, from the resolvent. However, finding the complete (infinite) set of moments is impractical. In the next section, we discuss strategies for dealing with knowledge of only a finite set.

## 7. Reconstruction, termination, and convergence

The problem then comes down to evaluating  $\tau_k$  (or  $g_0(\omega = 0)$ ) where we know some number of moments of the function  $g_0(\omega)$ . Based on dimensional analysis [30], and noting that the moment  $\mu_m$  has dimension  $\omega^m$ , we can re-write  $\tau_k$  (Eq. (22)) as a function of all the moments as

$$\tau_k = \mu_2^{-1/2} G(\gamma_4, \gamma_6, \dots)$$

so that the scale of  $\tau_k$  is set by the second moment of the distribution. The function  $G$  depends then on the dimensionless parameters  $\gamma_{2m} \equiv \mu_{2m} / \mu_2^m$  which measure only the relative *shape* of the distribution. It is very unlikely that we will ever find  $G$  exactly, but using physical arguments we should be able to find some close approximations to it. The hypothesis proposed here is that a useful approximation can be obtained by considering only a few low moments, the trade-off being that higher moments are increasingly difficult to calculate. Some possible approximations involving only low moments are discussed here. Ultimately, the quality of these approximations will need to be judged numerically (see [27]).

A simple approach would be to express the problem as one of reconstructing the function from its low order moments, as one would do in applying the principle of maximum entropy. In this fashion, we determine  $g_0(\omega)$  from its lowest non-vanishing  $l$  moments by minimizing the functional

$$A[g_0(\omega)] = \int_{-\infty}^{+\infty} d\omega \{ g_0(\omega) \ln(g_0(\omega)) - \sum_{k=0}^{l-1} \lambda_k \omega^{2k} g_0(\omega) \}$$

with respect to  $g_0(\omega)$ . At the lowest (second moment) level, then,

$$g_0^{(2)}(\omega) = \frac{1}{\sqrt{2\pi b_1}} \exp\left(\frac{-\omega^2}{2b_1}\right)$$

and

$$\tau_2^{ME} = \sqrt{2\pi / \mu_2}$$

Incorporating higher moments involves exponentials of quartic and higher powers in  $\omega$ . At the level of fourth moment, the spectrum will have the form

$$g_0^{(4)}(\omega) = A \exp(-B\omega^2 - C\omega^4)$$

but the relationship between the constants and the moments of the spectrum is now transcendental, so that we cannot write an analytical form for  $B(b_1, b_2)$ , for example. In that case, the relationship between the lifetime and the moments is purely numerical.

It is helpful to note that we can incorporate more knowledge about the resolvent than simply its lowest moments. We know that  $\chi_k(t)$  is infinitely differentiable, which means that  $R_0(\omega)$  must fall off faster than any power of  $\omega$ . Additionally, as pointed out by Haydock et al. [23], we know generally about the analytical behavior of the projected  $R_0(\omega)$  as a function of complex  $\omega$ . Haydock and Nex [24] build on this insight by proposing a general scheme for reconstructing the density of states from the moments. They apply the physically motivated constraint that states of the macroscopic system have minimal lifetimes consistent with the moments, expressed alternatively as maximal breaking of time-reversal symmetry (MBTS) in finite subsystems. This they show can be

expressed in terms of the tails  $T_N(\omega)$  of the continued fraction, defined at each level of recursion by

$$R_0(\omega) = 1/\{\omega - b_1^2/[\omega - \dots - b_N T_N(\omega)]\}$$

Because of the analytical properties of  $T_N(\omega)$ , inferred from that of  $R_0$ , it is demonstrated that the continued fraction expansion of  $R_0$  converges within a circle of radius  $\rho$  which decreases exponentially with increasing  $N$ , which also produces the same bounds on  $g_0(\omega)$ . The application of MBTS then constrains the analytic properties sufficiently that a convergent calculation of  $g_0(\omega)$  is demonstrated.

At the lowest (second moment) level the power spectrum is Lorentzian, that is

$$g_0^{(2)}(\omega) = \frac{b_1}{\pi(\omega^2 + b_1^2)}$$

which gives

$$\tau_2^{MBTS} = 2/\sqrt{\mu_2}$$

However, the resulting auto-correlation function would be  $\chi(t) = \exp(-b_1|t|)$  which is not differentiable at  $t = 0$ .

The next (fourth moment level) gives

$$g_0^{(4)}(\omega) = \frac{b_1 b_2 \sqrt{\omega^2 + b_1^2 + b_2^2}}{\pi[(\omega^2 - b_1^2)^2 + (\omega^2 + b_1^2)b_2^2]}$$

which gives

$$\tau_4^{MBTS} = \tau_2^{MBTS} \sqrt{1 - \gamma_4^{-1}}$$

Another approximation offered by Haydock and Nex [24] is the single-band, where the spectrum  $g_0(\omega)$  is non-zero only inside of a finite range of frequency. In this case, the lowest level gives

$$g_0^{(2)}(\omega) = \frac{\sqrt{4b_1^2 - \omega^2}}{2\pi b_1^2}$$

and

$$\tau_2^{SB} = 2/\sqrt{\mu_2}$$

The next level gives

$$g_0^{(4)}(\omega) = \frac{2b_1 b_2 \sqrt{4b_1 b_2^2 - \omega^2}}{\pi[(2b_2 - b_1)^2 \omega^2 + b_1^2(4b_1 b_2 - \omega^2)]}$$

and

$$\tau_4^{SB} = \tau_2^{SB} \sqrt{\gamma_4 - 1}$$

We note that the single-band approximation will always give an oscillatory  $\chi(t)$ .

Among these offerings, none is optimal. The maximum entropy approach becomes analytically unwieldy at fourth moment. The MBTS leads to power spectra which are power-law in  $\omega$  and so do not fall off fast enough, resulting in a  $\chi(t)$  which has unphysical derivatives at  $t = 0$ . By contrast the SB gives oscillatory behavior for  $\chi(t)$ , which is not appropriate for the examples above. However,

they all give somewhat similar dependence of  $\tau$  on the lowest moments, and it would seem that the final result is somewhat insensitive to the details of the model. With some work on appropriate numerical solutions, it may be possible to obtain a model for the power spectrum which has all of the right properties and gives a usable but robust expression for  $\chi(t)$ .

## 8. Conclusions

A formalism is presented here for improved calculations of vibrational mode lifetimes in solids. The mode lifetime is calculated in terms of moments of the power spectrum of the resolvent of the Liouvillian. The lowest level (second moment) should provide a reasonably good approximation to the lifetime, with refinement given by the next order (fourth moment). In the companion piece [27], we will compare the approximations to the numerically exact calculation using the Green-Kubo relation for some simple models of lattice vibrations.

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