Using low moments of the Liouvillian to calculate mode lifetimes in low dimensional models

Yang Gao,1 Doyl Dickel,1,2 David Harrison,1,3 and Murray S. Daw1

1Department of Physics & Astronomy, Clemson University, Clemson, SC 29634
2Now at Karlsruhe Institute of Technology, Institute of Applied Materials (IAM-ZBS), Kaiserstr. 12, 76131 Karlsruhe
3Now at Department of Physics, Wake Forest University, Winston-Salem, NC

Abstract

A recent proposal for practical calculation of vibrational mode lifetimes is tested on simple, low-dimensional anharmonic models. The proposed scheme approximates the mode lifetime in terms of ensemble averages of specific functions in phase-space; various levels of approximation correspond to ensemble moments of the Liouvillian. It is shown that, for systems where the vibrational density of states is well-approximated by a single broadened peak, the fourth-moment approximation works well over the full range of temperature.

PACS numbers: 05.40.-a, 05.45.-a, 05.60.Cd, 63.20.Ry
I. INTRODUCTION

Dickel & Daw\textsuperscript{[1,2]} recently proposed an efficient, approximate means of calculating vibrational mode lifetimes in solids. The method involves ensemble averages of appropriate functions in phase space that 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 illustrated on a lattice model of non-linear interactions, where the dependence of the mode lifetimes on cell size and temperature was investigated numerically.

While the aim of the original work was to further calculations of vibrational mode lifetimes in solids, the purpose of the present work is to examine in more detail the approximations involved in the method. To this end we take up the same method as applied to very simple systems of just one or two degrees of freedom. In considering systems of such simplicity, we analyzed some aspects of the problem analytically as well as numerically, and the insights obtained are reported here. These insights are expected to prove fruitful in the application of this method to the original target (vibrational lifetimes in solids).

This paper is organized as follows. First, we recap briefly the proposal of Dickel & Daw (DD). Then we apply the proposed method to the simple dynamical models considered here. Our analysis of the results focuses on the density of states, by which we can understand when and why the approximations work as they do. Finally, we draw our conclusions.

II. BACKGROUND & SCOPE OF THE PRESENT WORK

We summarize here the proposed method of DD, who began by examining the momentum Auto-Correlation Function (MACF)

$$\chi_p(t) = \frac{\langle p(0)p(t) \rangle}{\langle p^2 \rangle}$$

where the angular brackets indicate phase-space averages over the canonical ensemble at temperature $T$ ($\rho = \exp \left( -\frac{H}{T} \right)$).

The auto-correlation can be studied in terms of the Liouvillian\textsuperscript{[3,4]}, which governs the time evolution of functions $f(x, p, t)$ in phase space according to

$$\frac{\partial f}{\partial t} = -iL f$$

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where the (hermitian) Liouvillian operator is
\[ \hat{L} = i \{ H, \} = i \sum_i \left( \frac{\partial H}{\partial x_i} \frac{\partial}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial}{\partial x_i} \right) \]

The equation of motion can be integrated formally, so that
\[ f(x, p, t) = e^{-i\hat{L}t} f(x, p, 0) \]
and we can express the auto-correlation explicitly in terms of \( \hat{L} \):
\[ \chi(t) = \frac{\langle pe^{-i\hat{L}t} p \rangle}{\langle p^2 \rangle} \]

The Taylor Series of \( \chi(t) \)
\[ \chi(t) = 1 - \mu_2 \frac{t^2}{2!} + \mu_4 \frac{t^4}{4!} - \mu_6 \frac{t^6}{6!} + ... \]
relates the derivatives of \( \chi(t) \) at \( t = 0 \) to the moments of the Liouvillian acting on the momentum:
\[ \mu_n = \frac{\langle \hat{L}^n p \rangle}{\langle p^2 \rangle} \]
These moments 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
\[ \mu_m = \int_{-\infty}^{+\infty} d\omega \omega^m n(\omega) \]

Auto-correlation functions considered in this work typically have strong oscillations dampened by some sort of decaying envelope (for examples, see Figs. 1-2). We propose here to use the area under the square of the MACF as a measure of the lifetime
\[ \tau = \int_{-\infty}^{+\infty} dt \chi(t)^2 \] (2)
This is not intended to correspond to a 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, as we shall see. Using Parseval’s Theorem, the lifetime is also given as the area under the \( n(\omega)^2 \) curve:
\[ \tau = \int_{-\infty}^{\infty} dt \chi(t)^2 = \int_{-\infty}^{\infty} d\omega n(\omega)^2 \] (3)
DD observed that the lifetime $\tau$ can be expressed as a function of the moments

$$\tau = F(\mu_2, \mu_4, \mu_6, \ldots)$$

which can be re-expressed (using dimensional analysis) as

$$\tau/\tau_2 = G(\gamma_4, \gamma_6, \ldots)$$

where $\tau_2 = \mu_2^{-1/2}$ and the $\gamma$’s are dimensionless parameters

$$\gamma_n = \frac{\mu_n}{(\mu_2)^{n/2}}$$

that characterize the shape of the DOS. 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

$$\tau = c\tau_2$$  \hspace{2cm} (4)

and including successively higher moments. The fourth moment approximation would then be

$$\tau = \tau_2 F(\gamma_4)$$ \hspace{2cm} (5)

where $F$ 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.

DD then went on (in part 2) to test the lowest approximation on a simple model of non-linear lattice vibrations as a function of cell size and temperature. First, much as done by Ladd, et al.\[15]\, DD calculated from ordinary molecular dynamics the auto-correlation function for each normal mode a periodic cell of a given size (appropriately sampled at the specified temperature) and from there the lifetime. Second, they calculated using standard Monte Carlo the second moment $\mu_2$ (hence $\tau_2$) for each mode. (This second part of the demonstration is, of course, requires much less computational time than the first.) They then plotted $\tau/\tau_2$ vs. temperature for all modes, and found that at high temperatures the lifetime was simply proportional to $\tau_2$. Furthermore, at high temperature, the auto-correlation functions scaled in a simple way. That is, plotting all of the calculated $\chi$ vs. $t/\tau_2$ exhibited a data collapse, 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).

DD ended by speculating that the behavior over the full range of temperature might be accounted for by including fourth moment, but that was not tested. Also, that paper did not offer much insight as to why the second moment approximation should work well at high temperature but be insufficient at low temperatures.

The present study uses several simple dynamical models as the basis for testing the fourth moment approximation and also in using the density of states to provide an analysis of why the approximation might work and when it would be expected to fail.

III. MODELS CONSIDERED

We consider three simple model hamiltonians in one \((x)\) and two \((x\) and \(y)\) dimensions. These models are chosen because they are simple, non-linear, and the ensemble averages can be obtained analytically. The momentum conjugate to \(x\) is \(p\); that to \(y\) is \(q\).

**\(x^4\) model:**

\[
H(p, x) = p^2 + x^2 + x^4
\]  

(6)

The auto-correlation in the \(x^4\) model has been studied extensively before\(^6,7\). In that work, an analytic approximation to \(\chi(t)\) was obtained at low temperature:

\[
\chi(t) = \frac{\cos(t) - 3Tt \sin(t)}{9T^2 t^2 + 1}
\]  

(7)

showing an oscillatory behavior with an algebraically decaying envelope. Our calculated auto-correlation conforms well to this analytical form at low temperatures.

**\(x^2y^2\) model:**

\[
H(p, x, q, y) = p^2 + q^2/M + x^2 + y^2 + x^2y^2
\]  

(8)

The \(x^2y^2\) model is a simple extension to two modes coupled nonlinearly. In this model, we investigate various values of the ratio \((M)\) of the masses between the two modes, which controls the degree of resonance.
The “cubic” model for certain parameters has multiple minima in the $x - y$ plane and exhibits a “structural” transformation (from multiple attractors to a single attractor) with temperature, which makes it interesting to include in the present study. To explore the effects produced by this transition, we tried various values of the strength ($\lambda$) of the cubic term. For $\lambda < 2/9$, there are 3 off-center global minima with one local minimum on-center. For $\lambda > 1/4$ only there is only 1 global minimum on-center.

Some examples of a calculated MACF are shown in Figs. 1-2. For the $x^4$ model, the function exhibits a simple oscillation and decay. In the “cubic model”, the function displays less regularity because of the less symmetrical potential.

\[ H(p, x, q, y) = p^2 + q^2 + x^2 + y^2 + \frac{\lambda}{4}(x^2 + y^2)^2 + \frac{1}{3}(x^3 - 3xy^2) \]
IV. TESTING THE FOURTH MOMENT APPROXIMATION

We want to determine if the form in Eq. 5 is robust enough to approximate the lifetimes in the various simple models we have chosen. In the $x^4$ model, for example, we can perform ensemble dynamics at various temperatures and extract the lifetime by Eq. 5. The lifetime vs. temperature for the $x^4$ model is then shown in Fig. 3.
In view of Eq. [5], we represent these results as a scatterplot of $\tau/\tau_2$ vs. $\gamma_4$, where the temperature-dependent $\tau_2$ and $\gamma_4$ are calculated analytically. Noting that $\gamma_4 \geq 1$, and the power-law behavior of $\tau$ and the moments with $T$, we will plot $\log(\tau/\tau_2)$ vs. $\log(\gamma_4 - 1)$. This is shown in Fig. [4]
FIG. 4. Scatterplot of $\tau/\tau_2$ vs $\gamma_4$ for the $x^4$ model. The straight line is a fit using Eq. 10.

Similar results can be seen for the $x^2y^2$ model (see Fig. 5).

FIG. 5. $\tau/\tau_2$ vs $\gamma_4$ of the $x$-mode for the $x^2y^2$ model. The straight line is a fit using Eq. 10.
The relations in Figs. 4-5 are fit well by

\[ \tau / \tau_2 \propto (\gamma_4 - 1)^{-1/2} \]  

From the analytic approximation to MACF for the $x^4$ model at low temperature (Eq. 7), we can also calculate $\tau$, $\mu_2$, and $\mu_4$, and we find

\[ \tau / \tau_2 = \pi (\gamma_4 - 1)^{-1/2} \]  

The analytical form for $\chi(t)$ was derived by Sen, et al. only for low temperatures, by noting the dependence of the oscillator frequency on energy and the contributions of different energies in the canonical ensemble. However, here we find the relationship between $\tau$, $\tau_2$, and $\gamma_4$ extends over a large range of temperature. The reason for this extended range will be understood better below.

At low $T$, the low moments for both $x^4$ and $x^2y^2$ models behave similarly, in that $\mu_2 \approx 1 + aT$ and $\mu_4 \approx 1 + 2aT$ so that $\gamma_4$ approaches 1 as $T^2$. Thus $\tau_2$ is approaches a constant while $\gamma_4 - 1$ goes to zero, and the lifetime diverges like $\tau \approx T^{-1}$ at low temperature. The temperature dependence at low $T$ is dominated by the approach of $\gamma_4$ to 1.

At high temperature, the moments for the $x^4$ model go as $\mu_2 \approx aT^{1/2} + b$ and $\mu_4 \approx cT - dT^{1/2}$. So $\gamma_4$ saturates to a constant as $T^{-1/2}$, leaving only the variation in $\tau_2$ to account for the change in lifetime. Thus the lifetime at high $T$, is governed by the behavior of $\tau_2$ and $\tau \approx T^{-1/4}$.

This accounts well for the two power-law regimes visible in Fig. 3.

For the $x^2y^2$ model, by contrast, at high temperature, the moments go as $\mu_2 \approx 2T / \log T + 1/2$ and $\mu_4 \approx 4T^2 / \log T + 4T / M$ which makes $\gamma_4$ go as $\log T$. This cancels a $\log T$ dependence in $\tau_2$ leaving $\tau \approx T^{-1/2}$.

The $x^4$ and $x^2y^2$ models seem to be well-described by the simple combination of the first two moments. However, by contrast, the corresponding scatterplot for the “cubic model” deviates significantly (Fig. 6), so that there is no simple relationship between $\tau$ and the first two moments. Evidently, higher moments will be required to capture the dynamical behavior of the cubic model over a wide range of temperatures and parameters.
FIG. 6. Scatterplot of $\tau/\tau_2$ vs $\gamma_4$ of the $x$-mode for the “cubic” model, showing irregular behavior as compared to the other models (Figs. 4-5).

V. ANALYSIS

From the previous results, we see that the behavior of the lifetime for the $x^4$ and $x^2y^2$ models over a wide range of parameters and temperature is captured in the behavior of the two lowest moments ($\mu_2$ and $\mu_4$) which can be calculated analytically. However, for the cubic model, the behavior is more complex, requiring at least higher moments in the description. We investigate here the reasons for success in one case and not in the other.

Fig. 7 shows the insight gained from checking for a data-collapse for $\chi(t)$, by scaling the time $t$ by the lifetime $\tau$ (Fig. 3) for the $x^4$ model. The results illustrate that while the oscillations of auto-correlation functions vary with temperature, they are contained by one decaying envelope, which is what we are trying to capture.
As one might expect from the data-collapse, the DOS for the $x^4$ model is also simple, as shown in Fig. 8 for various temperatures.
The DOS of this model is characterized by a single dominant peak that shifts and broadens with temperature, as one would typically expect of a vibrational mode in an anharmonic solid. In such a case, the lifetime depends mostly on the shape of the DOS around the peak, and two parameters (peak value of the DOS and the width) are sufficient to describe it. At low temperatures, $\gamma_4 \rightarrow 1$, while at high temperatures $\gamma_4 \rightarrow 2.2$ (for this model). Recalling $\gamma_4$ as the (dimensionless) ratio $\mu_4/\mu_2^2$, it is aptly designated as a “shape parameter” of the DOS.

The DOS of the $x^2y^2$ model (Fig. 9) is only somewhat more complex than that of the $x^4$ model.
The simple evolution of the DOS with the temperature and other parameters for these models explains why a simple, generic relationship can exist between $\tau$ and the first two moments of the DOS. To explore this point further, let us consider a generic, single-mode DOS that is peaked at an oscillator frequency $\omega_0$ and broadened to a width $\Omega$. Both the oscillator frequency and width will depend on temperature. At low temperatures, $\Omega \ll \omega_0$, and from Eq. 3 we have

$$\tau \approx \Omega^{-1}$$

The leading behavior of the lowest two moments is

$$\mu_2 \approx \omega_0^2 (1 + a\Omega^2/\omega_0^2)$$

$$\mu_4 \approx \omega_0^4 (1 + b\Omega^2/\omega_0^2)$$

where $a$ and $b$ depend on the details of the DOS. Then

$$\tau/\tau_2 \approx \omega_0/\Omega$$

and

$$\gamma_4 - 1 \approx \Omega^2/\omega_0^2$$
Eliminating $\Omega$ and $\omega_0$ among the two relations gives

$$\frac{\tau}{\tau_2} \approx (\gamma_4 - 1)^{-1/2}$$

just as we found in Eq. 10. So long as the DOS has this simple, generic behavior, the same relationship obtained here should hold.

At high temperatures, if the DOS can be assumed to be a mostly featureless and broad distribution with width $\Omega$ and height $\Omega^{-1}$, then $\tau \approx \Omega^{-1}$ and $\mu_2 \approx \Omega^2$ so $\tau_2 \approx \Omega^{-1}$. While the shape parameter saturates at some value ($\gamma_4 \approx c$), in which case the variation in $\tau$ is tracked by that of $\tau_2$, so that

$$\tau \approx \tau_2$$

which is the behavior reported by DD.

The DOS of cubic model (Fig. 10) is much more complicated than that of $x^4$ and $x^2y^2$ model, which explains why the simple 2-parameter scatterplot (Fig. 3) does not capture the behavior.

![Figure 10](image-url)  
**FIG. 10.** Density of states of the $x$-mode at $\lambda = 0.2$ and various temperatures for the cubic model.

Finally we note that $\gamma_4$, in addition to being a simple measure of the shape of the DOS, is also a direct measure of the degree of anharmonicity of the mode as averaged over the
ensemble. Specifically, $\gamma_4$ for a given mode can be re-written as

$$\gamma_4 = \frac{\langle x^2 \rangle \langle f^2 \rangle}{\langle xf \rangle^2}$$

(12)

where $f$ is the force associated with a displacement $x$. A harmonic system is, of course, defined where the force obeys $f + kx = 0$. In the anharmonic ensemble, we could define an effective $k$ by that which minimizes the deviation from linear. That is, define the effective $k$ by minimizing $\alpha = \langle (f + kx)^2 \rangle$. The minimum value of $\alpha$ then measures the degree of anharmonicity of the system as effective for the ensemble. For a harmonic system, $\alpha_{\text{min}} = 0$. In general, $k_{\text{eff}} = -\langle xf \rangle / \langle x^2 \rangle$ and

$$\alpha_{\text{min}} = \frac{\langle xf \rangle^2}{\langle x^2 \rangle} (\gamma_4 - 1)$$

(13)

showing how the deviation $\gamma_4 - 1$ is directly related to the effective anharmonicity of the ensemble.

VI. CONCLUSIONS

We have investigated using low-dimensional models the proposal that the mode lifetime in equilibrium might be approximated from the two lowest moments of the Liouvillian. For the generic case of a DOS dominated by a single peak broadened and shifted, as is the case here for the $x^4$ and $x^2y^2$ models, we see that the fourth moment approximation works well. In the case of the cubic model, the fourth moment approximation is insufficient, which can be understood in terms of the more complex structure of the DOS. The multiple minima of the cubic model creates a more complex dynamics that cannot be captured with just two parameters.

ACKNOWLEDGEMENT

Research supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering under Award ER 46871.

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