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Improved calculation of vibrational mode lifetimes in anharmonic solids – Part III: Extension to fourth moment

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ABSTRACT

A recent scheme for calculating approximate vibrational mode lifetimes in solids (Dickel and Daw, 2010) is extended to the next level (fourth-moment). The extension is tested in two cases: (1) simple, low-dimensional anharmonic systems, and (2) on a simple lattice model of vibrations. We show that, for systems where the mode-resolved density of states is well-approximated by a single broadened peak, the fourth-moment approximation works well over a wide range of temperatures.

1. Introduction

Dickel and Daw [1,2] recently proposed an approximate method to calculate lifetimes of vibrational modes in non-linear solids which 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. In particular, calculations based on averages of the second power of the Liouvillian (that is, so-called "second-moment" approximation) accounted for the mode lifetimes very well at high temperatures but diverged at lower temperatures.

While the aim of the original work was to lay out the formalism and carry out first-level (that is, second-moment) calculations, the purpose of the present work is to examine in more depth the approximations involved and to investigate the improvement gained by including fourth moment. To this end we take up the same idea as applied to very simple systems of just one or two degrees of freedom. In considering systems of such simplicity, we analyze some aspects of the problem analytically as well as numerically. These insights prove fruitful, especially by indicating how the next level of approximation (that is, "fourth-moment") is able to account for vibrational mode lifetimes even at much lower temperatures. We then return to the normal modes of lattice model, and find that the fourth moment results are reliable to much lower temperatures than the second moment.

This paper is organized as follows. First, we recap briefly the approximation proposed by Dickel and Daw (DD). Then we consider the approximation as applied to some simple dynamical systems. 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. Then we re-examine the lattice model with the fourth-moment calculations. Finally, we draw our conclusions.

2. Background and scope of the present work

We summarize here the proposed approximation of DD, who began by examining the Auto-Correlation Function (ACF)[3]

$$\chi_k(t) = \frac{\langle A_k(0)A_k(t)\rangle}{\langle A_k^2\rangle} \tag{1}$$

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[3] DD used the auto-correlation of fluctuations in the mode occupancy, $\delta n_k = n_k - \bar{n}_k$. We examine here the auto-correlation based on mode amplitude, A_k, which we find more convenient. In particular, for finite systems the ACF using mode occupancy does not go to zero as t goes large; the "residual" value of the mode occupancy must necessarily be dealt with in calculations. Switching to the displacement ACF avoids that difficulty.

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where A_k is the amplitude in a normal mode indexed by k. The angular brackets indicate phase-space averages over the canonical ensemble at temperature T ($\rho = \exp(-H/T)$).

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

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

where the (Hermitian) Liouvillian operator is

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

The dynamics are expressed primarily in terms of the positions and momenta of the atoms ($\{x_l, p_l\}$) and the normal mode amplitudes and conjugate momenta ($\{A_k, \Pi_k\}$) are related to the atomic coordinates via the normal mode transformation X_{kl}: ($A_k = \sum_l X_{kl}x_l$ and $\Pi_k = \sum_l X_{kl}p_l$). The equation of motion can be integrated formally, so that

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

(where by x and p we mean here the set of atomic coordinates). We can express the mode auto-correlation explicitly in terms of $\widehat{L}$:

$$\chi_k(t) = \frac{\langle A_k e^{-it\widehat{L}} A_k\rangle}{\langle A_k^2\rangle}$$

The Taylor Series of $\chi(t)$

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

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

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

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

$$\mu_{k,2} = \langle \Pi_k^2\rangle / \langle A_k^2\rangle = -\langle F_k A_k\rangle / \langle A_k^2\rangle \quad (2)$$

(via the virial theorem) and

$$\mu_{k,4} = \langle F_k^2\rangle / \langle A_k^2\rangle \quad (3)$$

where the F_k is the mode-resolved set of atomic forces ($F_k = \sum_l X_{kl} f_l$).

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

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

Auto-correlation functions corresponding to decaying modes typically have strong oscillations dampened by some sort of dying envelope (for examples, see Figs. 1 and 2). We propose here to use the area under the square of the ACF as a measure of the lifetime[4]

$$\tau_k = \int_{-\infty}^{+\infty} dt\ \chi_k(t)^2 \quad (4)$$

[4] DD, basing their auto-correlation on the mode occupancy – which is usually non-negative – evaluated the mode lifetime as the area under that ACF. In the present case, because we are now using the displacement ACF, which oscillates strongly about zero, we find it more convenient to evaluate the mode lifetime in terms of the area under the square of the ACF.

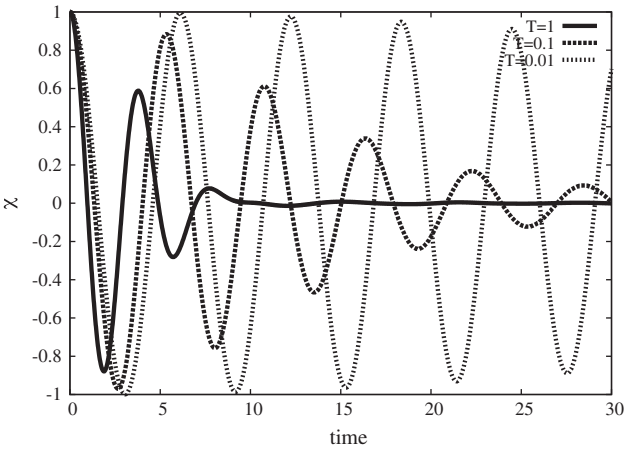

Fig. 1. The ACF at three temperatures for the x^4 model.

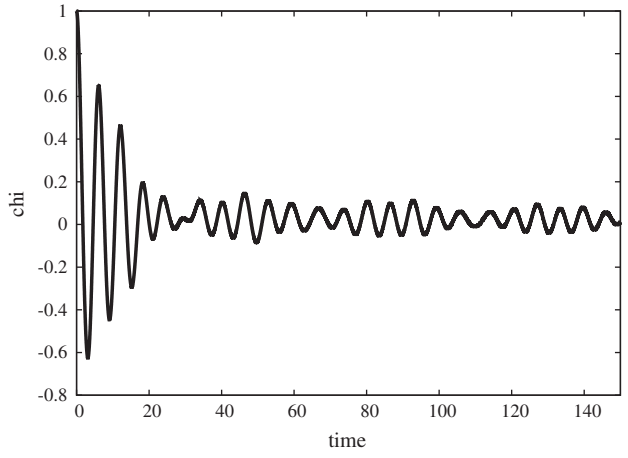

Fig. 2. The ACF of the x-mode at $\lambda = 0.5$ and $T = 0.2$ for the "cubic" model.

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:

$$\tau = \int_{-\infty}^{\infty} dt\ \chi(t)^2 = \int_{-\infty}^{\infty} d\omega\ n(\omega)^2 \quad (5)$$

DD observed that the lifetime τ can be expressed as a (generally unknown) function of the moments

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

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

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

where $\tau_{k,2} = \mu_{k,2}^{-1/2}$, G is a generally unknown function, and the γ's are dimensionless parameters

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

that characterize the shape of the DOS for each mode. (Note that $\gamma_n \geqslant 1$.) 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

$$\tau = c\tau_2 \tag{6}$$

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

$$\tau = \tau_2 K(\gamma_4) \tag{7}$$

where K 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. [5] DD calculated from ordinary molecular dynamics the auto-correlation function for each normal mode in a periodic cell of a given size and from there 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. They then scatter-plotted τ/τ_2 vs. 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).[5]

DD ended by speculating that the behavior over the full range of temperature might be accounted for by including fourth moments, 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, or much detailed reasoning as to why the fourth-moment approximation might be more successful.

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. In particular, we turn our focus to dynamical systems with only one or two modes, in order to simplify the analysis. As we will see, the DOS of these simple models closely resembles the mode-resolved DOS from the lattice model and even most solids. The insights gained with the simpler systems are then applied again to the lattice model.

3. 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:

$$H(p,x) = p^2 + x^2 + x^4 \tag{8}$$

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:

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

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

x^2y^2 model:

$$H(p,x,q,y) = p^2 + q^2/M + x^2 + y^2 + x^2y^2 \tag{10}$$

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.

"cubic" model:

$$H(p,x,q,y) = p^2 + q^2 + x^2 + y^2 + \frac{\lambda}{4}(x^2+y^2)^2 + \frac{1}{3}(x^3 - 3xy^2) \tag{11}$$

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 (λ) of the quartic term. For $\lambda < 1/9$, there are three off-center global minima with one local minimum on-center. For $1/9 < \lambda < 1/8$, there is one global minimum at the center and three off-center local minima. Finally, for $\lambda > 1/8$, there is only one global minimum at the center.

Some examples of a calculated ACF are shown in Figs. 1 and 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.

4. Fourth-moment approximation for low dimensional models

We want to determine if the fourth-moment approximation (Eq. (7)) is robust enough to describe 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 from the ACF (Eq. (5)). The numerical lifetime vs. temperature for the x^4 model is then shown in Fig. 3.

In view of the proposed fourth-moment approximation (Eq. (7)), we represent these results as a scatterplot (Fig. 4) of τ/τ_2 vs. γ_4, where the temperature-dependent τ_2 and γ_4 are calculated analytically. Noting that $\gamma_4 \geqslant 1$, and the power-law behavior of τ and the moments with T, we will plot $\ln(\tau/\tau_2)$ vs. $\ln(\gamma_4 - 1)$.

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

The behavior displayed in Figs. 4 and 5 is captured well by

$$\tau/\tau_2 = c/\sqrt{\gamma_4 - 1} \tag{12}$$

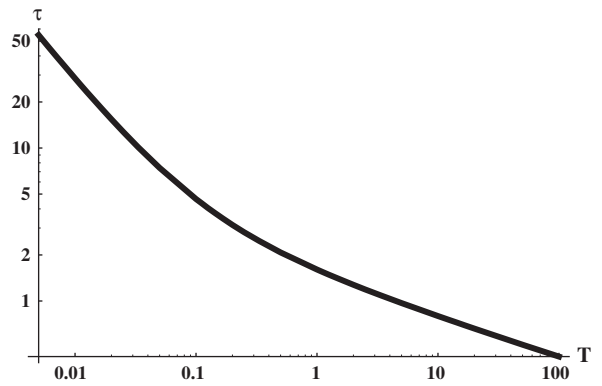

Fig. 3. Lifetime (Eq. (4)) vs. temperature in the x^4 model. For low temperatures, $\tau \sim T^{-1}$, while at high temperatures $\tau \sim T^{-1/4}$.

[5] 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.

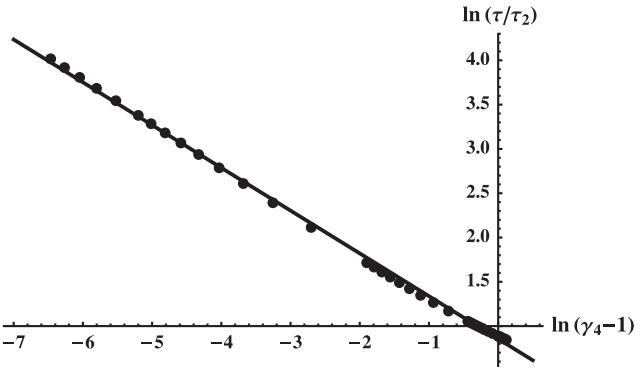

Fig. 4. Scatterplot of τ/τ_2 vs. $\gamma_4 - 1$ for the x^4 model. The straight line is a fit using Eq. (12).

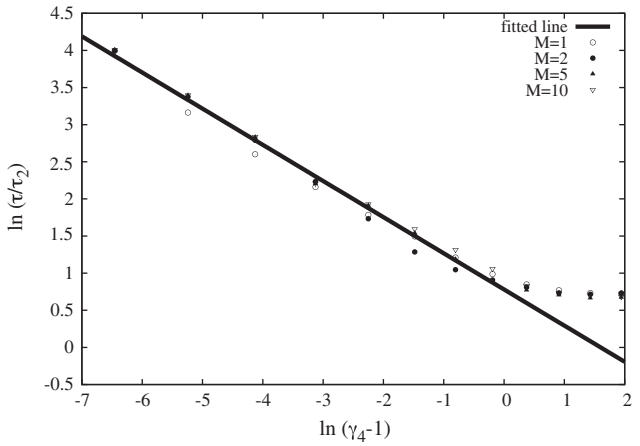

Fig. 5. Scatterplot of τ/τ_2 vs. γ_4 of the x-mode for the x^2y^2 model. The straight line is a fit using Eq. (12).

(c is a constant). From the analytic approximation to ACF for the x^4 model at low temperature (Eq. (9)), we can also calculate τ, μ_2, and μ_4, and we find $c = \pi$. 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 τ, τ_2, and γ_4 (Eq. (12)) 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 γ_4 approaches 1 as T^2. Thus τ_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 γ_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 γ_4 saturates to a constant as $T^{-1/2}$, leaving only the variation in τ_2 to account for the change in lifetime. Thus the lifetime at high T, is governed by the behavior of τ_2 giving $\tau \approx T^{-1/4}$.

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 $\mu_2 \approx 2T/\ln T + 1/2$ and $\mu_4 \approx 4T^2/\ln T + 4T/M$ which makes γ_4 go as $\ln T$. This cancels a $\ln T$ dependence in τ_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 τ 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.

5. Analysis for low dimensional models

From the present 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 (μ_2 and μ_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 τ (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 increasing temperature (as one would typically expect of a the *mode-resolved* DOS 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, $\gamma_4 \to 1$, while at high temperatures $\gamma_4 \to 2.2$ (for this model). Recalling γ_4 as the (dimensionless) ratio μ_4/μ_2^2, it is aptly designated as a "shape parameter" of the DOS.

The DOS of each of the two modes in the x^2y^2 model (Fig. 9) is only somewhat more complex than that of the single mode in 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 τ 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 ω_0 and broadened to a width Ω. Both the oscillator frequency and width depend on temperature. At low temperatures, $\Omega \ll \omega_0$. Obtaining the lifetime from the DOS (Eq. (5)) we have

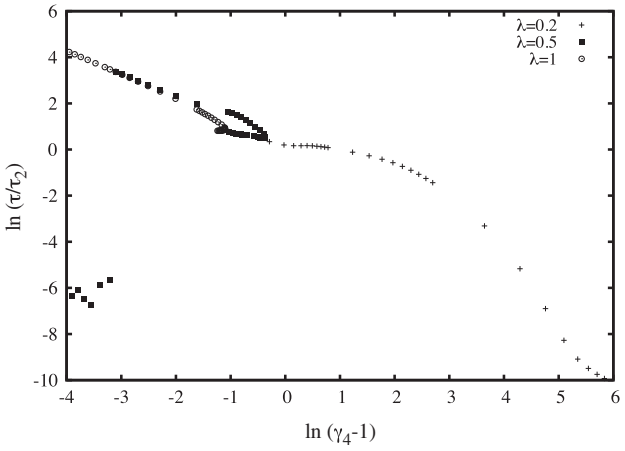

Fig. 6. Scatterplot of τ/τ_2 vs. $\gamma_4 - 1$ of the x-mode for the "cubic" model, showing irregular behavior as compared to the other models (Figs. 4 and 5).

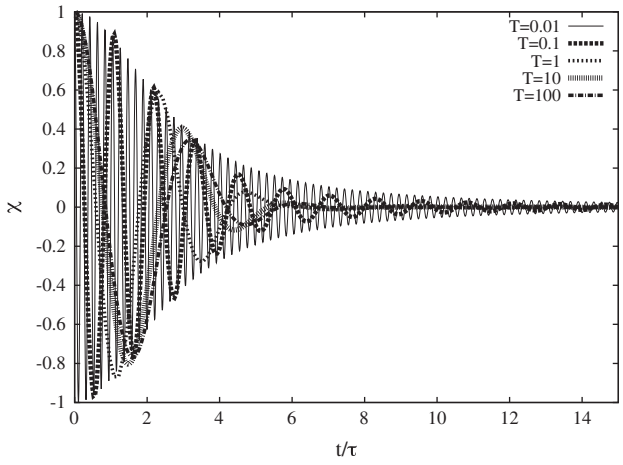

Fig. 7. Data collapse of ACF for the x^4 model (as explained in the text).

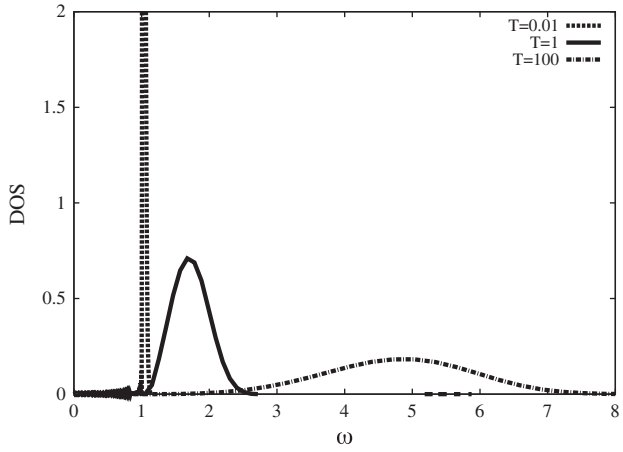

Fig. 8. Density of states at various temperatures for the x^4 model.

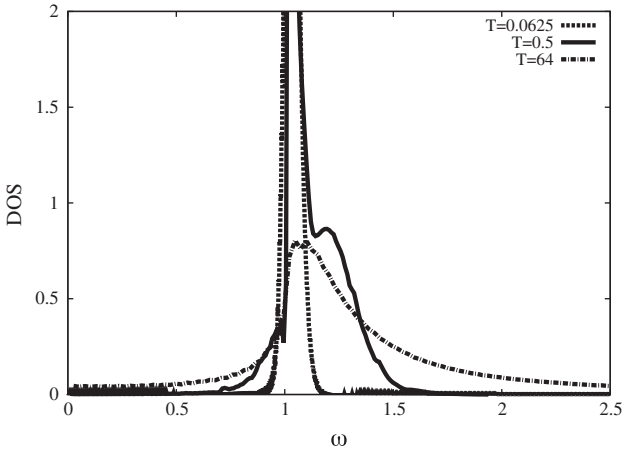

Fig. 9. Density of states of the y-mode at $M = 1$ for the x^2y^2 model.

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

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 Ω and ω_0 among the two relations gives

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

just as we found in Eq. (12). 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 Ω and height Ω^{-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 τ is tracked by that of τ_2, so that

$$\tau \approx \tau_2$$

which is consistent with the high-T 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. 6) does not capture the behavior.

Finally we note that γ_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, γ_4 is

$$\gamma_4 = \frac{\langle x^2\rangle\langle f^2\rangle}{\langle xf\rangle^2} \tag{13}$$

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 harmonic. That is, we construct the function

$$\alpha = \langle (f + kx)^2\rangle / \langle f^2\rangle \tag{14}$$

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, $k_{\text{eff}} = -\langle xf\rangle/\langle x^2\rangle = \mu_2$, from which the degree of anharmonicity is

$$\alpha_{\min} = 1 - \gamma_4^{-1} \tag{15}$$

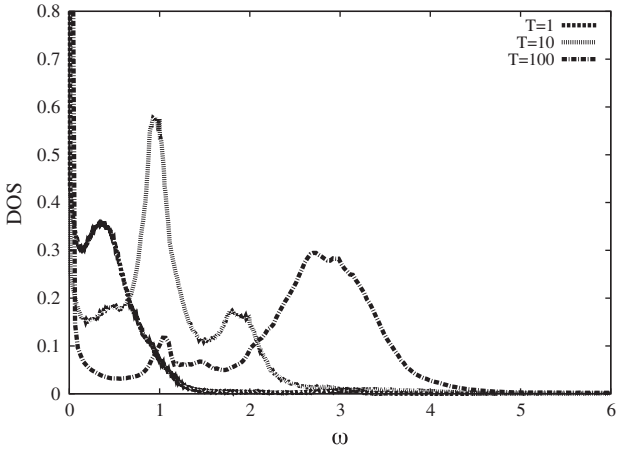

Fig. 10. Density of states of the x-mode at $\lambda = 0.2$ and various temperatures for the cubic model.

showing how the deviation $\gamma_4 - 1$ is directly related to the temperature-dependent anharmonicity of the system, which highlights again the significance of the observed trend in Eq. (12).

6. Reevaluation of the lattice models at fourth-moment

Armed by new insights about the fourth-moment approximation, we return to the lattice model originally explored by DD. This model is based a continuous vector-like quantity defined on a three-dimensional lattice. The underlying lattice structure is simple cubic ($L \times L \times L$, with L^3 sites) with periodic boundaries. Nearest neighbor lattice sites are connected by anharmonic potentials such that the Hamiltonian of the system is given by

$$H = \sum_i \frac{1}{2}|\vec{p}_i|^2 + \sum_{\langle i,j \rangle} V(\vec{d}_i - \vec{d}_j) \tag{16}$$

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

$$V(\vec{d}) = \frac{1}{2}|\vec{d}|^2 + \frac{1}{24}|\vec{d}|^4 \tag{17}$$

The coupling occurs for every pair (i,j) which are nearest-neighbors.

As in DD, we resolve the site-by-site dynamics onto normal mode coordinates, which is quite easy to do in this case. The resulting mode-resolved DOS are quite simple, as would be expected for the usual case of mode-resolved DOS for real solids, with the exception that the quartic potential becomes stiffer with increasing amplitude and results in an up-shift of the mode with temperature. (In a more realistic model, the potential should soften with amplitude and result in a down-shift.) This difference should not be important in terms of the ability of the moments to capture the overall behavior, because the moments will reflect the shift correctly whichever way it goes.[6]

We performed numerical calculations for systems with different size ($L = 2$, 4, and 8) at a wide range of temperatures (from 2^{-9} to 2^{10} for the smaller systems and down to a temperature of 2^{-1} for $L = 8$).

Improvement of the fourth-moment approximation over the second-moment in predicting τ can be gauged by scatter-plotting, as before, $\ln(\tau_k/\tau_{k,2})$ vs. $\ln(\gamma_{k,4} - 1)$, as in Fig. 11. There is some scatter among the data, but generally they span a straight line with the same slope $(-1/2)$ as seen in the simple low-dimensional models.

The mode-resolved DOS for the a typical mode for $L = 8$ is displayed at varying temperatures in Fig. 12. We see in the lattice model the same evolution of broadening and up-shift with temperature that was seen in the low-dimensional models, and the degree of change in the DOS is easily simple enough to be described well by two parameters.

(We emphasize again that our analysis is done on a mode-by-mode basis, that the DOS shown in the figure is for a *single mode*, and that this DOS is very much like what one sees in an experiment that selects by mode, such as inelastic neutron scattering. By contrast, the *total* DOS, which is composed of all modes together, is much more structured.)

[6] There is one other more subtle way in which all of the models discussed here do not capture an important aspect of vibrations in real solids. The models here all (except for the cubic model) have only *fourth order* anharmonicity; that is to say, no *third order* anharmonicity. This was done both to connect to the historically interesting and well-studied 4th-order anharmonic FPU (Fermi–Pasta–Ulam) model [8] as well as to make possible analytical treatment of the ensemble averages. Third-order anharmonicity is clearly important in solids but including such terms in the polynomial approximation of the potential would introduce divergent integrals in the ensemble averages. A systematic study of third- and fourth-order anharmonicities must be done in the context of a more realistic potential which does not have such divergent integrals. For example, considering a solid with Lennard–Jones or some other more realistic potential [9].

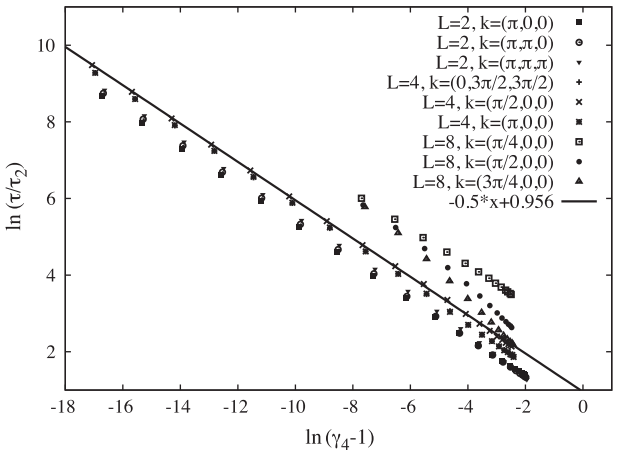

Fig. 11. Scatterplot of $\ln \tau_k/\tau_{k,2}$ vs. $\ln(\gamma_{k,4} - 1)$ for representative normal modes of systems of varying size. For clarity of illustration, not all of the modes are plotted, but all of the modes not displayed here have behavior very similar to those shown.

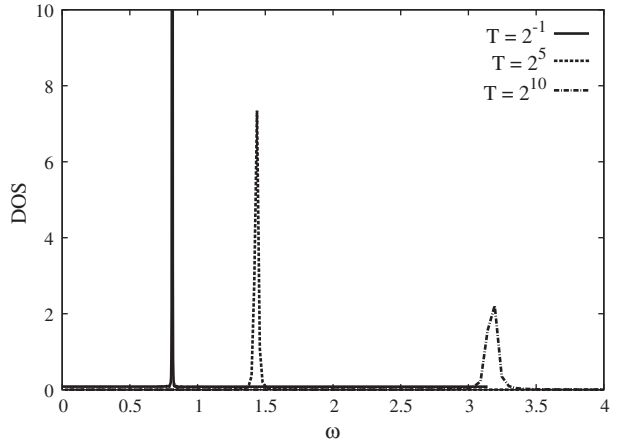

Fig. 12. Density of states for $\vec{k} = (0, 0, \pi/4)$ in the $L = 8$ system at a low, medium, and high temperature.

7. Conclusions

We have investigated using low-dimensional models the proposal that the mode lifetime in equilibrium might be approximated from the two lowest, non-vanishing moments of the Liouvillian. For the generic case of a DOS dominated by a single peak broadened and shifted, as is the case for the x^4 and x^2y^2 models and the non-linear lattice model presented here, we see that the fourth-moment approximation works well. In the case of the "cubic" model with two degrees of freedom, 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.

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