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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.

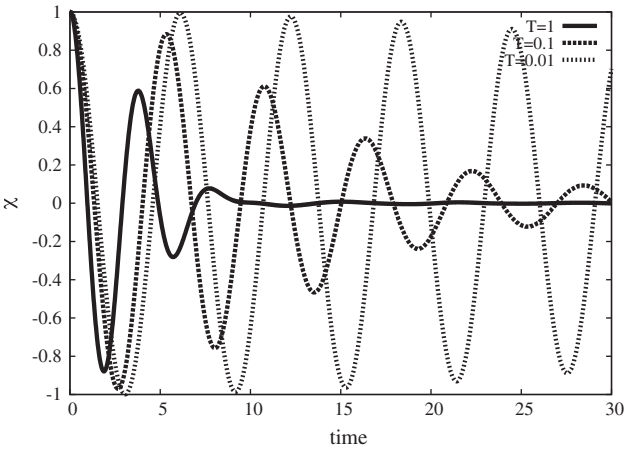

Fig. 1. The ACF at three temperatures for the x^4 model.

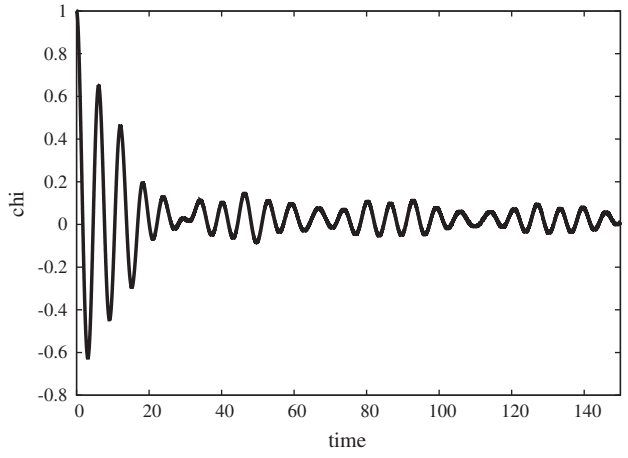

Fig. 2. The ACF of the x-mode at $\lambda = 0.5$ and $T = 0.2$ for the "cubic" model.

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