Asymptotic solutions for localized vibrational modes in strongly anharmonic periodic systems

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Sievers and Takeno (ST) have recently argued that a *periodic* system of particles interacting through harmonic and quartic anharmonic potentials can exhibit odd-parity *localized* vibrational modes for sufficiently strong anharmonicity. In the present paper, we demonstrate that this behavior is a fundamental property of the underlying pure anharmonic system. For a monatomic one-dimensional periodic chain of particles interacting via nearest-neighbor *purely anharmonic* potentials of any even order, it is shown that within the rotating-wave approximation of ST, the odd-parity vibrational mode pattern of a simple linear triatomic molecule, and the even-parity mode pattern of a simple diatomic molecule, yield *exact* solutions of the classical equations of motion in the asymptotic limit of increasing order of anharmonicity. These localized vibrational modes may be centered on any lattice site. The odd-parity solution remains a very good approximation even for the lowest-order case of pure quartic anharmonicity, whereas the new even-parity solution requires a relatively minor correction for this case. Our results are obtained by directly studying the equations of motion. For a system with just harmonic plus sufficiently strong quartic anharmonic interactions, our odd-parity solution corresponds to that found by ST using lattice Green's-function techniques.

I. INTRODUCTION

Recent theoretical studies[1-3] of the vibrational dynamics of periodic arrays of atoms interacting via strongly anharmonic potentials have argued for the existence of localized and resonance vibrational modes, reminiscent of those which are known to occur in purely harmonic lattices containing point defects. These striking results were obtained by analytic studies of the classical systems, within a "rotating-wave" approximation (RWA) whereby only a single frequency component was included in the time dependence. Within this approximation, spatially inhomogeneous, stable solutions were found, having amplitude-dependent frequencies either above (localized mode) or below (resonant mode) the maximum harmonic phonon frequency, depending on whether the anharmonicity was "hard" or "soft." Furthermore, it was argued in Refs. 1 and 2 that the configurational entropy arising from the fact that these new excitations can occur at any lattice site, leads to a temperature-dependent equilibrium density analogous to that for vacancies. It is expected that these excitations are mobile, thereby restoring the system's periodicity. The picture which emerges is that the vibrational spectrum at $T=0$ K is dominated by homogeneous plane-wave-like anharmonic phonons, but with increasing temperature the intrinsic anharmonic localized or resonant modes are created and should be included in describing the dynamical properties.

In Ref. 4, these ideas were extended and applied to the problem of the anomalous low-temperature specific heat of glasses. It was postulated that disorder results in anharmonic resonant modes moving diffusively, and this was shown to lead to a linear temperature dependence of the specific heat, as is observed. The theory was able to provide a consistent phenomenological description of the low-temperature specific-heat data for a wide variety of glassy materials ranging in type from covalent, van der Waals, ionic, metallic, inorganic, and organic.

The analytic work of Sievers and Takeno in Ref. 1 involved a simple linear monatomic chain of particles interacting via nearest-neighbor harmonic and quartic anharmonic springs, denoted here by k_2 and k_4, respectively. By making the RWA and using harmonic lattice Green's-function techniques, these authors argued that for sufficiently strong anharmonicity, stable odd-parity localized excitations are possible at any lattice site, with a frequency given by

$$\omega^2 \approx \frac{3}{m}(k_2 + \tfrac{27}{16}k_4 A^2) , \tag{1}$$

where m is the mass of each atom and A is the vibrational amplitude of the "central" atom in the mode pattern. This pattern is $\approx A(\ldots,0,-\frac{1}{2},1,-\frac{1}{2},0,\ldots)$, with the approximation being better for larger $(k_4/k_2)A^2$. More precisely, this solution was argued to be valid provided the inequality $3k_4A^2/(4k_2) \gg \frac{4}{27}$ is satisfied.[5] Again it is to be emphasized that this mode pattern may be centered on any lattice site. We have found via molecular dynamics simulations, which of course do not employ the rotating-wave approximation, that the above solution is indeed well realized.[6]

In the present paper it is shown that within the RWA and for a *purely anharmonic* lattice having anharmonicity of any even order, the above mode pattern plays a special role, in that it gives an *exact* solution to the equations of motion in the limit of increasing order of anharmonicity. It will be seen that this mode pattern, which is the most localized odd-parity displacement pattern consistent with

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the center of mass remaining at rest, is still a very good approximation for the "worst" case, a lattice with just pure k_4 anharmonicity. In the presence of harmonic forces, this solution breaks down in favor of (delocalized) plane waves, so that only for sufficiently strong anharmonicities, as determined through inequalities analogous to that given in the preceding paragraph, can one obtain a valid localized-mode solution.

The above results are obtained and discussed in Sec. II, by means of a direct study of the equations of motion. In Sec. III A they are generalized so as to encompass an arbitrary superposition of even-order anharmonicity. A different generalization is made in Sec. III B, where we demonstrate the existence of a new, *even* parity, localized mode in strongly anharmonic periodic systems. The paper is concluded in Sec. IV.

II. THEORY

We consider a linear monatomic chain of particles of mass m, interacting via nearest-neighbor purely anharmonic springs k_r of even order (i.e., even r). Considering just longitudinal displacements and letting $u_n(t)$ denote the displacement of the nth particle from its equilibrium position, we write the potential energy as

$$V=\frac{k_r}{r}\sum_n (u_{n+1}-u_n)^r . \tag{2}$$

Writing the equation of motion for the nth particle and substituting the trial solution $u_n(t)=A\xi_n\cos(\omega t)$, we have

$$\begin{aligned}-\omega^2 m\xi_n A\cos(\omega t)=k_r A^{r-1}&\cos^{r-1}(\omega t)\\ &\times[(\xi_{n+1}-\xi_n)^{r-1}\\ &\quad-(\xi_n-\xi_{n-1})^{r-1}] .\end{aligned} \tag{3}$$

The relative displacement pattern is $\{\xi_n\}$, and A is the overall amplitude. We now follow Ref. 1 and make the RWA, keeping just the $\cos(\omega t)$ term on the right-hand side of this equation. The identity

$$\cos^p(\theta)=\frac{p!}{2^{p-1}}\sum_{k=1}^{p}\frac{\cos(k\theta)}{[(p+k)/2]![(p-k)/2]!} \quad (p,k\ \ \text{odd}) , \tag{4}$$

gives

$$\cos^{r-1}(\omega t)=C_r\cos(\omega t)+\text{higher harmonics} , \tag{5}$$

where the coefficient C_r is

$$C_r=\frac{(r-1)!}{2^{r-2}(r/2)!(r/2-1)!} . \tag{6}$$

Retaining just the first term in Eq. (5) and substituting into Eq. (3), we have

$$\omega_r^2=\frac{k_r C_r A^{r-2}}{m\xi_n}[(\xi_n-\xi_{n+1})^{r-1}+(\xi_n-\xi_{n-1})^{r-1}] , \tag{7}$$

where a subscript r has been added to the frequency ω, for clarity.

We now seek highly localized, odd-parity solutions to the above system of equations. Accordingly, we let the mode be centered on the site $n=0$ and take $\xi_0=1$, $\xi_{-n}=\xi_n$, and $|\xi_n|\ll|\xi_1|$ for $|n|>1$. Equation (7) for $n=0$ then yields

$$\omega_r^2=\frac{2k_r C_r A^{r-2}}{m}(1-\xi_1)^{r-1} , \tag{8}$$

and for $n=1$ we have

$$\omega_r^2\approx\frac{k_r C_r A^{r-2}}{m\xi_1}[\xi_1^{r-1}+(\xi_1-1)^{r-1}] . \tag{9}$$

The above two equations must, of course, give the same frequency, and we see clearly that $\xi_1=-\frac{1}{2}$ will be an approximate solution. Substituting this value of ξ_1, we obtain for $n=0$

$$\omega_r^2=\frac{2k_r C_r A^{r-2}}{m}\left[\frac{3}{2}\right]^{r-1} \tag{10}$$

and for $n=1$

$$\omega_r^2=\frac{2k_r C_r A^{r-2}}{m}\left[\frac{3}{2}\right]^{r-1}[1+(\tfrac{1}{3})^{r-1}] . \tag{11}$$

Equations (10) and (11) are obviously identical in the limit of increasing anharmonic order r. Moreover, even for the worst case $r=4$, Eq. (11) only differs from Eq. (10) by the factor $1+\frac{1}{27}\approx 1$. Substituting the explicit expression for C_r given by Eq. (6), we thus obtain the squared frequency for the odd-parity localized mode in a purely anharmonic linear chain with anharmonicity of order r:

$$\omega_r^2\approx\frac{2k_r A^{r-2}}{m}\left[\frac{3}{2}\right]^{r-1}\frac{(r-1)!}{2^{r-2}(r/2)!(r/2-1)!} . \tag{12}$$

In particular, we have for the case of pure quartic anharmonicity

$$\omega_4^2\approx\frac{81k_4A^2}{16m} , \tag{13}$$

and we have found by numerical molecular dynamics simulations,[6] which involve no RWA, that this solution is accurate.

Of course, for consistency we must still investigate the validity of our assumption on the smallness of the $\{\xi_n\}$ for $|n|>1$. We will first study Eq. (7) for $n=2$, namely

$$\omega_r^2=\frac{k_r C_r A^{r-2}}{m\xi_2}[(\xi_2-\xi_3)^{r-1}+(\xi_2-\xi_1)^{r-1}] . \tag{14}$$

Setting $\xi_2-\xi_1\approx\frac{1}{2}$ and neglecting $\xi_2-\xi_3$ compared with this, we obtain

$$\omega_r^2\approx\frac{k_r C_r A^{r-2}}{m\xi_2 2^{r-1}} . \tag{15}$$

In order that we have a solution, this equation must give the same frequency as Eq. (10). This yields an expression for ξ_2:

$$\xi_2 \approx \frac{1}{(2)3^{r-1}} . \quad (16)$$

Obviously, $\xi_2 \to 0$ in the limit of large r. Even in the $r=4$ worst case we have $\xi_2 = \frac{1}{54} \ll \frac{1}{2} = |\xi_1|$. Finally, we consider Eq. (7) for arbitrary $|n| \geq 2$. In analogy with the $n=2$ case just treated, we assume $|\xi_{n+1}| \ll |\xi_n|$ for all $n \geq 2$. Equation (7) then leads to the recursion relation for $n \geq 2$

$$\frac{\xi_{n+1}}{\xi_n} \approx \left[\frac{\xi_n}{\xi_{n-1}} \right]^{r-1} ,$$

so that all of the ξ_n's for $|n| \geq 2$ very rapidly approach zero with increasing n, even for the $r=4$ worst case. Hence, the localized relative displacement pattern $(\ldots,0,-\frac{1}{2},1,-\frac{1}{2},0,\ldots)$ is indeed an exact solution in the limit of large r, with the corresponding squared frequency being given by Eq. (12). Moreover, this solution is seen to give a very good approximation even in the $r=4$ worst case of pure quartic anharmonicity.

III. GENERALIZATIONS

A. Arbitrary superposition of even-order anharmonicity

Because we have obtained the same localized relative displacement pattern for every (even) order of anharmonicity, we can simply use superposition to get an expression for the corresponding localized mode frequency when the anharmonicity is an arbitrary admixture of such terms. Thus, for

$$V = \sum_{r \text{ even}} \frac{k_r}{r} \sum_n (u_{n+1} - u_n)^r \quad (17)$$

we obtain

$$\omega^2 \approx \frac{2}{m} \sum_{r=2,4,6,\ldots} k_r C_r (\tfrac{3}{2})^{r-1} A^{r-2} , \quad (18)$$

where a harmonic term (k_2) has also been included. Without the harmonic term, Eq. (18) gives a very good approximation, according to the arguments presented above. However, it is easy to see that the localized solution $A(\ldots,0,-\frac{1}{2},1,-\frac{1}{2},0,\ldots)$ does *not* solve the purely harmonic equations of motion; in that case one recovers the familiar homogeneous plane-wave solutions. Hence, for Eq. (18) to be a good approximation in the presence of nonzero k_2, the anharmonic terms must be sufficiently large relative to the harmonic term. Note that the anharmonic terms involve both the anharmonic force constants *and* the mode amplitude. In particular, for the case when only harmonic and quartic anharmonic terms (k_2,k_4) are present, Eq. (18) reduces to Eq. (1), which was obtained in Ref. 1 and was argued there to be valid when the inequality $3k_4A^2/(4k_2) \gg 4/27$ holds.

B. Even-parity localized modes

We now investigate the possibility of a new type of localized mode, namely one of even parity ($\xi_{-n} = -\xi_n$), in the periodic chain described by the potential given by Eq. (2). The most localized such mode has the relative displacement pattern $(\ldots,0,-1,1,0,\ldots)$. It is convenient to change the particle labeling such that the two particles with nonzero displacements are labeled $n=\pm 1$, and there is no particle labeled $n=0$. We then have $\xi_1 = 1 = -\xi_{-1}$. The substitution of this pattern into the $n=\pm 1$ versions of Eq. (7) leads to the frequency condition

$$\omega_r^2 \approx \frac{k_r C_r A^{r-2}}{m}(1+2^{r-1}) \text{ (even parity)} . \quad (19)$$

The approximation arises from the fact that the $|n|>1$ version of Eq. (7) is not exactly satisfied by the above displacement pattern, analogous to the situation discussed above for the odd-parity case. The $n=2$ version of Eq. (7) is given by Eq. (14), and an argument like that leading to Eq. (15) yields the following approximate expression for ξ_2 for the even-parity case:

$$\xi_2 \approx \frac{-1}{1+2^{r-1}} . \quad (20)$$

This is the even-parity analog of Eq. (16), and we again see that $\xi_2 \to 0$ in the large-r limit; hence, the localized relative displacement pattern $(\ldots,0,-1,1,0,\ldots)$ is an exact solution in this limit. Note that for the worst case ($r=4$) we have $\xi_2 \approx -\frac{1}{9}$, which is small compared to 1. However, in the corresponding pure k_4 case for the *odd*-parity localized mode, we obtained $\xi_2 \approx \frac{1}{54}$, which was to be compared with $\frac{1}{2}$. Thus, our approximate even-parity localized-mode solution for the pure k_4 case, while a fairly good approximation, is less good than the corresponding odd-parity local-mode solution.

It is straightforward to obtain a much more accurate approximation for the pure k_4 case. By equating the $n=1$ and $n=2$ versions of Eq. (7) for $r=4$, and neglecting $|\xi_3|$ compared with $|\xi_2|$, one readily obtains $\xi_2 = -0.166 \approx -\frac{1}{6}$. Using the latter value and the fact that $C_4 = \frac{3}{4}$, we find that the squared frequency is then given by

$$\omega_4^2 \approx \frac{k_4 A^2}{m} 6[1+(\tfrac{7}{12})^3] \text{ (even parity)} . \quad (21)$$

For a given amplitude A, the frequencies obtained from Eqs. (19) and (21) differ by just 3%. To investigate the magnitude of ξ_3, we use the $n=3$ version of Eq. (7), taking $\xi_2 = -\frac{1}{6}$ and assuming $|\xi_3|$ and $|\xi_4|$ are each $\ll |\xi_2|$. This gives the squared frequency as $3k_4A^2/[4m(6)^3\xi_3]$, and comparison with Eq. (21) then yields $\xi_3 \approx 1/2071 \approx 0$.

Summarizing, the even-parity localized-mode displacement pattern for the pure k_4 case is accurately given by $A(\ldots,0,\frac{1}{6},-1,1,-\frac{1}{6},0,\ldots)$, with the corresponding squared frequency given by Eq. (21). For the higher-order anharmonicity cases $r=6,8,\ldots$, the earlier approximations of Eqs. (19) and (20) are excellent, and the mode pattern is very close to its asymptotic limit $A(\ldots,0,-1,1,0,\ldots)$.[7] Direct numerical molecular-dynamics simulations have verified the accuracy of the above solution for the pure k_4 case.[6]

IV. CONCLUSION

This work has explored the nature of localized vibrational modes in strongly anharmonic periodic one-dimensional systems. By directly studying the classical equations of motion, we have shown that in the asymptotic limit of increasing even orders of nearest-neighbor anharmonic interactions, the "molecular"-like odd-parity and even-parity localized displacement patterns $A(\ldots,0,-\frac{1}{2},1,-\frac{1}{2},0,\ldots)$ and $A(\ldots,0,-1,1,0,\ldots)$ are exact solutions within the rotating-wave approximation. For the lowest-order case (pure quartic anharmonicity), the above odd-parity solution remains a very good approximation, whereas the above pure quartic even-parity mode solution requires a relatively small correction. These modes may be centered on any lattice site. For a system containing just harmonic (k_2) and quartic (k_4) terms in the potential energy, the odd-parity solutions correspond to those found previously in Ref. 1 for the case of sufficiently strong anharmonicity.

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[5]This inequality and the frequency condition given here as Eq. (1) were given in Refs. 1 and 3 in terms of a quantity $\alpha = A/2$. It is the quantity A which is the actual amplitude of the central particle.

[6]J. B. Page, S. Bickham, A. J. Sievers, O. F. Sankey, and J. P. Sethna (unpublished).

[7]The *odd*-parity localized-mode relative displacement pattern $(\ldots,0,-\frac{1}{2},1,-\frac{1}{2},0,\ldots)$ discussed in Sec. II was seen there to be very accurate even in the $r=4$ worst case. Indeed, if one investigates the corrections for $r=4$, just as we have done here for the $r=4$ even-parity localized mode, one finds that the above pattern is only corrected to $(\ldots,0,0.02,-0.52,1,-0.52,0.02,0,\ldots)$.