Journal of Statistical Physics, Vol. 78, Nos. 3/4, 1995

New Equipartition Results for Normal Mode Energies of Anharmonic Chains

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Received October 20, 1993; final July 7, 1994

The canonical and microcanonical distributions of energy among the normal modes of an anharmonic chain with nearest-neighbor interactions and free ends are examined. If the interparticle potential is an even function, then energy is distributed uniformly among the normal modes at all energy densities. If the interparticle potential is not an even function but includes quadratic, cubic, and quartic terms, then the energy sharing among the normal modes is also uniform in both the small- and large-energy density limits. At large energies, in this latter case the energy per normal mode scales as the square root of the energy density. Thus we find equipartition of energy among the normal modes of an anharmonic chain. The sum of the normal mode energies is less than the total energy of the chain.

KEY WORDS: Equipartition of energy; ergodic hypothesis; anharmonic chains; normal modes; nonlinear lattice dynamics.

1. INTRODUCTION

In the harmonic approximation the vibrations of a lattice can be represented by a superposition of normal mode vibrations.[1] The equilibrium statistical mechanics principle of equipartition of energy asserts that in the harmonic approximation the energy of the lattice should be equally shared among these normal modes.[2] This result is in agreement with experimental measurements on the specific heat of crystals in a temperature

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0022-4715/95/0200-1039$07.50/0

regime where the classical approximation is valid (see, for example, ref. 3). However, equilibrium statistical mechanics is founded on the postulate of *a priori* equal probabilities for all microstates subject to the macroscopic constraints (e.g., constant energy, constant pressure, constant temperature) and there is no dynamical justification for this postulate in the case of an isolated harmonic chain with two or more degrees of freedom.

The traditional dynamical justification of equilibrium statistical mechanics rests on establishing the ergodic hypothesis. This hypothesis states that in an isolated system the dynamical trajectory uniformly visits (or comes arbitrarily close to) all points on the energy surface.[4] However, the harmonic lattice at constant energy (with two or more degrees of freedom) is not ergodic. The energy of each mode is itself a conserved dynamical quantity and hence the dynamics is confined to a lower-dimensional surface than the energy surface. More generally, systems with more than one degree of freedom that can be decoupled into normal modes are not ergodic.

It used to be assumed that the introduction of small nonlinearities in the interparticle interactions could provide a dynamical basis for energy sharing and ergodicity while still (to a good approximation) preserving the equipartition principle among the normal modes. Commencing with the classic numerical studies of Fermi, Pasta, and Ulam,[5] it was found that the introduction of small nonlinearities did not, in fact, provide a mechanism for uniform energy sharing among the normal modes. Concurrent and subsequent algebraic work now known as the KAM theorem (see, for example, ref. 6 for a discussion in the context of anharmonic chains) showed that the inclusion of small nonlinearities is in general insufficient to bring about ergodicity. As demonstrated in the numerical work of Henon and Heiles,[7] larger nonlinearities are required to destroy the conserved dynamical quantities and thus allow the possibility of ergodicity. However, at larger energies the total system energy can no longer be represented by a sum of the normal mode energies and it is far from clear in this case if equipartition of energy among the normal modes should still apply—even if the system is now ergodic. One possibility is to define a new set of nonlinear mode energies, each of which contains a normal mode energy as a subset but the sum of which is equal to the total system energy. This prescription is, however, not unique and numerical studies have demonstrated no energy equipartition among such a set.[8] Furthermore, Tolman's generalized equipartion principle[2] when applied to anharmonic chains defines a new set of quantities (not identifiable as modes) among which equipartition must occur. Despite this, numerous researchers have pursued the question of uniform energy sharing among the normal modes

of anharmonic chains in higher nonlinear regimes (see, for example, refs. 6, 9, and 10 and references therein). Moreover, equipartition of energy among the normal modes has been postulated as a test for ergodicity in some of these studies. A major aim of this research has been to establish whether or not there is a critical energy density threshold above which equipartition is obtained.

It is clear that normal mode energies and the principle of equipartition of energy have been and still are important concepts in analyzing both linear and nonlinear systems. Yet to our knowledge, no one has pursued the question of *whether or not there should be* equipartition of energy among the normal modes of an anharmonic lattice *assuming at the outset* that the postulate of *a priori* equal probabilities for all microstates is satisfied (e.g., assuming ergodicity from the outset). This important question is the focus of our work. We find that if the interparticle potential is an even function, then energy is distributed uniformly among the normal modes at all energy densities. If the interparticle potential is not an even function but includes quadratic, cubic, and quartic terms (the generic case for an archetypical anharmonic chain), then the energy sharing among the normal modes is also uniform in both the small- and large-energy density limits. We thus come to the rather surprising conclusion that even in a regime where most of the energy is contained in the nonlinear terms there is still equipartition of the remaining energy among the normal modes. As an added result, we identify a set of nonlinear mode energies for the quadratic plus quartic nonlinear Hamiltonian which equipartition the total system energy.

2. MODEL ANHARMONIC LATTICE

We consider a chain of $N=(2n+1)$ equimass particles coupled by nearest-neighbor linear and nonlinear forces with free ends. Let x_j denote the displacement of the jth particle from its equilibrium position and p_j denote its conjugate momentum; then the Hamiltonian (in dimensionless variables) describing the chain is given by

$$H = H_0 + \sum_{j=-n}^{n} f(x_{j+1} - x_j) \tag{1}$$

where

$$H_0 = \sum_{j=-n}^{n} \frac{p_j^2}{2} + \sum_{j=-n}^{n} \frac{1}{2}(x_{j+1} - x_j)^2 \tag{2}$$

is the harmonic Hamiltonian and $f(x_{j+1}-x_j)$ is an arbitrary anharmonic function which depends only on the difference $(x_{j+1}-x_j)$. The free-end boundary conditions are given by

$$\begin{aligned} x_{-n} &= x_{-(n+1)} \\ x_n &= x_{n+1} \end{aligned} \tag{3}$$

The harmonic Hamiltonian with free end boundaries may be diagonalized by the normal mode transformations

$$\begin{aligned} a_0 &= \frac{1}{\sqrt{N}} \sum_{j=-n}^{n} x_j \\ a_m &= \left(\frac{2}{N}\right)^{1/2} \sum_{j=-n}^{n} x_j \cos\left(\frac{\pi j 2m}{N}\right), \qquad m = 1, 2, \ldots, n \\ b_m &= \left(\frac{2}{N}\right)^{1/2} \sum_{j=-n}^{n} x_j \sin\left(\frac{\pi j(2m-1)}{N}\right), \qquad m = 1, 2, \ldots, n \end{aligned} \tag{4}$$

together with the identities

$$\begin{aligned} \sum_{j=-n}^{n} \cos\left(\frac{\pi j 2m}{N}\right) \cos\left(\frac{\pi j 2m'}{N}\right) &= \frac{N}{2}\delta_{m,m'} \\ \sum_{j=-n}^{n} \sin\left(\frac{\pi j(2m-1)}{N}\right) \sin\left(\frac{\pi j(2m'-1)}{N}\right) &= \frac{N}{2}\delta_{m,m'} \end{aligned} \tag{5}$$

Explicitly

$$H_0 = \frac{1}{2}\left(\dot{a}_0^2 + \sum_{m=1}^{n} \dot{a}_m^2 + \dot{b}_m^2\right) + \frac{1}{2}\left(\sum_{m=1}^{n} \omega_{2m}^2 a_m^2 + \omega_{2m-1}^2 b_m^2\right) \tag{6}$$

where the normal mode frequencies are defined by

$$\omega_k = 2 \sin\left(\frac{\pi k}{2N}\right) \tag{7}$$

Note that a_0 does not appear in the Hamiltonian (6), and hence $\dot{a}_0 = (1/\sqrt{N})(\sum_{j=-n}^{n} \dot{x}_j)$ is a constant of the motion. This is simply interpreted by noting that the center-of-mass momentum is conserved. The harmonic Hamiltonian is now a sum of normal mode energies, $H_0 = \sum_{k=0}^{N-1} \varepsilon_k$, where

$$\varepsilon_k = \tfrac{1}{2}\dot{c}_k^2 + \tfrac{1}{2}\omega_k^2 c_k^2 \tag{8}$$

$c_0 = a_0$, $c_{2m} = a_m$, and $c_{2m-1} = b_m$ for $m = 1, 2, \ldots, n$.

3. CANONICAL ENSEMBLE AVERAGE MODE ENERGIES

In this section we describe the calculation of the canonical averages of the mode energies ε_k. The canonical averages are defined by

$$\langle \varepsilon_k \rangle = \frac{1}{Z(N,\beta)} \int_{-\infty}^{\infty} \prod_{i=-n}^{n} dp_i\, dx_i\, \varepsilon_k \exp(-\beta H) \tag{9}$$

where the normalization is the partition function

$$Z(N,\beta) = \int_{-\infty}^{\infty} \prod_{i=-n}^{n} dp_i\, dx_i \exp(-\beta H) \tag{10}$$

We shall have need to refer to both the normalized $\langle \cdot \rangle$ and the unnormalized $\langle \cdot \rangle^*$ canonical ensemble averages in the following. The partition function for the anharmonic chain described by Eqs. (1)–(3) factors as

$$Z(N,\beta) = Z_p(N,\beta)\, Z_x(N,\beta) \tag{11}$$

where the momentum contribution is

$$Z_p(N,\beta) = \int_{-\infty}^{\infty} \prod_{i=-n}^{n} dp_i \prod_{i=-n}^{n} \exp\left(-\beta \frac{p_i^2}{2}\right) \delta\left(\frac{1}{N} \sum_{i=-n}^{n} p_i\right) \tag{12}$$

and the configurational contribution is

$$Z_x(N,\beta) = \int_{-\infty}^{\infty} \prod_{i=-n}^{n} dx_i \prod_{i=-n}^{n} \exp\left\{-\beta\left[\frac{1}{2}(x_{i+1}-x_i)^2 + f(x_{i+1}-x_i)\right]\right\} \times \delta\left(\frac{1}{N} \sum_{i=-n}^{n} x_i - \bar{\phi}\right) \tag{13}$$

The delta functions appearing in Eqs. (12) and (13) ensure that the center of mass of the chain is held fixed (at $\bar{\phi}$); without this constraint the free energy would in general be infinite.

The momentum contribution readily simplifies after a transformation to the normal mode coordinates (the Jacobian of the transformation is unity) as follows:

$$\begin{aligned} Z_p(N,\beta) &= \int_{-\infty}^{\infty} \prod_{i=0}^{N-1} d\dot{c}_i \delta\left(\frac{\dot{c}_0}{\sqrt{N}}\right) \prod_{i=0}^{N-1} \exp\left(-\beta \frac{\dot{c}_i^2}{2}\right) \\ &= \prod_{i=1}^{N-1} \int_{\infty}^{\infty} \exp\left(-\beta \frac{\dot{c}_i^2}{2}\right) d\dot{c}_i \end{aligned} \tag{14}$$

The remaining integration is now trivial, resulting in

$$Z_p(N, \beta) = \left(\frac{2\pi}{\beta}\right)^{(N-1)/2} \tag{15}$$

The canonical average mode kinetic energy is now readily calculated as

$$\left\langle \frac{1}{2}\dot{c}_k^2 \right\rangle = \frac{1}{2\beta} \qquad \text{for} \quad k = 1, 2, \ldots, N-1 \tag{16}$$

in accordance with the equipartition principle.[2]

To simplify the configurational contribution we first introduce the relative coordinate and center-of-mass coordinate transformations

$$\begin{aligned} \phi_i &= x_{-n+i} - x_{-n+i-1} \qquad \text{for} \quad i = 1, 2, \ldots, N-1 \\ \phi_N &= \frac{1}{N}\sum_{i=-n}^{n} x_i \end{aligned} \tag{17}$$

It is a simple exercise to confirm that the Jacobian of the transformation is unity and the inverse transformation is defined by

$$x_{-n+i-1} = \sum_{j=1}^{N} A_{i,j}^{-1}\phi_j \qquad \text{for} \quad i = 1, 2, \ldots, N \tag{18}$$

where

$$A_{ij}^{-1} = \begin{cases} (j-N)/N & \text{for} \quad j \geqslant i, \quad j = 1, 2, \ldots, N-1 \\ j/N & \text{for} \quad j < i, \quad j = 1, 2, \ldots, N-1 \\ 1 & \text{for} \quad j = N \end{cases} \tag{19}$$

With the above transformations the configurational contribution to the partition function simplifies to

$$Z_x(N, \beta) = \int_{-\infty}^{\infty} \delta(\phi_N - \bar{\phi})\, d\phi_N \prod_{i=1}^{N-1} \int_{-\infty}^{\infty} \exp\left\{-\beta\left[\frac{\phi_i^2}{2} + f(\phi_i)\right]\right\} d\phi_i \tag{20}$$

It is convenient to write this as

$$Z_x(N, \beta) = z_0^{N-1} \tag{21}$$

where

$$z_0 = \int_{-\infty}^{\infty} \exp\left\{-\beta\left[\frac{\phi^2}{2} + f(\phi)\right]\right\} d\phi \tag{22}$$

Combining the normal mode transformations, Eq. (4), with the coordinate transformations defined by Eqs. (18) and (19), we can write the canonical ensemble average mode potential energies in the form

$$\begin{aligned}\left\langle \frac{1}{2}\omega_{2m}^2 a_m^2 \right\rangle &= \frac{\omega_{2m}^2}{N} \sum_{j,j'=-n}^{n} \cos\left(\frac{2\pi mj}{N}\right)\cos\left(\frac{2\pi mj'}{N}\right) B_{jj'} \\ \left\langle \frac{1}{2}\omega_{2m-1}^2 b_m^2 \right\rangle &= \frac{\omega_{2m-1}^2}{N} \sum_{j,j'=-n}^{n} \sin\left(\frac{(2m-1)\pi j}{N}\right)\sin\left(\frac{(2m-1)\pi j'}{N}\right) B_{jj'}\end{aligned} \tag{23}$$

where

$$B_{jj'} = \sum_{k,k'=1}^{N} A_{jk}^{-1} A_{j'k'}^{-1} \langle \phi_k \phi_{k'} \rangle \tag{24}$$

The canonical ensemble averages $\langle \phi_k \phi_{k'} \rangle = \langle \phi_{k'} \phi_k \rangle$ simplify as follows:

$$\langle \phi_i \phi_j \rangle = \begin{cases} (z_1/z_0)^2 & \text{for} \quad i \neq j \quad (\neq N) \\ z_2/z_0 & \text{for} \quad i = j \quad (\neq N) \\ (z_1/z_0)\bar{\phi} & \text{for} \quad i \neq j \quad (=N) \\ \bar{\phi}^2 & \text{for} \quad i = j \quad (=N) \end{cases} \tag{25}$$

where

$$z_k = \int_{-\infty}^{\infty} \phi^k \exp\left\{-\beta\left[\frac{\phi^2}{2} + f(\phi)\right]\right\} \qquad \text{for} \quad k = 0, 1, 2 \tag{26}$$

The canonical ensemble averages defined by Eqs. (23)–(26) appear to be cumbersome, but evaluating the sums leads to remarkable simplifications. We first consider the case where $f(\phi)$ is an even function. In this case the potential is also an even function and $z_1 = 0$. The canonical average mode potential energies now reduce to

$$\begin{aligned}\left\langle \frac{1}{2}\omega_{2m}^2 a_m^2 \right\rangle &= \frac{z_2}{2z_0} \\ \left\langle \frac{1}{2}\omega_{2m-1}^2 b_m^2 \right\rangle &= \frac{z_2}{2z_0}\end{aligned} \tag{27}$$

Hence the canonical average mode energy is the same for all modes and is given by

$$\langle \varepsilon_k \rangle = \frac{1}{2\beta} + \frac{z_2}{2z_0} \tag{28}$$

This result establishes that, starting with the assumptions of equilibrium statistical mechanics, energy will be uniformly shared among the normal modes of the anharmonic chain described by Eqs. (1)–(3) provided that the anharmonic function $f(\phi)$ is an even function of ϕ.

In the case of more general potentials there is equipartition of energy among half the modes (a_m) but not among the other half (b_m). The result for the a_m modes is

$$\left\langle \frac{1}{2}\omega_{2m}^2 a_m^2 \right\rangle = \frac{1}{2}\left[\frac{z_2}{z_0} - \left(\frac{z_1}{z_0}\right)^2\right] \quad \text{for} \quad m = 1, 2, \ldots, n \tag{29}$$

We have been unable to find explicit algebraic expressions for the canonical ensemble average potential energy in the b_m modes as a function of the number of particles in the chain. However, using the algebraic symbol manipulation package MAPLE, we have identified the following pattern of behavior:

$$\left\langle \frac{1}{2}\omega_{2m-1}^2 b_m^2 \right\rangle = \frac{1}{2}\left[\frac{z_2}{z_0} + d_m(N)\left(\frac{z_1}{z_0}\right)^2\right] \quad \text{for} \quad m = 1, 2, \ldots, n \tag{30}$$

where $d_1(3) = 1$; $d_1(N)$ increases monotonically with N; $d_m(N) < 0$ for $m > 1$; $d_j(N) > d_k(N)$ for $j < k$; and $\lim_{N \to \infty} d_n(N) \to -1$. We have also found that the sum rule

$$\sum_{m=1}^{n} \frac{1}{2}\omega_{2m}^2 \langle a_m^2 \rangle + \frac{1}{2}\omega_{2m-1}^2 \langle b_m^2 \rangle = \frac{n z_2}{z_0} \tag{31}$$

holds in general for both even and noneven potentials. It follows from Eq. (30) that we can expect approximate equipartition of energy among the b_m modes, too, in regimes where $(z_1/z_0)^2$ is negligible compared with (z_2/z_0).

4. MICROCANONICAL ENSEMBLE AVERAGE MODE ENERGIES

The microcanonical averages of the mode energies are defined by

$$\langle \varepsilon_k \rangle_\Omega = \frac{1}{\Omega(N, E)} \int_{-\infty}^{\infty} \prod_{i=-n}^{n} dp_i \, dx_i \, \varepsilon_k \delta(H - E) \tag{32}$$

where the normalization is the phase space volume of the energy shell,

$$\Omega(N, E) = \int_{-\infty}^{\infty} \prod_{i=-n}^{n} dp_i \, dx_i \, \delta(H - E) \tag{33}$$

It can be readily seen from Eqs. (10) and (33) that the canonical partition function $Z(N, \beta)$ is the Laplace transform of the energy shell volume $\Omega(N, E)$,

$$Z(N, \beta) = \int_0^\infty \Omega(N, E) e^{-\beta E} \, dE \tag{34}$$

Similarly the unnormalized ensemble averages are related by

$$\langle \varepsilon \rangle^* = \int_0^\infty \langle \varepsilon \rangle_\Omega^* \, e^{-\beta E} \, dE \tag{35}$$

Hence

$$\langle \varepsilon_k \rangle_\Omega = \frac{\mathscr{L}^{-1}[\langle \varepsilon_k \rangle^*]}{\mathscr{L}^{-1}[Z(N, \beta)]} \tag{36}$$

where $\mathscr{L}^{-1}$ denotes the inverse Laplace transform operator (with respect to β). We shall use Eq. (36) to calculate the microcanonical ensemble averages in the following.

We first note that it follows immediately from Eq. (36) that if $\langle \varepsilon_k \rangle^*$ are the same for all modes, then $\langle \varepsilon_k \rangle_\Omega$ are also the same for all modes. Hence from Eq. (28) we deduce that if the isolated anharmonic chain described by Eqs. (1)–(3), with $f(\phi)$ an even function of ϕ, was ergodic, then starting from any initial energy distribution, eventually all modes would acquire, on average, uniform energy content. This result would still hold if the sum of the average mode energies was much less than the total energy of the chain.

In more general potentials where $f(\phi)$ is not an even function of ϕ the microcanonical average mode kinetic energies are the same for all modes, whereas the microcanonical average potential energies are, from Eqs. (29), (30), and (36), given by

$$\left\langle \frac{1}{2} \omega_{2m}^2 a_m^2 \right\rangle_\Omega = \mathscr{L}^{-1} \left\{ \frac{1}{2} [z_0 z_2 - z_1^2] \, z_0^{N-3} \left(\frac{2\pi}{\beta} \right)^{(N-1)/2} \right\} \Big/ \mathscr{L}^{-1}[Z(N, \beta)] \tag{37}$$

$$\left\langle \frac{1}{2} \omega_{2m-1}^2 b_m^2 \right\rangle_\Omega = \mathscr{L}^{-1} \left\{ \frac{1}{2} [z_0 z_2 + d_m(N) z_1^2] \times z_0^{N-3} \left(\frac{2\pi}{\beta} \right)^{(N-1)/2} \right\} \Big/ \mathscr{L}^{-1}[Z(N, \beta)] \tag{38}$$

Recognizing that the inverse Laplace transform operator is a linear operator and expanding the denominator in the above, we expect equipartition of the normal mode energies in regimes where

$$\hat{\alpha}(N, E) = \frac{\mathscr{L}^{-1}[z_1^2 z_0^{N-3}(2\pi/\beta)^{(N-1)/2}]}{\mathscr{L}^{-1}[z_0^{N-1}(2\pi/\beta)^{(N-1)/2}]} \tag{39}$$

is negligible compared with

$$\alpha(N, E) = \frac{\mathscr{L}^{-1}[z_2 z_0^{N-2}(2\pi/\beta)^{(N-1)/2}]}{\mathscr{L}^{-1}[z_0^{N-1}(2\pi/\beta)^{(N-1)/2}]} \tag{40}$$

We are particularly interested in the scaling of these terms with the energy density E/N.

5. ASYMPTOTIC RESULTS

In the following we carry out an asymptotic analysis of $\hat{\alpha}(N, E)$ in the small- and large-energy density limits for the anharmonic chain described by Eqs. (1)–(3) with $f(\phi) = -(\lambda/3)\phi^3 + (\mu/4)\phi^4$, where λ and μ are positive constants. The potential in this model,

$$V(\phi) = \frac{1}{2}\phi^2 - \frac{\lambda}{3}\phi^3 + \frac{\mu}{4}\phi^4 \tag{41}$$

can be regarded as the first few terms in a Taylor series expansion for more general potentials. This potential is "archetypical" for anharmonic chains. It encompasses the paradigmatic anharmonic models studied by Fermi *et al.*[5] and Henon and Heiles.[7] The physically interesting Lennard-Jones potential[3] expanded about its equilibrium points can also be written in this form (as indeed can any other interparticle potential with a minimum). For example, it is a simple exercise to show that in the Lennard-Jones approximation $\lambda = 10.5$ and $\mu = 61.8$. The Lennard-Jones potential gives us physically realistic parameters which will guide us in assessing the accuracy of our approximations in the following analysis.

First we consider the large-β behavior of the integrals appearing in Eqs. (39) and (40),

$$z_k = \int_{-\infty}^{\infty} \phi^k \exp[-\beta V(\phi)]\, d\phi \qquad \text{for} \quad k = 0, 1, 2 \tag{42}$$

The asymptotic analysis is straightforward using the method of Laplace (see, for example, Chapter 2 of ref. 11). The major contribution to the

integral z_k as $\beta \to \infty$, comes from the neighborhood of the point where $V(\phi)$ has its minimum value. For the potential considered in Eq. (41) with parameter values in the vicinity of the Lennard-Jones approximation there is a single minimum at $\bar{\phi}=0$, $V(\bar{\phi})=0$. The integral, Eq. (42), is approximated by expanding $V(\phi)$ about its minimum and introducing a change of variables $x^2 = V(\phi) - V(\bar{\phi})$. Retaining the dominant two terms in the expansion for the change of variables gives

$$\phi \approx \left(\frac{2}{V^{(2)}}\right)^{1/2} x - \frac{V^{(3)}}{3(V^{(2)})^2} x^2 + O(x^3) \tag{43}$$

where $V^{(n)}$ denotes the nth derivative of $V(\phi)$ evaluated at $\phi=0$. In Laplace's method only the leading term in the expansion of $V(\phi)$ is retained in the exponential contribution and hence

$$z_k(\beta) \sim \left(\frac{2}{V^{(2)}}\right)^{(k+1)/2} \int_{-\infty}^{\infty} x^k \exp(-\beta x^2)\, dx$$
$$- (k+2)\left(\frac{2}{V^{(2)}}\right)^{k/2} \frac{V^{(3)}}{3(V^{(2)})^2} \int_{-\infty}^{\infty} x^{k+1} \exp(-\beta x^2)\, dx \tag{44}$$

For the potential in Eq. (41) we now obtain the asymptotic results

$$\left(\frac{z_1}{z_0}\right)^2 \sim \frac{\lambda^2}{\beta^2}, \qquad \frac{z_2}{z_0} \sim \frac{1}{\beta} \tag{45}$$

Thus in the large-β limit, $\hat{\alpha}(N, E)$ is dominated by $\alpha(N, E)$ and Eq. (38) predicts equipartition of energy among the normal modes. This is not surprising because the large-β limit is essentially the small-energy limit where the harmonic behavior should dominate. The dependence on the energy density is found by calculating the inverse Laplace transforms in Eqs. (39) and (40). This yields the small-E asymptotic scaling $\hat{\alpha} \sim \lambda^2 (E/N)^2$ and $\alpha \sim E/N$, which establishes equipartition of energy in the small-energy density limit.

To investigate the small-β limit we first introduce a change of variables $y = \phi \beta^{1/2}$; then for β small

$$z_k \sim \left(\frac{1}{\beta}\right)^{(k+1)/2} \int_{-\infty}^{\infty} y^k \exp\left(\frac{\lambda}{3\sqrt{\beta}} y^3 - \frac{\mu}{4\beta} y^4\right) dy \tag{46}$$

where the approximation omits the factor $\exp(-\frac{1}{2}y^2)$ from the integrand. The accuracy of the approximation can be quickly assessed through numerical comparisons. For example, at $\beta = 10^{-4}$ with λ and μ values appropriate for the Lennard-Jones approximation the "exact" values are

$z_0 = 9.134\ldots$, $z_1 = 0.515\ldots$, $z_2 = 78.5\ldots$, whereas the approximate values are $z_0 \approx 9.138\ldots$, $z_1 \approx 0.516\ldots$, $z_2 \approx 78.4\ldots$. The usefulness of the approximations is that each of the integrals in Eq. (46) can now be calculated algebraically. Using the algebraic symbol manipulation package MATHEMATICA, we find

$$
\begin{aligned}
z_0 &\approx \frac{\Gamma(1/4)}{2^{1/2}\mu^{1/4}}\,{}_2F_2\left[\left(\frac{1}{12},\frac{5}{12}\right),\left(\frac{1}{4},\frac{1}{2}\right),\frac{\lambda^4}{12\mu^3}\beta\right]\beta^{-1/4} \\
&\quad + \frac{2^{3/2}\lambda^2\Gamma(7/4)}{9\mu^{7/4}}\,{}_2F_2\left[\left(\frac{7}{12},\frac{11}{12}\right),\left(\frac{3}{4},\frac{3}{2}\right),\frac{\lambda^4}{12\mu^3}\beta\right]\beta^{1/4} \\
z_1 &\approx \frac{2^{1/2}\lambda\Gamma(1/4)}{6\mu^{5/4}}\,{}_2F_2\left[\left(\frac{5}{12},\frac{13}{12}\right),\left(\frac{1}{2},\frac{5}{4}\right),\frac{\lambda^4}{12\mu^3}\beta\right]\beta^{-1/4} \\
&\quad + \frac{2^{7/2}\lambda^3\Gamma(11/4)}{81\mu^{11/4}}\,{}_2F_2\left[\left(\frac{11}{12},\frac{19}{12}\right),\left(\frac{3}{2},\frac{7}{4}\right),\frac{\lambda^4}{12\mu^3}\beta\right]\beta^{1/4} \\
z_2 &\approx \frac{2^{1/2}\Gamma(3/4)}{\mu^{3/4}}\,{}_2F_2\left[\left(\frac{7}{12},\frac{11}{12}\right),\left(\frac{1}{2},\frac{3}{4}\right),\frac{\lambda^4}{12\mu^3}\beta\right]\beta^{-3/4} \\
&\quad + \frac{2^{5/2}\lambda^2\Gamma(9/4)}{9\mu^{9/4}}\,{}_2F_2\left[\left(\frac{13}{12},\frac{17}{12}\right),\left(\frac{5}{4},\frac{3}{2}\right),\frac{\lambda^4}{12\mu^3}\beta\right]\beta^{-1/4}
\end{aligned}
\tag{47}
$$

where ${}_2F_2[\cdot]$ denotes the generalized hypergeometric function, whose behavior for small β goes as $\sim 1 + O(\beta)$ (see, for example, ref. 12, p. 585). We now substitute the above approximations into Eqs. (39) and (40), retaining only the first two leading-order terms in an expansion for small β. Finally, after carrying out the inverse Laplace transforms (see, for example, ref. 12) in the numerators and denominators we obtain the limiting (large E) behavior

$$
\begin{aligned}
\hat{\alpha}(N, E) &\sim \frac{\lambda^2}{9\mu^2}\left(1 + \frac{8\lambda^2\Gamma(3/4)}{9\mu^{3/2}\Gamma(1/4)}\frac{\Gamma((3N-3)/4)}{\Gamma((3N-5)/4)}E^{-1/2}\right) \\
\alpha(N, E) &\sim \frac{2\Gamma(3/4)}{\mu^{1/2}\Gamma(1/4)}\frac{\Gamma((3N-3)/4)}{\Gamma((3N-1)/4)}E^{1/2} \\
&\quad \times\left(1 + \frac{\lambda^2}{9\mu^{3/2}}\frac{1}{\Gamma((3N-3)/4)\,\Gamma(3/4)\,\Gamma(1/4)}\right. \\
&\quad \times\left\{\frac{3(1-n)\,\Gamma(3/4)^2\,\Gamma((3N-3)/4)^2}{\Gamma((3N-5)/4)}\right. \\
&\quad \left.\left. + \Gamma\left(\frac{3N-1}{4}\right)\left[(3n-8)\,\Gamma\left(\frac{3}{4}\right)^2 + \frac{5}{4}\,\Gamma\left(\frac{1}{4}\right)^2\right]\right\}E^{-1/2}\right)
\end{aligned}
\tag{48}
$$

Thus the small-β analysis reveals that at large energies, $\alpha(N, E)$ dominates $\hat{\alpha}(N, E)$ and again we expect equipartition of energy among the normal modes. In the limit $N \to \infty$ the expressions in Eq. (48) can be simplified further using Stirling's asymptotic result, $\lim_{x\to\infty} \Gamma(x+1) \sim (2\pi x)^{1/2} \times x^x e^{-x}[1 + O(x^{-1})]$, together with the identity $e^{-ab} = \lim_{N\to\infty}(1 - a/N)^{bN}$; we have

$$\begin{aligned} \hat{\alpha}(N, E) &\sim \frac{\lambda^2}{9\mu^2}\left\{1 + O\left(\left[\frac{N}{E}\right]^{1/2}\right)\right\} \\ \alpha(N, E) &\sim \frac{4\Gamma(3/4)}{3^{1/2}\Gamma(1/4)\mu^{1/2}}\left(\frac{E}{N}\right)^{1/2}\left\{1 + O\left(\left[\frac{E}{N}\right]^{-1/2}\right)\right\} \end{aligned} \tag{49}$$

Hence equipartition of energy also holds for large N when the energy density E/N is large. We note in this latter case that the energy in the normal modes $[\sim\alpha(N, E)]$ scales as the square root of the energy density rather than directly as the energy density.

6. SUMMARY AND DISCUSSION

The equilibrium statistical mechanics principle of equipartition of energy among the normal modes of a harmonic chain has long been a puzzling result. It is experimentally supported by specific heat measurements at temperatures where the classical approximation is valid. However, there is no theoretical dynamical justification for the application of equilibrium statistical mechanics to the harmonic chain. Efforts to circumvent the theoretical difficulties by considering anharmonic chains face an immediate paradox: Anharmonic interactions are required to allow exchanges of energies among the normal modes, but in an anharmonic lattice the equilibrium statistical mechanics generalized equipartition principle[2] should be employed and it is not clear that this is consistent with equipartition of energy among the normal modes. The anharmonicity should be sufficiently strong to overcome the restrictions of the KAM theorem, but sufficiently weak to approximate the conditions for equipartition of energy among the normal modes. The situation has been made all the more puzzling by a series of numerical experiments that report equipartition of energy among the normal modes of an anharmonic chain above a critical energy density threshold[13] (i.e., for sufficiently strong anharmonicity).

In this paper we assumed that the conditions for equilibrium statistical mechanics were satisfied at the outset for an anharmonic chain with nearest-neighbor interactions and free ends, and we calculated the canonical and microcanonical averages for the normal mode energies of the chain. We found the surprising result that in the case where the interparticle

potential is an even function of its argument, equipartition of energy among the normal mode energies is still an exact result independent of how strong the anharmonicity is (how much energy is contained in the anharmonic terms). Noneven potentials including quadratic, cubic, and quartic terms were also considered and here, too, using an asymptotic analysis it was found that there is equipartition of energy among the normal modes in both the low- and high-energy regimes.

As a final remark we note that in the (quartic) Hamiltonian described by Eq. (1) with $f(\phi)=(\mu/4)\phi^4$ we can identify a set of nonlinear mode energies whose sum is equal to the total energy of the chain and which equipartition the energy among them. Following ref. 8, we define the nonlinear mode energies by

$$\varepsilon_k^* = \frac{1}{2}\dot{c}_k \frac{\partial H_0}{\partial \dot{c}_k} + \frac{1}{2} c_k \frac{\partial H_0}{\partial c_k} + \frac{1}{4} c_k \frac{\partial (H - H_0)}{\partial c_k} \tag{50}$$

where c_k is a mode position coordinate. The change of ε_k^* with time is a function only of intermode energy flows, whereas the change in the normal mode energies ε_k with time depends on both intermode energy flows and intramode energy flows.[8] It is a simple exercise to show that $\sum_k \varepsilon_k^* = E$. Furthermore, combining the results that $\langle \dot{c}_k \, \partial H_0/\partial \dot{c}_k \rangle$ is the same for all modes and $\langle c_k \, \partial H_0/\partial c_k \rangle$ is the same for all modes (equipartition of energy among the normal modes) together with the result that $\langle c_k \, \partial H/\partial c_k \rangle$ is the same for all modes (Tolman's generalized equipartition principle), it follows immediately that $\langle \varepsilon_k^* \rangle$ is also the same for all modes.

ACKNOWLEDGMENTS

This work was supported by the Australian Commonwealth Government. One of the authors (B.I.H.) would like to thank John Grindlay for the benefits of his insights on energy sharing in nonlinear lattices.

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