Fourier heat conduction characteristics of a lattice chain arising from considerations in intermolecular potentials and the Second law

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Abstract

Two aspects of conductive heat are considered here (i) its definition and characterization and (ii) the intermolecular potentials that induce both energy flow and the temperature profile at the steady state for a 1-D lattice chain. It is found from NEMD simulations and theory, such as that of Rieder, Lebowitz and Lieb (RLL) that the fundamental presuppositions maintained by persons like Joseph Fourier and others do not always obtain locally for some potentials since the Fourier Principle (FP), with stated form $J_q \cdot \nabla T \leq 0$ in standard terminology and which is sometimes interpreted as reflecting the local form of the Second law, is violated. This result necessitates here a discussion of the nature of heat energy as defined in the First and Second laws of thermodynamics. A variational principle of form $\delta J_q = 0$ for conductive heat is proposed in general, which also accounts for those regions that seem to violate the FP and local statements of the Second law. The 1-D simulations were conducted without recourse to synthetic algorithms utilizing coupling coefficients under very large temperature gradients leading to results that differ somewhat from some theories including that of RLL for harmonic potentials, that feature single particle thermostats with coupling coefficients. Here, we define control volumes at the right and left ends of the chain of 200 particles for each control volume and apply the non-synthetic thermostatting algorithm there for total chain length of 1000 particles. If the method used here is considered feasible, then a re-evaluation of some of the standard theoretical methodology would prove beneficial in order to design and implement more extended paradigms with enrichment of the axiomatic basis. The sinusoidal temperature profiles observed here and perhaps elsewhere for the harmonic lattice suggest that thermal integrated circuits with several thermal P–N junctions may be constructed at the coordinate positions of the peaks and troughs of the profile which serve as sources and sinks of thermal energy, which might open the possibility of creating more complex thermal transistor circuits. The simulation results indicate that the presence of an anharmonic term per se does not guarantee diffusive behavior or the Fourier law obtaining because for any strength of an anharmonic symmetric contribution $k_b$, a high enough value of the harmonic parameter $|k_b|$ induces “ballistic” behavior with the breakdown of the conventional Fourier law. It is noted that current research in the lattice problem subjected to temperature forces has perhaps unfortunately veered away from the original trajectory of FPU’s research that focused on dynamics, and which also spawned much of the entire field of KdV and KAM analysis. © 2017 Elsevier Masson SAS. All rights reserved.

1. Introduction

Whenever the Fourier law obtains, (here confined to the linear first order version) $J_q = \kappa \nabla T(\mathbf{r})$ where $J_q$ is the heat current vector, $\kappa$ the thermal conductivity and $T(\mathbf{r})$ the temperature at coordinate $\mathbf{r}$, then Fourier maintained that [1, Sec. III, no. 57–64, pp.41–45] (a) net heat energy flow cannot occur in the absence of a temperature gradient, and (b) net heat flow occurs from hot to cold temperature regions that are connected if a temperature gradient exists. With the implication of local behavior, his postulates (a) and (b) are taken to imply

$$J_q \cdot \nabla T \leq 0.$$  \hspace{1cm} (1)

where (a) and (b) taken together refer to the Fourier Principle (FP).
in (1). Fourier and subsequently his followers claim that conductive heat is local in nature (within the limits of molecular volumes and particle interaction times) with (1) obtaining. In comparatively recent times, Benofy and Quay [2, p.11] following Fourier have argued that the Fourier law is essentially local in nature, where whenever a temperature gradient is present, there can be a flow of heat but there cannot be such conductive heat transfer in the absence of a thermal gradient. BQ also argue that the Second law statements of Kelvin and Clausius are global, so that with compensation, there can be transfer of heat from cold to hot, but never by conduction [2, p.10, par. 2–3]. The fundamental definition of heat, according to some authorities, on the other hand is that it is that form of energy that traverses a boundary as a result of a temperature difference [3, p.73], [4, p.229], [5]. Further a direction of traverse is also implied. Carathéodory defines heat [4, J. Kestin ed., Introduction, p.229] as follows: “Furthermore, when two bodies of different temperatures are brought into contact, heat always passes from the hotter to the colder, and never in the reverse direction.” In passing, the more restricted previous work [6] identifies Fourier conductive heat transfer as thermodynamical “heat” and showed that this heat actually conforms to a Carnot optimized trajectory. From these definitions, one can surmise that a contradiction to (1) implies that conductive heat is not only local within the afore-mentioned limits, but could involve some sort of “optimised” trajectory where global principles apply even within a localized region. This is another result which is postulated in what follows as suggested by the simulation results. The objectives of this work are several which is surveyed below. Firstly, we examine the nature of the RLL model. The RLL result for the harmonic lattice has been assumed implicitly by many workers to be the unique solution irrespective of the thermostating mechanisms, and temperature difference between thermostats and for the entire length of the lattice chain if the end particles are thermostatted to different fixed temperatures although the authors have stated some of the assumptions used in their derivations with the attending derivations. Other assumptions are implied rather than explicitly stated. It has been implicitly assumed by many that single particle thermostating at the ends is absolutely equivalent to the general case and more physically reasonable instance where an extended region is thermostatted, and that the specialized thermostating algorithm used by RLL is universally valid in that it yields equivalent results to all other thermostating algorithms. In particular, their use of the coupling coefficient $\lambda$ in (12) is deemed a natural and general method of constructing thermostating algorithms. It should be noted that standard kinetic theory of heat transfer [7, Chap. VI] expresses rates in terms of (local) gradients - which are the thermodynamical forces - of thermodynamical potentials of functions of state, and where the kinetic coefficients are not dependent on the reservoir couplings for instance, in the case of heat transfer. Quantum mechanics can calculate $\kappa$ the thermal conductivity [8] without thermostating assumptions. The use of these phenomenological laws in scientific and technological applications with no reference to reservoir coupling coefficients other than material properties is standard. Within the relatively mild regimes of applied temperature gradients in reduced units found in the literature, (our gradients and temperature difference between the two ends of the lattice chain are typically about 30–40 times greater), a 10th order move algorithm study [5, Fig. 1(a)] with a temperature difference of 0.1 does not reproduce the characteristic pronounced loops of the temperature profile at the ends that RLL predict for the FPU harmonic lattice. RLL cannot provide an explanation, referring to a possible “mismatch” between the reservoir and lattice oscillator frequencies [10, p.1074]. There is a hint of a weak sinusoidal oscillation of temperature with lattice index for the FPU simulation over and above the noise fluctuation and superimposition of the Toda spectrum at the plateau region [9, Fig. 1(a)]. It will be demonstrated in the following sections that the RLL and allied treatments seem to be a third development developed later in time to the still dominant KdV and KAM theories of dynamical systems. A work very much in the spirit of RLL for anharmonic lattices is that of Eckmann et al. [11], where as with RLL certain uniqueness theorems are addressed only under certain mathematical boundary conditions existing. Essentially, such works as these are mathematical constructs that refer to few physical objects whose state variables are invested with mathematical properties so as to guarantee a solution to the defined mathematical problem. What bearing this method has in actually suggesting physically reasonable solutions to physical reality is debatable. In our work here, the system being considered is a 1-D lattice of finite length with fixed boundaries to mirror the physical arrangement of nanoscale devices as with the original FPU study [12, p.9–19] that allows for wave reflection at the “walls” of the system without periodic boundary conditions leading to constructive and destructive interference of the traveling waves. The system is thermostatted along two segments of the chain, mirroring physical conditions which may not be mathematically convenient. In [11, eqn.(2.3)], the total system has Hamiltonian form

$$H = H_p(p.q) + H_{BL} + H_{BR} + q_1 \cdot F_1 + q_n \cdot F_R$$

(2)

where $H_p(p,q)$ is the lattice Hamiltonian not containing the thermostated particle spatial coordinates $(q_1, q_n)$ and is a $C^\infty$ function of a chain of particles with indexes $(1, 2 \ldots n)$, $n \to \infty$ with anharmonic nearest neighbor (NN) and next nearest neighbor (NNN) interactions, which is not the system simulated here nor in the original FPU study, nor in many of the works reported here; an infinite lattice chain is assumed. In (2), the $H_p$s are the Hamiltonians for the free heat baths, and $F_{(LR)}$ are integrated functions of charge density functions and a dynamical wave equation expression [11, p.660]. The choice of the thermostat factor $H_T$ was motivated by the dipole approximation of classical electrodynamics. How this abstract and convenient mathematical definition relates to the various standard MD thermostating algorithms [13, Chap.6] remains undemonstrated. In order to achieve the mathematical result of the Markov process associated with the stochastic dynamical equations having unique invariant measure with mixing, (which is assumed to correspond to the unique physical steady state without qualification), various assumptions had to be devised, such as described by hypothesis H1 and H2 and small enough temperature gradients none of which obtains for the elementary system explored here under more extreme conditions of temperature gradients and more extreme than reported in the literature [11, p.659]. To arrive at their proofs of the existence of the steady state, and uniqueness under added conditions, they introduced [11, p.659, Introduction] non-Newtonian equations of motion by the addition of two kinds of force, a random force exerted by the heat baths on the chain of oscillators and a dissipative force with memory which “... describes the genuine retro-action from the heat bath on the small system...” ($H_e$). How this translates into a description of the Newtonian dynamics that we are using here is difficult to establish. The abstract Hamiltonian form in (2) has no immediate application to our finite system - theirs is infinite - with strict, non-stochastic, Newtonian dynamics along both the chain and thermostatted control volumes having several particles; the introduction or removal of energy follows the conservation laws along the thermostatted segments. The work here is similar to those referred to in what follows, except for temperature differentials (e.g.1.1 to 1.0 [14] or 0.3 to 0.2 [9] in reduced units compared to our 4.0 to 1.0) which therefore adds to the common pool of data.

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over the decades. The study here does not focus on bulk properties, where periodic boundary conditions should be used. Whilst this is routine for equitemperature systems [13], problems arise when intensive variables differ at the extremities of the simulation box, leading to singularities as particles are mirrored across the boundaries. An interesting solution by Hafskjold and Ikeshoji (H−I) is to have a symmetrically divided box with gradients imposed at the centers and the ends [15]. This technique was what we used for our own NEMD studies where bulk properties were probed [16] and should be used for any NEMD study of bulk properties such as thermal conductivity and its changes with size and gradients of intensive variables. An interesting application of a bathfree method for NEMD simulations with Lennard Jones (LJ) particles using (R) NEMD and H−I boundary conditions is by Müller-Plathe [17] where particle velocities (but not position coordinates) are exchanged at the hot and cold slabs or sections of the system, leading to a temperature gradient and where the energy inputs/outputs are monitored. The time interval of exchange W is varied and in every instance, for different W, different gradients were obtained with essentially the same value of the thermal conductivity. Two related methods were used, constant E where there is no intermediate coupling and a so-called constant T type thermostatting of Berendsen et al. [17, Ref.7]. Doubtless, these methods were used to show the consistency of the bathless method with those of the coupling coefficients using standard coupling coefficient values. However, we notice here that many workers in this field of heat transfer show that the rate of heat transfer is related to these coefficients, including the RLL solution for harmonic lattices [18]. So far, this problem has not been definitely overcome, to my knowledge. In reduced * units, the thermal conductivity is ~ 6.70 ± 20 with accuracy ranging 4–8% compared to experiment. The method was taken over by Xiong et al. [19] with a bathless (constant E) system with semicircular periodic boundary conditions for an anharmonic lattice to study the divergence of k_L, the conductivity with L the system size where it is inferred that \( \kappa \sim L^2 \) and where it was previously thought that \( \alpha \) may belong to either one or two universal classes with associated values for each of the universal classes; Xiong et al. showed that depending on the NN and NNN coupling coefficient ratio \( \gamma \), there was a continuous dependence of \( \alpha \) on \( \gamma \) for the FPU-\( \beta \) lattice. For these studies, the NN potential coupling parameters accord with the values that we use in reduced units, and there is no violation of the FP in these works, which is what we also obtain for these typical values of the potential coupling parameters albeit under higher temperature and temperature gradients. We note that the Hβ boundary conditions do not involve interference effects because we are dealing with a symmetrical loop motion of particles without interference, and therefore cannot be used for problems where such interference is significant, such as a system with fixed boundary conditions.

Eckmann et al.'s system [11] is different from ours which does not have NNN interactions, but we might surmise that where the FP holds, the distribution is unique. For non-constant values and ratios of the coupling coefficients of (3) for the FPU-\( \beta \) lattice, we suggest that one possibility of departure from the FP principle is that apart from the very large gradients and thermostatting methods, these coefficients are related to the assumptions and axiomatics of the Eckmann [11] development that are only valid for a certain regime of values of the reduced variables. On the other hand, in highly chaotic dynamical systems [20, Sec. 1.2, Limit sets], the initial conditions of the system can lead to a particular and unique steady state realization; in standard MD simulations, this possibility has hardly been explored. Treatises have been devoted to the “warm-up” portion of simulations, implying that the impressed thermodynamical state variables determine uniquely the state of the system; this follows from the equation of state. However, there is no reason whatsoever for this state of affairs to obtain for non-equilibrium systems; a simple perusal of time-dependent boundary value problems should suggest that the uniqueness is related to the distribution profile at time \( t = 0 \). The \( b_k \) value of the potential in (24) was chosen to correspond to the tungsten solid state still under the melting point at \( T = 4.0 \). The \( b_0 \) mixing coefficient has been interpreted as indicating the degree of “diffuseness” by physicists [21]. In this context, I make comparisons by choosing a reference to be \( b_0 = 0.5 \) which is a standard value, and the standard value of \( k_0 = 1.0 \) is chosen to illustrate the regime where the FP holds at our fixed temperature difference of 3.0, which is relatively large. The \( k_0 \) harmonic coupling factor refers to the “ballistic” factor by physicists such as Hu et al. [21, p.2994]. Hence for fixed diffusive factor, one can gauge the effect of \( k_0 \) on the “ballistic” trajectory, which seems to refer to a type of mechanical vibrational motion. The temperature gradient imposed is about 30 times larger than the standard gradients, and at much higher temperature; the absolute values of the temperature also matters, and not just ratios or differences in the reduced values. In the Eckmann [11] development, such assumptions as “small enough temperature gradient” to guarantee his conclusions may not apply here, leading to possible anomalies even if NN and NNN interactions were used as prescribed in his system. Concerning the uniqueness of steady states, it is stated that if an invariant measure exists, then it indicates the existence of steady states for any temperature difference in the lattice chain, and in addition, if the temperature difference is sufficiently small, then the invariant measure is unique and mixing [11, Abstract]. Assuming some correlation between the mathematics of [11] with our system despite all the differences, then we have perhaps shown that some invariant measure exists for our systems whenever a steady state exists; all the work here refer to steady state outcomes. Further, given the very large temperature differences, there is no reason to suppose that the steady state is in fact unique; that requires another massive study beyond the scope of this work.

Here, we are interested in finite size systems with fixed conditions that allow for wave interference in both directions of propagation, leading to a stationary state that may be applicable to thermal microcircuits with very large thermal gradients. For this purpose 5 Figures are provided. Fig. 1 is a sketch of the RLL solution, Fig. 2 that of a harmonic lattice under a large temperature difference of the coupled reservoirs, Fig. 3 illustrates the results where FP obtains for the standard coupling coefficients used (\( k_0 = 1.0, b_0 = 0.5 \)), Fig. 4 the graph of the temperature profile for a large ballistic component without any anharmonic coupling.

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**Fig. 1.** Sketch of the RLL solution [10] where the FP is violated at the ends of the lattice chain as indicated and \( \kappa \sim \infty \) at the plateau region; \( j \) is the particle index and \( T \) a scaled temperature.
(\(k_h = 593.355, b_h = 0.0\)) and lastly Fig. 5 graphs the result for our standard diffusive \(b_h\) value with a very large ballistic coefficient \((k_h = 593.355, b_h = 0.5)\). Various conclusions will be drawn from these choices of coefficients.

If so much theory and applications are based on the truth of the above assumptions of RLL and related work, then the exploration of other possibilities founded on plausible physical principles could provide alternate practical physical realizations of phenomena not considered possible relative to their axiomatics or assumptions. In the case of the harmonic lattice following RLL theory, a “ballistic” trajectory is envisaged (see Fig. 1) at the central portion of the graph, where \(\nabla T \rightarrow 0 \Rightarrow \kappa \rightarrow \infty\) if the Fourier form \(I_q = -\kappa \nabla T\) is retained. This is a standard interpretation, even for well-behaved systems [21] where a propagation at the acoustic speed is expected. If the FP obtains for the RLL model with the temperature profile as in Fig. 1, then RLL seem to suggest that no immediate explanation can be given for heat conduction at those regions with a positive gradient and heat flow direction if \(\kappa \geq 0\). Hence this is another critical issue not addressed by RLL, where the mathematical structure breaks down in terms of being able to provide a conventional explanation. Here, from previous work in recoverability theory [6], a principle is posited to allow for heat conduction that apparently violates the FP and perhaps local forms of the Second law that is framed in terms of the impossibility of pure heat only without work compensation – conductive heat only - traversing along a temperature gradient [2]. In terms of applying a thermostatting algorithm, we apply one with no apparent coupling parameters [22] and with strict conservation of energy and momentum in the control volumes maintained at different temperatures, where each control volume consists of 200 particles. The conditions imposed on the system are all physically realistic with no assumptions concerning the nature of the thermostats; the laws
of mechanics (including the conservation of energy and momentum) are implemented and a non-synthetic simplectic algorithm integrates the Hamiltonian equations, unlike many algorithms that incorporates the thermostats into the move algorithms [13]. This system for a harmonic lattice (Series 1 and 3 below) is simply not equivalent to the RLL model with the temperature profile sketched in Fig. 1 and hence it would be of interest to investigate whether such profiles are realizable in nature. One point of commonality with the RLL result and ours is that both show violations of the FP. Although numerical integration of hybrid dynamical systems - of the kind presented here - which incorportates a stochastic component such as when thermostat algorithms are employed cannot be independently verified via simulations without comparison to an equivalent mathematical solution to the differential equations of the dynamical system which is not given here, and to the best of my knowledge has never been provided, nevertheless the numerical results derived is suggestive of other possibilities other than the conventional descriptions found in the current literature. This then is one objective of the work here. These simulation outcomes can be explored in experiments and in theoretical modeling and descriptions that are closer to the real system interactions than idealized and simplistic descriptions which are of course important first order approximations.

A second objective is to briefly comment on the nature of the anharmonic term (associated with the variable $b_h$). The current theoretical understanding is that these terms contribute to the ‘diffusive’ flow of energy associated with heat, exemplified by Fourier heat conduction. The results in Series 3 and 4 address and rationalize this issue. Series 2 is a reference run for the model, where the Fourier law is applicable and where the results agree with the results of the temperature profile as found in the literature. Series 2 runs therefore indicates that the results relative to the model are plausible for Series 1, 3, 4. A third objective is to suggest that perhaps the way workers have framed their differential equations may be extended for the harmonic lattice at least to cover hybrid systems that incorporates both deterministic solutions and perhaps stochastic elements at the thermostat control volumes. Our thermostats do not have a stochastic element, since the algorithm is deterministic, because the scaling of velocities in the algorithm used is derived from the velocity distribution that arises from the dynamical laws. A fourth objective is to suggest that if this model does capture aspects of real systems, then various new types of thermal circuits may be designed that exploits the temperature variation with distance observed in this model in simulations.

We note that simulations are usually most useful when performed in conjunction with a theoretical structure with analytic solutions and experimental measurements, where an interplay of the various factors exists. Here, the other two elements of the interplay are largely absent, both experimental studies and the differential equations associated with a precisely stated model. Hence it would seem that another fifth unintended objective of this work is to suggest experimental and theoretical investigations that might encourage a need for interplay between the different aspects mentioned above.

2. Materials and methods

Aspects of the historical background to the current state of the methodology that might significantly influence the future developments will be sketched here. The focus in present nonequilibrium lattice dynamics is an augmentation and direct consequence of a work due to Fermi, Pasta and Ulam (FPU) [12, Appendix 1.3 reprint] that began the era of experimental mathematics via computer simulation. It was an unpublished Los Alamos document LA-1940 issued in May, 1955, and was only made available to the public a decade later, entitled “Studies in Non Linear Problems”. At least one entire study of this pivotal work and its consequences has been made [23] and a recent status report too has been published [12]. Debye as early as 1913 realized that heat as a diffusion or scattering process was due to the non-linear conservative forces acting on the energy-conveying particles in a crystal [24]. This concept was further refined by Peierls [25]. Cognizant of these facts, Fermi et al. proposed the following Hamiltonian $\mathcal{H}$ for simulation of a lattice chain

$$\mathcal{H} = \sum_{i} \left[ \frac{p_i^2}{2} + \frac{(q_{i+1} - q_i)^2}{2} + \alpha \frac{(q_{i+1} - q_i)^3}{3} + \beta \frac{(q_{i+1} - q_i)^4}{4} \right]$$

with unit harmonic coupling and where the $\alpha$ and $\beta$ coefficients are associated by convention to the power of the exponents, either the anharmonic $\alpha$ term (FPU-$\alpha$) or the $\beta$ term (FPU-$\beta$) being present (but not both in the early studies); $(p_i, q_i)$ are the conjugate momentum position of particle $i$ with equidistant equilibrium separation distance $d$. We note that no thermostatting is featured, and the equations of motion were numerically integrated. Fermi et al. were interested in how the normal modes of the unperturbed Hamiltonian of (3) written

$$\mathcal{H}_0(q, p) = \frac{1}{2} \sum_{i=1}^{N} \left[ p_i^2 + (q_i - q_{i-1})^2 \right]$$

(with $p_{N+1} = 0$) in some way relates to the actual coupled system that was being simulated.

Since we are dealing with a coupled problem, the so called unperturbed system is a different system, and so the metric used for comparison is merely virtual. However, FPU felt that one can make deduction between virtual systems and a physical system that is being simulated, leading to “unexpected” results. Writing the $a_k$ normal mode coordinates as

$$a_k = \sqrt{\frac{2}{n+1}} \sum_{j=1}^{n} q_j \sin \left( \frac{jk \pi}{n+1} \right) \quad k = 1, 2, \ldots n$$

then the normal modes in terms of the unperturbed Hamiltonian is

$$\mathcal{H}(a, \dot{a}) = \frac{1}{2} \sum_{k} \left( \dot{a}_k^2 + \omega_k^2 a_k^2 \right) \quad \omega_k = 2 \sin \left( \frac{k \pi}{2(n+1)} \right)$$

whilst the full Hamiltonian is

$$\mathcal{H}(a, \dot{a}) = \frac{1}{2} \sum_{k} \left( \dot{a}_k^2 + \omega_k^2 a_k^2 \right) + \alpha \sum_{k,m=1}^{N} C_{km} a_k a_m$$

The unperturbed Hamiltonian has modes that are said to be independent and are said to be unrelated, while (7) on the other hand is said to allow energy to transfer from one mode to another. The simulation did not have any thermostating stochastic interference which would indeed cause “coupling” between even independent modes, from which equipartition results, where for instance, $<a_1^2>$ = $\frac{1}{2}kT$, $<a_2^2>$ = $\frac{1}{2}kT$ for any quadratic term in the Hamiltonian with ($a_1, a_2$) constants [26, sec.17, pg.79]. Indeed, with thermostating, a Hamiltonian $\mathcal{H}(q, p)$ with form
\[ \mathbf{H} = p^2/(2m) - \Delta_i q_i^2/2 - \beta_i q_i^4 \]

would yield a Virial equation [26, pg.83]

\[ (1/2)\Delta_i q_i^2 - 2\beta_i q_i^4 = (1/2)\Theta \]

where the modulus is taken to be \( \Theta = kT \) with mean energy \( \mathcal{E} = \Theta + \beta_i q_i^4 \). We therefore note a “shift” from the so-called independent mode by amount \( \beta_i q_i^4 \). It would appear that even for this case a “shift” is observed relative to the virtual “independent” mode. The results of the FPU simulation where \( E_0 \), the virtual total energy is defined as \( E_0 = \sum_i E_{i,\alpha} \) where

\[ E_{i,\alpha} = \frac{1}{2}\dot{q}_i^2 + \frac{1}{2}(q_i - q_{i-1})^2 \]

is the instantaneous energy of the virtual mode \( i \). What surprised FPU was that the averaged “modal” energy converged to different averages about the first mode; this might not appear surprising to others in view of the anharmonic terms in an oscillator given by (9) for instance. The other result, perhaps influenced by the Poincaré-Zermelo recurrence theorem ([26, Sec. 7, pg.38–39]) is the observation of quasi-periodicity in the different virtual modes ([23, Fig. 1.3]) whose features were further characterized with increasing computational power by workers like Tuck and Menzel where they conclude that “superperiodicity” was observed but where by checking the results for energy conservation, it was inferred that the recurrence of a particular mode was not “exact” within experimental observation time for any of these “supermodes”. As a result of these observations, two dominant mutually exclusive schools [23, p.30] came to dominate the interpretation of FPU systems, one school believed that they exemplified Kolmogorov-Arnold-Moser (KAM) stability, whilst the other interpreted these systems in terms of Korteweg-de Vries (KdV) solitons, and these models continue to dominate the current discourse of heat conduction problems [23, p.30]. Proponents of both approaches, KdV and KAM agree that none of their formulations to date have been able to offer a full explanation of FPU system phenomena; no existence proofs of solutions to the problem from both these approaches are forthcoming [23, p.30]. The KAM method refers to perturbations of the original Hamiltonian in the approach of Poincaré in his study of mechanics, where many of the bottlenecks which he encountered were resolved by KAM methodology. It has been opined that the whole field of dynamical systems theory has been advanced by these two methodologies associated with KAM and KdV. It is interesting that others have actually solved the n-body problem at least formally by a direct method not immediately related to perturbations in a succinct manner [27], a problem that Poincaré was preoccupied with in his development of perturbation methods used in mechanics which also influenced the whole KAM and other departments of mechanics. The above arguments and developments have been influenced by recurrence theorems of the Poincaré type, which has been proven to be incorrect, as with the pivotal Liouville equation, save for some trivial linear systems [28], but where a stochastic or probabilistic form exists with a precisely stated stochastic form derived [28]. We also note that ergodicity concepts have been moderated by the Poincaré derivation [23, p.56]. The KAM theory [23, p.44] applies to discrete lattices. It overcame the problem of small divisors [23, p.59] associated with the perturbation method of Poincaré in solving complex dynamical systems, where a rational number in the denominator of a series expansion of a canonical transformation [23, p.59] does not lead to series convergence, in addition to the slow convergence of such series expansions. It is clear here that according to this approach, numerical simulation with digital computers will not yield the solutions that comes from the KAM methodology no matter what the length of the computer runs are. KAM theory describes the stability of quasiperiodic orbits when a weak perturbation is introduced. Since KAM theories refer to Hamiltonians, then some of the anomalies described in the investigation of the classical Liouville equation [28] would have to be accounted for in KAM theory if elements of KAM theory are found useful in describing the FPU lattice. We note that none of the theories above, that refer to dynamical motion are immediately applicable without further consideration to the study here that refer to steady state averaged distribution over 1-D space, such as the FPU determination for converged values - relative to their computer run - of the averaged values of the various virtual modes - to within experimental fluctuation [23, e.g. Fig. 1.4, pg.24]. In short, even for non-thermostatted systems, the jury is still out concerning the appropriateness and correctness of the theory that is used. It follows that for the systems referred to here, which are thermostatted and which are subjected to thermodynamical gradients and energy flows far from equilibrium, the theoretical underpinnings appear even more ambiguous; the situation is rather vague at the current time concerning the appropriateness of the FPU lattice. There is no systematic history which can be applied to historical results, and this is a well received opinion [29]. However, for the steady state (s.s.), the total energy of the system is constant, and hence the dynamics is confined to a phase space volume element and much of the thinking concerning “ergodicity” could be applied to such a system. Concerning ergodicity, if the system is integrable, then averages would exist under the Gibbs’ assumption, and the fluctuations of those averages would reflect the motion in phase space; each complete cycle would lead to the exact average value and then there would be apparent departures from this average as the system begins another orbit. If a system is not ergodic, it implies that no matter how long, there is a confinement of the motion about the phase space, but an average would still exist. Of course it would be impossible to analytically compute when convergence in the averages has been achieved; some type of measure of the departure from the average and the persistence of the magnitude about the average are some of the factors used in real simulations. Later in time, as described above, workers determine refinements to the values determined. Objectively, one can compute averages and their fluctuations and compare these results with the run time, and in the case of steady state nonequilibrium systems, one can also determine the degree of conservation of conserved quantities such as the flow rates of energy or mass and compare these to the mean fluctuations. This is the method that we adopt, which is also the standard method that is employed. There is no coherent theory available to characterize the nature of many of the most elementary systems such as the FPU lattice, and its so-called ergodic properties or lack of, depending on definition. As in the historic FPU experiment then, which was to spur theoretical and computational development by observing the evolution of the system numerically (within the domain of rational numbers, which according to theory makes simulation of some systems that depend on the property of the irrationality of some coefficients impossible, producing anomalous or incomplete results) the current work seeks to report certain computer results or outcomes which mainstream work has avoided or ignored even if there are implications concerning the nature of the actual physical state that a system could potentially manifest of significance in applications. The reason why the FPU lattice Hamiltonian is used in studies now is because of historical legacy; it became the norm for the theoretical development for those interested in heat conduction studies, where the equilibrium non-thermostatted systems are superimposed with nonequilibrium currents and forces, adding further complication to the
structure of the theory advanced over many decades for essentially microcanonical equilibrium systems because workers feel that these theories that pertain to the equilibrium state with specified Hamiltonians can be extended to systems that are interrupted stochastically through thermostatting mechanisms and temperature gradients and energy fluxes, making these theories a suitable reference and foundation for their elaborations. The current work will adhere to the trajectory set by these conventions, but the motivation and theoretical suggestions are not necessarily along the standard trajectory, and where many of the core descriptions and rationalizations are considered to be still open questions in the current approach.

The method used here was numerical NEMD computer simulation to investigate various theoretical models of the harmonic lattice chain and also the effect of the anharmonic perturbation, which is the reason why the FPU system is used, because they were also interested in a restricted context of how the anharmonic terms affects the energy distribution of the modes, and also in the time dependent irreversible behavior of the system. Here the steady state average temperature profile and current flows are investigated against the backdrop of prevailing theories and interpretations. The current dominant paradigm of the harmonic lattice is that due to RLL [10]. This work of considerable prescience has proved influential to the entire field of low-dimensional heat transfer where for the first time a unique solution to the harmonic lattice chain was provided (officially) under restricted thermostatting conditions complementing and also without joining the mainstream FPU development with its emphasis on mechanics and wave motion in the KAM and KdV elaborations. The restrictions probably include many other unspecified energy-coupling and temperature factors in the thermostats and main system, judging from the Eckmann [11] study. There is mention of an unpublished work of O.Bills as having foundation significance in their derivation [10, their ref. 6f], as well as other official works referenced. Here the s.s. temperature profile \( T(j) \) and total current density \( j(\lambda, \omega) \) [10, eq.4.6] are some of the quantities derived for a harmonic inter-particle potential 1-D lattice of equal masses; \( j \) is the particle index 1 to \( N \), counting from left \( L \) to right \( R \). The model is at times vaguely described. RLL speaks of “pistons” of systems interacting with heat baths and then later revert to the two endpoint particles that are thermostatted, where the Hamiltonian on the other hand is of their standard form [10, their eq.2.1] below in (11).

\[
H = \frac{1}{2} \sum_{i=N}^{2N} x_i^2 + \frac{N}{2} \sum_{i=1}^{N} \Phi_i x_i x_i \quad N = \text{index} \quad (11)
\]

where \( \Phi \) is the force matrix, the \( x \)'s are position \( (i = 1, N) \)-momentum \( (i = N, 2N) \) coordinates with \( \lambda \)' being the number of particles of dimension \( s \) each. The input and output thermal energy channels are at the first particle 1 at the left at temperature \( T_L \) and particle \( \lambda \)' on the right of the lattice at temperature \( T_R \). There is derived [10, eq.3.1] a heat reservoir interaction parameter \( \lambda \), \( \lambda_1 = \lambda_N = \lambda \) where the heat transfer rate \( j(\lambda, \omega) \) is given by

\[
j(\lambda, \omega) = \left\{ \begin{array}{ll}
\frac{1}{2} \omega^2 \lambda \kappa(T_1 - T_N), & \lambda \gg \omega \\
\frac{1}{2} \lambda \kappa(T_1 - T_N), & \lambda \ll \omega 
\end{array} \right. \quad (12)
\]

Here, the energy transfer rate is proportional to \( (T_1 - T_N) \) and not on any gradient with respect to distance or particle index \( j \). A sketch of the solution profile is given in Fig. 1. The RLL result has been taken to be generally true for all regimes of temperatures and numbers of particles thermostatted [30], also substantiated by their refs. 43–45 where it is stated that [30, pg. 159] the profile of a homotactic lattice has a fairly flat region along most of the curve at temperature \( T \) where \( T = (T_R + T_L)/2 \), where the standard assumption is that this temperature is the actual temperature about this region. In actuality, for a purely harmonic potential \( \vec{q}, \lambda \) is the coordinate vector of the equilibrium position), the RLL solution profile is

\[
T(j, \nu) = T\left[1 - \eta(\varphi_1)^{\lambda - 1}\right], 1 < j < \frac{1}{2} N, T(j, \nu) = T\left[1 + \eta(\varphi_1)^{\lambda - 1}\right], 1 < j' = N - j < \frac{1}{2} N. \quad (13)
\]

where \( \eta, r \) and \( \varphi_1 \) may be considered to be small parameters \((\eta j \leq 1)\) about a mean temperature \( T \). The mean profile \( T(j) \) shows slight gradients at the plateau region that does not correspond to the FP; in particular the gradients seem to be contrary to Fourier’s claims at the endpoints; it is explicitly stated that the hot thermal reservoir on the left hand side of Fig. 1 has a temperature profile that dips below the mean temperature \( T \) whilst conducting heat to the colder reservoir on the right hand side. This contradicts the BQ and Fourier assumption at least, and perhaps the Clausius assumption of the Second law if stated in non-cyclic process terms [31]. The temperature difference, on the other hand for the two endpoint thermostats is typically only 0.1, which might seem to validate the RLL result. The simulation here has a temperature difference 30 times greater. A 10th order NEMD integrating scheme [9, p.3829, Fig.1A] for the harmonic lattice has a relatively flat, mild sinusoidal curve with no evidence of the two characteristic humps seen at the ends of the RLL solution in Fig. 1. In particular Hu et al. used single particle Nosé-Hoover reversible motion thermostatting described in their eqn. (2) [9, p.3829]. Hence there appears to be significant discrepancies between theory and simulations that have arisen merely as a result of theoretical assumptions that require further investigation. One of many assumptions supposes that thermostats with coupling parameters are universally valid in modeling the kinetics.

2.1. Description of simulation method and system

In all the simulations conducted, the chain length was 1000 particles, of unit mass. The first \( N_L = 200 \) particles were thermostatted at \( T_L = 4.0 \) and the last 200 at \( T_R = 1.0 \). This method is to be contrasted to those where the last two particles at the extreme ends only are thermostatted by various unspecified or synthetic algorithms [32] such as the “reversible” Nosé-Hoover thermostat when it has been proven that time reversible motion as utilized in mathematical physics is often misused and misconstrued [33–35]. Since several particles are thermostatted, this system differs from the standard RLL and allied models where only the end-point particles are thermostatted and where the algorithm for thermostating differs. The thermostating method used here is non-synthetic in terms of equations of motion where direct classical mechanics is used [22.36,37], and there is conservation of both momentum and energy in the control volume so that no extraneous forces are introduced into the system with time that could affect the dynamics of nonequilibrium systems. Primes denote the state after the thermostatic move, where for a 3-D system we scale the velocities according to \( \vec{q} = (1 + q_1) \vec{q}_1 + \vec{q}_2 \) with \( q_1 \) and \( q_2 \) being the parameters to be determined. If \( P \) is the total momentum of a control volume or region, (denoted L and R in this case for the two ends), then conservation of momentum implies \( \Delta \vec{P}_L = \vec{P}_L - \vec{P}_R = 0. \quad (L, R) \). Defining \( \vec{V}_1 = \sum_{i=1}^{N_L} \vec{q}_1, \vec{W}_1 = \sum_{i=N_L+1}^{N} \vec{q}_1, \) then to set the temperature we write for a 3-D system \((N_D = 3)\),

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\[ W_i = \frac{N_i k T}{m_i} \] (14)

\[ W_i = (1 + \alpha_i) W_i + N_i \beta_i \] (15)

to determine the scaling parameters \( \beta_i \) and \( \alpha_i \). The simplified 1-D version of the above equations is solved here. The updating for this thermostat is carried out every \( s \text{th} \) time-step to ensure that the temperature of the thermostatted control volumes remains invariant. Currently, no coupling parameters are used for these thermostats, as opposed to the more synthetic methods, where in these descriptions, the rate of heat transfer is dependent on the thermodynamical variables only. On the other hand, Lepri et al. \[39, Sec 3.3\] give quantitative values of how energy transfer rates vary with the thermodynamical variables and many phenomenological laws, such as the Fourier heat conduction laws conform to this structure where the kinetic coefficients and the gradients of the thermodynamic potentials or variables, and many phenomenological laws, such as the Fourier heat conduction laws conform to this structure where the kinetic coefficients are dependent on the thermodynamical variables only. On the other hand, Leipri et al. \[39, Sec 3.3\] give quantitative values of how energy transfer rates vary with the microscopic coupling values, which is not a feature of conventional descriptions of simulation results. Clearly these factors are very challenging issues as noted by prominent workers \[29\] and so far it is not clear whether a comprehensive treatment has been made to remove ambiguity in terms of the actual energy transfer rates so essential for characterizing these systems. Dhar mentions the need for calibration \[18, p.467\]. Variants of the Langevin type thermostats has been utilized \[30\] that is related to the Hoover-Nose type where one has a dynamical equation for the particles at the \( L \) and \( R \) sides, maintained at temperatures \( T_L, T_R \) with particle index 1 and \( N \) respectively of form:

\[ M_i \ddot{q}_i = F_i - F_{i-1,1} - (\ddot{z}_L - \lambda_i \dot{q}_1) \delta_{i,1} - (\ddot{z}_R - \lambda_i \dot{q}_N) \delta_{i,N} \] (16)

where the force on the particle is \( F_i = -\partial H/\partial q_i \) and \( \lambda_i \) are the coupling or variance parameters and where each of the stochastic (velocity) variables \( \dot{z}_R \) satisfies the Wiener process with frictional coefficients \( \gamma \):

\[ \langle \dot{z}_R(t) \dot{z}_R(t') \rangle = 2k_B T \gamma \delta(t-t'), \]

\[ \langle \dot{z}_R(t) \dot{z}_R(t') \rangle = 0. \] (17)

It is unclear whether momentum is conserved in these algorithms; no explicit equations have been introduced for such conservation. Again the coupling parameters are featured which determines the rate of heat transfer, which means that at the current state of development, NEMD may not in general be an ab initio method where nonequilibrium energetics is concerned. For the MD algorithm here, unlike the use of standard Verlet algorithm for previous studies (e.g. Ref. [6]), the modified 5 stage 4th order method of Calvo and Sanz-Serna \[40\] tested in Ref. \[41\] was utilized. The parameters \( (\tau, \alpha_k, \beta_k) \) for this symplectic algorithm was taken from \[41, Table 2\] where the pseudo-code for the iterations \( k = 1, M, M = 5 \) are:

\[ p^{(k)} = p^{(k-1)} + b_k \tau F(q^{(k-1)}) \] (18)

\[ q^{(k)} = q^{(k-1)} + a_k \tau G(p^{(k)}) \] (19)

where \( F(q) = -\partial V(q)/\partial q, G(p) = -\partial T(p)/\partial p \).

3. Theory and calculations

Relative to their many assumptions, which are not used here, the RLL solutions are shown to be unique \[10, p.1077, last par., 1st column\]. The RLL system does not seem to follow the FPU trajectory of interpretation in a general sense, and attempts to directly derive the results with thermal gradients and single thermostats at the ends of the lattice by recourse to the various elaborations of the fluctuation-dissipation theorem with its assumption of local equilibrium and time reversibility, which has been proven not to obtain in general as analytical principles \[35,42\]. The assumption of many workers is that the thermostating algorithm with its use of coupling parameters that determines the flow rates that contradicts basic kinetic theory that relates these rates to the thermodynamical forces and the natural intermolecular forces within the system is universally valid, including the use of single thermostats that is equivalent under this belief system to multiple control volume thermostating. A sketch of the solution for the temperature profile is given in Fig. 1. The plateau in the middle portion is not constant but close to \( T = (T_L + T_R)/2 \) although this is the result quoted in simulations. Of importance is that the curve at \( j = 2 \) falls below the mean temperature, and if the Fourier inequality \( q_j \nabla T \leq 0 \) is deemed valid, where \( j = 0 \) (a fundamental kinetic assumption in thermodynamics), then the FP falls along this temperature profile segment, which is a fundamental contradiction to the principle. The plateau portion is widely quoted in numerical and theoretical studies, over the last half century, where the harmonic potential yields “ballistic trajectories” \[14, p.361\]. The profile presented in Fig. 1 is taken to imply the failure of the Fourier law, for the plateau region suggests \( k(j) \to \infty \) there, whereas portions of the end-point regions suggests \( k(j) \leq 0 \). Dhar has opined that \[18, p.459\] Fourier’s law is “probably not valid in one- and two-dimensional systems, except when the system is attached to an external substrate potential.”

The FPU lattice was considered too simplistic for “real” systems and elaborations have been made \[12, e.2.16,p.38\] with the addition of site potentials etc. which is not relevant to the core issues investigated by FPU and others, that is, the role of anharmonicity in moderating the energy flow from the speed of sound ballistic trajectory which is considered “mechanical” to diffusive behavior as exemplified by the Fourier heat conduction law with flow rates proportional to the local gradient. One more elaborate well behaved system \[12, e.2.16,p.38\] has the Hamiltonian form \( H \) \[18, eq.(3)\] where

\[ H = \sum_{l=1}^{N} \left[ \frac{p_l^2}{2m_l} + V(x_l) \right] + \sum_{l=1}^{N-1} U(x_l - x_{l+1}) \] (20)

and \( V(x_l) \) is the position coordinate dependent site or substrate potential and \( U(x_l - x_{l+1}) \) the interparticle nearest neighbor interactions, where the \( x \)'s are the spatial coordinates relative to the equilibrium position. Shah et al. \[14, p.361\] on the other hand seem to indicate from their extensive numerical work that the “general outcome of these studies is that anharmonicity is the necessary ingredient for the formation of a temperature gradient”.

This was verified extensively \[6\] for the most basic model in line with the FPU potential given in (3), a quartic term in the potential leading to
a cubic force term, known as the FPU-β model. It was pointed out [6] that one factor hardly considered in current theory in that the size-dependency of κ, the conductivity may be due to the fact that higher order terms \( \frac{\partial^4 T}{\partial x^4} \) were not considered; accounting for higher order terms could perhaps remove the enigma of \( \kappa \rightarrow \infty \) limits for varying chain length for fixed thermostat temperatures [12, Sec.2.7,p.g.89]. This point was mentioned in Mathematical Reviews for the work [43, MR3162538]. For BQ, the local first order form \( \mathbf{j}_0 = \kappa(T) \cdot \nabla T \) sufficed, with the possibility of higher order terms being incorporated (e.g., \( \mathbf{j}_0 = \kappa(T) : \nabla^2 T + \kappa_2 \cdot \nabla^4 T + \infty \ldots \) but for them the first order term sufficed in the steady state development of thermomagnetic effects [2]. On the other hand, Dhar [18] uses the form \( \mathbf{j}(\mathbf{x}, t) = -\kappa \nabla T(\mathbf{x}, t) \) and admits the following: However there is no rigorous derivation of this law starting from a microscopic Hamiltonian description and this basic question has motivated a large number of studies on heat conduction in model systems. The earlier work of Rieder et al. [10] on the harmonic linear crystal of length \( N \) lead to the conclusion that in the limit \( N \rightarrow \infty \), the heat current flow was proportional to the temperature difference of the reservoirs at the end of the chains \( T_1 - T_N \), rather than to the temperature gradient \( (T_1 - T_N)/N \). By adhering to the first order Fourier law and by parameterizing approximating theories with this form, a belief arose that even for anharmonic systems, Fourier heat conduction was anomalous in that the thermal conductivity diverges as the system size goes to infinity. These beliefs may well have their basis in the use of the ubiquitous first order treatment of heat conduction, in assuming a constant \( \kappa \), and in perhaps not taking other effects into consideration, such as the pressure, whose value over the chain is determined by several factors, such as the mean temperature, and which would be particle potential dependent; i.e., \( \kappa \) may not be only temperature dependent. Be that as it may, in this work Dhar claims that the paper was written to answer the question posed by Zhong et al. [44] who find normal transport at low temperatures and anomalous transport at high temperatures, which leads to the inquiry: Is there a nonequilibrium phase-transition in this system as a function of temperature, or are finite size effects stronger at low temperatures, so that the true asymptotic behavior is only seen for much larger system sizes? The conclusion given as a result of applying many theoretical models, including those of the Green-Kubo variety for the conductivity transport coefficient, is that the unexpected finite conductivity of the \( a \rightarrow b \) Fermi-Pasta-Ulam chain is due to finite sized effects. The impression one gets from all these studies is that a common global vocabulary was being generated in the wave if \( \tau \) varies in time for the same spatial location. A well known extension to non-steady state is the Maxwell-Cattaneo equation

\[
\left(1 + \frac{\partial}{\partial \tau}\right) \mathbf{j} = -\kappa \nabla T
\]

where \( \tau \) is the relaxation time of the system to reach the steady state heat current value of the instantaneous gradient \( \nabla T \) leading to a hyperbolic differential equation of form

\[
\frac{\partial^2 T}{\partial \tau^2} + \frac{\partial T}{\partial \tau} = \alpha \frac{\partial^2 T}{\partial x^2}
\]

(22)

where the temperature conduction coefficient \( \alpha = \frac{a}{\kappa} \) with \( \rho \) the density and \( c \) the specific heat. Solutions to the equation leads to the transmission of temperature waves with finite speed \( v = \sqrt{\alpha/\tau} \). Imposing the spatial periodic boundary condition in the \( 1 - D \) case \( T(L, t) = T(0, t) \) immediately makes the problem solvable within Fourier analysis, even if the physical boundary conditions are open to question. Writing the solution as

\[
T(x, t) = \sum_{m=-\infty}^{\infty} a_m(t) \exp(2\pi imx/L)
\]

(23)

leads to two regimes, the oscillatory wave relaxation due to complex numbers appearing in the \( a_m(t) \) factor whenever \( m > L/4\pi\sqrt{\alpha/\tau} \) and a diffusive non-oscillatory factor otherwise [46, eq. (6)]. We hypothesize that such equations might be relevant in our system of fixed boundary conditions whereby oscillatory waves propagate in both directions from the cold to the hot reservoir and vice versa such that a resultant non-varying in time sinusoidal temperature profile over spatial coordinates might result in the steady state situation. We can also hypothesize that for the FP to obtain, diffusive waves propagate in both directions leading to a stationary distribution with the Fourier law evidenced in the steady state. The above realizations would depend on whether there exists some type of detailed balancing that would result in a stationary state from two dynamical processes. It is also conceivable that two oscillatory waves propagating in opposite directions could result in a stationary profile that does not have sinusoidal variation over distance. In this case, the Fourier law would still obtain.

Taking the remark made by Shah et al. above as an observation which accords with the original FPU rationalizations, we carry out simulations where the site potential in (20), \( V(x) = 0 \) (which is more basic than Dhar who admits this factor but affirming Shah et al. and also the work in Ref. [6] which is used as a reference for the runs performed here) and consider the anharmonic portion \( U \) written as

\[
U(x_{n-1}, x_n) = k_0 \frac{(x_n - x_{n-1})^2}{2} + b_0 \frac{(x_n - x_{n-1})^4}{4}
\]

(24)

which is the FPU-β standard model for the anharmonic contribution to the interparticle potentials [14, eq.2]. There is a history to the FPU model which is constantly referred to in the literature concerning heat conduction but where a link to the original work has not been discussed. Clearly the potentials used are arbitrary. We conform to the standard models of potentials representing the most basic representative potentials used in simulation and which is referenced so that comparisons between theories and simulations may be made with standard values of the potential coupling coefficients in reduced units. In our case, the differences with previous work may be enumerated as follows: (a) more than one particle per control volume is used, (200 in this case) (b) a non-synthetic algorithm is used for thermostatting, (c) a 5th order symplectic MD algorithm is used, (d) a relatively larger number of particles \( (N = 1000) \) (e) a high rate of thermostating frequency where the thermostats are activated every 5th time step compared to about 20 in normal NEMD applications [22,37] for this type of thermostats, (f) a relatively very large sampling of 1 Billion time steps per run, and (g) using a relatively large temperature difference between the set thermostat values but which is moderated by the longer chain length to observe features that arise from larger
temperature differences.

Thus any differences that are found between the results found here and in other work can be attributed to at least any of the above differences in system or thermostatting algorithm.

3.1. Note on reduced units and temperature

In this note, reduced units for physical quantities are denoted by asterisks *, and are in laboratory (e.g. SI.) units if not denoted by an asterisk. All the given computations and graphical expressions are according to reduced units. The system is a homoatomic 1-D lattice chain with masses $m_i = M_i$. If the interatomic equilibrium distance is $L$, then for any length measurement $x$, a convenient reduced length is defined as $x^* = x/L$ and thus $L^* = 1$ where the reduced unit length is our equilibrium interatomic spacing and similarly $m_i^* = m_i^L = 1$ for the masses. Clearly in all cases, the laboratory unit of measure must be specified (e.g. L, $m_i$) to recalculate the measured variable from reduced to laboratory units. If the energy unit is $e$ then for any energy measurement yielding value $E$, then $E^* = E/e$. The temperature in reduced units is defined as $(kT^*) = k^* T^* = k^*/e$ ($k$ is the Boltzmann constant) and since it is conventionally interpreted that $k^* = 1$ in magnitude, (another interpretation is given in Ref. [48]), then $T^* = k^*/e$. We define the temperature by assuming the equipartition of energy theory applies to our s.s. system, which is defined similarly by practically all workers in the field [18], where $N_i \langle v_i^2 \rangle = \frac{1}{2} \sum_i m_i \langle v_i^2 \rangle$ or $N_T^* = \langle \sum_i N_i \langle v_i^2 \rangle \rangle$ where $N_D = 1$ for a 1-D system and $N_D$ is as before the number of particles in the control volume. So $T^*$ is defined via equipartition and this parameter is used to characterize the temperature profiles. Thus there exists continuous and differentiable vector function mapping laboratory units to laboratory units [48] $\mathbf{F}(\mathbf{D}_L) = \mathbf{F}_R$ where $\mathbf{D}_L$ is the vector domain of laboratory units. All mainstream MD research platforms, e.g. Ref. [49] convert the inputted $\mathbf{D}_L$ variables to reduced $\mathbf{F}_R$ values which are used for the computation proper from reconverting back to the appropriate laboratory units for the output. For very large systems, such as in biochemical systems, laboratory units are used because the focus is not on basic measurement of physical parameters but on bulk properties of thermodynamical variables. In fundamental Physics studies on the other hand invariably use reduced units to ensure that there is no reporting of duplicate data where in laboratory units, the variables may appear to be different, but are the same in reduced units, since the function $\mathbf{F}$ is not a $1 - 1$ mapping.

4. Results

The MD runs each time were $1 \times 10^9$ = 1B time steps after an initial relaxation run of 10 M (1M = $10^6$) time steps where the coordinates from the previous run are used for the subsequent one at the commencement of any particular MD run. The results presented in the graphs of Figs. (2–5) are typically for the last 3 runs in the 17–21 runs; more details are provided in the paragraph discussing Table 1 results. The total “warm up” of time steps prior to sampling is in the vicinity of $17 \times 10^9$ time steps. This figure is based on monitoring the energetics and temperature profile. Before reaching the particular s.s. equilibrium with the heat inputs being equal and opposite for the cold and hot reservoirs, the time steps were varied from one run to another, even up to $\delta t = 1$. The input coordinate files for Series 1 were used as initial inputs for Series 3. It took over 20 days of runs to arrive at a s.s. when all the variables and the temperature profiles did not vary up to the standard deviation of fluctuation. The object here is to present examples of numerically derived s.s. profiles which can be contrasted with some the abstract mathematical solutions not of the KdV and KAM trajectory alluded to and with others that might be forthcoming so that inferences might be drawn concerning the BQ discussion of Fourier heat and the FP and not to prove uniqueness of solutions since as discussed previously, no one theory is able to account for all the observations, and so the question of uniqueness of solution is a moot point at the current time for the regime under which the simulations were conducted. Furthermore, the KdV and KAM developments seem dialectically positioned, with the situation far from clear. Given the circumstances, what might be more useful is to comment on the results as determined by the MD algorithm. We note that in theories, blow-ups and singularities appear whenever rational coefficient exist in the denominator of perturbation expansions [23, Eq. (3.8), p.59]; also whenever the action angle frequency variable ratios [23, A.6 p.146] are rational, then periodic motion about the torii energy hypersurface occurs, and the hypersurface is not covered, meaning the motion is not ergodic; this implies that relative to these theories, computer simulations are of limited applicability in determining full system properties. The results here are relative to systems specified by the Hamiltonian, and where the dynamics uses the specified move and thermostatting algorithms, within the domain of rational numbers. In the absence of proven theories, the approach here is to oscillate between possible applicable concepts, culminating in the proposal of a dynamical heat principle in subsection 5.1. Indeed, by analogy with zero current equilibrium systems, one may expect an infinite number of neighboring s.s. solutions to exist [50] for any one specified temperature difference, since for purely harmonic motion of a lattice, an infinite number of solutions exists. An inhomogeneous stochastic addition to the homogeneous equation could yield a multiplicity of solutions dependent on the boundary conditions, and sources of noise. These objectives were also touched upon in Sec. (3). There is reason to suppose that the output profile might not be unique for “ballistic” trajectories close to harmonic normal mode behavior since there are no unique solutions for these purely mechanical motions which depend on the initial boundary conditions.

In the figure legends, $n$ represents the data for the $n^{th}$ run. The statistics for the energy transfer were averaged over 30 dumps where each dump sampled 33 M steps. The reduced time increment $\delta t$ was $\delta t = 0.001$. Table 1 contain data for the heat transfer characteristics for the runs in Series 1 (–4). All fluctuations in quantities are expressed as the uncorrected standard deviation

<table>
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<tr>
<th>Series #:</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
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</table>
u.s.d. and the error ± are expressed in terms of this u.s.d. The u.s.d. is the ordinary standard deviation σ where \( \sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (y_i - \mu)^2} \) with mean \( \mu = \frac{1}{N} \sum_{i=1}^{N} y_i \); \( y_i \) are the experimental values with \( N \) sample points. The E notation signifies base 10 exponents.

The main reference here is the harmonic system \((b_h = 0.0)\) where comparisons are made to this system whenever the diffusive term \(b_d \neq 0.0\). For anharmonic systems, the main reference is when \(b_h = 0.5\) and the “ballistic” indicating coefficient \(k_b\) is made to vary. The objective is to determine whether there exists possible steady-state configurations that might be encountered in real systems as suggested by simulation results, especially if they differ from abstract theories of systems that are not equivalent to ours. Series 1 suggested by simulation results, especially if they differ from ab-

bh

similarly Series 4 contrasts with Series 1, where in either case k

ous work [6] based on the

given in Fig. 3 as Series 2; the choice conforms to the pure FPU-β approach of CMT is encouraging because of the resultant expression of propagating waves and oscillations as a result of introducing scalar advance-delay differential equations, pulsating traveling waves [12, pg.209] and time-periodic oscillations determined from iterative maps of periodic functions. For instance [12, Fig. (6.1) pg.209] an oscillatory tail wave amplitude results from a pulse profile at time \( t = 0 \) which are analogous to the pulses introduced by the hybrid elements of the thermostat energy impulses which are all solutions to their dynamical equation [12, eq. (6.3), pg.208] having form

\[
\frac{d^2x_n}{dt^2} + V'(x_n) = \gamma (x_{n-1} - 2x_n + x_{n+1}), \quad n \in \mathbb{Z}
\]

where \( x_n \) is the coordinate of particle \( n \), \( \gamma \) the coupling constant, and \( V \) the potential term, and \( V' \) a presumed gradient to the potential. Other solutions to the same equation for different \( V \) and coupling coefficients have been reported [12, Fig. (6.9),pg.235, Figs.(6.10–6.11), pg. 236]. An attempt to relate the KdV and FPU equations has been discussed by B. Rink [12, Chap. 8, p.283] where KdV unidirectional waves could be partially related to the results of the FPU lattice [12, pg.283]. It seems plausible that these approaches that refer to unidirectional waves, when coupled to the appropriate boundary conditions and to the stochasticity of the thermostats, could serve as a backdrop to a development of a theory that can account for the stationary oscillations encountered in the simulation results here. Finally, the KdV, CMT and other approaches mentioned all seem to have wave-solutions and concepts of periodicity, and the simulation results too seem to mirror
these features, unlike the RLL model, and so it is surmised here that the results are not all that extraordinary when viewed within the context of the mainstream developments briefly surveyed here.

The NEMD stimulation studies reported in the literature often use values in the vicinity of $k_h \approx 1$, $b_h \approx 0.5$ for the standard harmonic and anharmonic term. We increased the value of $k_h$ to observe whether any s.s. solutions exists for these exaggerated $k_h$ values. These are reported in Series 3 and 4. Current theory and investigations seem to focus on either the presence or absence of the $b_h$ term, and not on the relative magnitudes. As proof that relative magnitudes does affect the s.s. temperature profile, both $b_h$ and $k_h$ are varied and compared. We used the converged position-momentum values of Series 1 for Series 3 with the original intention of hastening the convergence process by providing some initial starting point which lead to the Series 3 convergence.

As side note, the $k_h$ value for the exaggerated case was computed very roughly for tungsten instead of choosing an artificial large whole number not related to physical properties. The (large) value of $k_h = 593.355$ for Series 3 in Fig. 4 was estimated very approximately by assuming the harmonic potential for the element tungsten (W) with lattice constant 316.52 pm, BCC structure, bulk modulus 310 GPa, where we set the reduced temperature $T^* = 1$ when $T = 300K$ and where there are 2 atoms per unit cell. There is nothing else remarkable about this particular choice. If asterisks represents the reduced units variable, then the energy scaling parameter $e_s$ is such that $k^* t^* = kT^* e_s$ so that $e_s = 4.14196 - 21$. The harmonic energy of a crystal is $E_h = 2k_0/\Delta^2$ with the harmonic constant $k_0$ and so $k^*_h = b^*_h/2c^*_h$. The bulk modulus $B$ can be written approximately $B = (\partial P/\partial V)_{T, V}$ for changes $\Delta$ in the pressure $P$ and volume $V$. Equating the forces of compression with the harmonic force law with the harmonic constant half of what it would be for a single atom per unit cell leads to $k_h = 49.06/\text{nm}^3$.

Thus $k^*_h = 49.06/316.52 \cdot e^{-24} = 593.355$ which is close to our choice of $k^*_h = 593.355$ in the simulations.

The anharmonicity constant is the same $b_h = 0.5$ for all simulations whenever $b_h \neq 0$, where the ratio $b_h/k_h = 8.42 \times 10^{-4}$ and 0.5 respectively for Series 4 and Series 2. The Series 3 profile coincides with the Series 1 profile, but the rate of heat transfer is radically different for the converged flow rate. Finally, we include the $b_h$ anharmonicity factor to study the s.s. profile for a Series 3 system where $b_h = 0.5$ in Fig. 5 for Series 4.

Some comments are in order: Series 1 and 3 both have zero anharmonic contribution $b_h = 0$ to the potential, but it is possible to have coincident stationary temperature/kinetic energy profiles but with radically different stationary thermal energy fluxes. We can infer or surmise that one is dealing with a type of vibrational energy transfer mediated by the thermal reservoirs that allows for solutions to the dynamical system of exactly coincident thermal profiles, but not of energy flow rates. Since the $k_h$ values differ, the speed of “sound” or the wave velocity differs, and so it is clear that in this case, the flow rates are due to the different values of $k_h$ that determines the group velocity of propagation of the wave which is proportional to $\sqrt{k_h}$ in a harmonic lattice in addition to other factors related to Brillouin zones. Table 1 shows indeed that the flow rate is $\approx 24.35$ larger, as expected from the above argument concerning group velocities. Of course, since we are dealing with a stationary wave, there is the reverse energy flow as well that must be taken into account in any coherent theory. We can also infer that the mechanism of non-diffusive heat transfer - meaning transfer of heat by the harmonic potential interactions - is a process that can decouple itself from amplitudes and the stationary state temperature profile distribution when comparing the results of Series 1 and 3. The comparison of Series 3 and 4 is interesting in that here the common factor is the same value of $k_h$ and not $b_h$ as in the case of Series 1 and 3. We note that there is an obliteration of the coincidence of the temperature profiles, where in Series 4 the peaks are not so pronounced and ordered, due to the anharmonicity part that seems to confer diffusive behavior that smudges the distinctness of the peaks found in Series 3. We therefore suspect that the temperature profile distribution is affected or coupled to the $b_h$ factor. Another interesting observation is that the heat transfer rates are fairly similar, the ratio of Series 4 to 3 being 1.032 with the rate in Series 3 slightly higher than for Series 4. We can infer that the main carrier of energy is the harmonic term $k_h$ in the potential, and that the diffuse $b_h$ factor creates a scattering process that retards the energy transfer by a relatively small amount for that particular pair of runs we are considering. Comparing Series 1 and 2 shows that for this, the $b_h$ term seems to contribute positively to the flow rate, rather than retard it. These comparisons seems to suggest that the ratios of the two factors ($k_h, b_h$) might indicate the degree of interplay between work-heat transformations within the phenomenon of heat conduction [5, Materials and Methods]. Based on the observations in the simulations and the theoretical result of RLL where there is clear violation of the FP, then if steady state heat conduction is to encompass all the temperature profile possibilities including RLL and the results here, then one possible rationalization is to propose that these work-heat transformations occur not just when the Fourier principle is maintained, but also when there is violation of it. This proposal is embodied in the hypothesis of subsection (5.1). It was observed in these simulations conducted over several months that at the initial stages when the s.s. had not yet been attained judging from the flow rates at either ends of the lattice chain, the temperature profile on the other hand was reasonably stable and coincided to within 0.1 or less in temperature units with respect to the particle index when compared to the converged values. For such systems, the molecular distribution function and the associated properties arising from this distribution (e.g. density, energy etc.) cannot be used as the sole criteria for the steady state “equilibrium” and therefore both flow rate and the temperature profile distribution were used to indicate the regime of the s.s. for Series 1–4; initially, even if the temperature-particle index profile in Series 1–4 were slowly varying, the heat input and output currents were not equal to within experimental fluctuation; indeed, the energy current flow rate at both ends differed by some orders of magnitude relative to the fluctuation. Table 1 provides the data with the following heading: (e) and (g) are heat input per unit time in the L and R thermostatted control volume; (f) and (h) are the standard deviation of the heat input per unit time in L and R thermostatted control volume. Table 1 provides the data for the convergence criteria where the absolute value of the rate in the (L) left arm varies by $10^{-3} - 10^{-5}$ of the current fluctuation (columns (e) and (f) respectively) and $10^{-3} - 10^{-6}$ for the (R)ight arm (columns (g) and (h) respectively), in keeping with the different temperatures that would affect the fluctuation magnitude. More importantly, the difference of rate relative to the random fluctuation error is of the order of $10^{-5} - 10^{-7}$; at this point, we could not discern any more improvement relative to the fluctuational error. This was achieved after ~ 17B time steps which is not the length of runs typically encountered in the literature. For normal precision, 1B is about the order of magnitude for the limit of integer arithmetic magnitude. A large number of steps were taken in order to ensure that s.s. heat current equilibrium had been reached, where subsequent runs did not improve accuracy. The equilibrium values were finally averaged typically between the 18–20th runs where we “preequilibrated” by $10^{-2}$ time steps between runs before sampling with dumps, where each run lasts 1B timesteps. Thus, the
total “warming up” or thermalization steps is in the vicinity of $17 \times (10^2 + 10^3)$, which is a large number for pre-equilibrium for systems of this size. In nonequilibrium measurements conducted in the past, in one instance to disprove the principle of local equilibrium [16], the relative error in the difference of the rates relative to the past, in one instance to disprove the principle of local equilibrium. In nonequilibrium measurements conducted in current relative fluctuations of $10^{-5}$ which is a minute figure for NEMD simulation fluctuations. Here the method used included using varying $\delta t$ time step increments at the preliminary stages of the runs with 1B time steps each time over 20 days until no further improvement could be observed, in that the average for each run fluctuated in both directions about the average of the run averages.

5. Discussion

The Series 2 results partially verifies Shah et al. [14, p.361] in Sec. (3) and many others concerning anharmonicity contributions allowing for Fourier’s law to hold without a site potential. The data from the Series 2 system was used to construct a theory of recoverable conversions for heat-work energy transitions along the so-called recoverable trajectory $\delta \mathcal{V} = 0$ [68] as exemplified by Fourier heat conduction where the heat flow direction was consonant with the FP for that particular system throughout. The construct was verified as obtaining for Fourier heat conduction through simulations using the ordinary velocity Verlet algorithm for the Series 2 result. Various force and work terms had to be computed at each time step to verify the theorem for a well-behaved non-pathological system where the FP applied locally [6, eqs.(68–82)]. The Series 2 runs here were just to ensure that the FP applied here and that the system was well behaved with the new MD algorithm and was compatible with previous results.

In current terminology, the term “ballistic” terminology applies to solutions given for instance by the RLL system where the FP breaks down [14, 1. Introduction] and where presumably, because of the flattish curve, the conductivity would tend to a very large number. Dhar opines that the Green’s function approach can explain harmonic systems but does not produce any temperature fluctuations. Here the Fourier-phonon interactions can be neglected”. How one can describe phonons in classical simulations is one area that is not always apparent. Indeed, the well known solution of the harmonic lattice without thermostating in (27) shows that the modes are all independent, and that if the role of the thermostat was essentially to modify the coordinates of the first and last particle, then the energy transfer would be through all the independent modes where the boundary conditions are modified for the first and last particles. Thus, one could interpret “phonons” classically as these independent modes of sinusoidal vibrations that arise from the harmonic potential that transmits energy as a traveling wave. The role then of “anharmonicity” would be at each increment of time $\delta t$, to perturb the position and momentum of the particle away from the path it would take if the harmonic potential only were operative, thereby leading to “phonon” interaction or coupling amongst the different modes. Hu et al. [21, p.2394] write: “If the lattice is absent, and the interparticle potential is harmonic, then no phonon-phonon interaction exists; thus the heat transfer would take place at the speed of sound and the thermal conductivity would be infinite, as pointed out by Debye in 1914. However, if we add a dissipative term to the harmonic oscillator chain, then we could obtain the Fourier heat law, even though we do not have a lattice.” Here, within this interpretative framework, the Fourier law is thought to arise from constant perturbation of the path from the harmonic trajectory due to the anharmonic term. This then is an interpretation of the phonon interaction mechanism alluded to by Dhar for classical systems. We note however that this interpretation would suggest that the strength or intensity of the interaction would be significant, and not just the fact that a minute perturbation only is required, as perhaps suggested by Hu et al. above [21] since magnitudes are not mentioned. Concerning profiles for heat conduction, the originators of the RLL theory [10] claim “no explanation is offered for this paradoxical result” which could refer to the entire temperature profile of Fig. 1, or to the portions that violate the FP, where the principle or other thermodynamic principles are not explicitly discussed in the text. However, the remark has a prescient ring to it, in that despite the mathematics, there seems to be an awareness of possible thermodynamical anomalies that attend their solution. There seems to be a diversity of opinion at the current times in the absence of comprehensively stated theories, as noted in Ref. [29]. We note that RLL used the Liouville equation in conjunction with the Hamiltonian. It was pointed out that the Liouville equation could not in general obtain as a mathematical truth for most systems, although it and the quantum version is a basis for describing systems and might be considered good approximations as a result of their continuity [5, see refs. 66 and 67]. The RLL system and the one studied here are not equivalent since we use a control volume of 200 particles at the R and L ends of the lattice chain for thermostating using a non-synthetic algorithm with no coupling coefficients. Furthermore, assuming RLL uniqueness to their solution, and that the number of particles thermostatted do not matter, then perhaps the method of coupling of the reservoirs to the particles play a role in leading to the solution depicted in Fig. 1. Another possibility is that these coupling mechanisms may be dependent on the number of particles thermostatted, and the temperature and temperature differences, as mentioned previously in the case of the anomaly concerning ergodicity in KAM and statistical physics theories. It could be that the solution of the stochastic equations would require some type of propagation term from the particle that is thermostatted to all the other non-thermostatted particles in a time retarded manner. The RLL method has the Liouville equation to generate densities. Perhaps other methods such as stochastic differential equations (SDE) [52] with forms [53, eq.(4.1)]

$$X(t) = X_0 + \int_0^t f(X(s)) ds + \int_0^t g(X(s)) dW(s), \quad 0 \leq t \leq T.$$  

(26)

where noise terms $W$ could be incorporated into a known solution, such as the harmonic lattice could be attempted, but then there must be expressions that also cater to the propagation and energy transfer terms in a non-local sense at the s.s. where (26) is however a local expression. Exact solutions to the anharmonic lattice is limited and at the present time and numerical solutions are plagued with many convergence issues. Numerical solution of stochastic differential equations and especially stochastic partial differential equations is a relatively young field and most if not nearly all algorithms that are used for the solution of ordinary differential equations work poorly for SDEs, with poor numerical convergence [54]. As such, it follows that numerical simulation data will continue to play a major role in at least heat transfer processes, and could also inspire the direction of the mathematical development from the results generated. If indeed non-synthetic thermostating of regions involving multiple particles are deemed to be reasonable representations of physically realizable systems, and that this feature is significant in the steady-state profiles that...
are generated in real world applications, then some consideration of work over the last several decades in theoretical heat transfer might prove beneficial to incorporate some of these added features that have been neglected in some of the theoretical modeling. Another deduction attempted in this work is related to the problem of the anharmonic contribution to the potential. Is the presence of the anharmonic term a necessary and sufficient condition to ensure that the FP and in particular, the Fourier law obtains? Comparing Fig. 4 for Series 3 and Fig. 5 for Series 4 allows for a deduction. The purely harmonic Series 1 profile has 5 well defined peaks for $k_B = 1$ and Series 3 with the harmonic constant $k_B = 593.355$ has remarkably a nearly exact profile with exact coincidence of the temperature-particle index graph, but with radically different heat transfer rates ($\sim 0.388$ unit time) for Series 3 as opposed to ($\sim 0.344$ unit time) for Series 1 when the input coordinates for Series 3 were derived from the output for Series 1 at an earlier stage prior to relaxation to a new s.s. We note also the well developed curves of Series 1 and 3 seem to indicate the formation of quasi-mechanical standing “thermal waves” despite a net dissipative transfer of heat from hot to cold reservoirs at different rates. The introduction of anharmonicity ($\delta_B = 0$) with the same reservoir algorithm and harmonic coupling coefficient $k_B$ value destroys or smooths out the standing wave pattern, and further another peak (6 peaks) are added with a heat transfer rate of $\sim 0.81257$/unit time for Series 4; however, we do not observe a linear temperature profile for this series and more importantly, the FP is violated along the chain. We therefore conclude that anharmonicity is a necessary but not sufficient condition for the Fourier law to obtain. Indeed the ratio of the force field parameters $\delta_B/k_B$ in Series 4 seems to determine whether the Fourier law is obeyed or not. In addition, whether absolute magnitudes of ($\delta_B$, $k_B$) are also featured in the criterion for the FP to hold is not known at the present time, as with the temperature difference magnitude $T_1 - T_2$. Here, we interpret the phonon coupling via $h_B$ as determining the degree in which “diffusive” energy transfer predominates, traditionally also interpreted as thermal energy. In Series 4, there is violation of the FP despite the presence of the anharmonic term. The question that could be posed therefore is: can “heat” energy still be defined locally or microscopically within the system in the light of the RLL solution and the results of simulation, and the First and Second law formulations? We note that heat energy is thermodynamically defined as that form of energy transferred due to a temperature difference and therefore the RLL system of a purely harmonic lattice chain would be defined as transferring solely thermal energy despite its “ballistic” trajectory; further, in Series 4, there is violation of the FP principle with a nonzero anharmonic $b_B$ term.

As a result of these considerations, it seems that the energy transferred due to the harmonic and anharmonic terms both qualify as “heat”, and the criterion for pure local heat transfer cannot be merely compliance to the FP, but also pure heat transfer can occur in physical processes that violate the FP. A more general criterion for the definition of heat is conformation to the variation principle construct of subsection (5.1) as defining pure heat flow without global compensation.

Table 1 might indicate the degree of admixing of the “ballistic” or mechanical component of the harmonic potential with the anharmonic modification; one would expect that the “ballistic” trajectory would not have a large fluctuation in the energy transfer. For the same Series, the higher temperature reservoir has a higher thermal temperature fluctuation in the u.s.d. as compared to the lower, as would be expected from the higher kinetic energy. That is the static aspect. Where the rate of energy transfer is concerned, Table 1 indicates that purely harmonic ballistic trajectories of Series 1 and 3 have much smaller u.s.d. fluctuations (heading (f) and (h)) than their analogs with some anharmonic contribution (Series 2 and 4 respectively). However, they have comparable heat exchange rates. This seems to indicate that the Debye argument quoted by Hu above requires qualification or modification in that the combined modes in the ballistic trajectories have a kinetic description in energy transfer that is comparable to the one with “phonon” coupling. The relatively very low u.s.d. fluctuations in the energy transfer rate in the reservoirs (Series 1 and 3) seems to indicate a quasi-mechanical trajectory, where the anharmonic contribution adds to the spread of energy distribution in the thermostats. The general solution for a purely mechanical system of an array of $n$ oscillators with coordinates $q_k$ relative to the equilibrium position all evenly placed is given by

$$q_k(t) = \sum_{N=1}^{n} A_N \sin \left( \frac{N x k}{n - 1} \right) \cos \left( \omega_N t - \epsilon_N \right)$$

with $\omega_N = 2\omega_0 \sin \left( \frac{N x k}{n - 1} \right)$ and $\omega_0 = \left( \frac{x}{m} \right)^{1/2}$ where $K$ is the elastic constant and may be inferred from Ref. [55]. Hence between thermostat activation, the above equation would be relevant for each of the particles in the lattice chain in Series 1 and 3, leading to a relatively small energy transfer fluctuation. The contribution of the anharmonic factor for at least this simulation algorithm seems to be not so much to retard the motion, but to contribute more to a greater fluctuation in the energy transfer process.

The data from the simulations, including the RLL solution, indicates that the FP does not apply locally. Also, the RLL solution has regions where the temperature is lower and higher than the adjacent or neighboring thermostatted particles. These results imply that such peaks and troughs in the distribution may be used as energy sources and sinks, so that thermal rectifier junctions could be created at the microlevel, not involving only anharmonic lattice chains which is currently the standard model of construction [14,32,56–59] where each chain constituting a junction or gate in a 3 terminal device is of the same type in terms of constitution and force fields.

5.1. A fundamental hypothesis concerning heat transfer

The FP does not apparently apply locally to some regions in RLL-like theories and from the various simulation data. If these results are also physically realizable, then this fact has implications for the definition of heat given by some in the First law and for any other measurement based on this definition. The Clausius statement without reference to cycles of the form: [31, 2. Clausius statement of 2nd law] “No process is possible whose sole result is the transfer of heat from a cooler to a hotter body” might require some refinement in having to extend the system beyond a locally defined region to conform to the law, since microscopically, we observe the transfer of energy from a colder adjacent particle to a hotter one; if each particle is a body with a defined temperature, then the definition is not complete. In order to overcome some of these difficulties associated with the direction of energy flow and the definition of heat, we resort to a principle verified for a 1-D anharmonic lattice where the FP holds and where the theory of “recoverable transitions” [60] was applied to Fourier conduction [6]. Whilst the current simulation reported here and elsewhere and theoretical considerations such as the RLL theory does not contradict or invalidate the theory developed in Ref. [6] for a system that complied with the FP everywhere, we postulate that the same theory can explain the transfer of energy.
along a positive temperature gradient, and which can still be considered as thermal energy (extending the concept of heat as defined by Carathéodory and the definition of heat in thermodynamics) if we simply state that even in regions where the Fourier law is apparently violated, the entropy change along the trajectory is invariant and may be written [6, eq.(1)]

$$\delta \left[ \int_U dS \right] = \delta \mathcal{S} \bigg|_{\text{Traj}} = 0. \quad (28)$$

where the variation of the entropy $S$ is over the system trajectory $\partial C$ of a "macroparticle" subject to the constraints of fixed energy content $U$ and external constraints $(x)$ and where $U$ has a specialized meaning. In multivariable calculus, the subscripts refer to constant terms; here the energy is in one sense not constant because a portion of the energy may be transferred to the force constant terms; here the energy is in one sense not constant and other portions retained. This entire trajectory, but not locally. This energy

where (30) has an entropic form locally but which incorporates the same constant $k$ in the discrete model described below for particle $i$ is written as follows where subscripts $a, b$ refer to states with the same potential energy just after or before a collisional interaction with particle $i + 1$ and is written [6, eq.(48)]

$$Q_{b(a)} = \left\langle k.e.(i) + V_i \right\rangle_{p_j} \quad \text{(averaged over all j collisions with i + 1)} \quad (29)$$

where $p_j$ represents the coordinates at the point of interaction; there is also an interaction with particle $i - 1$ which is discussed for the above equation [6, eq.(48)]. Then it can be shown that at the s.s. [6, eq.(54)],

$$\frac{(Q_b)}{T_b} - \frac{(Q_a)}{T_a} = 0 \quad (30)$$

where the same constant $k'$ applies for $x \in (a, b)$ where $k' = \frac{Q_b}{T_b}$ where (30) has an entropic form locally but which incorporates potential energy factors and where trivially the equation is $k' - k' = 0$. Defining an interval of time $\Delta t = dt$ and $F = F_{i+1,i}$ where $F$ is the force exerted by particle $i$ on $i + 1$, where for $n$ time intervals, $n \mathcal{S} = n dt$, then it can be shown that the continuous analog (reduced to per unit time) to the discrete case leads to equations such as the ones below [6, eq.(73-82)]

$$Q_a = \int k.e.(i) dt / \Delta t. \quad (31)$$

with heat content $Q_a$ and work quantity $\delta w$ given respectively by

$$Q_a = k.e.(i) - F \frac{dq_{i+1}}{dt} dt_j \quad (32)$$

$$\delta w = (Q_0 - Q_a) \quad \text{spanning } [t_1, t_2]. \quad (33)$$

Over $n$ time intervals, the averaged $\delta w$ have values

$$n \delta w = \int_{t_1}^{t_2} k.e.(i) dt / \Delta t - \int_{t_1}^{t_2} \left( k.e.(i) - F \frac{dq_{i+1}}{dt} \right) dt / \Delta t \quad (34)$$

$$= + \left( \int_{t_1}^{t_2} F \frac{dq_{i+1}}{dt} dt \right). \quad (35)$$

where for a single time interval

$$<Q_a> = \frac{\int k.e.(i)}{n dt} - \frac{\left( \int \frac{F dq_{i+1}}{dt} dt \right)}{n}. \quad (36)$$

and so $<Q_a> = <Q_0> / 2$ where at all times the above construct is centered about the identity $k' - k' = 0$.

Since the above is based on a localized Carnot-type engine, where in the case of the global Carnot engine, heat energy can be conveyed in a cycle from a hotter to a colder region provided work is done on it, so likewise if the force fields are orientated in a manner to do work on the “macroparticles”, heat could locally flow from a colder region to a hotter region if the force-fields permit it. One could therefore also suppose that the above equations would not need to be modified significantly to verify this principle for regions within a system that exhibits such FP violations. One could also interpret the $k_h$ “ballistic” and $b_h$ “diffusive” parameters as influencing the $V_i$ potential of (29) in the discrete version depicting the principle, that would locally permit the FF to fail.

6. Conclusion

The data presented indicates that the RLL interpretation, remarkable as a first attempt in describing anomalous heat diffusion or Fourier conduction that has in some positive ways influenced nearly all subsequent work over the last half century is probably a model that could be augmented by a more flexible set of conditions including the nature of thermostatting in terms of coupling mechanisms, the number of particles in the control volumes of the thermostatted particles, and the dynamical equations. This is a major project. On the other hand, during the intervening time since the RLL method was mooted, many other lattice dynamical theories have gained ascendency or popularity in addressing the FPU lattice problem [23, pg.29], several of which are variants of the KAM theory of stability, or the wave theories of KdV. It is suggested here that the simulation results based on our non-synthetic algorithms could perhaps be described by recourse to some of the mathematical structures and methods found in the KdV and KAM and Maxwell-Cattaneo developments, suitably modified. The remarkable quasi-mechanical sinusoidal curves of the s.s. profile for harmonic interparticle potentials relative to this simulation algorithm imply that the peaks in those graphs, as well as the troughs can be coupled to other lattice chains to produce more complex integrated thermal circuits than is currently being investigated [32]. We showed that anharmonicity is a necessary but not sufficient condition for traditional Fourier heat conduction mechanisms to apply. We inferred that the relative magnitudes of the $k_h, b_h$ terms determine the degree of ballistic and diffusive energy flow in the lattice. We also present a hypothesis that even for harmonic potential lattices, heat flow can occur along a temperature gradient, without contradicting recoverable heat transition theory [60] as expressed in (28), which generalizes the nature of heat and its direction of flow in a temperature gradient as
defined in some versions of the First and Second laws of thermodynamics. Perhaps more true now than at any other time in the past, the discussion given in Ref. [29] should be heeded and a very open view be maintained as regards these fundamental issues of the nature of heat and thermodynamics in general. Furthermore, we have shown how applied mathematicians devise boundary conditions and invent assumptions to force a solution to their supposedly physical system. Escularta et al. [61] are of the opinion that all too often mathematical physicists are actually solving differential equations and other mathematically predefined algebras rather than creating an axiomatic base stemming from the experience of reality that can become the structure for mathematical invention which has a physical correspondence whenever solutions to physical problems are attempted. Perhaps this insight should gain more influence in providing a means to solving problems related to the physical world.

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I thank one of the reviewers for indicating the need to mention the history of the FPU lattice problem and how it stimulated the activity of reality that can become the structure for mathematical invention which has a physical correspondence whenever solutions to physical problems are attempted. Perhaps this insight should gain more influence in providing a means to solving problems related to the physical world.

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