Steady State NEMD Investigation of Heat Conduction of a 1-D Lattice Chain Subjected to a Temperature Gradient and Statement of a Variational Principle for Second Law Compliance of Heat Transfer

Christopher G. Jesudason

Center for Theoretical Physics and Chemistry Department
Science Faculty, University of Malaya, 50603 Kuala Lumpur, Malaysia
Email: chrysostomg@gmail.com

(Received: 31.1.2018 ; Published: 7.6.2018)

Abstract. Two aspects of conductive heat are reviewed here, (i) its basic definitions and (ii) the results of nonequilibrium molecular dynamics (NEMD) simulation for a 1-D lattice chain for the harmonic and non-harmonic FPU-β standard model potentials subjected to a temperature gradient that results in both thermal energy flow and a distinct temperature profile at the steady state. Ever since the publication of the Rieder-Lebowitz-Lieb (RLL) theory approximately half a century ago, it has been taken as axiomatic by the global Physics community that their rationalization and prediction of a near flat temperature profile along the central region of the harmonic lattice is unique and the only one possible for the ballistic trajectory that ensues for such intermolecular potentials. We note that the RLL theory is replete with assumptions concerning the nature of how the particles interact with the potential field which was mathematically convenient in providing the boundary conditions that allows one to derive exact solutions to the matrix differential equations. Using non-synthetic NEMD algorithms that conserves energy and momentum, we observe that other solutions to the steady state problem exists, where the temperature profile varies sinusoidally, which also obtains for non- harmonic potentials depending on the strength of the potential coefficients for the harmonic part of the potential. This investigation will describe some of the potentials used and the ensuing results. Apart from the obvious theoretical implications of these results, we surmise that systems exhibiting a near harmonic potential could be used for the construction of thermal PN junctions in regulating heat flows in applications.

Keywords: local violation of Fourier law and Second law statements, NEMD simulation of FPU-β standard lattice chain model, Rieder-Lebowitz-Lieb theory violation, thermal transistor applications.

I. INTRODUCTION

We investigate steady state heat conduction on a 1-D FPU-β lattice chain of N particles albeit for a non-equilibrium system where the thermostats at the ends of the chain are at different temperatures [1, Appendix 1.3 reprint]; the FPU work initiated research in numerical and probabilistic and experimental mathematics utilizing electronic computers. For a consecutive

sequence of material particles i numbered from left to right the intermolecular potential U has form:

$$U(x_{i-1}, x_i) = k_h \frac{(x_i - x_{i-1})^2}{2} + b_h \frac{(x_i - x_{i-1})^4}{4}, \quad (1)$$

with different k_h, b_h values (Case 1-Case 4) with thermostatted particles for the first N_s at the left hand side (lhs) and last N_s particles on the right (rhs) with particles 1 and N. The study is to rule out anomalies in current First and Second law formulations by extending concepts and definitions to self-consistency. Henceforth the x axis refers to particle index number from $1 - N$.

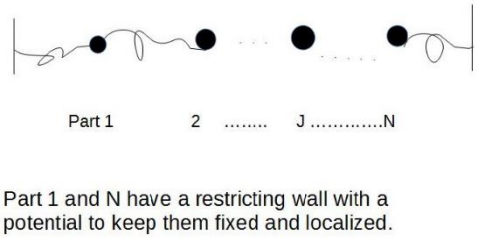

FIGURE 1. A cartoon of the system consisting of a chain of material particles with mass with nearest neighbor potential interactions.

The system and the non-synthetic NEMD methodology has already been described [2] and the work follows from a theory of "recoverable" zero-entropy trajectories presented in [3].

By "anomalies" or "anomalous behavior", we mean steady state heat flow rates and direction which appears to contradict the stated laws and descriptions in thermodynamics.

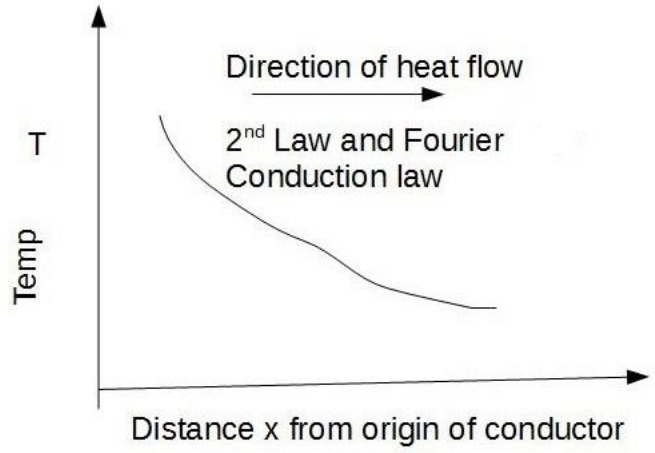

FIGURE 2. A sketch of expected behavior that conforms to the Second law definition of heat and the Fourier Principle.

The linear form of Fourier's law is given as $\mathbf{J_q} = -\kappa \nabla T(\mathbf{r})$ where $\mathbf{J_q}$ is the heat current vector, κ the thermal conductivity and $T(\mathbf{r})$ the temperature at coordinate $\mathbf{r}$. Fourier and the Second law maintains that

(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.

For the linear form for Fourier's law, (a) and (b) embody the Fourier (**F**) principle:

$$\mathbf{J_q}.\nabla T \leq 0, \tag{2}$$

where the inequality follows from $\kappa \geq 0$ and $||\nabla T||^2 \geq 0$. Thus, this inequality leads to the expected behavior depicted in Figure (2), where heat flows from a hotter region to a colder region always and never in the other direction. Indeed, Carathéodory, the pioneer who developed an alternative formulation of the Second law defines heat in accordance with convention [4] in the following manner: "*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*".

The following is noted concerning the above conventions:

1. In this definition, there is no mention of equilibrium conditions.
2. Thus if the above definition is shown not to apply in any particular local region of a non-equilibrium system (and this is what simulation and theory indicate), then the energy transfer in that locality cannot be characterized as heat.
3. Whereas the form of energy that is transferred to the reservoirs at either end is heat because there is transfer from a hotter region to a cooler region.

There is therefore ambiguity with regard to definitions created exclusively for thermodynamical quasi-static equilibrium systems which are neverthless used to characterize dynamical systems not in equilibrium. More recent simulation using alternating differing masses leads to a saw-tooth temperature profile [5], which violates the conventional descriptions and definitions of heat as provided by thermodynamics, and even Carathéodory. Thus a study was initiated to address some of these issues.

Investigation of the Second Law and Fourier Principles

To address the above situation, the following are investigated here:

1. Investigate the form of the steady state temperature profile for systems that do not conform to local Fourier heat conduction mechanism via MD computer simulations.
2. Choose parameters in the MD simulation that can shed light on the various ideas and interpretations of heat conduction, such as the fundamental RLL theory [6], which is the current most basic foundation of heat conduction theory for anomalous systems and related theories.
3. Compare and contrast the various simulation results.
4. Suggest possible factors for discrepancies between theory and results.
5. Suggest practical applications and resolutions to thermodyanmical theory for ambiguity of definitions and concepts.

Description of System, Simulation Method and Intermolecular Forces

The system is a 1000 atom chain, labeled 1 to 1000 from left (L) to right (R), with the first 200 atoms thermostatted to 4.0 (reduced units) whilst atoms 800-1000 were maintained at 1.0; the choice of more than one particle per region is to provide a counter example to 1 used in the

RLL solution. The thermostatting was accomplished by using a classical, non-synthetic algorithm [7] that conserved energy and momentum. The interparticle potential [8] $\mathcal{V}$ between particles i and $i+1$ was defined as:

$$\mathcal{V} = k_h \frac{(q_{i+1} - q_i)^2}{2} + b_h \frac{(q_{i+1} - q_i)^4}{4} + V_{site} \tag{3}$$

a simplified version of the standard FPU-β potential neglecting site potentials that appears frequently [8] in the works of Shah and Gajjar where $V_{site} = 0$.

Outline of System

In phenomenological thermodynamical theory, flow rates are dependent on the material properties, which are time independent and thermodynamical forces, which feature gradients of thermodynamical state variables, but this is not the case in recent formulations where coupling parameters of thermostats that give rise to different heat flow rates for the same material can occur. No coupling parameters feature in our thermostats, c.f. ([9] p.467), Lepri et al. [10]. The MD move algorithm is a 5 stage 4th order method of Calvo and Sanz-Serna analyzed by Gray et al. [11, Table 2]. The MD runs each time were $1 \times 10^9 = 1\ B$ time steps that provided the input for subsequent runs until the steady state was achieved after 17 consecutive runs. The results presented are the average for the last 3 runs where in the figure legends, vx represents run x. The lattice equilibrium spacing is an arbitrary distance a which does not feature in any of the dynamical equations and interparticle potential, for it cancels out in the force laws.

II. DISCUSSION OF SOLUTIONS AND CURRENT OPINION

It has been taken as axiomatic that the RLL solution [6] represents *the unique* solution for this class of problems. The general Steady State RLL solution for a 1-D lattice with harmonic intermolecular potential is sketched in Figure (3).

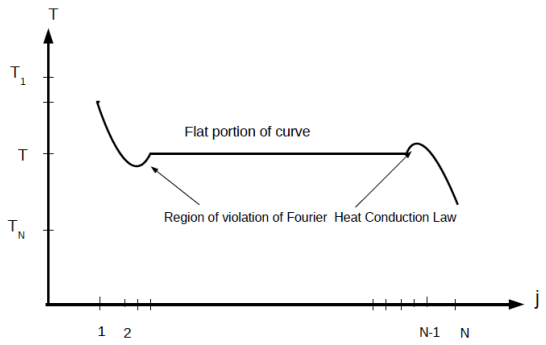

Figure 3. RLL solution; j is the particle index. T_N, T_1 are the temperatures of the first and last particles on the chain. The solution includes regions that have temperatures higher and lower than the average $T = (T_1 + T_N)/2$.

The primary assumptions of the RLL model interpreted by the physics community as being universal and unique for all harmonic potentials include the following:

1. RLL used the Liouville equation in conjunction with Hamilton's equations in modeling these heat conduction problems. It was proved [12] that the fundamental Liouville equation did not, in general, obtain as a mathematical truth for systems.
2. RLL speaks of "pistons" of systems interacting with heat baths and then later revert to the two endpoint particles that are thermostatted at T_1, T_N, where the Hamiltonian is of the standard form [their equation 2.1] below in (4),

$$H = \frac{1}{2}\sum_{i=N}^{2N} x_i^2 + \frac{1}{2}\sum_{i,j=N}^{N} \Phi_{ij} x_i x_j, \qquad N = s\mathcal{N}\ ; \tag{4}$$

Φ is the force matrix, the x's are position-momentum coordinates with $\mathcal{N}$ being the number of particles of dimension s each where particle with index 1 is at temperature T_l at the left of the lattice and where particle $\mathcal{N}$ is at the right of the lattice at temperature T_N. The somewhat awkward RLL convention states that $x_i\ ,\ i = 1, N$ are the Cartesian coordinates whilst $x_j\ ,\ j = i + N$ is the momentum conjugate of x_i , where it is implicitly understood that the summation over the force matrix involving j is coupled to the i index.

3. Only the endpoint particles $1, N$ at T_1, T_N thermostatted. The heat reservoir interaction parameters are used: $\lambda = \lambda_1 = \lambda_N$ where the heat transfer rate $J(\lambda, \omega)$ is

$$J(\lambda, \omega) = \frac{1}{2}(\omega^2/\lambda)k(T_1 - T_N), \qquad \lambda \gg \omega \tag{5}$$

$$J(\lambda, \omega) = \frac{1}{2}\lambda k(T_1 - T_N). \qquad \lambda \ll \omega \tag{6}$$

Here, the energy transfer rate is proportional to $(T_1 - T_N)$.
On physical grounds, the heat flow rate for a fixed temperature difference across the ends of a lattice would be expected to be a function of the time independent kinetic parameters of the system, and not on the coupling terms of the thermal reservoir as for the kinetic phenomenological equations used in engineering and physics.

4. The RLL solutions are deemed unique by them as well [6, p.1077,last par.,1st column]. The following salient characteristics of their solution is evident from Figure (3) :
• Plateau gradient ≈ 0 in middle segment where $\approx (T_1 + T_N)/2$. T at $j = 2$ falls below the mean temperature, and from $\mathbf{J_q}.\nabla T \leq 0$, $\kappa(j) > 0$, it follows that the **F** principle fails along one arm of profile segment.
• The plateau portion widely quoted in numerical and theoretical studies, over the last half century, as yielding "ballistic trajectories" [8,13] with $\kappa = \infty$.
Given the above general characteristics taken as axiomatic, Dhar opines that [9, 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."

Shah et al. [8, p.361] on the other hand 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".

Taking this remark as an observation, we carry out simulations where the site potential in eqn.(3), $V_{site} = 0$ contradicting Dhar [9] but affirming Shah et al.[8] and consider the anharmonic contribution to U via b_h written

$$U(x_{i-1}, x_i) = k_h \frac{(x_i - x_{i-1})^2}{2} + b_h \frac{(x_i - x_{i-1})^4}{4}, \tag{7}$$

which is the FPU-β model [8, eq.(2)].

For our simulations, the NEMD steady state was achieved for the following values of k_h and b_h:

(a) Case 1, $k_h = 1.0, b_h = 0.0$
(b) Case 2, $k_h = 1.0, b_h = 0.5$
(c) Case 3, $k_h = 593.355, b_h = 0.0$
(d) Case 4, $k_h = 593.355, b_h = 0.5$

The anharmonic b_h coefficients have values that feature in publications so that comparisons with the literature [8] can be made, and k_h was chosen for typical values ($k_h = 1$) and for extreme values $k_h = 593.355$ to check for universality claims, such as in the RLL solution [6], and also to decide on the views of Dhar and Shah et al. mentioned previously. The value $k_h = 593.355$ is a rough estimate of the force constant for element W.

III. DISCUSSION OF RESULTS

The results are presented graphically in what follows. In Case 2, The values $k_h = 1.0, b_h = 0.5, T_L = 4.0, T_R = 1.0$ were chosen from previous work [2] based on the b_h value from Shah et al. [8] without the site potential $V(x_l) = 0$. Case 2 was a reference run to ensure the algorithm was performing as expected. These values ensured that the **F** principle could never be violated as found in numerous numerical simulations in the literature, and so the transport energy is deemed to be characterized by Fourier heat transfer. This run was also used to check on the MD algorithm consistency for all the other runs. The temperature difference of $(4.0 - 1.0) = 3.0$ is approximately $30 \times$ greater than than used in the majority of contemporary simulations.

Figure (4) for the Case 2 results partially verifies Shah et al. [8] concerning anharmonicity contributions allowing for Fourier's law to hold without a site potential. The data from the Case 2 system was used to construct a theory of recoverable conversions for heat/work energy transitions along the so-called recoverable trajectory where it was numerically and theoretically demonstrated that $\delta\mathcal{S} = 0$ [2] as exemplified by Fourier heat conduction where the heat flow direction was consonant with the **F** principle for that particular system.

In current terminology, the term "ballistic" applies to solutions given for instance by the RLL system of Figure (3) where the **F** principle breaks down [8, 1. Introduction] and where presumably, because of the flat curve of Figure (3), the conductivity would tend to infinity. These are some of the difficult issues concerning heat conduction. The authors of RLL theory claim [6] "no explanation is offered for this paradoxical result" which could refer to the entire temperature profile, or to the portions that violate the **F** principle. Hu et al. [14, p.2994] with Shah et al. [8] opine anharmonicity seems to add "resistance" or diffusion or "dissipation" to the system leading to Fourier conduction, which can be shown by elementary conservation to be a diffusion equation in terms of energy. There seems to be a diversity of opinion with little consistent theoretical backing. Thus the flat RLL curve is viewed as a non-dissipative process at the speed of sound as in thermal superconduction in analogy to electronic superconduction.

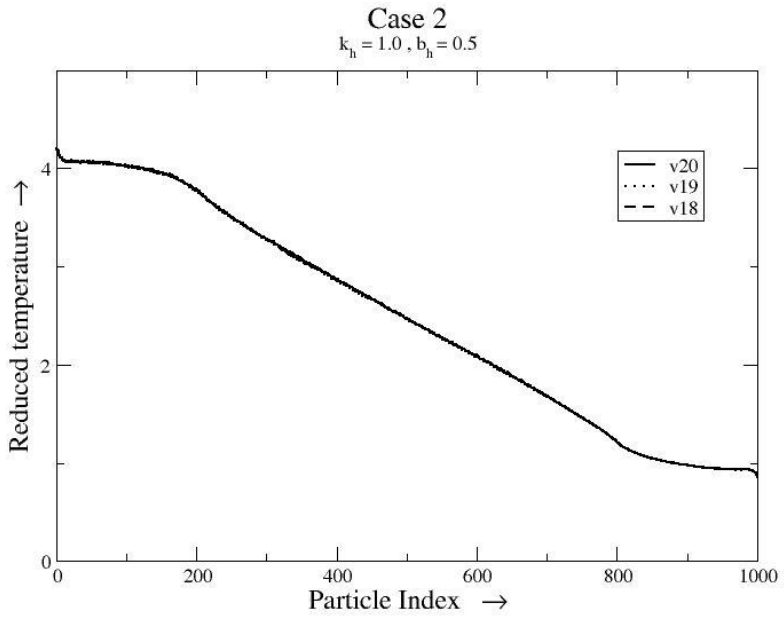

FIGURE 4. Case 2 results where the Fourier principle and local form of the Second law is obeyed everywhere along the lattice chain in the steady state.

Thus we next examine the simulation results at elevated temperature differences (the literature mentions typically gradients where $T_L = 1.1, T_R = 1.0$ (Shah et al. [8]) since RLL pertains to all temperature differences and examine the profile for the Harmonic and non-Harmonic (anharmonic) system where $b_h \neq 0.0$ to check for possibility of exceptions. Here $T_L = 4.0, T_R = 1.0$. We examine for instance Case 1, A steady state solution for harmonic intermolecular potential with parameters $k_h = 1.0, b_h = 0.0$. No flat plateau in the temperature is indicated in the middle portion of the graph, contradicting the RLL result. Some type of thermal standing wave is observed and it seems that "phonon-phonon" coupling at least with the heat reservoirs are evident in this simulation representation in conjunction to a system that is able to generate cavity waves of some sort. The sinusoidal representation implies that the **F** principle does not obtain if the transport energy is deemed to be due to heat transfer.

In Figure (5), there is little resemblance between the Case 1 profile to the RLL profile sketched in Figure (3). RLL used the Liouville equation in conjunction with the Hamiltonian. The Liouville equation did not in general obtain as a mathematical truth for systems [12]. In addition, there may be other compounding reasons such as:

(a) Method of coupling of the reservoirs, and number of particles.

The RLL theory presumed single particles that are thermostatted and some type of rate coupling mechanism was introduced. We realize that in classical nonequilibirum theories thermodynamical flows are dependent on forces due to the gradient of potentials only, and no microscopic time constants concerning coupling coefficients are normally included.

(b) Cavity mode buildup.

RLL and the physics community currently do not normally include the possibility of cavity buildup of thermal resonance modes in a steady state chain.

(c) Non-universal temperature and potential parameter dependent solutions.

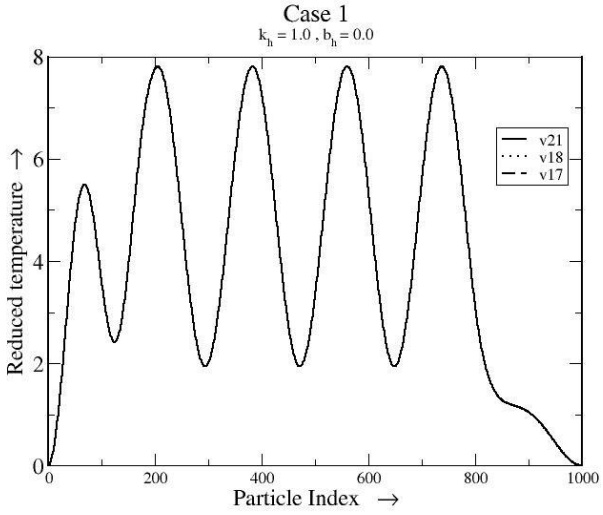

FIGURE 5. Case 1 which conforms to the RLL theory boundary conditions but which does not in any way resemble the results that are supposed to obtain for the universally unique solution

The definition of temperature follows the classical equilibrium equipartition of energy with the temperature parameter being linearly related to the average kinetic energy for instance. Clearly a theoretical justification is in order for such assumptions which has barely been considered. If there is cavity buidup, then the profile would be related to the potential energy of the system which would describe the steady state distribution of the temperature which is determined by the kinetic energy. Such studies are at their infancy.

Thus, a re-evaluation of work over the last 1/2 century in some of these aspects of theoretical heat transfer would be beneficial.

Solutions for large $k_h = 593.355$ yields the same result in terms of curves but with different heat transfer rates are derived when the steady state numerical solutions for Case 1 are used as inputs for the NEMD simulations as shown in the next figure, Figure (6) For Case 3. The full details of the simulation results are given in [15] where for Case 3, $k_h = 593.355, b_h = 0.0$. Well defined sinusoidal curves with the same profile as for Case 1 is observed, but with different energy rates. Cases 1, 3 and 4 violate the **F** principle in regions with positive gradient and so the transport energy cannot be characterized by heat transfer if the **F** principle is taken to be always true and which refers to conductive heat. This is a paradox and inconsistency from the point of view of basic definition because one the one hand, heat is defined in thermodynamics as that form of energy that traverses a boundary as a result of a temperature difference, but local Second law statements demand that this energy flow is from a higher temperature to a lower temperature. We postulate that heat can be defined in accordance with thermodynamics but which need not flow from a hotter to a colder temperature only: in either case, we suggest that the variational principle for entropy along a heat flow streamline is δS=0 as discussed below in greater detail. More computational work would have to be performed to validate this postulate.

The purely harmonic Case 1 profile has 5 well defined peaks for $k_h = 1$ and Case 3 with the harmonic constant $k_h = 593.355$ has amazingly a nearly exact profile with exact coincidence of the temperature-particle index graph, but with significantly different heat transfer rates

($\sim.8388/\ unit\ \ time$) for Case 3 as opposed to ($\sim.3443/\ unit\ \ time$) for Case 1. We note also the well developed curves that seem to indicate the formation of standing "thermal waves" despite a net dissipative transfer of heat from hot to cold reservoirs at different rates.

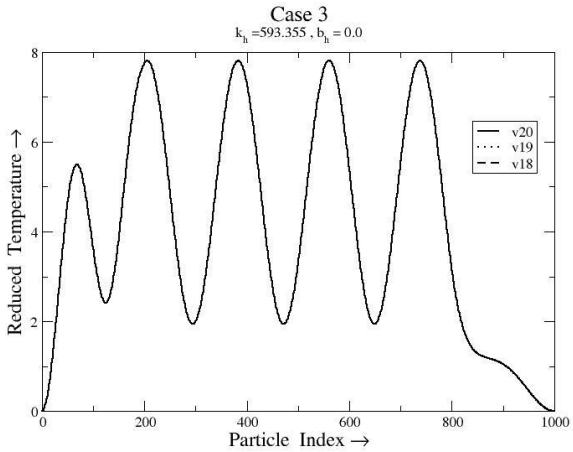

FIGURE 6. Case 3 simulation with identical profile as for Case 1 but with different heat conduction rates.

The next deduction in this work is related to the problem of anharmonicity which is discussed below. The question that we pose is: Is it a necessary and sufficient condition to ensure that the **F** principle and in particular, the Fourier law necessarily obtains if there is an anharmonic term? The results for Case 4 attempts to shed light on this question. We remark that the value of $k_h = 593.355$ 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 $T^* = 1 \Rightarrow 300K$. The ratio $b_h/k_h = 8.42 \times 10^{-4}$ and 0.5 for Case 4 and Case 2, respectively.

Case 4 is the steady state solution for anharmonic intermolecular potential parameters $k_h = 593.355, b_h = 0.5$. A smudged out less sinusoidal curve is observed. We note that anharmonicity does not imply that the **F** principle holds necessarily: **F** is violated in regions with positive gradient and so the transport energy cannot be characterized by heat transfer if the **F** principle is taken to be true.

The introduction of anharmonicity ($b_h \neq 0$) in the simulation yields the output profile in Figure (7). Presumably the coupling strength destroys or smoothes out the standing wave pattern, and further another peak (6 peaks) are added with a heat transfer rate of $\sim 0.81257/\ unit\ time$ We can 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 (b_h/k_h) seems to determine whether the Fourier law is obeyed or not. In addition, whether absolute magnitudes of (k_h, b_h) are also featured in the criterion is not known at the present time. Also not known is whether absolute values of the temperature parameter and temperature differentials affects the results where the RLL solution does not indicate that they are significant variables.

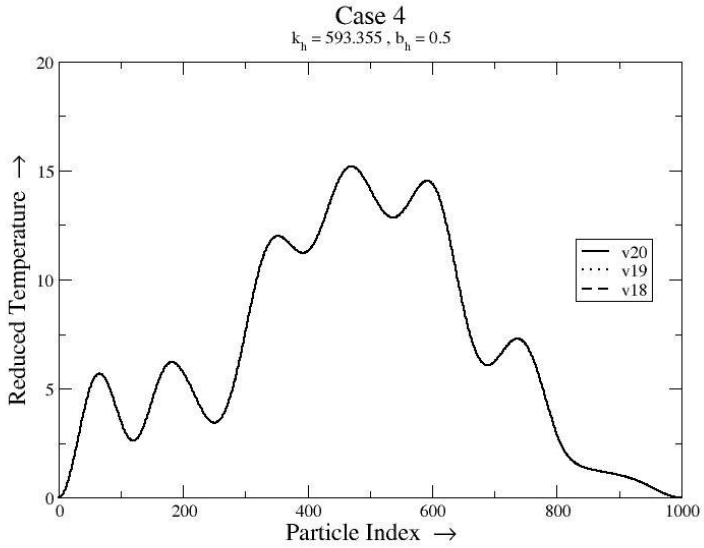

FIGURE 7. Case 4 steady state profile for parameters $k_h = 593.355, b_h = 0.5$ where there is some anharmonicity contribution in the force fields.

Considerations in Extension of First and Second Law Statements

When the theory of "recoverable transitions" [3] was applied to Fourier conduction [2] the current data was unavailable and the RLL result seemed controversial. The current data indicates (as with some portions of the RLL result) that energy is flowing in the direction that invalidates the **F** principle.

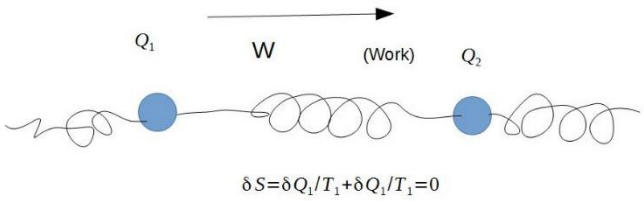

FIGURE 8. Zero entropy change recoverable trajectory for Fourier conduction.

The "recoverable" or zero entropy pathway [3] with a cartoon description provided in Figure (8) describes a system along a streamline that does work to the environment or to itself and as a result loses thermal energy along a zero-entropy streamline where the variation in entropy $\delta S=0$. This concept was applied in [2] to pure thermal conduction, where the work term W along the streamline is actually the heat current vector for Fourier heat conduction.

The theory developed in [2] only considered work-heat interchange in a potential field, with no preferred direction of energy transfer implied, but which was applied to the Case 2 situation where the **F** (principle) applied. The variational principle in more complete form can be stated as follows [15]:

$$\boxed{\delta \mathcal{S}|_{Traj} = 0.} \tag{8}$$

This variational principle was demonstrated numerically to be feasible in the restricted case for heat conduction where the **F** principle obtained [2]. The same principle was used in rudimentary form to derive thermoelectric equations [16] where the transfer of heat along gradients were dependent on the (electrical) work performed which suggests that regions considered "anomalous" are subjected to the same considerations of work heat transformation as found for instance in more complex thermoelectric systems. Hence work-heat transfomations are perhaps not distinct but form a relational pair.

The systems with harmonic interparticle potentials have well developed peaks, and we surmise that these regions can serve as sources and sinks of thermal energy. This implies that thermal integrated circuits may be created by taking advantage in the spatial location along the chain where these maxima/minima occur. Currently, the creation of thermal transistors etc. do not make use of such properties where convention potentials [17] are used

IV. CONCLUSIONS

Traditionally, (a) thermodynamics partitioned energy into two distinct forms, work W and heat Q, from which the entropy differential dS for a closed system is $dS = dQ/T$, and (b) in the field of statistical theory, these concepts were cast in terms of the Liouville equation and the associated Hamiltonian and time reversible dependent equations which we have shown to be largely incorrect but still forms the basis of statistical and dynamical theories.

A method of conflating both these quantities via the concept of recoverable transitions was outlined [2] which meant that heat can be considered to be both locally defined and is bounded by an optimized trajectory whereas Benofy and Quay [18] on the other hand argued it is local and is not global, not embodying optimized energy flows, which is also how conventional thermodynamics views heat.

The view developed here [2,3] is that Fourier heat conduction is both local (up to molecular dimensions and relaxation times) and global with respect to work- heat transformation optimized efficiencies.

The data presented indicates that the RLL derivation [6], that has influenced nearly all subsequent work over the last half century is probably a model which might not be as general as it was assumed to be.

The remarkable sinusoidal curves of the steady state profile for harmonic interparticle potentials imply that those regions are potentially sources and sinks for thermal energy if the simulation model and MD methodology is good enough, as well as the troughs can be coupled to other lattice chains to produce complex integrated thermal circuits. Technologically, thermal transistors and integrated circuits may be constructed by exploiting the maxima/minima along chains with a predominantly harmonic potential.

We show that anharmonicity is a necessary but not sufficient condition for traditional Fourier heat conduction mechanisms to apply. The relative ratio of the potential coefficients in the expansion of the intermolecular potentials are significant in determining the degree of diffusion or ballistic behavior.

We present a hypothesis that even for harmonic potential lattices, heat flow can occur along a temperature gradient; and extend the Carathéodory definition that cannot account for this

behavior by recourse to the principle that defines heat as that form of energy that traverses a boundary as a result of a temperature difference such that its entropy trajectory along the streamline ∂C is invariant:

$$\boxed{\delta \mathcal{S}|_{\partial C} = 0.} \tag{9}$$

ACKNOWLEDGMENTS

I am very grateful to the IMFP2017 leadership for their kind invitation to the conference and their monetary considerations in view of my being retired by University of Malaya.

REFERENCES

1. Giovanni Gallavotti. *The Fermi–Pasta–Ulam Problem: A status report.* Number 728 in Lecture Notes in Physics. Springer, 2008. Electronic resource by Springer publications.
2. C. G. Jesudason, *PLoS ONE,* p.e0145026 (2016).
3. C. G. Jesudason, *Indian J. Pure Ap. Phy.* **29**, 163 – 182 (1991).
4. C. Carathéodory," The Second Law of Thermodynamics" translation of C. Carathéodory Math Ann. 1909; 67: 355– 386, edited by J. Kestin, Stroudsburg, Penn: Dowden, Hutchinson and Ross Publications, Introduction, Chap. 12, p.229.
5. T. Mai, A. Dhar, and O. Narayan, *PRL* **98,** 184301 (2007).
6. Z. Rieder, J. L. Lebowitz, and E. Lieb, *J. Math. Phys*, **8**(5),1073–1078 (1967).
7. B. Hafskjold, and T. Ikeshoji, *Fluid Phase Equilibria,* **104**, 173–184 (1995).
8. N. Shah and P. N. Gajjar, *Commun. Theor. Phys.* **59**, 361-364 (2013).
9. A. Dhar, Adv Phys, **57**, p. 459 (2008).
10. S. Lepri, R. Livi, and A. Politi, *Phys. Rep***. 377**, 1-80, Sec 3.3, (2003).
11. S. K. Gray, D. Noid, and B. G. Sumpter, *J. Chem. Phys*, 101(5), 4062-4072 (1994)xe1
12. C. G. Jesudason, Stoch Anal Appl, **21**(5), pp.1097-1114. Erratum provided with publisher's apology for their wrong typesetting of key equations and some inline equations in 22(4), pp.1131-1132 (2004): inline equations and phrases p.1102; p1108 eq. (17); p. 1108 eq.(18), inline equations and eq.(19);p.1109, inline equation ; p.1110 eq.(20).
13. J-W Mao and Y-Q Li,,*Front. Phys. China* **4**, 428-441 (2006).
14. B. Hu, B. Li, and H. Zhao, *Phys Rev E* **57,** 2992-2995 (1997).
15. C. G. Jesudason, *Int. J Therm Sci*. **120**,491–507 (2017).
16. C.G. Jesudason, Asian Journal of Physics **9**(1):1-14 (2000).
17. M. Vachhani, T.K. Patel, and P. Gajjar, Int. J. Therm. Sci. **108**, 159-164 (2016).
18. S. J. Benofy, and P. M. Quay, S.J., "Fourier inequality as a principle of thermodynamics, with applications to magnetothermoelectric effects," in Physics as natural philosophy, M.I.T. Press, 1982, chap. 1, pp. 7-24.