Fourier Heat Conduction as a phenomenon described within the scope of the Second Law

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Abstract. The historical development of the Carnot cycle necessitated the construction of isothermal and adiabatic pathways within the cycle that were also mechanically "reversible" which lead eventually to the Kelvin-Clausius development of the entropy function $S$ where for any reversible closed path $\oint dS = 0$ based on an infinite number of concatenated Carnot engines that approximated the said path and where for each engine $\Delta Q_1/T_1 + \Delta Q_2/T_2 = 0$ where the $Q$'s and $T$'s are the heat absorption increments and temperature respectively with the subscripts indicating the isothermal paths (1, 2) where for the Carnot engine, the heat absorption is for the diathermal (isothermal) paths of the cycle only. Since 'heat' has been defined as that form of energy that is transferred as a result of a temperature difference and a corollary of the Clausius statement of the Second law is that it is impossible for heat to be transferred from a hot to a cold reservoir with no other effect on the environment, these statements suggested that the local mode of transfer of 'heat' in the isothermal segments of the pathway does imply a Fourier heat conduction mechanism (to conform to the definition of 'heat') albeit of a "reversible" kind, but on the other hand, the Fourier mechanism is apparently irreversible, leading to an increase in entropy of the combined reservoirs at either end of the material involved in the conveyance of the heat energy. These and several other considerations lead Benofy and Quay (BQ) to postulate the Fourier heat conduction phenomenon to be an ancillary principle in thermodynamics, with this principle being strictly local in nature, where the global Second law statements could not be applied to this local process. Here we present equations that model heat conduction as a thermodynamically reversible but mechanically irreversible process where due to the belief in mechanical time reversible symmetry, thermodynamical reversibility has been unfortunately linked to mechanical reversibility, that has discouraged such an association. The modeling is based on an application of a "recoverable transition", defined and developed earlier on ideas derived from thermal desorption of particles from a surface where the Fourier heat conduction process is approximated as a series of such desorption processes. We recall that the original Carnot engine required both adiabatic and isothermal steps to complete the zero entropy cycle, and this construct lead to the consequent deduction that any Second law statement that refers to heat-work conversion processes are only globally relevant. Here, on the other hand, we examine Fourier heat conduction from MD simulation and model this process as a zero-entropy forward scattering process relative to each of the atoms in the lattice chain being treated as a system where the Carnot cycle can be applied individually. The equations developed predicts the "work" done to be equal to the energy transfer rate. The MD simulations conducted shows excellent agreement with the theory. Such views and results as these, if developed to a successful conclusion could imply that the Carnot cycle be viewed as describing a local process of energy-work conversion and that irreversible local processes might be brought within the scope of this cycle, implying a unified treatment of thermodynamically (i) irreversible, (ii) reversible, (iii) isothermal and (iv) adiabatic processes.

Keywords: Heat Conduction, Molecular Dynamics Simulation, Recoverable transitions, Zero entropy trajectory

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INTRODUCTION

Some principles were developed in connection with the thermal desorption problem, where it was proven that the irreversible desorption of particles on a surface [1] within a relaxation time $\tau$ conforms to an adiabatic scattering zero entropy process along the center-of-mass frame of the desorbing particles. To summarize the more detailed treatment in [1, Sec. 4.4], for states $i$ with probability $p_i$ before a transition and $p'_i$ after where state $i$ transmutes into another state (denoted by primes), the entropy change $\Delta S$

$$\Delta S = k'k \Delta \sum_{i=1}^{N} p_i \ln p_i = 0$$

for the entire transition implied

$$p_i(E_i, T) = p'_i(E'_i, T')$$
$$E_i/(kT) = E'_i/(kT')$$
where the $E$’s are energy variables between the two states with defined temperatures $T, T'$ and where the partition function $Z$ too is conserved, i.e. $Z = Z'$, and where if we summed the energies in (2), we have the heat energy $Q$ conforming to

$$\frac{Q}{kT} - \frac{Q'}{kT'} = 0 \quad (4)$$

or the entropy is conserved for this “heat pulse” movement called a recoverable trajectory. We note that the prime and unprimed variables refer to the same system making a transition. These transitions are “thermodynamically reversible” in the sense of zero entropy change, but is clearly mechanically irreversible [2]. For the above system, we observe that the system is disintegrating, and that the ad-atoms on the surface of the substrate eventually all leave the surface, and each of these ad-atoms have instantaneous energy $E'$, where $E' = E - \deltaW$ where $\deltaW$ is the work done by the particle on the force-field it traverses, which is absorbed into the field. The particles then move on to infinity in space if no work potentials are present along the trajectory when the kinetic energy of the particles are still positive. Clearly in this situation, no structure is preserved. Of interest then is to investigate the possibility of modeling energy transfer processes that has something of the form above of zero entropy trajectories relative to the defined heat terms, but where the system is not disintegrating. A simple example of such a structured assembly would be a lattice chain where the particles have a mean time independent position whilst involved in the process of transferring energy between the two ends of the lattice chain that are maintained at different temperatures. Since modeling such a process is a very involved task, with possibly unproven assumptions being surreptitiously imported into the creation of the theoretical structure that could be simulated and computed, the following methodology is being currently pursued to ensure that no extraneous concepts are imported:

1. Identify a discrete non-disintegrating model system that, from theoretical considerations would have to conform to the above process of a recoverable process
2. Apply that model to the continuous lattice chain, even in a restricted system to extend concepts that would have to be used for a more comprehensive treatment of irreversible phenomena
3. Quantitatively check the model for numerical agreement with total heat flow terms
4. Extend the model from just one particle interaction with the adjacent pair to longer ranges of interactions so that one might be able to predict the kinetics and thermodynamical variable profile over the entire lattice
5. Lastly, from the above, it may be possible to construct a more comprehensive and extensive thermodynamical theory by generalization of the above item (4) that might be able to encompass both equilibrium and non-equilibrium interactions.

So far we seem to have promising results for items (1-3) which will be discussed here. The other items in the methodology list (4-5) are work in progress.

It was demonstrated before [2, 3, 4] that the pivotal concept of time reversibility is mathematical incorrect in its major applications to wide-ranging phenomena, and that these fallacies have been incorporated into mainstream thermodynamical interpretation (e.g. see [5, pp.36,52,141:7,356-7]). The above remarks require some qualification. The original work of Carnot [6] describes essentially a work cycle whose work energy variable $w$ is not a perfect differential and where the introduction of heat [6, Fig. 2, 3 p.70] into the working substance involves the transfer of heat about vanishing temperature gradients where there is “…no contact between bodies of sensibly different temperatures”[6, p.68]. Such views developed in modern times to conceiving heat as a degraded form of energy that increased the entropy of a system by traversing a thermal gradient from hot to cold (thus increasing the entropy of the system). Indeed the calorimetric definition of heat [7, 1968 5th Ed, p.73] is “…that which is transferred between a system and its surroundings by virtue of a temperature difference only.” Carathéodory conceives of heat [8, J. Kestin ed., Introduction, p.229] in the following manner: “Furthermoe, 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.”. Here we shall show for recoverable transitions, which includes heat conduction, the energy transferred is actually “work”, although the movement is from hot to cold, in accordance with previous definitions. The degradation idea is also evident in É. Clapeyron’s 1834 work [9, p.38]:”...in any mechanism designed to produce motive power from heat, there is a loss of force whenever there is a direct communication of heat between two bodies at different temperatures and it follows that the maximum effect can be produced only by a mechanism in which contact is made only between bodies at equal temperatures”. This coupled with the definition of heat above lead to the concept of “reversible transfer”, where the concept of “reversibility” is a rationalization imported from mechanics with its belief in the reversibility of its laws in quantum and classical physics and thermodynamics [5]. The derivation of the Onsager reciprocity relations and the Boltzmann H-theorem are examples of misapplications of such time-reversible assumptions [2, 3, 4].
Finally, it was proven that the celebrated Liouville equation, derived from the Hamiltonian in \((\mathbf{p}, \mathbf{q})\) Liouville phase space is in general not valid as a continuous equation, where a stochastic analog of the same form was derived in its place \([10]\). In particular, attempts to deduce zero-entropy paths from Liouville space were shown to be flawed \([10\) see reference therein\]. It was expressly stated in \([1]\) that the zero-entropy “recoverable trajectory” developed there is not described in Liouville space, and that further, as illustrated in the current work, there is a stochastic back-scattering of energy involving a non-conservation of energy about a stochastic work cycle that at first sight would not readily follow from a standard mechanical Hamiltonian using continuous, non-stochastic variables as will be demonstrated. If such Hamiltonians \(H(\mathbf{p}, \mathbf{q})\) are used in describing non-equilibrium mechanical systems, then assuming a general average \(\{mb\mathbf{p}_i, \mathbf{q}_i\}\) for all coordinates \(j\) where \(j \neq i\), then \(\int \frac{\partial H}{\partial \mathbf{q}_i}(q_i, \mathbf{p}_i, \mathbf{q}_j) dq_i = 0\) which is not observed in the simulation result, implying that the introduction of hybrid elements (random energy impulses at the ends of a chain of vibrating atoms in this case) to for instance simulate thermostated regions destroys the continuum description of the mechanical Hamiltonian and that in addition some very complex cooperative phenomena may be involved with the standard Hamiltonian where the assumption of averaged coordinates do not apply. The conventional description of conductive heat transfer which is viewed as the transport of “heat” energy occurs through reversible dynamical laws, and which involves a positive local internal entropy production rate(\(S = \int_{V} \mathbf{J}_q \nabla T / T^2 \neq 0\)) in a temperature gradient with a non-zero heat current present and indeed in conventional descriptions, \(\sigma\) has the above component due to the conductive heat contribution \([11, \text{Ch.III} , p.24, \text{eq. (21)}]\). One important aspect of the expressions for \(\sigma\) is that it allows for the identification of the Onsager reciprocity coefficients that couple forces and fluxes \([11, \text{Ch.IV} , pp.33-36]\). Previously, it was remarked \([1, \text{p.163, Sec.2}\), in keeping with the Clausius definition, that for closed atoms in this case) to for instance simulate thermostated regions destroys the continuum description of the mechanical Hamiltonian and that in addition some very complex cooperative phenomena may be involved with the standard Hamiltonian where the assumption of averaged coordinates do not apply. The conventional description of conductive heat transfer which is viewed as the transport of “heat” energy occurs through reversible dynamical laws, and which involves a positive local internal entropy production rate(\(S = \int_{V} \mathbf{J}_q \nabla T / T^2 \neq 0\)) in a temperature gradient with a non-zero heat current present and indeed in conventional descriptions, \(\sigma\) has the above component due to the conductive heat contribution \([11, \text{Ch.III} , p.24, \text{eq. (21)}]\). One important aspect of the expressions for \(\sigma\) is that it allows for the identification of the Onsager reciprocity coefficients that couple forces and fluxes \([11, \text{Ch.IV} , pp.33-36]\). Previously, it was remarked \([1, \text{p.163, Sec.2}\), in keeping with the Clausius definition, that for closed systems a more appropriate definition would be \(S = \int_{V} \mathbf{J}_q \nabla T / T^2 \neq 0\) which would yield zero entropy production apart from the system boundaries. Further, Benofy and Quay have argued that Fourier’s inequality (following (5) with \(J_q = -\kappa \nabla T\))

\[
\kappa(\nabla T)^2 / T^2 \geq 0
\]

is a local principle, not subject to the Second law since the latter refers to global work-heat transitions, and may well be an independent principle. Recall that the modern Carnot cycle is strictly developed with 2 types of heat transitions of the working substance, the “”isothermal”” and the “”adiabatic””. One conclusion of Carathéodory thermodynamics \([12]\) for “”macroscopic”” systems is found in Axiom II: \(\text{In every arbitrary close neighborhood of a given initial state, there exists states that cannot be approached arbitrarily closely by adiabatic processes.}\) In what follows, we show that relative to a particular subsystem, within the heat conducting chain constituting atom \(i\) and the adjacent one \(i + 1\), pure heat energy transfer according to Carathéodory occurs and in accord with conventional definition, but at the same time according to the major assumptions of recoverable transitions \([1]\) and as illustrated here in our modeling, the following conditions obtain:

1. A net adiabatic process in the forward direction occurs
2. The energy transfer being the work done, conventionally considered the heat increment
3. The work is mechanically irreversible, but thermodynamically reversible (zero entropy) where the micro-transitions complete a Carnot-type loop within the subsystem
4. The stochastic integral for the energy about a loop is not zero, implying that the mechanical Hamiltonian is non-conservative in such hybrid systems
5. There is a distant implication that both adiabatic and isothermal processes may be unified, at least at the micro-level, which would require answering challenging questions as to how macroscopic descriptions, such as due to Carathéodory, emerge from the micro-processes, which encompasses both adiabatic and isothermal ones.

The above seems to indicate that if the direction of this research project is deemed reasonable, then there are gaps that need to be bridged between some of the more conventional definitions and the deductions that are being made here.
DESCRIPTION OF THE SIMULATION SYSTEM

The sample results presented here refers to a 1000 atom chain, labeled 1 to 1000 from left to right, with the first 200 atoms on the left thermostated to 4.0 (reduced units) whilst atoms 800-1000 were maintained at 1.0. The method of thermostating used a classical, non-synthetic algorithm developed or popularized by Hafskjold and Ikeshoji [13] where the thermostated atoms were scaled according to \( \dot{q}_i = \alpha + \beta q_i \), with \( \alpha \) and \( \beta \) common to all relevant atoms to maintain the temperature \( T \) where \( T = \sum_{i=1}^{N} m \dot{q}_i^2 \) and in reduced units, \( m = 1 \). As is well know, the harmonic potential only [14] does not yield the expected Fourier heat conduction law \( \mathbf{J}_h = -\kappa \nabla T \), with near constant \( \kappa \), but one might also say that for the harmonic interaction potential between particles, the thermal conductivity \( \kappa \) is a very sensitive function of the temperature, and that it is also not a local property but may be a function of the entire temperature distribution. These and others are very interesting research questions, as Lebowitz et al. have testified to [15]. The interparticle potential \( \mathcal{V} \) between particles \( i \) and \( i+1 \) was defined as

\[
\mathcal{V} = k_h (q_{i+1} - q_i)^2 / 2 + b_h (q_{i+1} - q_i)^4 / 4.
\]

Here \( k_h = 1.0, b_h = 0.5 \) with these parameter values chosen for good reproducibility in the work on Tejal et al. [16, Fig.6]. The \( q \)’s are the displacement from the equilibrium position with the separation distance of unity, and the force \( \mathcal{F} \) from particle \( i \) due to particle \( i+1 \) is defined as \( \mathcal{F}_{i,i+1} = -\frac{\partial}{\partial q_i} \mathcal{V} \). We define the partitioned work done on \( i \) due to the force from \( i+1 \) as

\[
\Delta w_{i+1 \rightarrow i} = \int_{t_1}^{t_2} \mathcal{F}_{i,i+1} \dot{q}_i dt \approx m \int_{\text{stoch}} \mathcal{F}_{i,i+1} dq_i
\]

between the time interval \([t_1, t_2]\), and the work done on \( i+1 \) due to the force from \( i \) as

\[
\Delta w_{i \rightarrow i+1} = \int_{t_1}^{t_2} \mathcal{F}_{i+1,i} \dot{q}_{i+1} dt \approx m \int_{\text{stoch}} \mathcal{F}_{i+1,i} dq_{i+1}.
\]

The above equations normalized over unit time are defined thus:

\[
\delta w_{2 \rightarrow 1} = \Delta w_{i+1 \rightarrow i} / (t_2 - t_1)
\]

\[
\delta w_{1 \rightarrow 2} = \Delta w_{i \rightarrow i+1} / (t_2 - t_1).
\]

We make use of the standard Simpson second order 3-point formula (fourth order error) numerical integration [17, 18] for the over 3 million (M) consecutive time steps of stepsize 0.001, equal to the MD timestep. Since all the particles are oscillating, particles \( i \) and \( i+1 \) too can be viewed as oscillating back and forth an average of approximately \( m \) times (to the nearest integer) about their mean position. If this partition force were conservative, then

\[
\lim_{m \to \infty} \Delta w_{i+1 \rightarrow i} / m = 0
\]

\[
\lim_{m \to \infty} \Delta w_{i \rightarrow i+1} / m = 0
\]

and the above limits for large values of time intervals are not observed in all the simulations carried out (see Table (1) ) with varying lengths from 3 to 10 M time step intervals, where, when these integrations of different time lengths are normalized to per unit time, yielded the same numerical quantities. Hence these stochastic path integrals (involving a hybrid system of random energy and momentum impulses at the reservoir coupled to a standard system Hamiltonian without a time dependent variable) have non-conservative “Hamiltonians” even if the classical Hamiltonian is continuous with continuous variables having no explicit time dependence. We note that distinguished theorists routinely use the Liouville and Hamilton equations in modeling these heat conduction problems [14, 15, etc.] etc.

FORMULATION OF THEORETICAL REFERENCE MODEL

Assuming the validity of equipartition, this particular model will exhibit recoverable transitions in the manner described below. Of note here is that the localized particle exhibits two temperatures as it interacts with adjacent particles;
there is the mean kinetic energy temperature and the temperature associated with the transfer of energy to the adjacent particle (on the right, particle \( i + 1 \)) in a basic adiabatic transition. Once the model is described, then we actually use it for the continuously interacting case that we validate by simulation; the key link to the continuum is to realize that each moment of time constitutes a “collision” interaction of the coupled particles relative to this “isolated” reference model.

The theoretical model is “isolated” in the sense that its energy is well defined and localized except for the time of collision with elastic hard sphere energy interchange as shown in Figure 1(a) where they oscillate in the horizontal direction due to a potential \( V \) acting vertically with a small horizontal projection which we can assume to be harmonic with regard to its displacement \( q_i \) from the horizontal equilibrium position at \( q_i = 0 \), (this assumption is not mandatory but it simplifies matters) and so \( V_i = k q_i^2 \), the kinetic energy is \( k.e.(i) = \frac{m q_i^2}{2} \) and the total energy \( E_i = V_i + k.e.(i) \). We will eventually modify this model to cover the situation in Figure 1(b) by appropriate choice of subsystem where even in the coupled state, one can conceptualize each particle as being isolated at each instance of time. For what follows, we refer to particle \( i \) simply as \( i \). The proof of the workability of this model is that a simulation of an allied system with the same dynamics has been described in detail [19].

The above (14) is computable. The equilibrium distance between particles is set to 1 in reduced units. Let \( p_{l_j} \) denote both the plane perpendicular to the vector \( q_i - q_{i+1} \) which contains the \( q \) coordinate point of contact between the particles during the \( j \)th collision of \( i \) and \( i + 1 \), and the \( q \) coordinate during this collision process. The collision would impart a change of kinetic energy \( \delta q_i \). By energy conservation, the average energy up to the time of collision for \( i \), \( Q_b \) is

\[
Q_b = \langle k.e.(i) + V_i |_{pl_j} \rangle \quad \text{(averaged over all \( j \) collisions)}.
\]

We note that \( Q_b \) is also dependent on interaction with particle \( i - 1 \) which is not relevant here for the transfer energetics of \( i \) to \( i + 1 \). Then the dynamical laws can be utilized to compute the change of k.e. for \( i \) (since the potential energy remains unchanged at \( q_i = p_{l_j} \) and we can compute \( Q_a \) the energy just after the collision as

\[
Q_a = \langle k.e.'(i) + V'_i |_{pl_j} \rangle \quad \text{(averaged over all \( j \) collisions)}
\]

over the time duration between the previous collision \( j - 1 \) denoted \( \Delta \); we define the mean time between collisions as \( \tau_{mc} \). Averaging over the sampling time, we can compute average quantities such as the \( Q \)'s, denoted by brackets \( <> \) and so over time \( \tau_{mc} \), the energy transfer \( \delta w \) is

\[
\delta w = < Q_b > - < Q_a >
\]
or \(\delta w/\tau_{mc}\) per unit time over a continuous time period. Note that the normalized units used here are not the same as for the un-normalized work terms in (8-9). From (14), the following array of equations become evident:

\[
T_b = k < E_b > = k < Q_b >
\]

(18)

\[
T_a = k < E_a > = k < E_a - \delta w >
\]

(19)

\[
T_a = k < E_a > = k < E_b + \delta E > = k < Q_a >
\]

(20)

\[
\frac{1}{k} = \frac{Q_a}{T_a} = \frac{Q_b}{T_b}.
\]

(21)

From one of the field properties of number theory [20, p.15, Field Axiom A4],

\[
\frac{1}{k} + \left(\frac{-1}{k}\right) = 0
\]

(22)

we deduce

\[
\delta S = \frac{< Q_b >}{T_b} - \frac{< Q_a >}{T_a} = 0
\]

(23)

which defines the recoverable trajectory. Some elementary remarks are in order concerning the averaging process. We note that

\[
< Q_a > = \left(\sum_{i=1}^{N} \frac{Q_{a,i}}{N}\right)
\]

(24)

Then from (22) or (23) and some \(k'\) (here \(k = k'\)),

\[
< T_a > = \frac{k' \sum Q_{a,i}}{N} = k' < Q_a >
\]

(25)

\[
\Rightarrow \frac{< Q_b >}{T_b} - \frac{< Q_a >}{T_a} = 0
\]

(26)

and the mean rate of energy transfer is \(\delta w/\tau_{mc}\).

A generalization of the Zeroth law based on recoverable trajectory

The equilibrium understanding of the Zeroth law is that if two bodies are in diathermal contact, and there is no net exchange of energy, then they are at the same temperature. Another entropic approach is to examine the exchange of energy across the diathermal boundary between two systems 1 and 2 (these labels determine the heat and temperature of the systems) and if there is no net exchange of energy \(< \delta Q_1 > = -< \delta Q_2 > = 0\), then for any instant of time \(\delta Q_1 = -\delta Q_2 = 0\) for non-work energy exchange, and

\[
\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = \frac{\delta Q_1}{T_1} - \frac{\delta Q_1}{T_2}.
\]

(27)

\[
\delta S = \frac{\delta Q_1}{T_1} - \frac{\delta Q_1}{T_2} = 0 \Rightarrow \delta Q_1(T_2 - T_1) = 0
\]

(28)

or \(T_2 = T_1\) if \(|\delta Q_1| \neq 0\). Since in dynamic equilibrium \(|\delta Q_1| \neq 0\) most of the time, we conclude \(T_2 = T_1\). If we therefore define the Zeroth law in terms of Zero entropy transitions, then recoverable trajectories \(\delta(E/T) = 0\) can conform to the Zeroth law even if their temperatures differ across a boundary if the criterion refers to zero entropy changes rather than energy (in at least closed systems). From the above model, we note that the isolated system \(i\) can be viewed as having “adiabatic”-like transitions in terms of energy transfer at the time of collision, leading to a double temperature characterization for the particle; thus we can say that the two temperatures refer to the same particle in equilibrium with itself.

We have theoretically demonstrated that subsystem (a) of Figure 1 must have the particle behaving as a recoverable trajectory based on the generalized equipartition theorem. Hence if the above model is applied to a system that conforms to case (b) of the same Figure, and where there is numerical confirmation that the vector “work term”
\( \delta \dot{w} \equiv \delta w / \tau_{mc} \) in unit time arising from recoverability theory is exactly equal to the energy transfer across the thermostated ends of the chain in unit time, then one can conclude that a verification of conductive heat as a recoverable process has been made. We demonstrate this to be the case for the 9 atoms/particles situated uniformly over the conductive lattice, where there is close numerical agreement between the independently determined heat transfer rate due to the thermostats and the numerical integrations of various defined energy processes for all of the above labeled particles.

**APPLICATION OF THE THEORETICAL REFERENCE MODEL DESCRIBED ABOVE TO LATTICE PARTICLES INTERACTING CONTINUOUSLY VIA POTENTIALS**

Here we apply the results of the previous section for discontinuous energy interactions to continuous heat conduction (Figure 1 (b)). This can be achieved by isolating the system to the "particle" with \( \text{coordinates}(q_i, \dot{q}_i) \) and where with \( k/2 = k' \) we have \( k' < T_i =< k.e.(i) > \). For what follows we determine the stochastic averages omitting the angle brackets \(<>\) normally indicative of this in the equations about (26), but the context should indicate if averages are implied or not. We define the partial heat to be \( Q = k.e.(i) \) for (particle) \( i \), where \( k'T(i) = Q = k.e.(i) \). We then correlate the reference system above to the current model by realizing that each moment of time involves an interaction via a potential, which takes the place of the transfer of energy due to elastic collisions and the conservation of momentum in the reference system. Thus we can envisage an interaction over time interval \( dt \), and for the \( j \)th interval, the work performed on \( i+1 \) because of the force from \( i \) is

\[
\delta w_j = F_{i+1,i} \frac{dq_{i+1}}{dt} dt_j. \tag{29}
\]

Then \( Q_b = k' \) and after the interaction time \( dt_j \), we have the following results where subscripts \( a \) and \( b \) refer to \textit{after} and \textit{before} the interaction over time interval \( dt \) at the \( j \)th interval respectively:

\[
Q_a = (k.e.(i) - \delta w_j) \tag{30}
\]

\[
k'T_{a} = (k.e.(i) - \delta w_j) = Q_a \tag{31}
\]

and \( k' = k' \Rightarrow Q_b / T_b - Q_a / T_a = \delta S = 0 \tag{32} \]

where (32) defines a recoverable process. Then over \( n \) time intervals, where \( \Delta \mathcal{T} = n dt \),

\[
< Q_b > = \int k.e.(i) dt / \Delta \mathcal{T}. \tag{33}
\]

Define \( \Delta t = dt \) and \( F = F_{i+1,i} \). For any one time interval \( \Delta t \), the loss of \( k.e.(i) \) which would give it some of the characteristics of \( i+1 \), such as a lower temperature would also yield a heat content \( Q_a \) given as

\[
Q_a = k.e.(i) - F \frac{dq_{i+1}}{dt} dt_j \tag{34}
\]

\[
\delta w = (Q_b - Q_a) \text{ spanning } [t_1, t_2]. \tag{35}
\]

Over \( n \) time intervals, the averaged \( n \delta w \) has value

\[
n \delta w = \int_{t_1}^{t_2} k.e.(i) dt / \Delta t - \int_{t_1}^{t_2} (k.e.(i)) - F \frac{dq_{i+1}}{dt} dt \Delta t / \Delta t \tag{36}
\]

\[
+ \left( \int_{t_1}^{t_2} F \frac{dq_{i+1}}{dt} dt \right). \tag{37}
\]

Thus \( \delta w \text{ per unit time} \) is given by

\[
\left( \int_{t_1}^{t_2} F \frac{dq_{i+1}}{dt} dt \right) / n \Delta t \tag{38}
\]
which is identical to $\delta w_{1\rightarrow 2}$ in Table (1) and (11). We note therefore complete concordance between the two models. We have modeled transitions here in terms of one particle that exhibits recoverable transitions. Relative to the work transitions, one might wish to also characterize the lower exchange temperature and heat energy $Q_a$ that allows for work to be performed on the adjacent elements. Over $n$ time intervals $dt$, we have

$$Q_a |_n = \int_{t_1}^{t_2} \left( k.e.(i) - \frac{F dq_{i+1}}{dt} dt \right) dt.$$

Then $< Q_a >$ for one interval is

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

Hence,

$$< Q_a > = \{ < Q_b > - \delta w_{1\rightarrow 2} \times dt \} = \alpha \quad (41)$$

and

$$< T_a > = 2 \alpha \quad (42)$$

The results for $< T_a >$ are provided in Table 1. We observe that it is lower, as it should be, and this temperature is associated with the particle $i$. Thus in any one location, we observe that we can evoke 2 temperatures that are consistent with the energy transfer across the crystal and the extended Zeroth law.

**RESULTS AND DISCUSSIONS**

![Figure 2](tp1.eps)

**FIGURE 2.** Temperature Profile across chain. From Table 1, the u.s.d. for the freely vibrating particles is of the order of 0.14 whereas the thermalized particles 1-200 are maintained at the average temperature $T=0.40014E+01$, u.s.d.0.8E-02, and the colder thermalized particles 800-1000 have the average temperature $T=0.99987E+00$, u.s.d.0.2E-02.

The use of an anharmonic potential allows for the system to exhibit a near linear temperature gradient as shown in Figure 2. The details of the simulations are as follows: all fluctuations in quantities are expressed as the uncorrected standard deviation $u.s.d.$ and the error $\pm$ are expressed in terms of $u.s.d.$, The $E$ notation represents exponents to base 10. After many successive equilibration runs amounting to about 500M timesteps ( where $dt = 0.001$ for the timestep in reduced units), the production runs were initiated. The integrations utilized the well-established symplectic Velocity Verlet algorithm of Swope, Anderson,Berens and Wilson [21, 22, p.81,eqs.3.17-3.21 of Allen et al. reference], which is essentially second order. The production runs
Over the last two centuries, the main developments in thermodynamics include (a) the partitioning of the energy into two distinct forms, work $W$ and heat $Q$, from which the entropy is derived from the latter where the entropy differential $dS$ for a closed system is $dS = dQ/T$, and (b) where the field of statistical theory in concerned, these concepts were cast in terms of the Liouville equation and the associated Hamiltonian for both classical and quantum systems. We have shown the mathematical contradictions of both the Liouville equation and the time reversibility assumptions, both of which were incorporated into the more modern versions of thermodynamical theories. Here we have outlined a method of conflating both these quantities via the concept of recoverable transitions. We have demonstrated its feasibility for the case of single particle scattering. Of great interest, and of great challenge, is to extend these models to more than one particle, so that the kinetics and thermodynamical profile of the system might be computed from these elementary considerations. We also contradict the view that the Fourier law is a locally defined process, unrelated to the Second law or which cannot be deduced from the Second law, a claim central to the work of Benofy and Quay in their theory of thermolectric and thermomagnetic effects[23], by framing elementary theoretical propositions that are then based on recoverability theory is in excellent quantitative agreement to the $\Delta w$'s is approximately $0.12 \times 10^{-1}$ and that of the temperatures $0.14 \times 10^3$.

### TABLE 1.

| part.# | $\Delta w_{2 \rightarrow 1}$ | $\Delta w_{1 \rightarrow 2}$ | temp. # | temp. #+1 | $< T_o >$ |
|--------|----------------------------|----------------------------|---------|-----------|----------|
| 250    | -0.21070E+00               | 0.21110E+00                | 0.35166E+01 | 0.35038E+01 | 0.35162E+01 |
| 300    | -0.21031E+00               | 0.21046E+00                | 0.33159E+01 | 0.33037E+01 | 0.33154E+01 |
| 350    | -0.20958E+00               | 0.20976E+00                | 0.31287E+01 | 0.31141E+01 | 0.31283E+01 |
| 450    | -0.20978E+00               | 0.20988E+00                | 0.27131E+01 | 0.26945E+01 | 0.27127E+01 |
| 500    | -0.21036E+00               | 0.21034E+00                | 0.24834E+01 | 0.24830E+01 | 0.24830E+01 |
| 550    | -0.21185E+00               | 0.21182E+00                | 0.23192E+01 | 0.23078E+01 | 0.23187E+01 |
| 650    | -0.21076E+00               | 0.21086E+00                | 0.18816E+01 | 0.18692E+01 | 0.18812E+01 |
| 700    | -0.21149E+00               | 0.21146E+00                | 0.16796E+01 | 0.16676E+01 | 0.16792E+01 |
| 750    | -0.21236E+00               | 0.21231E+00                | 0.14668E+01 | 0.14619E+01 | 0.14664E+01 |

The rate of energy transfer into the 200 hot thermostated atoms at the left hand side of the system is $21747E+00 \pm 0.34577E-01$ and for the 200 colder atoms is $-0.21229E+00 \pm 0.12843E-01$. We find that the energy transferred to the adjacent atoms in Table 1, $\Delta w_{1 \rightarrow 2}$ based on recoverability theory is in excellent quantitative agreement to the independently determined energy flow into the thermostats in every instance. We note that the reverse work of particle $i+1 \rightarrow i$ is negative meaning that there is a gain of energy due to its own force field. The important point therefore is that one is observing a type of one way scattering of energy, from $i$ to $i+1$ due to the conservation of energy because atom $i-1$ would have to scatter energy into $i$ to compensate for the loss of energy through the force field on the work done to $i+1$.

### CONCLUSIONS

Over the last two centuries, the main developments in thermodynamics include (a) the partitioning of the energy into two distinct forms, work $W$ and heat $Q$, from which the entropy is derived from the latter where the entropy differential $dS$ for a closed system is $dS = dQ/T$, and (b) where the field of statistical theory in concerned, these concepts were cast in terms of the Liouville equation and the associated Hamiltonian for both classical and quantum systems. We have shown the mathematical contradictions of both the Liouville equation and the time reversibility assumptions, both of which were incorporated into the more modern versions of thermodynamical theories. Here we have outlined a method of conflating both these quantities via the concept of recoverable transitions. We have demonstrated its feasibility for the case of single particle scattering. Of great interest, and of great challenge, is to extend these models to more than one particle, so that the kinetics and thermodynamical profile of the system might be computed from these elementary considerations. We also contradict the view that the Fourier law is a locally defined process, unrelated to the Second law or which cannot be deduced from the Second law, a claim central to the work of Benofy and Quay in their theory of thermolectric and thermomagnetic effects[23], by framing elementary theoretical propositions that are then tested out numerically in simulations. Benofy and Quay interpreted the Second law as pertaining to globally coupled heat-work transitions, whereas (Fourier) heat conduction was viewed as local and also as only one component of the energy definition, and therefore had only local significance. It seems feasible from the preliminary results obtained here that thermodynamical processes, both equilibrium and otherwise may be expressed in terms of a single concept where equilibrium and non-equilibrium processes might appear as limiting cases of this singular interpretation. What is of interest in these initial forays is the nature of the representation; here we are able to model systems that seem to conform to recoverable trajectories for single particle interactions. Questions that immediately suggest themselves are whether these models are unique, and if not, do they imply a multiplicity of modes that recoverability theory can accommodate to interpret thermodynamical phenomena relative to the unified concept being proposed.
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