



EDELWEISS PUBLICATIONS
OPEN ACCESS

<https://doi.org/10.33805/2641-7383.104>
Volume 1 Issue 1 | PDF 104 | Pages 8

Edelweiss Chemical Science Journal

Research Article

ISSN 2641-7383

Flaw in Crooks Fluctuation Theorem

Gokaran Shukla*

Affiliation: School of Physics, Trinity College, Dublin, Ireland

***Corresponding author:** Gokaran Shukla, School of Physics, Trinity College, Dublin 2, Ireland, E- mail: shuklag@tcd.ie

Citation: Shukla G. Flaw in crooks fluctuation theorem (2018) Edelweiss Chem Sci J 1: 13-20

Received: Oct 31, 2018

Accepted: Nov 06, 2018

Published: Dec 01, 2018

Copyright: © 2018 Shukla G. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Abstract

The existence of Crooks fluctuation theorem (even at microscopic level, in a very short time period) is a direct threat to the second law of thermodynamics. In this paper, we will underline the flaw that exists in Crooks fluctuation theorem assumptions, and thus, we will confirm the validity of the second law of thermodynamics at any temperature, pressure, and at any scale (time, and length-scale) in nature. We will validate the Loschmidts paradox, and will show that no physical directional-process can be perfectly-reversible at any non-zero, finite temperature ($T > 0$ K) and pressure ($P > 0$) in nature.

Introduction

Fluctuation theorem is a consequence of time reversal symmetry. Gavin E. Crooks and other [1-4] uses the same theorem in thermodynamics and concluded that there can be a non-zero possibility during which entropy generation can becomes negatives in short time-period. And thus, they concluded that the second law of thermodynamics does not hold at nano-scale where work done by the system is the same order as the available ($k_B T$) thermal energy [2,3]. Gavin E. Crooks assumed that any thermo-dynamical process which happens with finite speed (could be very small speed, but still it come under finite category), still this process come under reversible category (he is completely unaware with this finding) [5]. These researchers think that entropy production at any time-step can be negative [1-4].

Also, Crooks [1] proposed that any directional process can be reversible (after using time reversibility) and can be used to calculate the change in equilibrium Helmholtz free energy of the system. Crooks argued that if one repeat any thermodynamics process multiple (ideally infinites) times and then taking time average (using fluctuation theorems) will provide the change in equilibrium Helmholtz free energy [1]. Crooks suggested that one can get equilibrium Helmholtz free energy using time reversal symmetry, even in ir-reversible process, where work done by the system or on the system is strictly process (speed, surrounding, polytropic exponent) dependent.

In this paper, we will show that, fluctuation theorem should not be used in thermodynamics, because, theorem has inherent flaw in the definition of entropy. We will show that any directional process (no matter how slow that process has been performed) has inherent ir-reversibility, and thus, entropy increases in every time-step during the evolution of the system (which is against the Crooks fluctuation theorem assumption). We will show that every real system (no dynamic system can be prefect ideal system due to it interaction with surrounding during evolution in every time step which induces ir-reversibility in the process) driven by non-zero finite chemical/electrical/magnetic/gravitational potential energy gradient which come under ir-reversible category and time reversal symmetry

Should not be used to infer any information of the system at any non-zero temperature ($T > 0$). We will discuss the flaw that exists in Crooks fluctuation theorems [1], and in some experimental analysis which have been done by various experimentalist group, and thus, we will show that the second law of thermodynamics is still valid in their experiment [2-4]. Before dealing this problem, we will discuss some very fundamentals rule of thermodynamics such as ir-reversibility, reversible thermodynamic process and evolution of process under reversible condition, chemical potential and time reversal symmetry.

Ir-Reversibility in Nature

We will start this topic from Carnot's statement: "A perpetuum mobile is impossible because of the irreversibility of thermodynamic processes" [6]. The key point in Carnot's statement is "perpetuum mobile", and "ir-reversibility" of the thermodynamics process. Question arises that is there any thermodynamics process in nature which is reversible (in absolute sense)?

In this section, we will validate Carnot's statements and will show that there will never be any thermodynamics process in nature, which will be perfectly reversible, no matter how slow (even infinitely slow process) one has perform the process. Before dealing this problem, we will discuss thermodynamics reversible system. Let see how this process can be performed in real system and how every real system will be associated with a finite non-zero entropy at every time-step.

Let's take system and surrounding. Both have the same average-temperature, and same thermodynamic states, so that reversible thermodynamics process can be performed. We know that the temperature is macroscopic average quantity. A macroscopic average quantity always evaluated using statistical rule. So, if there are many thousands of atoms/molecules, then one can define the average temperature of the system after adding all possible kinetic energy of the atoms/molecules (or one can use Maxwell-Boltzmann distribution curve), and equate it to them $< \frac{3}{2} n k T >$. Where, n is the total number

Citation: Shukla G. Flaw in crooks fluctuation theorem (2018) Edelweiss Chem Sci J 1: 13-20



of moles of gas atoms/molecules. This temperature is the average temperature in investigating volume. This temperature will not be uniform in the entire volume. There will be some zone in investigating volume, where actual temperature (depend on the velocity profile of atoms/molecules (Maxwell-Boltzmann distribution) in that zone) will be bit higher, and also there will be some zone where actual temperature will be bit lower than the average temperature. In our analysis, we will use average temperature (mean) and then we will put temperature error distribution (from mean value) function which will follow normal-distribution (we have taken this assumption). Now, let's take our investigating system from thermo-dynamical state A, and move (reversible) towards the thermodynamics state B. Let's take this process has completed in infinitely many step, during which system was always in thermodynamic equilibrium with surrounding (reversible). During this process, each and every step, we assume that system and surrounding was in thermo-dynamical equilibrium. Question arises that if both system and surrounding were always in thermodynamics equilibrium (reversible), then why system goes from one thermo-dynamical state A, into another thermo-dynamical state B? If system goes from one thermo-dynamical state A, into another thermo-dynamical state B, then there must be thermo-dynamical potential gradient in a very unique direction in which system has evolved. Presence of any non-zero, finite, (no matter how small this number is, still this number will be finite in absolute sense) thermodynamic potential gradient will generate irreversibility in the system and, if system have non-zero, finite (no matter how small this is), entropy at each and every step during the transition from thermodynamic state A, into thermodynamic state B, then why we call it reversible process? To answer this question, we will take average temperature of both system and surrounding at each and every step, as mean temperature, and then will put error distribution (deviation from mean-temperature) function of temperature which follows normal distribution. Let's take average (mean) temperature T_0 . If we follow normal distribution in temperature error distribution, then at any time system and surrounding instant temperatures can be written as $T_0 + \delta T$, and $T_0 - \delta T$, where δT has been sampled from normal distribution. If one takes average temperature of both system and surrounding at this time, then, still it is T_0 (mean-temperature). Presence of small temperature difference ($2\delta T$) between system and surrounding will allow the differential amount of heat (δQ) to flow from system into surrounding. We call this δQ is a reversible heat that has been flown between the system and surrounding at equilibrium (because heat δQ has been transferred at common temperature (system and surrounding have common average temperature T_0) with reversible process). During this time, the change in entropy in system, and in surrounding, can be written as,

$$ds_{\text{system}} = -\frac{\delta Q}{T_0 + \delta T} \quad (1)$$

$$ds_{\text{surrounding}} = +\frac{\delta Q}{T_0 - \delta T} \quad (2)$$

respectively. Now, the total change in entropy (system + surrounding) in this single-step can be written as,

$$ds_{\text{total}} = \frac{\delta Q}{T_0 - \delta T} - \frac{\delta Q}{T_0 + \delta T} = \frac{\delta Q}{T_0} \left(1 - \frac{\delta T}{T_0} \right)^{-1} - \frac{\delta Q}{T_0} \left(1 + \frac{\delta T}{T_0} \right)^{-1} \quad (3)$$

After using binomial expansion, one can write,

$$ds_{\text{Surrounding}} = \frac{\delta Q}{T_0} \left[1 + \frac{\delta T}{T_0} + \frac{(\delta T)^2}{T_0^2} + \frac{\delta T^3}{T_0^3} + \dots \right] \quad (4)$$

Similarly, ds_{system} , can be written as,

$$ds_{\text{System}} = -\frac{\delta Q}{T_0} \left[1 - \frac{\delta T}{T_0} + \frac{(\delta T)^2}{T_0^2} - \frac{\delta T^3}{T_0^3} + \dots \right] \quad (5)$$

After that, the net change in entropy in one time-step between the system and surroundings can be written as,

$$ds_{\text{total}} = \frac{2\delta Q}{T_0} \left[\frac{\delta T}{T_0} + \frac{\delta T^3}{T_0^3} - \frac{\delta T^5}{T_0^5} + \dots \right] \quad (6)$$

Let assume that δT ($\delta T > 0$) is very small, therefore, only linear term shall make any significant changes. Then, ds_{total} , can be written as,

$$ds_{\text{Total}} \approx \frac{2\delta Q}{T_0} \left[\frac{\delta T}{T_0} \right] \quad (7)$$

If one analyze this step closely, then one notice that the δQ amount of heat has been flown out from the system into the surrounding (infinite bath) without informing the agent (investigator who were watching this step very carefully during the performance of thermodynamic reversible process). If one asks with agent that what the entropy change at this-step is in thermo-dynamical reversible process, then instantly he/she will respond and say that it is absolutely zero. But, we have just shown that it is not exactly zero. It may be a very small number, but still non-zero, and finite. If one add this number infinites times (because whole transition process will take infinites step during transition from state A, into state B, if it has been performed under thermo-dynamical reversible process), then it will be very finite and significant. Now, let's assume that after one step, system temperature become T_1 , which is very close to T_0 . Now, repeat the same process again (now assume that you have different surrounding which average temperature is also T_1). In this process, the net change in entropy can be written as,

$$ds_{\text{Total}} [2] \approx \frac{2\delta Q}{T_1} \left[\frac{\delta T}{T_1} \right] \quad (8)$$

where [2] in above equation, represents the number of time-step, δQ is the amount of heat flow from system into surrounding in during the thermodynamic reversible process at step number 2 (we have taken the same amount of heat (δQ) flow in step 1, and in step 2, to make analysis simple), T_1 is the system temperature which is very close to step 1, temperature T_0 , but not exactly the same, and δT (positive, assume) is the instant change in temperature between system and surrounding, which follows the normal distribution. Similar process will be happened in step number 3, 4, 5, ... ∞ . Now, the total change in entropy in a thermodynamic reversible system which transit from state A into state B, can be written as,

$$\int_A^B ds_{\text{Total}} \approx 2\delta Q \int_{T_A}^{T_B} \frac{\delta T}{T^2} = 2\delta Q \left[\frac{1}{T_B} - \frac{1}{T_A} \right] \quad (9)$$

$$S_{\text{total}} = 2\delta Q \left[\frac{1}{T_B} - \frac{1}{T_A} \right], (T_A > T_B, \delta Q, \delta T > 0)$$

Where δQ , is the amount of differential heat that has been flown from the system into a surrounding in each time-step under the reversible thermodynamic process, δT , is the positive temperature difference that has been developed instantly between system and surrounding and it (δT) follows the normal distribution (we have assumed this distribution to make our analysis simple. Sometime δT will be negative, because it has been sampled from normal distribution, but in this case no heat can



flow from system into surrounding, and thus we have ignored this part and focused only when $\delta T > 0$). What we are concluding in this section is that, if one see the change in entropy (dS_{total}), in one time-steps, then, one notice that change in entropy (system +surrounding) is not absolutely zero during the thermodynamics reversible process. It could be a very small number, but still it is finite. We generally ignore it and loosely say that change in entropy during the thermodynamical reversible process is zero. Since transition process happens with infinitely many steps (thermodynamical reversible) in between state A to state B, therefore, the total change in entropy will be very significant, and thus it will induce ir-reversibility in the process (no matter how small is this, but still will be non-zero, finite in absolute sense). So no thermo-dynamical reversible process can be possible without increasing the net change in entropy of the system+surrounding. In absolute sense, no directional process (going from state A into state B come under directional process category) can be perfectly reversible. There will always be a non-zero, finite ir-reversibility in every process. It does not matter that how slow process has been performed. Similar process will be happened, if one takes thermodynamics state B, into state A. In this case, one can take surrounding temperature $T_0 + \delta T$, and system temperature $T_0 - \delta T$, and differential heat δQ will be flown from surrounding into system during single step process. Again, in this equation T_0 is the average temperature (mean-temperature) of system and surrounding, and δT is the temperature error distribution function (deviation from mean-temperature), which follows normal distribution (we have assumed it). Again, the total change in entropy when thermodynamics system goes from state B, into state A, can be written as (this time define $dS_{total} = dS_{system} + dS_{surrounding}$).

This time heat flows from surrounding into the system with surrounding temperature $T_0 + \delta T$, and system temperature $T_0 - \delta T$

$$S_{total} = 2\delta Q \left[\frac{1}{T_B} - \frac{1}{T_A} \right], (T_A > T_B, \delta Q, \delta T > 0) \quad (10)$$

If any cyclic reversible thermo-dynamical process has been performed between state A, and state B, then the net change in entropy will be $2S_{total}$, which is very small and we simply ignore it and says that change in entropy in a cyclic process under reversible thermodynamic condition is zero. But, if one arguing the validity the second law of thermodynamics at any scale, then one must include this entropy as well (which is non-zero, and finite) in discussion.

What we are concluding in this section is that no directional process can be reversible (in absolute sense) in nature. It does not matter that how slow that process has been performed, still there will be a finite ir-reversibility in the process, and thus, a finite net positive entropy will be outcome. Since every process in nature is ir-reversible (in absolute sense), therefore, the second law of thermo dynamics will be absolute and will always remain valid at any scale (time, length-scale).

Chemical Potential

To make our discussion simple, we will use ideal gas equation without losing any generality. In ideal gas, chemical potential is defined by the Gibbs-Helmholtz equation,

$$\mu(T, P) = \mu_0(T_0, P_0) + kT \ln \left[\frac{P}{P_0} \right] \quad (11)$$

Where μ_0 and P_0 is the chemical potential and pressure at equilibrium, k is the Boltzmann constant and T is system temperature in Kelvin. As we can see that, chemical potential $\mu(T, P)$, depends on temperature and pressure. Locally, the change in Gibbs free energy in two different part (space which has different concentrations, different chemical constituents, different pressure and temperature) can be written as,

$$dG_1 = VdP_1 - SdT_1 + \sum_{i=1}^{N_1} \mu_i(T_1, P_1) dN_i \quad (12)$$

$$dG_2 = VdP_2 - SdT_2 + \sum_{i=1}^{N_2} \mu_i(T_2, P_2) dN_i \quad (13)$$

Therefore, the net differential change in Gibbs free energy which is available as a useful work is equal to,

$$\int dG = \int (dG_2 - dG_1) \quad (14)$$

or

$$\int dG = \int (dG_1 - dG_2) \quad (15)$$

depend on the local differential space denoted by subscript 2, and subscript 1. We have assumed that the subscript 2 has the higher chemical potential. The net change in Gibbs free energy $\int dG$ will

develop the chemical potential gradient locally between two investigating space, and thus drive the system (composition of atoms/molecules) either from space 2, towards space 1, or from space 1, towards space 2. This is a directional process, and thus will come under ir-reversible category. If system evolves under chemical potential gradient and goes from investigating space 2, towards space 1, or from space 1, towards space 2, then, there will be a finite, non-zero, ir-reversible entropy associated with this process. It does not matter that in which direction process has been evolved, the entropy will keep adding in previous value, and thus, keep increasing during the process. If system move in either direction (due to presence of finite electrochemical potential gradient $\left(\frac{\partial \mu(T, P, N)}{\partial r} \right)$, which drive the

system in either direction), then the total entropy (system+surrounding) will increases. One can compare this system with spring-block system, in which gravitational potential is higher in extreme end, and there is finite gravitational potential gradient towards the center of the spring-block system (around which simple harmonic oscillation happen), thus block move toward the center and constantly interacting with dissipating surrounding media through which ir-reversibility induces in the system.

In this system, entropy (ir-reversibility) will always increases, and thus spring-block system will finally come to stop after certain number of oscillation. It does not matter that block moving towards the center or away from the center. In both cases, there will be dissipation in energy, and increases in ir-reversibility, and thus increases in entropy. In other system, it is quite possible that system has differential non-zero finite chemical potential gradient which is a function of time, and which change rapidly (because it depends on the concentrations, pressure and temperature of the constituents), and thus generates chaotic motion. Still entropy will increase in each time-step in which system has driven in certain direction (due to chemical/electrical/magnetic/gravitational potential energy gradient).

The working principle of mitochondria or any nano-scale devices (where common sense suggest that this process violate the second law of thermodynamics, because it is moving in backward direction, and thus one may assume that it is taking heat from surrounding and converting it into work, which seems violation of the second law of thermodynamics) can be explained using chemical potential energy gradient. Chemical potential energy gradient drives the mitochondria or any nano-scale device in the direction in which the net chemical potential energy gradient (thermodynamics force). The chemical potential gradient depends on the temperature, pressure, concentration which is indirectly dependent on time. If these quantity changes (evolves) with time, then, chemical potential gradient will also evolves with time (time dependent). Thus, motion of mitochondria or any nano



scale devices does not violate the second law of thermodynamics at any time and length-scale.

Time Reversal Symmetry

It is general belief in the scientific community that classical as well as quantum mechanical equations follows time -reversal symmetry. One should keep in mind that, time flow in one direction only. Also, every classical and quantum mechanical equation have been derived under very ideal condition, in which, if one reverse the time arrow, then past configuration of the system can be obtained (hypothetically). This is also called Lagrange paradox, because time reversal symmetry will ensure that every system will be 100% deterministic. So, time reversibility is an ideal concept, which only valid at zero Kelvin and zero pressure. Because, once system evolves or move in certain direction under chemical/electrical/magnetic/gravitational, potential-energy gradient, then there will be a non-zero, finite, ir-reversibility associated with the system. Because, if any system has been evolved under any non-zero finite chemical/electrical/magnetic/gravitational, potential energy-gradient, then this process will no longer called the reversible thermodynamics process. And, if process is not-reversible, then, there will be a finite ir-reversibility attached with the system. Also, ir-reversibility always increases the entropy of system and surrounding. If any system has non-zero finite ir-reversibility due to presence of chemical/electrical/magnetic/gravitational potential energy-gradient or due to the effect of surrounding (which is always present in any real life process), then, one should not invoke the time reversal symmetry during the analysis of real process. Every real process always interacts with the surrounding. Interaction with surrounding, and movement under any kind of chemical/electrical/magnetic/gravitational potential energy-gradient makes sure that no real-life process can be reversible. Any thermodynamics process is a real life process, in which thermodynamical system always interact with the surrounding, and evolves under finite thermodynamics potential energy-gradient, and thus, every thermodynamics process come under ir-reversible category. Classical and quantum mechanical dynamical equations come under ideal category, in which either we ignore the effect of surrounding, or, we pay no attention towards the evolution of surrounding. If any system move in either direction, then it will always interacts and will disrupt the surrounding. If one use time reversal symmetry in this case, and analyze the system, then disruption on/by the surrounding will not reverse. Because, disruption produces on/by the surrounding is always ir-reversible in nature. So, in real-life, no process can be qualified as a reversible process in absolute sense. Every real-life process is attached with a non-zero, finite ir-reversibility. Thermodynamics rules (such as second law of thermodynamics) deals real life process in which system and surrounding (infinite in size) are coupled to each other, and thus, they are ir-reversible by nature.

Thus, one will not get time-reversible classical or quantum mechanical equation (none of the equation are time reversible equation in real life, because surrounding effect (ir-reversibility) always continuously persistent in one direction only) from thermodynamics. This is exactly the Loschmidt's paradox". In real system, time reversal symmetry can only be invoked at zero Kelvin, because, at zero Kelvin, disruption due to the surrounding on a system will be zero. But, at zero Kelvin, everything will be frozen. Nothing can move in any direction, and thus no thermo-dynamical or real life process can occurs. So, time reversal symmetry is an ideal concept, which is only valid at zero Kelvin, and it has no implication in real process. One should not use time reversal symmetry in real life process, because disruption between system and surrounding flows in one direction (in time) only. Surrounding always drain the system, and if system move back in time (using time reversal symmetry), still then, surrounding will drain the system like it would have drained in forward time. Dispute between time reversal symmetry and second law of thermodynamics is very long. Boltzmann himself wrote: *as soon as one looks at bodies of such small dimension that they contain only very few molecules, the validity of this theorem [the*

second law of thermodynamics and its description of irreversibility] must cease [3]. However, if one investigate the microscopic system dynamics carefully, then one notice that microscopic system evolves under the time varying chemical potential gradient, which change in every time-step during the evolution. If system evolves under chemical potential gradient, then there will be a finite ir-reversibility inherently associated with the process, and thus this process will not be reversible in absolute sense. So, microscopic process also comes under the ir-reversible category, and thus this process can not violate the second law of thermodynamics.

Key Points in Crooks Fluctuation Theorem [1]

Crooks fluctuation theorem is purely based on key assumption that the microscopic reversibility is possible at any non-zero finite temperature and pressure ($T > 0\text{-K}$, $P > 0$). It assumes that if any directional-process happens at infinitely slow speed, then it can be put in a reversible category, which is inherently wrong [5]. No directional process can be reversible at any non-zero finite temperature ($T > 0\text{K}$), and pressure [5]. It does not matter that how slow the process has been performed. If process has been performed in certain direction even at very-very slow speed (infinitely slow), that means there is a non-zero, finite spatial chemical/electrical/magnetic/gravitational potential-energy gradient (could be very small, still it come under finite category) at each and every time-step during the process. If any system has finite spatial gradient at any temperature and pressure in any process, then, that process will be a directional process (at each time-step), and this directional process will generate the finite non-zero entropy in each time-step. So total, entropy of the system will increase in each and every time-step.

There will be no time-step in which entropy will decreases [5] it will always increase. Also, time reversibility is an ideal concept, which is only valid at absolute zero temperature (0-K) and zero pressure. At absolute zero Kelvin, nothing can be probe for measurement, because, everything will be completely frozen at zero kelvin. And if one probe for any measurement, then, locally temperature will rise and thus, system will no longer remain at absolute zero Kelvin. And, thus, every measurement process under any temperature and pressure come under directional-process category, which is itself ir-reversible by nature. Every ir-reversible process generates finite positive entropy (due to net non-zero finite chemical potential energy-gradient) in each and every step (no matter in which direction process move, there will always be a positive finite entropy), and thus, there will never be any step in any process in which entropy will be decreased. It will always increase [5]. And, thus, we can conclude that every directional-process or directional-motions either in classical mechanics or in quantum mechanics at any temperature and pressure ($T > 0\text{K}$, $P > 0$) is ir-reversible by nature (in an absolute sense).

Shortcoming in crooks fluctuation theorems [1]

There are many short coming in Crooks fluctuation theorem. We will go one by one. Gavin E. Crooks wrote:

(1) Another recently discovered far from equilibrium expression relates non-equilibrium measurements of the work done on a system to equilibrium free energy differences. In this paper, we derive a generalized version of the fluctuation theorem for stochastic, microscopically reversible dynamics.

If any system is far away from the equilibrium, then the work done by the system, or on the system, cannot be calculated unless or until all dissipative forces, and polytropic variation of thermo-dynamical variables are known completely, because, in such cases system always follows irreversible polytropic process. Also, no stochastic microscopic process is reversible in absolute sense. If system moves stochastically, then one must investigate each and every time-step in which system evolves. System can only evolve if there is a thermodynamic



chemical/electrical/magnetic/gravitational, potential-energy gradient present at each and every time-step. If system moves under any potential-energy gradient, then process will be ir-reversible by itself, which will increase the entropy of the system. Also, entropy and time is one way street. Both move in forward direction only.

(2)

$$\frac{p(+\sigma)}{p(-\sigma)} = e^{+\sigma},$$

"Here $P(+\sigma)$ is the probability of observing and entropy production rate, σ , measured over a trajectory of time τ .

This definition of positive and negative entropy production during forward and in time reversal situation is itself an absurd, because, there is no time-step in any system where system entropy will decrease. At each time-step, real system always moves under the presence of locally chemical/electrical/magnetic/gravitational, potential-energy gradient. Moving under any potential energy-gradient will generate ir-reversibility in process, and thus, increases the entropy.

(3) The piston is then moved inwards at a uniform rate, compressing the gas to some new, smaller volume. In the corresponding time-reversed process, the gas starts in equilibrium at the final volume of the forward process, and is then expanded back to the original volume at the same rate that it was compressed by the forward process. The microscopic dynamics of the system will differ for each repetition of this process, as will the entropy production, the heat transfer, and the work performed on the system. The probability distribution of the entropy production is measured over the ensemble of repetitions.

If piston move with some finite speed (no matter how small this speed is), then compression and expansion process will come under ir-reversible polytropic category [5]. If process is ir-reversible and polytropic then work done during compression and expansion cannot be calculated unless or until all dissipative forces and exponent η , is known completely. Also, due to presence of dissipative forces, this work will be the path and speed dependent. So, calculating entropy or any other thermodynamic variable under this condition after multiple repetition of the experiment has no solid thermodynamic foundation backing, and thus, cannot be trusted without any doubt.

(4) Another expression that is valid in the far-from equilibrium regime is the recently discovered relationship between the difference in free energies of two equilibrium ensembles, δF , and the amount of work, W , expended in switching between ensembles in a finite amount of time

$$\langle e^{-\beta W} \rangle = e^{-\beta F}$$

Here $\beta = \frac{1}{K_B T}$, K_B is the Boltzmann constant, T is the temperature of the heat bath that is coupled to the system, and $\langle \dots \rangle$ indicates an average over many repetitions of the switching process".

Strictly speaking, no direct relation can be obtained between Helmholtz free energy and work done in an ir-reversible process, until or unless all dissipative forces which are speed dependent, and polytropic exponents of gas are known completely. Because work done in an ir-reversible process will be path dependent. Any process which has been performed in a finite time will come under ir-reversible category.

(5) From state A to state B during some finite time interval. The stochastic dynamics that are typically used to model reversible physical systems coupled to a heat bath, such as the Langevin equation and Metropolis Monte Carlo, are microscopically reversible in the

sense of Equation [5]. Generally, if the dynamics of a system are detail balanced locally in time (i.e., each time step is detail balanced), then the system is microscopically reversible even if the system is driven from equilibrium by an external perturbation.

Langevin equation,

$$M\ddot{X} = -\nabla U - \gamma \dot{X} + \sqrt{2\gamma K_B T} \xi(t) \quad (16)$$

Has dissipative term ($\gamma \dot{X}$) which is velocity (\dot{X}) dependent. Presence of dissipative term will make whole equation ir-reversible which will always increase entropy. So, if one runs this equation back in time, then dissipative term behaves exactly the same way as it would have behaved when time flows in forward direction, and thus, increases the ir-reversibility. Thus entropy will keep increasing and flow in one direction, like time flow in real life.

Real system evolves under the presence of chemical/electrical/magnetic/gravitational, potential-energy gradient at each time-step, and thus Metropolis Monte Carlo must include ir-reversibility term in dynamic equation, otherwise this equation will never represent any real thermo-dynamical system, and thus, no final conclusion on entropy and second law of thermodynamics should have been made using Metropolis Monte Carlo outcome until or unless it represents the real system.

(6) Clearly there is a change in entropy due to the exchange of energy with the bath. If Q is the amount of energy that flows out of the bath and into the system, then the entropy of the bath must change by $-\beta Q$.

Strictly speaking, this statement is only correct when heat Q , has been exchanged under reversible condition (reversible condition is an ideal concept. It requires infinitely slow speed to perform any work. Under reversible condition, infinite amount of time will take to complete any process. If any process happens in finite amount of time, then it cannot be called reversible process). If heat Q , has been exchanged under ir-reversible condition (as in Crooks case), then total entropy will be higher than $-\beta Q$, due to the ir-reversibility contribution. And then change in entropy should be equal to $-\beta Q - \beta W_{\text{lost}}$ [7].

(7) For example, with the confined gas we compare the entropy production when the gas is compressed to the entropy production when the gas is expanded. To allow this comparison of forward and reverse processes, we will require that the entropy production is odd under a time reversal, i.e., $w_F = -w_R$, for the process under consideration.

Expansion and compression of a gas under ir-reversible condition is path, polytropic constant, and speed dependent. This dissipative process should not be made time reversible, because dissipative forces will always dissipate energy and increase entropy in every time-step. It does not matter in which direction process moves; entropy will keep increasing in one direction only. One can compare this process with a toll-tax collection done by some government/private agent on a road. If one uses road and goes in one direction, then toll-tax has to be paid, and if one comes back again on the same road then again toll-tax has to be paid. The total toll tax in one, two-way trip will be the double of one-way trip. Here toll-tax plays the same role as entropy plays in directional process. If one reverses time, still entropy will increase from previous value. It will never decrease, because entropy and time (in real situation) is only one way street (both move in forward direction only).

(8) Both baths are considered to be large, equilibrium, thermodynamic systems. Therefore, the change in entropy of the heat bath is $-\beta Q$ and the change in entropy of the volume bath is $-\beta \delta V$ where δV is the change in volume of the system.

This statement is only valid if heat, Q , and work, $\beta \delta V$, has been performed under thermo-dynamical reversible condition (which will take infinite amount of time). If process has been performed with non-



zero speed and completed in finite time, then above statement is wrong. Because entropy contribution due to ir-reversible process must be included (every process is ir-reversible process in real life. Only degree of ir-reversibility varies between processes to process, but no process can be 100% reversible).

(9) *We start from the appropriate non-equilibrium steady state, at a time symmetric point of $\lambda(t)$, and propagate forward in time a whole number of cycles. The corresponding time-reversed process is then identical to the forward process, with both starting and ending in the same steady-state ensemble. The entropy production for this system is odd under a time reversal and the fluctuation theorem is valid.*

No two ir-reversible process can be identical either in forward or in backward directions. Fluctuation theorem is not valid in thermodynamics. There is very inherent flaw in entropy definition itself in fluctuation theorem. Entropy can never be negative at any time-step. Thermo-dynamical system evolves under the chemical/electrical/magnetic/gravitational potential-energy gradient. If any system evolves under the presence of any gradient, then there will be inherent ir-reversibility associated with that process.

(10) *The dynamics are required to be stochastic, Markovian, and microscopically reversible, equation (5), and the entropy production, defined by equation (6), must be odd under a time reversal.*

Microscopic dynamics is driven by chemical/electrical/magnetic/gravitational potential-energy gradient. Microscopic system evolves under the presence of time varying finite chemical potential-energy gradient, and ir-reversibility keep getting accumulated in each and every time-step, and thus, no microscopic dynamics is reversible in absolute sense. Also, entropy always increases in ir-reversible process, and it is only one way street. Reversal of entropy is not possible by any means in any directional process which has been evolved under non-zero, finite chemical/electrical/magnetic/gravitational, potential-energy gradient. Every real life system only evolves on the presence of any type of potential-energy gradient (time dependent/independent driving force) and thus inherently ir-reversible.

Shortcoming in experimental analysis [2-4]

(1) GM Wang, et al. wrote, *we experimentally demonstrate the fluctuation theorem, which predicts appreciable and measurable violations of the second law of thermodynamics for small systems over short time scales, by following the trajectory of a colloidal particle captured in an optical trap that is translated relative to surrounding water molecules. From each particle trajectory, we calculate the entropy production/consumption over the duration of the trajectory and determine the fraction of second law defying trajectories. Our results show entropy consumption can occur over colloidal length and time scales [2].*

The key point in above statement is that, G.M. Wang et al has observed that colloidal particle deed second law of thermodynamics, and it move in opposite direction against the prediction of second law of thermodynamics. Question arises that on what fundamental ground G.M. Wang et al. have decided the direction of the second law of thermodynamics? The rule of thermo-dynamics says that it must be decided only after the careful evaluation of chemical/electrical/magnetic/gravitational potential-energy gradient. In G.M.Wang et al. experiment, colloidal particle will move in the direction in which chemical potential energy gradient will dictates. The time varying (due to external perturbation) chemical potential energy depends on temperature, pressure and concentration of colloidal particles in his experiment. Question is, did G.M. Wang et al. have included these key gradients in his analysis? Answer is absolutely no. Still, his team has the audacity to conclude the violation of the second law of thermodynamics in his experiment. It happens due to the pure ignorance effect.

(2) *If the work performed during the duty cycle of any machine is comparable to thermal energy per degree of freedom, then one can expect that the machine will operate in reverse over short time scales. That is, heat energy from the surroundings will be converted into useful work allowing the engine to run backwards. For larger engines, we would describe this as a violation of the second law of thermodynamics, as entropy is consumed rather than generated [2].*

Machine will operate only in that direction in which there will be finite chemical potential gradient. Chemical potential energy depends on the temperature, pressure, and concentrations of atoms/molecules locally where machine is situated. Chemical potential energy gradient will decide the direction in which machine will move. This motion is well accordance with the second law of thermodynamics (in-fact this directional movement will be dictated by the second law of thermodynamics itself). Moving under finite chemical potential energy gradient will generate ir-reversibility and thus increase finite entropy. No process can consume entropy in any time-step.

(3) *The only thermodynamic statement available was the second law itself, stating that, for large systems and over long times, the entropy production rate is necessarily positive. Even the foundations of statistical mechanics were unsettled as thermo-dynamists questioned how the second law of thermodynamics could be reconciled with reversible microscopic equations of motion. Loschmidts paradox states that in a time reversible system, for every phase-space trajectory there exists a time-reversed anti- trajectory [1]. As the entropy production of a trajectory and its conjugate anti-trajectory are of identical magnitude but opposite sign, then, so the argument goes, one cannot prove that entropy production is positive [2].*

The second law of thermodynamics only says that the evolution of any thermo-dynamical system will generate ir-reversibility and thus increase entropy. The second law of thermodynamics does not distinguish between small/large space dimension and time. The second law of thermodynamics is applicable to each and every time-step and any length-scale. Any real microscopic process is not reversible in any time-step and length-scale. Microscopic system drives under the chemical potential energy gradient, which is ir-reversible. It is only reversible in an imaginary computer simulation, in which outcome of the simulation has nothing to do with the real practical problems which happens in nature. No real process, either classical, or quantum mechanical is time-reversible at any time-step and length-scale. Classical and quantum mechanical equations are the ideal equation, and only applicable at the zero Kelvin. But, then, everything will be frozen at zero Kelvin and thus, no dynamics is possible. There is no real system in which the entropy can be absorbed during it evolution, because, evolution of any system is driven by chemical/electrical/magnetic/gravitational potential energy gradient, which is inherently ir-reversible.

(4) *That entropy-consuming trajectories can be discerned for micron-sized particles over time scales on the order of seconds is particularly important to applications of nano-machines and to the understanding of protein motors. The fluctuation theorem points out that as these thermodynamic engines are made smaller and as the time of operation is made shorter, these engines are not simple scaled-down versions of their larger counterparts. As they become smaller, the probability that they will run thermodynamically in reverse inescapably becomes greater. Consequently, these results imply that the fluctuation theorem has important ramifications for nanotechnology and indeed for how life itself functions [2].*

There is no trajectory in which entropy can get consumed. Because, every trajectory has been evolved under non-zero, finite chemical potential gradient, which inherently increases the ir-reversibility in the process and thus entropy, increases in each and every time-step. Thermodynamics process run under chemical potential energy



gradient, which depends on temperature, pressure and concentrations of atoms/molecules. Chemical potential energy gradient will decide the direction in which thermo-dynamical process will evolve. This evolution will be dictated by the finite potential energy gradients, which is nothing but the second law of thermodynamics itself.

Carberry DM, et al. wrote [6].

(1) *The puzzle of how time-reversible microscopic equations of mechanics lead to the time-irreversible macroscopic equations of thermodynamics have been a paradox since the days of Boltzmann. Boltzmann simply sidestepped this enigma by stating as soon as one looks at bodies of such small dimension that they contain only very few molecules, the validity of this theorem [the second law of thermodynamics and its description of irreversibility] must cease." Today we can state that the transient fluctuation theorem (TFT) of Evans and Searles is a generalized, second-law-like theorem that bridges the microscopic and macroscopic domains and links the time-reversible and irreversible descriptions. We apply this theorem to a colloidal particle in an optical trap. For the first time, we demonstrate the TFT in an experiment and show quantitative agreement with Langevin dynamics [3].*

There is no time-reversible process exist in nature at any temperature $T > 0K$. Fluctuation theorem has a very inherent flaw in defining the entropy. Under no circumstances entropy can be negative in any directional process at any-time steps. Therefore, fluctuation theorem will never be able to represent the second law of thermodynamics. If colloidal particles follows the Langevin dynamics,

$$M\ddot{X} = -\nabla U - \gamma\dot{X} + \sqrt{2\gamma K_B T} R(t) \quad (17)$$

Then how is the colloidal motion challenges the second law of thermodynamics? Because, Langevin equation is inherently irreversible in nature due to presence of dissipative term ($-\gamma\dot{X}$) which depends on the speed of the colloidal particle. If one reverses the dynamics of the Langevin equation back in time, then, this dissipative term will keep dissipating energy and will act like as process moving in the forward in time. Presence of this dissipative term will drive the process in ir-reversible direction. Also, no real process is reversible in nature in absolute sense.

(2) *The second law of thermodynamics states that for systems in the thermodynamic limit, the entropy production must be greater than or equal to zero. Although the underlying equations of motion are time reversible, the second law predicts an irreversible entropy production. This law applies to systems that are of infinite size and persist over long times. Despite this strict limitation, the second law is often treated as being universal in application because the size of most systems can be considered infinite when compared to atomic length and time scales. However, several systems of current scientific interest, such as nano-machines and protein motors, operate at length and time scales where the system cannot be considered infinite. At the nano and microscales the thermal energy available per degree of freedom can be comparable to the work performed by the system. Classical thermodynamics does not apply to these small systems [3].*

No directional motion is reversible in nature in absolute sense. Every directional process is driven by the chemical potential energy gradient, which is inherently ir-reversible by nature. The second law of thermodynamics is applicable to any system at any scale. This law only says that if any system evolves under chemical/electrical/magnetic/gravitational potential energy gradient, then the ir-reversibility of the process increases which will increase the entropy of the system. Even at the nano-scale, system evolves only under the presence of the chemical potential energy gradient, and thus, follows the second law of thermodynamics.

(3) *In this way the FT can be viewed as a generalization of the second law since the FT applies to finite systems observed over finite time and trivially recovers the second law in the thermodynamic limit [3].*

There is a fatal inherent flaw in the fluctuation theorem. Entropy can never be negative in any directional process. Entropy and time is only one way street. Both continuously flow in forward direction. Fluctuation theorems will never be able to represent the second law of thermodynamics any-day, anytime.

(4) If the probability of observing a trajectory in δV is equal to the probability of observing one in δV^* , then the system is thermodynamically reversible and $\Omega t = 0$ [3]. Thermodynamic reversibility is always defined between system and surrounding when process perform infinitely slow. Every thermodynamic variables, such as, temperature, pressure, Gibbs free energy, chemical potential, are in equilibrium between system and surrounding (there is no any type of spatial-gradient). Thermodynamic reversibility concept is not allowed if any system evolves under the non-zero, finite gradient (any-type). Tracing of any directional trajectory back in time after using time-reversal symmetry does not come under the thermodynamics reversible category.

(5) *The TFT quantitatively describes how irreversible macroscopic behavior evolves from time-reversible microscopic dynamics as either the system size or the observation time increases. This experiment confirms, for the first time, the predictions of this theorem. Furthermore, these experiments demonstrate that the effects predicted occur over colloidal length and time scales and, consequently, show that the TFT is relevant to nano-technological applications [3].*

There is no reversible process in nature at any finite temperature ($T > 0K$) in an absolute sense. Experiment confirms nothing about TFT. But, it does confirmed the validity of the second law of thermodynamics if one analyze the system and surrounding carefully, using the chemical potential energy gradient concept. FT/TFT will never be able to evaluate the exact change in a entropy of any system due to inherent fatal flaw that exists in the definition of entropy in FT/TFT.

Collin D, et al. wrote,

(1) *A consequence of the CFT is Jarzynski equality, which relates the equilibrium free-energy difference dG between two equilibrium states to an exponential average (denoted by angle brackets) of the work done on the system, W , taken over an infinite number of repeated non-equilibrium experiments [4],*

$$\exp\left(-\frac{G}{K_B T}\right) = \left\langle \exp\left(\frac{-W}{K_B T}\right) \right\rangle$$

The work done in an infinite numbers of repeated non-equilibrium experiment come under the ir-reversible category [5]. However, standard thermodynamics fundamentals suggest that, work must need to be performed under reversible process, (reversible process will take infinite amount of time for one cycle) only then work W and G can be equated. If process happens with infinite speed, or infinite time, then, it come under the irreversible category, and ir-reversible process rule needs to be invoked before reaching on any conclusion [5].

(2) *These results illustrate that when used in conjunction with an appropriate fluctuation theorem, non-equilibrium single-molecule force measurements can provide equilibrium information such as folding free energies, even if the process studied occurs under far-from-equilibrium conditions [4].*

The ir-reversible forces will never be able to provide the any information about the equilibrium thermodynamics variables. Also, unfolding and folding process of RNA molecules should have been explained using the chemical potential energy gradient, which depends



on the temperature, pressure and the local chemical compositions of atoms/molecules.

Fluctuation theorem has very inherent fatal flaw in the definition of entropy itself. Entropy will never become negative in any directional process in any time-step and length-scale. In nature, entropy and time is one way street, both flow in forward direction only.

Conclusion

In this paper, we have addressed the flaw that exist in Crooks fluctuation theorems. We have shown that the every directional process in nature evolves under the chemical/electrical/magnetic/gravitational potential energy gradient, which is inherently ir-reversible by nature; therefore, no reversible process exists in nature in absolute sense at any finite temperature. We have shown that the evolution of microscopic process is ir-reversible due to the presence of directional chemical potential energy gradient at each time-step, which drive the entire system in one direction. We have shown that if any process has been performed with infinite speed and in infinite time, then it will not come under the reversible process category. We have shown that fluctuation theorem has very inherent fatal flaw in the definition of entropy, and it will never be able to capture the second law of thermodynamics. We have shown that entropy and time are only one way Street, in which both will continuously increase and move in one direction only. We have shown that experiment in which the second law of thermodynamics violation has been claimed have inherent flaw in data analysis. We have shown that all experimented data can be explained using chemical potential energy gradient.

We have shown that the system will be evolved and governed by the chemical potential gradient and thus irreversibility will induce in the process itself which will increase entropy. We have shown that evolution of system under chemical potential energy gradient in each time step is governed by the second law of thermodynamics. We have shown that no directional process which have been evolved or will evolve can come under reversible category. We have discussed the reversible thermodynamics and its evolution which ultimately increases the non-zero entropy. We have shown that the every process which operates at any non-zero temperature ($T > 0K$) is inherently ir-reversible by nature, and thus fundamental thermodynamic quantity such as entropy will always increases in each and every time-step. We have shown that in nature entropy increases in every time-step and thus, validate the supremacy of the second law of thermodynamics.

We hope that this paper will clear the doubt which surrounds the second law of thermodynamics, and thus, stimulate the scientific community to start looking the fundamentals thermodynamics equations at microscopic levels very carefully.

Now, we can quote Arthur Eddington again: The second law of thermodynamics holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in dis-agreement with Maxwell's equations then so much the worse for Maxwell's equations. If it is found to be contradicted by observation, well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation [6].

References

1. Gavin CE. Entropy production fluctuation theorem and the non-equilibrium work relation for free energy differences (1999) *Phy Rev E* 60: 2721-2726. <https://doi.org/10.1103/PhysRevE.60.2721>
2. Wang GM, Sevick EM, Mittag E, Searles DJ and Evans DJ. Experimental demonstration of violations of the second law of thermodynamics for small systems and short time scales (2002) *Phys Rev Lett* 89: 050601. <https://doi.org/10.1103/PhysRevLett.89.050601>
3. Carberry DM, Reid JC, Wang GM, Sevick EM, Searles DJ, et al. Fluctuations and irreversibility: An experimental demonstration of a second-law-like theorem using a colloidal particle held in an optical trap (2004) *Evans Phy Rev Lett* 92: 14060. <https://doi.org/10.1103/PhysRevLett.92.140601>
4. Collin D, Ritort F, Jarzynski C, Smith SB, Tinoco I, et al. Verification of the crooks fluctuation theorem and recovery of RNA folding free energies (2005) *Nat lett* 437: 231-234.
5. Petrescu S, Borcila B, Costea M, Banches E, Popescu G, et al. Concepts and fundamental equations in Thermodynamics with Finite Speed (2016) IOP Conference Series: Materials Science and Engineering, UK 147: 012144.
6. Nikulov A and Sheehan D. Quantum limits to the second law of thermodynamics (2004) *Entropy* 6: 1-10. <https://web.mit.edu/16.unified/www/FALL/thermodynamic/s/notes/node48.html>