

Flaw in Crooks fluctuation theorem

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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 Loschmidt's paradox, and will show that no *physical directional-process* can be *perfectly-reversible* at any non-zero, finite temperature ($T > 0\text{K}$) and pressure ($P > 0$) in nature.

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I. INTRODUCTION

Fluctuation theorem is a consequence of a time reversal symmetry. Gavin E. Crooks⁴ and other⁵⁶⁷ uses the same theorem in thermodynamics and concluded that there can be a non-zero possibility during which entropy generation can become negative 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 energy⁵⁶. Gavin E. Crooks assumed that any thermodynamical process which happens with finite speed (could be very small speed, still it come under finite category), still this process come under reversible category (he is completely unaware with this² finding). These researchers⁴⁵⁶⁷ think that entropy production at any time-step can be negative. Also, Crooks⁴ 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 infinite) times and then taking time average (using fluctuation theorems) will provide the change in equilibrium Helmholtz free energy. Crooks, in-

fact argued 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 any real system driven by non-zero finite chemical/electrical/magnetic/gravitational potential energy gradient 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 theorems⁴, and in experimental analysis done by various experimentalist group⁵⁶⁷, and will show that the second law of thermodynamics is still valid in their experiment⁵⁶⁷. Before dealing this problem, we will discuss some very fundamental rule of thermodynamics such as, ir-reversibility, reversible thermodynamic

process, evolution of process under reversible condition, chemical potential and time-reversal symmetry.

II. IR-REVERSIBILITY IN NATURE

We will start from Carnot's statement: "*A perpetuum mobile is impossible because of the irreversibility of thermodynamic processes*"¹.

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 any cost. Lets 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 quantity always evaluated using statistical rule. So, if there are many thousands of atoms/molecules, 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 the $\langle \frac{3}{2}nKT \rangle$. Where, n is the total number 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, lets take our investigating system from thermodynamical state A, and move (reversible) towards the thermodynamics state B. Let 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 thermodynamical equilibrium. Question arises that if both system and surrounding were always in thermodynamics equilibrium (reversible), then why system goes from one thermodynamical state A, into another thermodynamical state B? If system goes from one thermodynamical state A, into another thermodynamical state B, then there must be thermodynamical 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 ir-reversibility 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. Lets 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 take 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 sys-

tem 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 temperature T_0) with reversible process). During this time, the change in entropy in system, and in surrounding, can be written as,

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

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

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

$$\begin{aligned} dS_{total} &= \frac{\delta Q}{T_0 - \delta T} - \frac{\delta Q}{T_0 + \delta T} \\ &= \frac{\delta Q}{T_0} \left(1 - \frac{\delta T}{T_0}\right)^{-1} - \frac{\delta Q}{T_0} \left(1 + \frac{\delta T}{T_0}\right)^{-1}. \end{aligned} \quad (3)$$

After using binomial expansion, one can write,

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

Similarly, dS_{system} , can we written as,

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

After that, the net change in entropy in one -step can be written as,

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

Let assume that δT ($\delta T > 0$) is very very small, therefore, only linear term shall make any significant changes.

Then, dS_{total} , can be written as,

$$dS_{total} \simeq \frac{2\delta Q}{T_0} \left[\frac{\delta T}{T_0}\right] \quad (7)$$

If one analyze this step closely, then one notice that δQ amount of heat has been flown out from system into surrounding (infinite bath) without informing the agent (investigator who were watching this step very carefully during the performance of thermodynamic reversible process). If one ask with agent that what is the entropy

changes in his thermodynamical 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 B, into state A, if it has been performed under thermodynamical reversible process), then it will be very finite and significant. Now, lets 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,

$$dS_{total}[2] \simeq \frac{2\delta Q}{T_1} \left[\frac{\delta T}{T_1}\right], \quad (8)$$

where [2], represent step number, 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-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,

$$\begin{aligned} \int_A^B dS_{total} &\simeq 2\delta Q \int_{T_A}^{T_B} \frac{\delta T}{T^2} \\ &= 2\delta Q \left[\frac{1}{T_B} - \frac{1}{T_A}\right] \\ S_{total} &= 2\delta Q \left[\frac{1}{T_B} - \frac{1}{T_A}\right], \quad (T_A > T_B, \delta Q, \delta T > 0). \end{aligned} \quad (9)$$

Where δQ , is the amount of differential heat that has been flown from the system into a surrounding in each-step under the reversible thermodynamic process, δT , is the positive temperature difference that has been devel-

oped instantly between system and surrounding and it (δT) follows the normal distribution (we have assumed this distribution to make our analysis simple. Some time 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 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 thermodynamical 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

$dS_{total} = dS_{system} - dS_{surrounding}$, because, this time heat flows from surrounding into the system with surrounding temperature $T_0 + \delta T$, and system temperature $T_0 - \delta T$)

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

If any cyclic reversible thermodynamical 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 thermodynamics will be absolute and will always remain valid at any scale (time, length-scale).

III. 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 have 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

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

depends on which, local, differential space denoted by subscript 2, or subscript 1, have the higher chemical potential. This net 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 it 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 surrounding media through which ir-reversibility arises in the system. In this system, entropy (ir-reversibility) will always increases. 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, 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 says that this process violate the second law of thermodynamics, because it is moving in backward direction, and thus one can think-of that it is taking heat from surrounding and converting it into work, which seems violation of second law of thermodynamics) can be explained using chemical potential energy gradient. Chemical potential gradient drive the mitochondria or any nano-scale device in the direction in which negative gradient exist. This chemical potential gradient is temperature, pressure, concentration and time dependent. 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.

IV. 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 of the system. 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 attach 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 interact 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 interact with the surrounding 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 produce 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 can 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, every thing will be frozen. Nothing can move in any direction, and thus no thermodynamical 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*"⁶. 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 come under the ir-reversible category, and thus these process can not violate the second law of thermodynamics.

V. KEY POINTS IN CROOKS FLUCTUATION THEOREM⁴

Crooks fluctuation theorem is purely based on key assumption that microscopic reversibility is possible at any non-zero finite temperature and pressure ($T > 0K, P > 0$). It assumes that if any *directional-process* happens at infinitely slow speed, then it can be put in reversible category, which is inherently wrong (see for example²). No directional process can be reversible at any non-zero, finite temperature ($T > 0K$), and pressure (see for example²). 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 was 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 decrease (see for example²). 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 (see for example²). 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 ($T > 0K, P > 0$) is ir-reversible by nature (in an absolute sense).

A. Shortcoming in Crooks fluctuation theorems⁴

There are too many shortcoming in Crooks fluctuation theorem. We will go one by one.

Gavin E.Crooks wrote (1), *“Another recently discovered far from equilibrium expression relates nonequilibrium 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 system is far away from equilibrium, then work done either by the system, or on the system, can not be calculated unless or until all dissipative forces, and polytropic variation of thermodynamical 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 move stochastically, then one must observe each and every time-step in which system evolves. System can only evolves if there is a thermodynamic chemical/electrical/magnetic/gravitational, potential-energy gradient present at each and every time-step. If system move 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 are one way street. Both can only move in forward direction.

$$\mathbf{2}, \quad \frac{P(+\sigma)}{P(-\sigma)} = e^{+\sigma},$$

“Here $P(+\sigma)$ is the probability of observing an 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 step in any system where system entropy decreases. At each step, any real system always move under the presence of locally chemical/electrical/magnetic/gravitational, potential-energy gradient. Moving under any potential energy-gradient will generates 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 (see for example²). If process is ir-reversible and polytropic then work done during compression and expansion can not be calculated unless or until all dissipative forces and exponent η , 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 these condition after multiple repetition of the experiment has no solid thermodynamic foundation, and thus, can not 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 $\langle .. \rangle$ indicates an average over many repetitions of the switching process”.

Strictly speaking, no direct relation can be obtain between Helmholtz free energy and work done in a ir-reversible process, until or unless all dissipative forces which is 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 Eq. [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 [see Eq. (9) of Ref.[19]].”

Langevin equation,

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

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 run this equation back in time, then dissipative term behaves exactly the same way as it would have behaved when time flow 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 thermodynamical 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 represent 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 require infinitely slow speed to perform any work. Under reversible condition, infinite amount of time will take to complete any process. If any process happen in finite amount of time, then it can not be called reversible process). If heat Q has 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 $-\beta Q - \beta W_{lost}$ (for more details, see³).

(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. These dissipative process should not be made time reversible, because dissipative forces will always dissipate energy and increase entropy every time-step. It does not matter in which direction process move, entropy will keep increasing in one direction only. One can compare this process with a toll-tax collection done

by some govt/private agent on a road. If one use road and goes in one direction, then toll-tax has to be paid, and if once come 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 play the same role as entropy play in directional process. If one reverse time, still entropy will increases from previous value. It will never decreases, because entropy and time (in real situation) are 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 $-P\delta V$ where δV is the change in volume of the system”*

This statement is only valid if heat, Q , and work, $P\delta V$, has been performed under thermodynamical 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 vary between process to process, but no process can be 100% reversible.)

(9), *“We start from the appropriate nonequilibrium 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. Thermodynamical system evolves under the chemi-

cal/electrical/magnetic/gravitational potential-energy gradient. If any system evolves under the presence of any gradient, then there will be a inherent ir-reversibility associated with that process.

(10), “The dynamics are required to be stochastic, Markovian, and microscopically reversible, Eq. (5), and the entropy production, defined by Eq. (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.

B. Shortcoming in experimental analysis⁵⁶⁷

(1), G.M. 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 lawdefying trajectories. Our results show entropy consumption can occur over colloidal length and time scales.”⁵

The key point in above statement is that, G.M. Wang et

al. has observed that colloidal particle defied 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? 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. includes these key gradient in his analysis? Answer is absolutely no! Still his team has concluded the violation of second law of thermodynamics in his experiment due to the 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”⁵

Machine will operate only in that direction in which there will be finite negative chemical potential gradient. Chemical potential energy dependent 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 . It is well accordance with the second law of thermodynamics (in-fact this is itself the second law of thermodynamics). 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 thermodynamicists questioned how the second law of thermodynamics could be reconciled with reversible microscopic equations of motion. Loschmidt’s 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”⁵

Second law of thermodynamics only says that evolution of any thermodynamical system will generate irreversibility and thus increase entropy. Second law of thermodynamics does not distinguish between small/large space dimension and time. 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 systems drive under the chemical potential energy gradient, which is irreversible. It is only reversible in imaginary computer simulation, which has nothing to do with real problems. No real process is time-reversible at any time and length-scale, classical or quantum mechanical level. Classical and quantum mechanical equations are ideal equations, and only applicable at zero Kelvin. But then everything will be frozen at zero Kelvin and no dynamics is possible. There is no real system in which entropy can be absorbed during its evolution, because evolution of any system driven by chemical/electrical/magnetic/gravitational potential energy gradient, which is inherently irreversible.

(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”⁵

There is no trajectory where entropy gets consumed. Because every trajectory has been evolved under non-zero, finite gradient, which increases irreversibility in the process and thus entropy increases in each and every time-step. Thermodynamic processes 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 thermodynamical processes will evolve. This evolution will be dictated by chemical potential energy gradients, which is nothing but the second law of thermodynamics itself.

D.M. Carberry et al. wrote (1), “The puzzle of how time-reversible microscopic equations of mechanics lead to the time-irreversible macroscopic equations of thermodynamics has 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”⁶

There is no time-reversible process that exists in nature at any temperature $T > 0K$. Fluctuation theorem has very in-

herent flaw in defining the entropy. Under no circumstances entropy can be negative in any directional process. Therefore, fluctuation theorem will never be able to represent second law of thermodynamics. If colloidal particles follows Langevin dynamics,

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

then how colloidal motion challenge second law of thermodynamics? Because, Langevin equation is inherently ir-reversible in nature due to presence of dissipative term ($\gamma\dot{X}$) which depends on the speed of the colloidal particle. If one reverse the dynamics of the Langevin equation back in time, then, this dissipative term will keep dissipating energy and will act like process moving 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 [1,2] 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 nanomachines 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.”*⁶

No directional motion is reversible in nature in absolute sense. Any directional process driven by chemical potential energy gradient, which is inherently ir-reversible by nature. Second law of thermodynamics apply 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 entropy of the system. Even the nano-scale system evolve only under the chemical potential energy gradient, and thus follows 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.”*⁶

There is fatal inherent flaw in fluctuation theorem. Entropy can never be negative in any directional process. Entropy and time are 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 $\Omega_t = 0$ ”*⁶.

Thermodynamic reversibility is always define between system and surrounding when process perform infinitely slow such that, 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 non-zero, finite gradient (any-type). Tracing any directional trajectory back in time after using time-reversal symmetry, does not come under 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.”*⁶

There is no reversible process in nature at any finite temperature ($T > 0K$) in an absolute sense. Experiment confirm nothing about TFT, however, experiment does confirm the validity of the second law of thermodynamics if one analyze carefully using 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.

D.Collin et al. wrote,(1), *“A consequence of the CFT is Jarzynskis 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 none-equilibrium experiments, $\exp(\frac{-G}{k_B T}) = \langle \exp(\frac{-W}{k_B T}) \rangle$ ”*⁷

Work done by infinite number of repeated non-equilibrium experiments come under ir-reversible category (see for example²). 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 happen with finite speed or in finite time then it come under ir-reversible category and ir-reversible process rule needed to be invoked before reaching any conclusion².

(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.”*⁷

Ir-reversible force will never be able to provide any thermodynamics equilibrium information beyond doubt. Also, unfolding and folding process of RNA molecules should have been explained using chemical potential-energy gradient, which depends on temperature, pressure, 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 are one way street, both can flow in forward direction only.

VI. CONCLUSION

In this paper, we have addressed the flaw that exist in Crooks fluctuation theorems. We have shown that 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 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 finite speed and in finite time, then it will not come under the reversible process category². 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 a 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 system will be evolved and governed by the chemical potential gradient and thus ir-reversibility 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 shown that how reversible thermodynamics evolves in nature and how there

is non-zero entropy associated even with this process (if one look process very closely in absolute sense). We have shown that every process which happens at any non-zero temperature ($T > 0K$) is inherently ir-reversible, and fundamental thermodynamic quantity entropy always increases in each and every time-step, which validate the supremacy of the second law of thermodynamics in nature.

We hope that this paper will clear the doubt about the second law of thermodynamics, and stimulate the scientific community to start looking the fundamentals thermodynamics equations at microscopic levels very care-

fully.

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 disagreement 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”*¹.

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