

Flaw in Maxwell's-demons paradox

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The existence of a Maxwell's-demons is a direct threat to the second law of thermodynamics. In this paper, we will underline the flaw that exists in Maxwell's-demons paradox, and thus, we confirm the validity of the second law of thermodynamics in nature.

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I. INTRODUCTION

Maxwell-demons was the thought-experiment by James Clerk Maxwell in 1867, in which he suggested that second law of thermodynamics can be violated if one able to segregate hot atoms/molecules in one compartment and cold atoms/molecules in other compartment from an equilibrium system without performing any extra work¹. Maxwell hypothesized a thought experiment and wrote *“if we conceive of a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are as essentially finite as our own, would be able to do what is impossible to us. For we have seen that molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower molecules to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics”*²

³⁴. Numerous paper have been written in a favor off Maxwell-demon as well as against about it. In this pa-

per, we will provide clear insight using standard thermodynamics rule such as thermodynamics potential, Gibbs free energy, and entropy, and will show that Maxwell-demon will never able to break the second law of thermodynamics, any-day, and anytime. Before dealing this problem, let see how chemical potential energy changes as a function of temperature and pressure. To make our analysis simpler, we will use ideal gas system in our analysis, without losing any generality. In ideal gas, chemical potential is defined by the Gibbs-Helmholtz equation, $\mu(T, P) = \mu_0(T_0, P_0) + kT \ln(\frac{P}{P_0})^5$, 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. As hot atom/molecule transfers from compartment A to compartment B (see in figure 1), then, temperature and pressure in compartment B start increasing, while in compartment A, both start decreasing from equilibrium value. As pressure and temperature changes in both compartments from equilibrium value, it shift the chemical potential of atoms/molecules in both compartment. In compartment A, chemical potential start decreasing, because both pressure and temperature start decreasing after Maxwell's demon intervention, while in compartment B, chemical potential start increasing, because, both pressure and temperature start increasing. Variation of chemical potential with pressure and

temperature in both compartment follows the relation, $\mu(T, P) = \mu_0(T_0, P_0) + kT \ln(\frac{P}{P_0})$, where $\mu_0(T_0, P_0)$ is the equilibrium chemical potential of the gas. Similarly, the change in Gibbs free energy in each compartment A, and in compartment B, can be written as,

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

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

Therefore, the net Gibbs free energy which will be available as a useful work is equal to

$\int dG = \int (dG_2 - dG_1)$. This is the minimum amount of work which demon must be performed on the gas-system during the segregation of cold and hot gas in two different compartment A, and B respectively.

II. SHORTCOMING IN MAXWELL'S-DEMON STATEMENT²³⁴

Maxwell wrote *“For we have seen that molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform.”*²³⁴

Temperature is a macroscopic average quantity. It is being calculated after statistical average of many particles having wide range of kinetic energy present in a certain volume, therefore, only average value of temperature in any small investigating volume which contains many numbers of particles (not few) make any sense in thermodynamics. So, there should not be any such term, like, *“uniform-temperature”* or *“uniform velocities”* in thermodynamics. However, average temperature or most probable velocity does make sense and these term are perfectly valid.

Maxwell further wrote *“Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower molecules to pass from B to*

*A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics.”*²³⁴.

There are two fatal flaw in this maxwell argument. First flaw is that, Maxwell thought that system will still remain in equilibrium all the time even after continuous segregating of hot (cold) atoms/molecules from one compartment A into other compartment B (see in figure 1). System equilibrium property defines through its temperature, pressure, Gibbs free energy and chemical potential of constituent atoms/molecules at that temperature and pressure. All these characteristic properties of the system changes as temperature and pressure changes continuously during the segregation of hot (cold) atoms/molecules into different A (B) compartment (see in figure 1). As the hot atoms/molecules start segregating in compartment B after demon intervention (see in figure 1), temperature in compartment B start increasing, while temperature in compartment A, start decreasing from equilibrium value (see in figure 1). As temperature start changing in both compartments, gas pressure in both compartment start changing as well (assume ideal gas equation $P = \frac{nRT}{V}$). Change in temperature and pressure in both compartment A and B, directly changes the chemical potential of the atoms/molecules in both compartment, and it vary as $\mu(T, P) = \mu_0(T_0, P_0) + kT \ln(\frac{P}{P_0})$, where μ_0 and P_0 are the equilibrium chemical potential and equilibrium pressure of the atoms/molecules. In compartment A, as segregation of atoms/molecules started, (see in figure 1) pressure and temperature start decreasing from equilibrium value, and thus, chemical potential also start decreasing from equilibrium value $\mu_0(T_0, P_0)$. While in compartment B, (see in figure) pressure and temperature start increasing from equilibrium value $\mu_0(T_0, P_0)$, and thus, chemical potential start increasing as well from equilibrium value $\mu_0(T_0, P_0)$. Thus, as the segregation of hot (cold), atoms/molecules started in different compartment A (B), by Maxwell's-demon, the net change in

chemical potential difference between two compartments A, and B also started as time progress. Thus system no longer remain in thermodynamics equilibrium during the transition of the hot atoms/molecules from the cold compartment A, into hot compartment B.

Second fatal flaw in Maxwell's argument is that demon did not perform any work on the system, and able to segregated the hot atoms/molecules in one compartment B (higher chemical potential), and cold atoms/molecules (low chemical potential) into other compartment A.

If one investigate the system closely, then, one notice that, there was always time varying finite chemical potential difference presented between hot compartment B, (higher chemical potential) and cold compartment A, (low chemical potential) during the segregation of the atoms/molecules into different compartments. This chemical potential difference was zero at the thermodynamics equilibrium. But, once the demons disturbed that thermodynamics equilibrium by allowing only one type of atoms/molecules in one compartment, and other type of atoms/molecules into other compartment, chemical potential difference start developing between the two compartments, A and B. This is a time varying chemical potential difference. Now, demon must work against this chemical potential difference to transfer any hot atom/molecule anytime from compartment A to compartment B. The minimum work done (during reversible equilibrium process at each-step, every time) by Maxwell's demon must be equal to change in chemical potential energy during the transition of hot atom/molecules from compartment A, to compartment B (see in figure 1). Also, as hot atoms/molecules goes in compartment B, temperature in compartment B start increasing, which increases the temperature of cold atoms/molecules, present in compartment B as well, and thus, number of cold atom in B start decreases (see Maxwell-Boltzmann speed distribution of N_2 -molecules of air as a function of temperature 2) as time progress. The minimum change in entropy in this process by

Maxwell's demon can be calculated as,

$\int \left(\frac{\mu_2(T_2, P_2, t)}{T_2} - \frac{\mu_1(T_1, P_1, t)}{T_1} \right) dN$, where, T_2, P_2, T_1, P_1 are the temperature and pressure in compartment B and A respectively at any time t. And, dN is the number of atoms/molecules that has been transferred from compartment A to compartment B, by demon at each step, because, chemical potential of atoms/molecules in both compartment changes continuously as a function of temperature T, and pressure P, as hot atom/molecules transfer from compartment A to compartment B (see in figure 1). Also, as time progress and demon transfer more and more hot atoms/molecules from compartment A to compartment B, the number of atoms/molecules in compartment B increases in comparison the compartment A (because cold atom in compartment B also get heated as temperature changes in B due to transfer of hot atom/molecule from compartment A (see the probability distribution profile in figure 2)). Thus, there will be an uneven distribution of atoms/molecules in both compartment rather than equal distributions (in contrast to Maxwell guess). Also, more than half of total (including both compartment) atoms/molecules will be at higher temperature in compartment B, and, thus they will have higher entropy, compare to compartment A, atoms/molecules, which have low entropy. The total change in entropy of the system must be equal to the change in entropy of compartment B, plus change in entropy of compartment A, plus minimum entropy contribution due to Maxwell's demons at each step when demon transfer hot atom/molecule from lower chemical potential (in compartment A) to higher electrochemical potential (in compartment B) using equation, $\int \left(\frac{\mu_2(T_2, P_2, t)}{T_2} - \frac{\mu_1(T_1, P_1, t)}{T_1} \right) dN$, where T_2, P_2 are the temperature and pressure in compartment B, while T_1, P_1 are the temperature and pressure in compartment A, at any time t. As we see that compartment B, accumulates more and more chemical potential energy (Gibbs free energy if one count total chemical potential energy associated with total number of atoms/molecules in compartment

B) as time progress, at the expense of the Maxwell's-demon work. One can say that the whole of the Gibbs free energy that has been buildup in compartment B, has directly come from Maxwell's demon work, and thus, no question for breaking of the second law of thermodynamics arises in Maxwell's-demons paradox. Maxwell's-demon working principle can be visualized and simplified further if one compare it with the working principle of rechargeable battery using electricity. In electrochemical battery, certain type of ion/molecules (depends upon the type of battery) move from cathode to anode and buildup higher chemical potential at anode during charging. As more and more ion/molecules move due to external agency (like external voltage source which recharge battery, or Maxwell's-demon) which move ion/molecules from cathode to anode, higher and higher electrochemical potential buildup at anode. Once, almost all ion/molecule (maximum) which can be moved from cathode material towards anode material has moved, highest chemical potential difference buildup between anode and cathode. And thus, we call battery is fully charged now, and stored electrochemical energy in battery is available for performing any useful work. The same total stored electrochemical energy is also called Gibbs free energy (because Josiah Willard Gibbs in 1873 himself defined such energy as maximum "available energy" for any work. Josiah Willard Gibbs wrote "*the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition*"⁷). Now, if one analyze the working principle of a charging battery, then, one notice that, battery will "never" be able to charge itself without external intervention, such as external source which will create require potential difference between cathode and anode electrodes, and will assist in movement of ion/molecules from cathode to anode. In this case, external source per-

forms at-least minimum amount of work, which is equal to the total electrochemical energy stored in the rechargeable battery. So, one can see that it is the external source, who has performed at-least minimum amount of work equal to the total electrochemical energy stored in the rechargeable battery. This is exactly what second law of thermodynamics wanted. As we see that the second law of thermodynamics does not violate in charging of the rechargeable battery. Similarly, in Maxwell's-demon case as well, it is demon, who must work during the segregation of the hot atoms/molecules in one compartment, and cold atoms/molecules in another compartment. Also, demon work must be at-least equal (if demon able to work using reversible process) to the stored Gibbs free energy, which arises in the system once atoms/molecules get segregated into different compartments. Thus, the second law of thermodynamics does not violate in Maxwell's demons case as well.

Till now we have discussed the case in which hot atoms/molecules have been transferred from compartment A, into compartment B. One can also discuss the other case in which demon will transfer cold atoms/molecules from compartment B, into compartment A. As demon start transferring cold atoms/molecules from compartment B, into compartment A, temperature in compartment B start increasing, because, there will be only fewer atoms/molecules in compartment B, whose temperature are below the average temperature (see in figure 2). As low temperature atoms/molecules number decreases, average temperature of the compartment B, increases, which indirectly increases the temperature of low temperature atoms/molecules as well. Thus, the temperature in compartment B, will always increases in both cases, that whether hot atoms/molecules has been transferred from compartment A, into compartment B, or cold atoms/molecules has been transferred from compartment B, into compartment A. Also, as time progress, and temperature in compartment B increases, only very few

atoms/molecules will remain in low temperature regime (see Maxwell-Boltzmann distribution of N_2 gas as a function of temperature 2). Due to rise in temperature in compartment B, pressure will also increase, and thus, chemical potential will increase in compartment B. While, in compartment A, temperature will decrease as more and more cold atoms/molecules come from compartment B, into compartment A. As time progresses, hot atoms/molecules (present in compartment A) temperature decreases as well. Also, pressure either increases or decreases in compartment A, seems very ambiguous, because, if one uses ideal gas equation, then, one notices that the gas pressure ($P = \frac{nRT}{V}$), proportional to both density and temperature of the ideal gas. So, although temperature has decreased, but gas density has increased. How these two quantities (n and T) will affect the pressure needs to be investigated further. It is quite possible that the effect of temperature is more than the change in gas density, therefore, pressure may fall down. Also, the effect of pressure and temperature on chemical potential also needs to be investigated. If both pressure and temperature fall down from equilibrium values, then chemical potential in compartment A will decrease, and follows, $\mu(T, P) = \mu_0(T_0, P_0) + kT \ln(\frac{P}{P_0})$. If pressure and temperature are interacting in such a way, that it increases the chemical potential in compartment A, then one needs to calculate the overall chemical potential gradient between compartment A, and in compartment B. It seems to the author that there will be a chemical potential gradient between compartment A, and in compartment B, for cold atoms/molecules. And, thus, the demon must need to work on the system during the transfer of cold atoms/molecules from compartment B, into compartment A. If one sees the change in Gibbs free energy in both compartments A, and B, then, one notices that,

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

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

From both of these equations, it is clear that concluding anything in this case is extremely difficult, because,

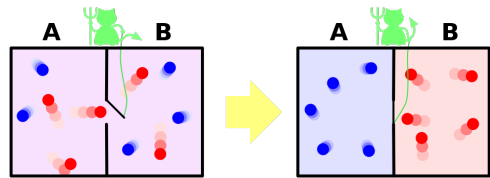


FIG. 1: Schematic diagram of Maxwell's demon⁵. Blue color atoms/molecules correspond to low temperature atoms/molecules, whereas the red color corresponds to high temperature atoms/molecules.

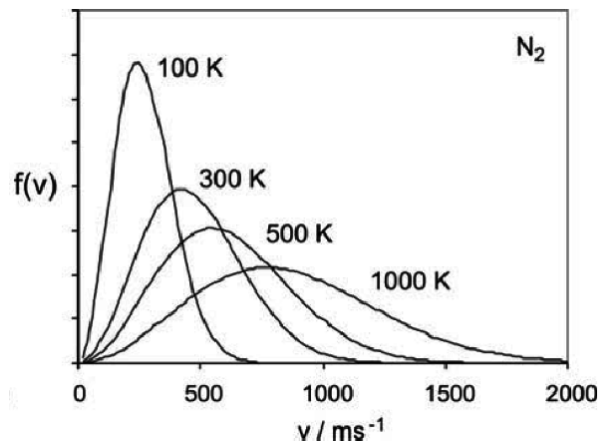


FIG. 2: Maxwell-Boltzmann speed-distribution of N_2 -molecules of air with temperature⁶.

change in Gibbs free energy in each compartment depends upon the change in pressure, change in temperature, change in atoms/molecules, and their chemical potential as a function of temperature and pressure. However, we assume that the system will evolve in such a way that the total change in Gibbs free energy will be equal to, $\int dG = \int (dG_2 - dG_1)$. Gibbs free energy which will be available for useful work is equal to $\int dG = \int (dG_2 - dG_1)$. And thus, this $\int dG$ will be the minimum amount of work (only possible with reversible process), which the demon must need to work on the gas system during the segregation of hot and cold gas in two different compartments.

III. CONCLUSION

In this paper, we have addressed the flaw that exist in Maxwell's-demon paradox. We have shown that due to chemical potential difference between hot compartment B, and cold compartment A, there is no way through which Maxwell demon can transfer hot atoms/molecules from cold compartment A, to hot compartment B, without performing any extra-work. Each time demon must perform at-least minimum amount of work, which is at-least equal to difference in chemical potential between hot compartment B, and cold compartment A, for each atom/molecule at that time. We have shown that as time progress, and demon continuously transfer hot atoms/molecules from cold compartment A, to hot compartment B, the chemical potential of hot compartment B, will increases, whereas cold compartment A, will decreases continuously. And, thus, there will be a chemical potential gradient develop between two compartment A, and B, which continuously increases till demon transfer last hot atom/molecule from cold compartment A, to hot compartment B. We have shown that demon must have to work against time varying chemical potential gradient each and every time during the

transfer of hot atoms/molecules from cold compartment A, into hot compartment B. We have shown that demon must perform at-least total minimum work, which must be equal to change in Gibbs free energy between the hot and cold compartment after the end of the process (when hot and cold atoms/molecules segregated completely into two different compartments). We have shown that if system has reached in thermodynamics equilibrium, then there is no way through which Gibbs free energy (maximum available energy for work, $E - TS$) can be extracted further without any external source intervention. We have shown that there is inherent flaw in Maxwell-demon thought experiment, and thus, this demon will never be able to segregate the hot atoms/molecules in one compartment B, and cold atom/molecules in other compartment A, without performing any extra-work on the system, and thus, this demon will never be able to break the second law of thermodynamics at any temperature or pressure.

We hope that this paper will clear the doubt about Maxwell's-demon paradox and stimulate the scientific community to start looking the thermodynamics fundamentals equations at microscopic levels carefully.

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