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INVESTIGATION ON SELECTED AREAS DEVIATING FROM THE SECOND LAW OF THERMODYNAMICS-CHALLENGES TO THE THERMODYNAMICS' SECOND LAW

Patrick Wanyonyi Munialo[1], Christopher K.Enwemeradu[2], James Owuor[3], Peter T. Cherop[4] and Seth Makokha[5]

[1,2,3,4,5]School of Engineering and Built Environment, Masinde Muliro University of Science and Technology, Kakamega, P.O Box 190- 50100, Kenya

ABSTRACT

Challenges to Thermodynamics' Second law

In this paper we undertake an investigation of the studies of the areas that show challenges to the second law of thermodynamics. This investigation has identified two areas causing a challenge to the second law of thermodynamics. The identified areas are Magneto Caloric Effect and Little Parks Effect

Keywords: Thermodynamics', second law, Magneto Caloric Effect, Little Parks Effect and Inhomogeneous Super Conducting Loop

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1. INTRODUCTION

Thermodynamics 'Second law challenges are diverse; they range from classical and quantum mechanical regimes, range from nanosomic to planetary in size, and operate from just above zero to more than 3,000K. They make use of ideal and non-ideal gases, plasmas, semiconductors, superconductors, Nano-, micro- and mesoscopic electrical circuits, chemical catalysts and biologically-inspired structures. The focus of this investigation is on two challenges to thermodynamics' second law. These challenges are share in details below:-

2. MAGNETO-CALORIC EFFECT

Type I normal super conductor undergoing transition, the super conductor is found to be first order and it is also established that the super conductor has associated latent heat. It is observed that a sample normally heats or cools when undergoing the transition to super conducting state (normal). This is referred to us the effect of magneto caloric. In another challenge of thermodynamics' second law, it is found that A non-quantum mechanical electrostatic analog, also referred to as electrostatic effect is employed by Trupp (Trupp 2002). Superconductors are known to be excellent diamagnets, excluding magnetic flux of the magnet from their bulk interior. The outer layer, from their bulk interior are shallowly penetrated by surfaces of parallel field , exponentially decaying in strength with characterization penetration depth, that is given by the equation below , $H(z)=H_o e^{-z/\lambda}$. Note that $\lambda \rightarrow \infty$ as $T \rightarrow T_c$ since $\lambda \propto 1/\sqrt{n_s}$ (Capek and Sheehan 2012), where $n_s \propto T_c - T$ is the density pair of superconductors, it is further observed that the sample normalizes at the transition temperature, even as the penetration depth increases in size i.e becoming large. In the transition period between normal to superconducting regions , a sample is caused to pass through intermediate state wherein lamellae of normal phase riddle the superconducting bulk. Small sized samples in the tune of ($\xi \geq d \geq 5\lambda$) can also undergo the normal-to-superconducting transition en masse, without going through an intermediate state. It is known that the samples are small sized in the tune of ξ and λ, d is narrowly restricted to roughly 10^{-6}m$\geq d \geq 10^{-7}$m. In such a transition, there can be no lamellae and the sample instantaneously can snap from one thermodynamic equilibrium to the other (Capek and Sheehan 2012).

It has been established that type-I elemental superconductors, which fit this criterion are Sn ((ξ/λ) = 4.5), In ((ξ/λ = 6.9), and Al ((ξ/λ) = 32). It is also found that the intermediate state in large samples of Type-I superconductors have been studied in details whereas very little investigation has been done on thermodynamics of small samples. Some questions and concerns were raised as early as 1952 by Pippard, in regard to reversibility effects in the cycle of magnetization of colloids which are super conductors in nature, (Pippard 1952), It is also known that in regard to type I super conductors, very little experimental work has been devoted to magnetization and transition between normal and supper conducting states of small samples of Type-I superconductors. The resistive measurements of thin tin whiskers were done by Lutes and Maxwell in 1955.

(Lutes and Maxwell 1955) made an observation that samples of suitably small size abrupt transition from the superconducting to normal state can occur without the intermediate state. It is only recently that techniques have developed (Geim et al 1997).Studies of quantitative nature to be done on thermodynamic properties of individual superconducting materials or particles at micron and sub-micron scale lengths. The outcome of (Geim et al 2000) showed the irreversible effects in the cyclic process of magnetization of All disks down to diameter > 0.3 μm (Geim et al 1997). However, it is important to emphasize that this irreversibility is conditioned by a high value of demagnetization coefficient typical of thin disks. Reversible behavior can be expected only in small samples with geometries like spheres.

The effect of magnetocaloric and reversible transition condition gives forth the *Coherent Magnetocaloric Effect* (CMCE). This is the current insight affecting Keefe's second law challenge. Inherently, this is a quantum mechanical process that relies on the superconductor's long-range order parameter (wave function) (Capek and Sheehan 2012).

3. KEEFE CMCE ENGINE

The other challenge to the thermodynamics' second law is illustrated through magneto calorific effect, which include a simple process of thermodynamics`. In this process a small sample of super conducting material is cycled through field-temperature (H-T) space and performs network solely at the expense of heat from a heat bath (Keefe, 2011). (We use Keefe's nomenclature.)

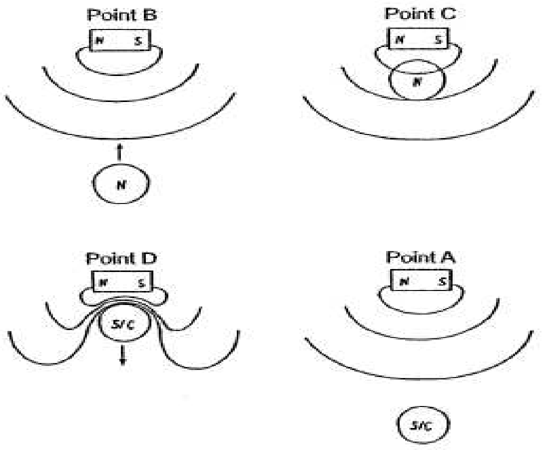

Figure 1 Pictorial overview of CMCE cycle. Source: (Capek and Sheehan 2012)

The CMCE Cycle uniquely invokes the Coherent Magneto caloric Effect It has facets of H-T standard cycles. Figures 2.1 and figure 2.2 shows two views of the cycle, namely graphically and pictorially. Whereas figure 2.2, views a small armature of superconductor (meeting CMCE requirements) getting in and out of field of magnet during a full cycle of thermodynamics. It is also established that "N" and "S/C" show states of superconductivity and normal states. Figure 2.2 graphs the armature's progress in H-T space and shows fluxes and effluxes of work and heat. The cycle commences with the armature (volume V) in the state of superconductivity (point A in Figure 2.2) at points (T_1, H_1) which are coordinates for thermodynamic. This continues to a point of thermally insulated armature and from this point the process proceeds adiabatically (Capek and Sheehan 2012).

When the armature is moved slightly closer to the magnet, it increases the magnetic field it experiences, so it passes to the normal side of the critical field (Tuyn) curve (point B, Figure 2.2) with coordinates (T_1, $H_1 + \Delta H$). (The magneto dynamic work to move the armature is assumed to be zero.) The armature coherently transitions to the normal state, evolves latent heat (LH_1) and magneto calorically cools to T_2, given by eqn 2.1. $LH_1 = T_1(S_{n1} - S_{s1}) = V.\int_{T_1}^{T_2} C_n dT$ ...(2.1)

With armature with accurately orchestrated motion. It is observed that cooling of the armature happens towards the magnet (process B , Figure 2.1) and it is also accompanied by its inward movement of the armature as it cools towards the magnet (Process B, Figure 2.1). This is done to skirt the side which is normal to the turn curve (B → C, Fig 2.2). When the armature is fully cooled (point C, Figure 2.2) at (T_2, H_2) coordinates, the armatures' field is reduced to $H_2 - \Delta H$. When it is slightly removed out of the field , this causes it to cross back to turn curves superconducting side (point D, Figure 2.1) at coordinates (T_2, $H_2 - \Delta H$). This causes heating of the armature to T_3 by evolution of Latent heat is given by equation 2.2

$$LH_2 = T_2(S_{n2} - S_{s2}) = V.\int_{T_2}^{T_3} C_s dT \ldots\ldots\ldots\ldots\ldots \quad .(2.2)$$

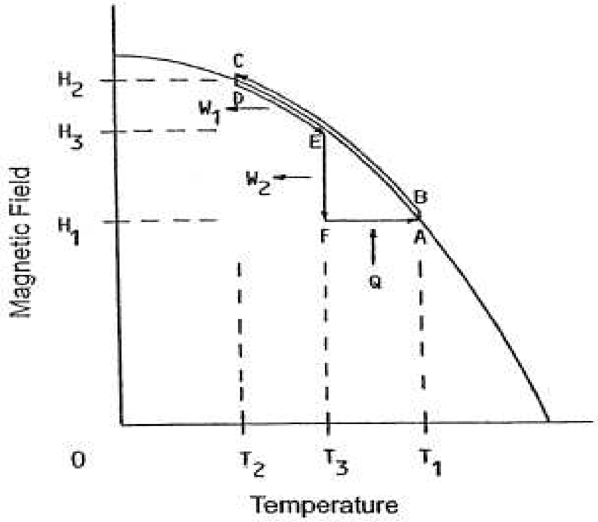

Figure 2 Coherent Magnetocaloric Effect (CMCE) cycle on H-T phase diagram

Source: (Capek and Sheehan 2012)

Considering the Turn curve's side of super conductor, it was established that the effect of Meissner kicks in and forcibly repels fields of magnet from the armatures' interior side. The armature is then expelled out of the region near the magnet but with high magnetic field. During the process of forcible expulsion the armature performs work (path D → E, Figure 2.2),

$$W_1 = \frac{\mu_0(H_2^2 - H_3^2)}{2}.V \quad \text{...(2.3)}$$

Likewise as for the segment path B → C in Figure 4.2, the armature moves in a fashionable calculated manner in terms of precision and coordination that is timed from D → E .This is done so as the side of turn curve of superconducting side is skirted in Magneto calorically heating to T_3 (and also while simultaneously performing work). From point E (Figure 2.2), the armature which is super conducting is again pushed out of the field (Process D, Figure 2.1), performing additional work and arrive at point F (Figure 2.2) with coordinates (T_3, H_1) (Capek and Sheehan 2012).

$$W_2 = \frac{\mu_0(H_3^2 - H_1^2)}{2}.V \quad \text{...(2.4)}$$

Until this point, it has been observed that the system has under gone adiabatic process up to this time of closing the cycle. From F → A (Fig 2.2), even though armature which is superconducting is thermally coupled to the surrounding heat bath (T_1) and heats ($T_3 \rightarrow T_1$), thus absorbing heat and at the sometime closing the cycle.

$$Q = V.\int_{T_3}^{T_1} C_s dT \quad \text{...(2.5)}$$

In the final stage of the cycle, there is heat transfer and absorption process taking place. It is also established that the armature performs positive work in the cycle. In case the cycle is under steady state operations then the heat being absorbed from the heat bath is transformed into work, this satisfies the first law requirement. (Capek and Sheehan 2012).

Keefe computed expected network output per cycle for an armature which is very tiny and cycle. The vortex conditions were specified in the cycle in fig 2.2. As concerns of tin's critical field (H_c) and critical temperature (T_c) were found to be :-.

$(T_1, H_1) = (0.6T_c, 0.64H_c)$, $(T_2, H2) = (0.186T_c, 0.965H_c)$, $(T_3, H_3) = (0.407T_c, 0.834H_c)$.

In the case of latent heat densities as per this cycle are: $LH_1 = 340$ J/m^3, $LH_2 = 50$ J/m^3. And work density/cycle is: $W_1 = 88$ J/m^3, $W_2 = 107$ J/m^3, and the heat density/cycle is: Q = 195 J/m^3. Satisfying the first law, $W_1 + W_2 = Q$, implies for the second law: ΔS is given by

$$\Delta S = -\int_{T_3}^{T_1} \frac{dQ(T)}{T} dT < 0 \qquad \ldots\ldots\ldots\ldots \qquad (2.6)$$

In principle, output network can be extracted from the CMCE cycle using a motor that is mechanically or using generator, that is electrical, or via a heat pump. Given the theoretical limitation due to small armatures, usable power would probably be extracted in large arrays. Because operating frequencies for mechanical devices of this size can be high ($f \approx 10^9$Hz – 10^{12}Hz), high output power densities might be achieved (Capek and Sheehan 2012). For example, assuming an individual tin CMCE motor is 10 times larger (10^3 times greater volume) than its armature ($d \approx 10^{-7}$m) and operates at $f = 10^{10}$ Hz, based on tin's calculated work density/cycle, based on his facts density the density of power is approximated at $\mathcal{P} \approx f(W_1 + W_2) \approx 2 \times 10^{12}$ W/m^3.

4. DISCUSSION OF THE FINDINGS

Phase electrons which are normal go past the external field of the magnet. This is also responsible for Production of eddy currents, Ohmic heating, and entropy, Rapidity of movement will determine the magnitude of these components.. The time in the magnitude of 10^{-12}s (i.e., 10^{-4} times the light travels across the armature) or even shorter than the above stated time. This is considered as sufficient time for coherent transition for the armature. As a temperature changes, within a few vibrational periods of the lattice ($\tau_{lattice} \approx 10^{-13}$s), it is expected that, the manifestation of the latent heat takes place. This is followed by the rapid and quick cycling of the armature and eventually trace the turn curve at approximately THz frequencies. At these level of frequencies, it is expected that there is heating due to eddy current of the normal electrons or even super electrons.(Capek and Sheehan 2012).

In super conducting samples, there is interaction between ac fields and normal electrons. This interaction causes dissipation and entropy production. Super electrons can absorb electromagnetic radiation near the necessary projected operating frequency of the armature. Dipole radiations for the magnet. is equally important (Capek and Sheehan 2012). The armatures external magnetic fields is due to the physical magnetic action. Due to this action ,the physical magnet experiences three things, first due to the action of armature , there is a possible distortion of field in a sizable manner , secondly a possibility of internal induced electric field and back reaction. Thirdly, because of being small in size, it is necessary that the account of thermal fluctuations is put into consideration, whether this may drive opportunely a cross transition line. There is also need to consider a possibility of hysteresis. The focus is not on microscopic mechanical engineering which is sophisticated and is required to realize a working engine of this study. MCE is beyond the present state of the art in micro –or nano –manufacturing, but may be on the horizon (Capek and Sheehan 2012).

Currently there are experiments being undertaken on this subject in Moscow, Russia, to have better understanding of the working of CMCE effect in relation to Keefe's engine. Even though they fall short of expectations of actual engine test they are laying the mandatory foundations for the task to be pursuit. The analysis will be done for Indium spheres with this specifications ($r \approx 1.25\times10^{-7}$m, $T_c = 3.7$K, $\xi/\lambda = 6.9$). The analysis was done with a ballistic Hall micro magnetometer. This was done as the sample was cycled through the normal-superconducting transition ($2.5\text{K} \leq T \leq 3\text{K}$) (Capek and Sheehan 2012). According to Capek and Sheehan 2012, research on predicted values of the transition field, will be checked for the transition time scale, and be investigated on hysteresis, which can then reduce the efficiency of the cycle of thermodynamics. To control the sphere size and purity tightly it will be mandatory because the CMCE effect is predicted to be controlling sphere size tightly and robust only within a narrow range of particle sizes (Capek and Sheehan 2012).

In a nut shell, it is clear that there are challenges, for example there are several uncertainties affecting superconducting and quantum processes in the mesoscopic regime. In spite of all these challenges the CMCE cycle appears compelling theoretically. It has also been established that undertaking of experiments is still problematic, even though investigation is ongoing to correct the problem. There is also a pronounced and formidable technical challenge or challenges in undertaking fabrication on a working mechanical CMCE engine (Capek and Sheehan 2012).

5. LITTLE – PARKS EFFECT

The quantum phenomenon due to momentum circulation quantization of superconducting pairs is referred to as the Meissner effect. The charge q is given by the equation given by $p = mv + qA$, where A is the magnetic vector potential. This equation is referred to generalized momentum equation of the charge q. In the case of pairs of cooper $q \rightarrow 2e$, where e is the electron charge. The momentum quantization due to circulation along a closed path is

$$\oint p.dl = nh = \oint mv.dl + \oint 2eA.dl = m\oint v.dl + 2e\Phi \text{ ………………………….. } \quad (3.1)$$

(Capek and Sheehan 2012), where n is taken as zero for path that is closed inside a super conductor that is simply connected and whose wave function has no singularity.

Hence, the persistent electrical current, $j_p=2evn_s$ in outer layer of super conductor should be maintained (where the velocity of superconducting pairs v is gotten by the relation $m\oint v.dl + 2e\,\Phi = 0$), while in its interior bulk, where $v = 0$, the magnetic flux should be absent ($\Phi=0$). (Capek and Sheehan 2012).

For a path that is closed in a multiply-connected superconductor - for example in a loop - the integer n in equation (3.1) can be any value and the velocity circulation of Cooper pairs should be

$$\oint v\, dl = \frac{h}{m}\left[n - \frac{\Phi}{\Phi_0}\right] \text{ ……………………………………………………………….} (3.2)$$

Where,

$\Phi_0 = h/2e$ is the flux quantum (fluxoid).

The magnetic flux inside the loop is $\Phi=BS+LI_p$, where B is the magnetic induction induced by an external magnet; S is the area of the loop;

L is the inductance of the loop;

$I_p = sj_p = s2evn_s$ is the persistent current around the loop.

The velocity (3.2) and the persistent loop current which is accompanied with screening that is weak. ($LI_p < \Phi_0$) is established to be a periodic function of the magnetic flux $\Phi \approx BS$. *This* is because circulation velocity (3.2) cannot be same as zero, until unless $\Phi=n\Phi_0$. The average thermodynamics value of the quantum number *n, this is* also referred to us quantum number and value of thermodynamics 'quantum number is n and is also found to be close to an integer number n corresponding to minimum kinetic energy. In the case cooper pairs, *i.e.*, to minimum $E \propto v^2 \propto (n - \Phi/\Phi_0)^2$. The periodicity of the quantum leads to effects due to experiment. (Capek and Sheehan 2012).

In 1962, Little and Parks were among the first people to observe such effects, therefore the effects were referred to as Little and Parks effect. The periodicity due to quantum in the temperature of transition T_c of a cylinder superconductor or a loop from enclosed magnetic flux following Φ was explained as a consequence of the periodic dependence of the free energy: $\Delta T_c \propto -E \propto -v^2 \propto -(n - \Phi/\Phi_0)^2$. It has also been established that for a cylinder or loop with a radius R, its dependence on critical temperature with flux varies as

$$T_c(\Phi) = T_c\left[1 - \left(\frac{\xi(0)}{R}\right)^2\left(n - \frac{\Phi}{\Phi_0}\right)^2\right] \text{...} (3.3)$$

Where $\xi(0)$ is its coherence length at $T = 0$. The values of $(n - \Phi/\Phi_0)$ is constrained between -0.5 and 0.5. The relation (3.3) describes well the experimental dependencies $T_c(\Phi)$ obtained from resistive measurements (Capek and Sheehan 2012).

The Little-Parks (LP) effect explanation is not complete. The investigation has also verified that, Little Parks effect has several shortcomings, these are , one there is no clear explanation why at non zero resistance ($R > 0$) there is presence of persistence current I_p as established in various studies. It is further established that at non zero Resistance ($R > 0$) , the presence and appearance of persistence current at ($R > 0$) , a case of under thermodynamic equilibrium conditions , there is a direct current observed as well. Appearance of power dissipationRI_p^2, and this being direct power source and happening under equilibrium conditions, hence this contradicts, however. It does not explain, for instance, why the persistent current I_p has been observed at non-zero resistances ($R > 0$) in a number of studies. It is emphasized that the observation of a persistent current I_p - *i.e.*, a direct current observed under thermodynamic equilibrium conditions, at a non-zero resistance $R>0$ contradicts standard expectations since it implies power dissipation RI_p^2 and, by inference, a direct current power source under equilibrium conditions. Nikulov advances this as evidence for the potential violability of the second law (Capek and Sheehan 2012).

6. CONCLUSION

The results of LP experiments are interpreted and extended to include the consideration of inhomogeneous superconducting loops. These loops are immersed in magnetic fields near their transition temperatures. Based on these happenings and Nikulov's key insight, it was concluded that thermal fluctuations can be used to drive electrical currents in the presence of nonzero resistance, and by this achieve nonzero electrical dissipation at the expense of thermal fluctuations. By doing these there is an achievement of dissipation of electrical currents at the expense of thermal fluctuations alone. This implies that the second law is violated by thermal energy being rectified into macroscopic current. Due to these happenings, a new force is proposed into existence called quantum force due to the exigencies of quantum to classical, from super conducting to transition to explain these fluctuation induced currents (Capek and Sheehan 2012).

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