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THERMODYNAMICS OF VIBRATIONS INDUCED BY CONTINUOUS LIGHT IN LIQUIDS

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Any amount of mechanical energy is known to be transformed into heat without any restriction. The principle of Carnot is to restrict any creation of mechanical energy from heat in heat engines on basis of entropy concept. The aim of this paper is to give an introduction to thermodynamics of the natural processes when effective generation of mechanical energy takes place without any devices owing to self-organization of a heat cycle. The main topics to discuss are: an advanced interpretation of Carnot principle and non-equilibrium entropy of light, the theorem of Carnot and maximum thermal efficiency available for generation of vibrations.

1   Introduction

The fundamental principle to the transformation of the thermal energy into work was formulated by Carnot [1] in 1824. According to Carnot's principle, the thermal energy alone is not sufficient to give birth to the impelling power. It is necessary, that there should be cold; without it the thermal energy would be useless. Carnot principle is the fundamental to consider a heat engine of any constructions.

The equilibrium treatment of Carnot's cycle by Clausius [3] is based on the model of equilibrium heat-transfer between a source and a sink of thermal energy by a work substance in a heat engine. The model of reversible heat engine is fundament of reversibility and background of all thermodynamics of reversible processes [4]. In the classical equilibrium thermodynamics [2] the all mechanical and thermal processes are supposed as reversible. It is essential, that equilibrium thermodynamics [3]deals with only a equilibrium state of a work-substance, while the behavior of the sink and the source of

the thermal energy by a constant temperature are beyond consideration (see, for example, [5])

In several experiments on interaction of the light with liquids the processes of self-organization of heat cycles have been found: the channeled phoresis of liquid particles towards laser beam was observed to be up to $10\, cm/\sec$ [6]; the generation of mechanical vibration in liquids by continuous wave light with threshold power around $0.1W$ [7] was observed. In these experiments, the creation of mechanical motion is due to the surface of phase discontinuity, which is involved into a periodic heat-cycle between hot and cold parts of the liquid. As a result, the continuous light induces the thermodynamic forces by the constant volume of system as a whole, which are much exceed the forces of radiation pressure.

The spontaneous decrease of mechanical energy in any systems is able to occur "by itself", no matter ether it is a natural system or a made artificial construction. But, when we want to renewable increase the mechanical energy using thermal one, we should use a result of a heat-cycle in a heat engine. The experiments on the creation of vibrations and extraction in liquids owing to absorption of thermal energy induced by continuous light without any *engineering* constructions "by itself" [9] make state the question about a more general treatment of the principle of Carnot [1] applicable for *natural* systems, when a heat cycle is able to be organized by itself.

The next problem is to involve the light as the radiation in non-equilibrium with matter in the general scope of the thermodynamic studies and to find a fundamental restriction as for the level of radiant energy available to be transformed into energy of mechanical motion. Besides, the statement of the problem around Carnot's principle for thermodynamic processes with light as motive power has quite define practical sense: to find fundamental restriction for direct transformation of solar light into the energy of mechanical vibration and its use in several vibration [8] and extraction [14] technologies. This is an additional argument, which pushes the statement of the problem around the maximum of efficiency available by the self-organization of heat cycles and its fundamental restriction.

The irreversibility of absorption of light in laser experiments [9], when work is produced by constant volume of system as a whole with variable temperature of matter, does not allow to use the standard approach of equilibrium linear thermodynamics [2]. This report is to make introduction into Carnot's principle applicable for creation of vibration in natural systems by itself powered by the light involved into scope of the thermodynamics on the known concept of non-equilibrium entropy [10]. The formula for maximum efficiency of generation of vibration will be obtained on the basis of such approach.

2 Carnot principle.

Any amount of mechanical energy H is known to be transformed into thermal energy E without any restriction (or with efficiency 100%). The aim of thermodynamics is to describe the inverse process $E \Rightarrow H$, when efficiency of transformation is restricted by Carnot principle. The keynote of this section is assumption that Carnot principle being formulated for heat engines can be also applied for any natural processes of transformation of thermal energy E induced by pumping energy of light L into mechanical one H.

The central point of thermodynamics as a science on creation of mechanical energy from heat is concept of entropy S. The problem is to use such definition of entropy, which will allow both to describe the natural process directed into growing of entropy and possibility of self-organization process $L \Rightarrow H$ without any heat engines. In other words, the concept of thermodynamics should involve mechanisms for natural processes occurred by itself:

accompanying by spontaneous both *disorder* and *order* of mechanical motion in framework of Second Law.

Again, let us suppose that Carnot principle for engines can also serve as a basis to build model of entropy for nonequilibrium interaction of light with matter. Let us consider as a thermodynamic *source* of heat the region with temperature T_h, where light is absorbed and as *a sink* the all system with temperature T_s beyond the source. If denote by dQ the heat spontaneously transferred between the source and the sink and suppose that it is much less of thermal energy which is kept in the source E_h and the sink E_s respectively energies we can define entropy production as

$$dS_i = \frac{dE_s}{T_s} - \frac{dE_h}{T_h} = dQ(\frac{T_h - T_s}{T_h T_s}) = \frac{dQ}{T_s}\eta_c > 0 \qquad (1)$$

where η_c is thermal efficiency of Carnot cycle [5]. Let us call process of production of entropy dS_i by heat transfer dQ when according Clausius's agreement to signs in definition of entropy $-dE_h = dE_s$ as *an idle cycle of the entropy production*

Let us suppose now that the transfer of thermal energy between the source and the sink is conducted by a working substance involving into a heat cycle. In this case, the thermal energy obtained by sink dE_s is not equal to the thermal energy dE_h given away by source because the part of thermal energy to transfer is able to be transformed into work dW according to energy balance

$$dE_h = dE_s + dW$$

Let us define the entropy production dS_w according the same relation (1)

$$dS_w = \frac{dE_s}{T_s} - \frac{dE_h}{T_h} \qquad (2)$$

But since the work of cycle equal to $dW = dE_h - dE_s$, then

$$dS_w = \frac{dE_h - dW}{T_s} - \frac{dE_h}{T_h} = dS_i - \frac{dW}{T_s} = \eta_c\frac{dQ}{T_s} - \frac{dW}{T_s} \succeq 0 \qquad (3)$$

Let us notice that since the process of heat transfer gives positive work $dW > 0$, then the entropy production according (3) is less than the entropy production of the idle cycle according (1) or $dS_w < dS_i$. Let us call such process of the entropy production as *a work cycle of the entropy production.*

3 Light and heat in thermodynamics

Let us consider the light as a motive power to excite an initial thermal non-equilibrium. In order to involve light into scope of thermodynamics, let us take a system of two bodies with difference temperatures, and consider two difference ways to transfer energy between them: by heat Q and by light L. According to the non-equilibrium definition of entropy (1) measured by thermal energy stored in sink and source separately with amount denoted by E_h and E_s, there are no principal difference in definition of entropy for two idle cycles: whether the entropy production occurs by contact (denoted by dQ) or by remote radiation transfer of energy with light (denoted by dL). In both cases, we can use the same differential form to find the entropy of system as a whole, if we exactly know: the energy has been lost in the source - dE_h and the energy is appeared in the sink - dE_s.

$$dS_i = dE_h\left(\frac{T_h - T_s}{T_h T_s}\right) = \frac{dQ}{T_s}\eta_c = \frac{dL}{T_s}\eta_c > 0 \qquad (4)$$

This follows from evident $|dE_s| = |dE_h| = |dL| = |dQ|$ in both cases. But such equivalent between contact dQ and remote dL transfer of thermal energy is applicable only for an idle cycle. As soon as we have a work substance involved into a work cycle of the entropy production, we should very differ dL and dQ.

To show this, let us again be back to cycle Carnot as a fundamental cycle to transfer energy between hot and cool bodies. In case of heat-transfer by a work substance, we can use again (3) with substitution dQ instead of dE_h

$$dS_w = \eta_c \frac{dQ}{T_s} - \frac{dW}{T_s} \qquad (5)$$

The light and the heat involved into the production of entropy of system by a work substance has an principal feature which differs them. Actually, by non-equilibrium interpretation of entropy, when energy of system described as thermal energy of source E_h and sink E_s, the thermodynamic heat (Q), is *no a kind of energy.* This means, that we can not associate any volume between two contacting bodies as filled by heat Q, because for thermal energy as the extensive quantity to describe thermal form of energy in two reservoirs has been reserved the symbol E. We can not duplicate the notation of the same thermal form of energy.

Another thing is the energy term, which we denoted as light L. The light, in its thermodynamic meaning, has two features: to be a way of energy-transfer and to be a kind of energy. The last means that , in opposite to heat Q, we can associate energy L with a volume between remote source and sink, which is filled by propagating light.

The fact that the light is a kind of energy in scope of thermodynamic studies gives a possibility to consider the entropy production in a following basic situation on interaction of light with matter. Let us image an opaque work substance and light alone in transparent surroundings. The light as a kind of energy with amount denoted by L propagating in cool medium is able to play a role of a thermal source *alone* without remote hot source. Let us define the entropy production, which follows from non-equilibrium interpretation of principle of Carnot by $dQ = 0$. Let us again emphasize the sign agreement with regards to the differentials dE_h and dE_s in definition of entropy production . According Clausius [3], if energy is obtained by system the differential of energy will be plus (+), and if energy is rejected the sign of differential will be minus (-). Keeping in mind this remark, we can write the entropy production for opaque work substance with define temperature T_w in transparent surroundings filled by light with temperature $T_s < T_w$ by following way (by $dQ = 0$)

$$dS_i = \frac{dL}{T_w} - \frac{dL}{T_s} = dL\left(\frac{T_s - T_w}{T_w T_s}\right) = -\frac{dL}{T_w}\eta_c < 0 \qquad (6)$$

While the sign (+) of entropy production in (1) is due to spontaneous heat transfer from the hot to the cold, the sign (-) in (6) regards spontaneous *local* transfer of energy form the cold to the hot. In other words, the fundamental thermodynamic feature of light (as radiation in non-equilibrium with matter) is the ability to energy-transfer in direction opposite spontaneous heat-transfer.

Let us show that sign (-) which appears here does not contradict Second Law. For this purpose, let us consider finite amount of energy of light ΔL, which is transferred between the source- and the sink-reservoirs. If we consider ΔL as form of energy-transfer with the source of light involved into

consideration, we can from (1) obtain entropy production by simple substitution ΔL instead of dL as

$$\Delta S_d = \frac{\Delta L}{T_s} - \frac{\Delta L}{T_h} = \Delta L(\frac{T_h - T_s}{T_h T_s}) > 0 \qquad (7)$$

But let us be back to the basic situation on the interaction of light with an opaque work substance given by T_s in transparent cold surroundings. Let us split such process by two: 1.*excitement*-absorption of light by work-substance $dL \neq 0$ in adiabatic conditions by $dQ = 0$; 2.*dissipation* -transfer of energy absorbed to the sink by heat $dQ \neq 0$ by $dL = 0$. For first process, the entropy production can be found as

$$\Delta S_1 = c_v \int_{Ts}^{T_w} \left(\frac{dT}{T} - \frac{dT}{T_h} \right) = c_v \left(\ln \frac{T_w}{T_s} - \frac{T_w - T_s}{T_h} \right) > 0 \qquad (8)$$

At the same time for second process we can write

$$\Delta S_2 = c_v \int_{Tw}^{Ts} \left(\frac{dT}{T} - \frac{dT}{T_s} \right) = c_v \left(\frac{T_w - T_s}{T_s} - \ln \frac{T_w}{T_s} \right) > 0 \qquad (9)$$

It is easy to see that the summary entropy production for direct absorption of light by the sink without work substance according (7) and the entropy production through an intermediate work body according (8) and (9) is the same

$$\Delta S_d = \Delta S_1 + \Delta S_2 > 0 \qquad (10)$$

because $\Delta L = c_v(T_w - T_s)$, where c_v-is heat capacity of opaque work substance by constant volume. Here we have assumed that $\Delta E \ll E_h, E_s$ and $E_h + E_s = const.$ In other words, the basic situation, when the source of light involved into consideration and the energy of system is *a constant,* the entropy production is in full coincidence with Second Law. Notice, that (10) expresses only the resulting entropy production during processes of excitement and dissipation of work substance without any references to its time behavior.

Let us now consider the same system, but when the remote source of light is replied by the light alone as the form of propagating energy and the system *becomes open.* If we have used (6) and integrated it from initial state of work substance with temperature equals to temperature of the sink, we will obtain for process of excitement

$$\Delta S^* = c_v \int_{Ts}^{Tw} \left(\frac{dT}{T} - \frac{dT}{T_s} \right) = c_v \left(\frac{T_s - T_w}{T_s} - \ln \frac{T_s}{T_w} \right) < 0 \qquad (11)$$

Sign minus here is result of fact that the basic scheme of the interaction of light with matter: an opaque body in transparent surroundings filled by propagating light is open system. For open system with *variable* energy, Second Law can not be formulated [10]. Again, the physical sense of the relation for negative entropy production (11) is due to the fundamental thermodynamic feature of the light filled transparent medium around an opaque work body to transfer of energy in direction against the direction of spontaneous heat-transfer. Notice, that the entropy of excited state is the quantity directly measured by thermal properties of matter after the light is absorbed. Such process of creation of the negative entropy of system (induced by L) in matter can be called as process of *the entropy consumption* in contrast to *the entropy production* (induced by Q). It is easy to see that the excited state with entropy $\Delta S^* = -\Delta S_2 < 0$ is a temporary deviation of entropy of system from equilibrium because $\Delta S_2 \to 0$ by $t \to \infty$ because of $T_s - T_w \to 0$ by $t \to \infty$. Generally, such a temporal state induced by entropy consumption

can be considered as a prime basic state for entropy production in theory of dissipative structures [10]. The principal possibility to have a thermodynamic states with the temporal negative entropy in non-equilibrium systems was qualitatively discussed, for example, in [12] by consideration of mechanics of liquids.

Resuming, the non-equilibrium interpretation of principle of Carnot allows to consider the interaction of light with matter for the creation of vibrations as two phases: the excitement of matter by consumption (flow) of entropy during absorption of light and the production of entropy during heat-transfer by a work substance. Let us call such sequence of consumption and production of entropy, which is able to renew by constant volume of system as a whole [9] as *the renewable cycle*. Notice, that according to the relation for entropy production (10) $\Delta S_d > 0$ any renewable cycle on $T - S$ diagram can not be presented by a close curve.

4   The theorem of Carnot

Briefly, the theorem of Carnot in the equilibrium thermodynamics has been based on the fact that closed equilibrium $T - S$ diagram of Carnot cycle is a rectangle restricted by temperatures of the source T_h and the sink T_s [5]. The thermal efficiency of any arbitrary equilibrium cycle can be found from the square of its $T - S$ diagram. The square of rectangle is bigger than the squares of any possible another $T - S$ diagram for an arbitrary non-Carnot cycle between the same T_h and T_s. This is a quantitative sense of Carnot theorem in brief. Thus, the problem is to find, how can be formulated the theorem of Carnot in case when we can not consider the square of closed curves at $T - S$ diagram at all and temperature of the source is variable.

Let us consider the entropy production by an excited state of two bodies: a source with temperature Th and a sink with temperature T_s which can occur by either cycle of Carnot or an arbitrary cycle. From definition entropy production we can write for an arbitrary cycle that

$$dS_w = \frac{dQ}{T_s}\left(\frac{T_h - T_s}{T_h}\right) - \eta\frac{dQ}{T_s} = \frac{dQ}{T_s}(\eta_c - \eta) \tag{12}$$

From theorem of Carnot [4] follows that for an arbitrary cycle should be valid $\eta \leq \eta_c$ that leads to

$$dS_w \geq 0$$

The theorem of Carnot for creation of work by an excited state of system can be formulated as follows.

The thermal efficiency of any work cycle of the entropy production by an initially exited system can not be more than efficiency of work cycle with the entropy production equals zero.

As an example of an useful methodological application of last interpretation of theorem of Carnot let us consider two bodies of equal mass with difference temperatures $\Delta T = T_1 - T_2$. Let us suppose that heat capacity of each is equal to c and excitement is induced by light absorption only in one of them, say in 2. Again, we will consider the consumption and the production of entropy separately for a while. Differential equation of heat transfer when each element of energy dE from heat to the sink is involved into an internal Carnot cycle has form

$$dT_2 = dT_1\left(1 - \frac{T_1 - T_2}{T_1}\right) = dT_1(1 - \eta_c) \tag{13}$$

that is coincident with transfer of thermal energy without transfer of entropy

$$\frac{dT_1}{T_1} = \frac{dT_2}{T_2} \tag{14}$$

Let us find maximum of work ΔW which can be produced in this system by given initial energy of light ΔL. We can integrate (13) in the finite interval of energy which is leaves the source $\Delta E_1 = c_v(T_1 - T_w)$ and energy which is obtained by the sink $\Delta E_2 = c_v(T_2 - T_w)$ and obtain that final temperature T_w of system after the work cycle of entropy production is equal to

$$T_w = (T_1 T_2)^{\frac{1}{2}}$$

that differs from final temperature

$$T_i = \frac{T_1 + T_2}{2}$$

of idle cycle by

$$\Delta W = \left(\frac{T_1 + T_2}{2} - (T_1 T_2)^{\frac{1}{2}} \right) 2c_v$$

The entropy production during work cycle is equal zero because of

$$\Delta S_w = c_v \ln \left(\frac{T_1}{T_2} \right) - 2c_v \ln \left(\frac{T_w}{T_2} \right) = 0$$

Let us use the theorem of Carnot in order to find the maximum of reversible work available in process of local heating by light [9]. Let us consider absorption of energy ΔL in volume v, which is part of large system of volume V and suppose, that the time of excitement is much shortest than the time of dissipation (thermal relaxation). In this case we can find entropy of excited state S^* with regard to $\bar{S}$ - entropy of volume V in equilibrium by integration (1) as

$$\Delta S_i = C \ln \frac{(1 + \alpha\beta)}{(1 + \alpha\beta)^{\frac{1}{\beta}}} > 0 \tag{15}$$

there $\alpha = \frac{\Delta L}{c_v V T_o}$, $\beta = \frac{V}{\Delta v}$, $C = c_v V$. This relation shows the entropy production by the idle cycle when a "lump" of hot volume v spontaneously relaxes to the large cold volume V.

Let us find the maximum of available work ΔW_c and efficiency η_c from Carnot's theorem in its non-equilibrium treatment. The efficiency of any arbitrary cycle in this case can not be more than the efficiency of work cycle with entropy production equals zero:

$$\Delta S_w^+ = \tilde{S} - \bar{S}_w = C \ln \frac{\left(1 + \frac{\Delta L - \Delta W_c}{CT_o} \right)}{(1 + \alpha\beta)^{\frac{1}{\beta}}} = 0 \tag{16}$$

Solving it with regard to ΔW_c

$$\Delta W_c = CT_o(1 + \alpha - (1 + \alpha\beta)^{\frac{1}{\beta}}) \tag{17}$$

we can find maximum thermal efficiency which can be reached as

$$\eta_c = 1 - \frac{1}{\alpha}\left[(1 + \alpha\beta)^{\frac{1}{\beta}} - 1\right] \tag{18}$$

At last, if we consider the case $v \ll V$ the thermal efficiency from (18) becomes function only two parameters: the temperature of surroundings T_o and maximum difference ΔT has been reached during optical pumping

$$\eta_c = 1 - \frac{T_o}{\Delta T}\ln\left(\frac{T_o + \Delta T}{T_o}\right) \tag{19}$$

that is expression of Carnot theorem for renewable cycles by interaction of light with matter, which can be used along with known ([5]) formula for reversible cycles

$$\eta_c^e = \frac{T - T_o}{T} = \frac{\Delta T}{\Delta T + T_o} \tag{20}$$

5   Conclusion

The maximum available efficiency of any reversible heat cycles are restricted by thermal efficiency of Carnot cycle. The elements of thermodynamics with light as motive power briefly introduced in this paper allow to give the form of Carnot theorem applicable for such kind of interaction of light with matter when work is produced by constant volume of system as a whole. It was shown, that the thermal efficiency any process of work production induced by light in the renewable conditions can not be more than the fundamental limit given by zero-entropy production.

These results should be taken into account by studies of vibrations induced by continuous light in liquids [8] and by the interpretation of other experiments on creation thermodynamic forces by light to estimate the efficiency of new technologies such as: recording of grating[13], extraction of mixtures [14], sound generation [15], pumping of liquids[16] and so on, when the heat-cycles is able to renew by constant volume of system as a whole.

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