Ramsey Theory and Thermodynamics

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Abstract

Re-shaping of thermodynamics with the graph theory and Ramsey theory is suggested. Maps built of thermodynamic states are addressed. Thermodynamic states may be attainable and non-attainable by the thermodynamic process in the system of constant mass. We address the following question how large should be a graph describing connections between discrete thermodynamic states to guarantee the appearance of thermodynamic cycles? The Ramsey theory supplies the answer to this question. Direct graphs emerging from the chains of irreversible thermodynamic processes are considered. In any complete directed graph, representing the thermodynamic states of the system the Hamiltonian path is found. Transitive thermodynamic tournaments are addressed. The entire transitive thermodynamic tournament built of irreversible processes does not contain a cycle of length 3, or in other words, the transitive thermodynamic tournament is acyclic and contains no directed thermodynamic cycles.

Keywords: thermodynamics; Ramsey theory; graph theory; directed graph; irreversible process.

Introduction

In 1900 David Hilbert presented a list of twenty-three problems that in his opinion would and should occupy the efforts of mathematicians in the future [1]. The sixth problem of the list deals with the axiomatization of physics [1]. Hilbert suggested "to treat in the same manner (as geometry), by means of axioms, those physical sciences in which mathematics plays an important part" [1]. This problem remains unsolved. The general fundamental physical axiomatic system does not exist. However, one of the branches of physics, namely thermodynamics, enables the self-consistent axiomatic formulation. The first successful attempt to reshape thermodynamic into the axiomatic theory was carried out by Constantin Carathéodory [2]. Carathéodory understood that just thermodynamics is well-suited for axiomatization. In particular, equations of thermodynamics, known as the First Law of Thermodynamics appear in a linear differential form that is known for mathematicians as Pfaff expressions or Pfaff differential forms, enabling a formal mathematical analysis of these equations [2-3]. Carathéodory also developed the axiomatic approach to the Second Law of Thermodynamics formulated as follows: "In the neighborhood of any equilibrium state of a system (of any number of thermodynamic coordinates), there exist states that are inaccessible by reversible adiabatic processes [3-4]". The aforementioned formulations of thermodynamics highlighted the role of the binary relation of adiabatic accessibility between two thermodynamic states. The idea that the binary relations interconnecting thermodynamic states are crucial for constituting thermodynamics hints to the hypothesis that the Ramsey Theory may be useful for the "mathematical thermodynamics".

Ramsey theory is a branch of graph theory that focuses on the appearance of interconnected substructures within a structure/graph of a known size [6-13]. Ramsey theory states that any structure will necessarily contain an interconnected substructure [7-10]. Ramsey's theorem, in one of its graph-theoretic forms, states that one will find monochromatic cliques in any edge labelling (with colours) of a sufficiently large complete graph [7]. One more example of the Ramsey-like thinking is delivered by the van der Waerden's theorem: colorings of the integers by finitely many colors must have long monochromatic arithmetic progressions [7]. An accessible introduction to the Ramsey theory is found in refs. 7, 9. More rigorous approach is laid out in refs. 10-11. Applications of the Ramsey theory for the theory of communication are addressed in ref. 13. Problems in Ramsey theory typically ask a question of the form: "how big must some structure be to guarantee that a particular property holds?" We re-shape this question for thermodynamics in a following form: how large should be a graph describing connections between discrete thermodynamic states to guarantee the appearance of thermodynamic cycles (which are crucial for modern thermodynamics) [14-15]?

2. Ramsey theory and unattainable thermodynamic states

Consider the map of thermodynamic states inherent for the thermodynamic system of constant mass, namely, a thermodynamic system enclosed by walls through which mass cannot pass, however heat could be delivered to the system [14]. Thermodynamic states of the system are fully identified by values of a triad of parameters known as state variables, namely: pressure, volume and temperature

(P, V, T). The addressed map contains six thermodynamic states and it is depicted in **Figure 1.** Every point depicts a certain thermodynamic state $(P_i, V_i, T_i, i = 1 \ldots 6)$. Two kinds of interrelations between the points numbered correspondingly n and k are possible, namely: i) the process $n \rightarrow k$ corresponding to the transition $(P_n, V_n, T_n) \rightarrow (P_k, V_k, T_k)$ is thermodynamically available (these points are connected with red lines), and ii) the process $n \rightarrow k$ corresponding to the transition $(P_n, V_n, T_n) \rightarrow (P_k, V_k, T_k)$ is thermodynamically unattainable (these points are connected with green lines in **Figure 1**).

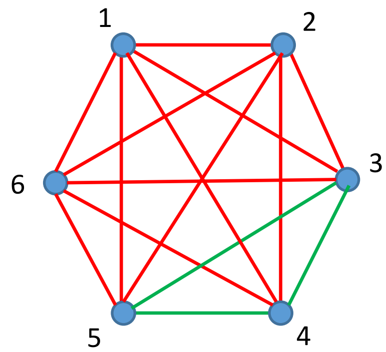

Figure 1. The map of thermodynamic states available for the constant mass thermodynamic system is depicted. Red lines connect the states which are attainable by the thermodynamic process. Green lines connect the states which are unattainable by the thermodynamic process. Cyclic process "124", "146", "256" and "345" are recognized in the map.

Why a thermodynamic transition (process) may be unavailable? The thermodynamic process in the system of the constant mass is possible, when Eq. 1 is fulfilled:

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \quad (1)$$

Eq. 1 means that the pressure and volume in the closed thermodynamic system cannot grow simultaneously within the isothermal process, and it is equivalent to the condition $C_V > 0$, where C_V is thermal capacity of the system under constant volume [14]. Eq. 1 actually emerges from the Second Law of Thermodynamics, and it is true for homogeneous physical systems [14]. For example, the transition from point "3" to point "4" (see Figure 1) corresponds to the isothermal process, for which Eq. (2) is true:

$$P_4 > P_3; V_4 > V_3; T = const \quad (2)$$

The algorithmic procedure of ordering of thermodynamic states is supplied in **Appendix A**. Processes (pathways) which are impossible in the closed thermodynamic systems are illustrated with **Figure 2**.

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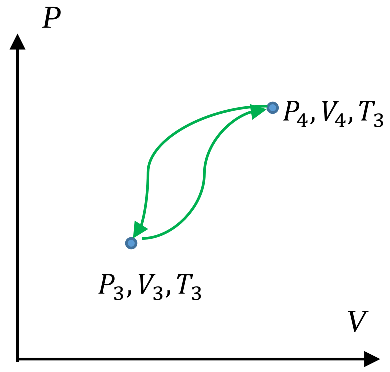

Figure 2. The processes impossible in the thermodynamic system of constant mass are depicted. $\left(\frac{\partial P}{\partial V}\right)_T \geq 0$ is true for the pathways $3 \rightarrow 4$ and $4 \rightarrow 3$.

The isothermal processes 3⟶4 and 4⟶3 are impossible in the thermodynamic system $m = const$), due to the fact that $\left(\frac{\partial P}{\partial V}\right)_T \geq 0$ takes place along the aforementioned pathways, shown in **Figure 2**. And it should be emphasized that both the "direct" 3⟶4 and "reverse" 4⟶3 processes are thermodynamically unattainable in the constant mass system [14].

Thus, two kinds of relationship are possible within the thermodynamic map depicted in **Figure 1**. These relationships form the complete graph, i.e. a graph in which each pair of thermodynamic states are connected by an edge, depicting the possibility of thermodynamic transition between the states. It is noteworthy, that any thermodynamic map, such as depicted in **Figure 1**, forms a complete graph, indeed, from a pure logical point of view, the thermodynamic transition from state labeled "*n*" to the state labeled "*k*" is or thermodynamically possible or alternatively, impossible. Thus, the ideal conditions for the application of the Ramsey theory to the analysis of the aforementioned thermodynamic maps/graphs are created.

We recognize a number of triangles, namely, the red triangles: "164", "162", "125". "136" and the green one "345" in **Figure 1**. Thus, a number of cyclic processes appear at our thermodynamic map. The green triangle "345" corresponds to the thermodynamically impossible cycle, whereas the cyclic process "164" is available for the system. The importance of cyclic processes for thermodynamics is crucial [14-15]. Let us ask the following fundamental question: what is the minimal number of points at our thermodynamic map in which cyclic processes (possible or forbidden) will necessarily appear? The minimal cyclic process includes three points at the thermodynamic map. The answer to this question is supplied by the Ramsey theory, and it is formulated as follows: what is the minimal number $R(3,3)$? The answer emerging from the Ramsey Theory is: $R(3,3) = 6$ (see refs. 7-11). Indeed, we recognize in the example illustrated with **Figure 1**, that in the thermodynamic map comprising six points corresponding to distinguishable thermodynamic states, in which the relationships "to be thermodynamically attainable" and "to be thermodynamically unattainable" are necessarily present we find triads of states forming the cyclic

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processes, some of which corresponds to the attainable and the other to the unattainable cycles (consider that possible *or* impossible cycles will necessary appear at the map). If the thermodynamically the attainable cycle "164" is present in the map, its maximal efficiency η_{max} is given by Eq. 3:

$$\eta_{max} = 1 - \frac{T_{min}}{T_{max}}, \tag{3}$$

where $T_{min} = min\{T_1, T_4, T_6\}$ and $T_{max} = max\{T_1, T_4, T_6\}$ correspondingly. It should be emphasized that the thermodynamically possible cycle does not necessarily present in the thermodynamic map. Simple, algorithmic procedure enabling ordering of the thermodynamic states is supplied in Appendix A.

Let us take a more close thermodynamic look on the thermodynamically attainable processes such as process $1 \rightarrow 2$; the reverse process $2 \rightarrow 1$ is also latently suggested to be available; thus, process $1 \rightarrow 2$ is reversible; from the logical point of view it means that thermodynamic attainability is the commutative property for the thermodynamic systems of constant mass.

3. Theory of graphs and irreversible thermodynamic processes

Now consider the thermodynamic map shown in **Figure 3**. Again, every point depicts a certain thermodynamic state $(P_i, V_i, T_i, i = 1 \dots 5)$. Now only irreversible processes occurring between the states are possible. We define the processes as "irreversible", when they create new entropy [15].

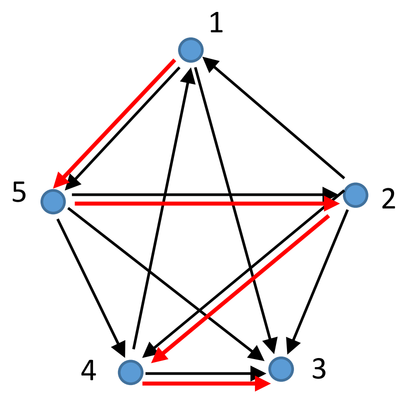

Figure 3. Vertices on the graph represent thermodynamic states $(P_i, V_i, T_i, i = 1 \dots 5)$. Only irreversible transitions between the states depicted by black arrows are possible. Red arrows demonstrate the Hamiltonian path.

The thermodynamic states, shown in **Figure 3** form a "tournament" which is a directed graph obtained by assigning a direction for each edge in an undirected complete graph [16-18]. Any tournament on a finite number *n* of vertices contains a Hamiltonian path, i.e., directed path on all *n* vertices, which is shown with red arrows in **Figure 3**. From the physical point of view, the pathway 15243 illustrates irreversible process involving all of the possible thermodynamic states. It should be emphasized, that in any complete directed graph, representing the thermodynamic states of the system the Hamiltonian path is found.

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The tournament may be transitive, in other words: $((a \to b)$ and $(b \to c)) \Rightarrow (a \to c)$ takes place in such a tournament. From the physical point of view this means, that the irreversible transition $1 \to 2$ followed by the irreversibly transition $2 \to 3$ implies the availability of the irreversible transition $1 \to 3$. If the thermodynamic states, form the map, in which only irreversible transitive processes are possible, they form the transitive tournament. This necessarily means that the entire tournament contain a no directed thermodynamic cycles. Consider, that real thermodynamic processes are always irreversible to some extent; thus, we proved that no directed thermodynamic cycles are possible in real thermodynamic systems, in which entropy growth is inevitable. This statement actually presents the re-formulation of the Second Law of Thermodynamics, as worded with the graphs theory notions. (по-моему здесь не ясно о каком утверждении именно речь)

Thermodynamic states may also form the "strongly connected graph", namely a graph in which every vertex is reachable from every other. Such a graph for a map of thermodynamic states $(P_i, V_i, T_i, i = 1 \dots 4)$ is shown in **Figure 4**.

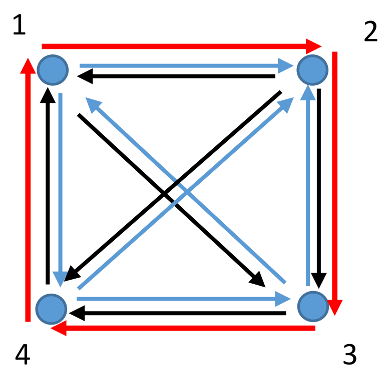

Figure 4. The strongly connected graph connected four thermodynamic states is shown. Red path depict the Hamiltonian cycle inherent for this thermodynamic map.

Every strongly connected tournament has a Hamiltonian cycle, which is shown with the red path in **Figure 4**. The opposite is also true: if the graph has a Hamiltonian cycle it is strongly connected. Cyclic reversible thermodynamic processes (such as the Carnot cycle) are seen in this context as strongly connected graphs, as shown in **Figure 5**. It is noteworthy that this graph *1234* is not complete and the edge *42* represents the process which is forbidden within the constant mass system.

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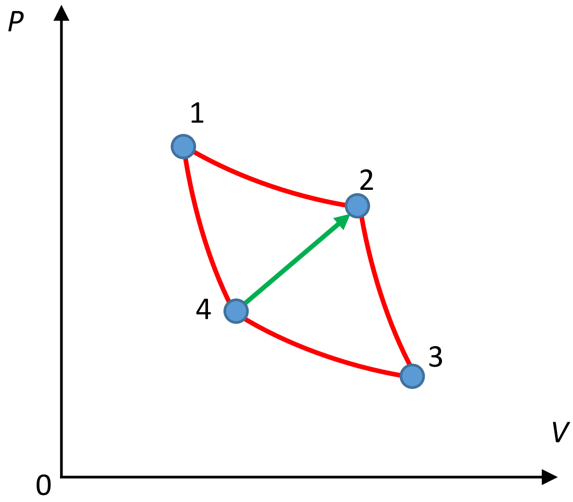

Figure 5. The Carnot cycle 12341 may be seen as the strongly connected graph; red solid line is the cyclic Hamiltonian path; the green arrow depicts the "forbidden thermodynamic process".

Now let us return to the Caratheodory axiomatic thermodynamics. Consider first the thermodynamic map representing the states, which all are attainable by reversible adiabatic processes within the system of the constant mass.

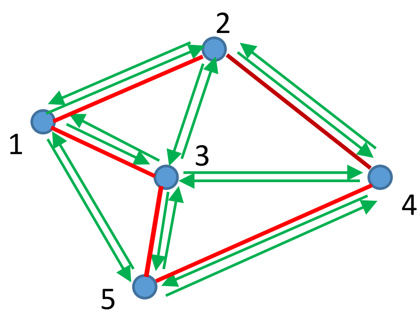

Figure 6. The graph presents five thermodynamic states between which reversible adiabatic processes are possible. Path *124351* depicts the Hamiltonian cycle for this map.

This graph is strongly connected and necessarily contains the Hamiltonian cycle *124351* shown in **Figure 6.**

Now consider the "mixed" map of states, which contains both kinds of thermodynamic processes, namely attainable and non-attainable with the reversible adiabatic process. Two types are possible for such graphs: i) non-transitive tournaments; ii) transitive tournaments. When three thermodynamic states are located on the same adiabatic curve, we deal with the transitive tournament. The transitive tournament contains no directed cycles and this is true for any number of vertices/thermodynamic states forming the complete graph [19]. Non-transitive

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complete graphs were discussed in Section 2. Applications of the Ramsey theory to physical problems are sparse, yet [20,21]. We demonstrate the possibility of such applications in thermodynamics.

Conclusions

Equilibrium thermodynamics is a branch of classical physics, which enables rigorous axiomatic mathematical treatment, such as axiomatic thermodynamics, suggested by Carathéodory. We demonstrate that the equilibrium thermodynamic may be re-shaped with the graph theory, in particular, exploiting the approaches developed within the Ramsey theory. The application of the Ramsey theory becomes possible when maps built of thermodynamic states are addressed. Ramsey theory enables treatment of the following problem: how large should be a graph describing connections between discrete thermodynamic states to guarantee the appearance of thermodynamic cycles, which play a crucial role in the classical thermodynamics. We introduce the following approach: thermodynamic states may be attainable and non-attainable by the thermodynamic process in the system of constant mass. The thermodynamic process in the system of the constant mass is possible, when the condition $\left(\frac{\partial P}{\partial V}\right)_T < 0$ is fulfilled. Thus, the processes for which $\left(\frac{\partial P}{\partial V}\right)_T > 0$ are forbidden; this makes possible the construction of the complete graph, connecting the states constituting the thermodynamic map. The Ramsey theory states that in the thermodynamic map comprising six or more points corresponding to distinguishable thermodynamic states, in which the relationships "to be thermodynamically attainable" and "to be thermodynamically unattainable" are present, we necessarily find at least one triad of states forming the cyclic processes, one of which corresponds to the attainable and the other to the unattainable cycles. Direct graphs emerging from the sequences of irreversible thermodynamic processes are considered. In any complete directed graph, representing the thermodynamic states of the system the Hamiltonian path, i.e. directed path on all n vertices/states is found. Transitive thermodynamic tournaments are addressed. The entire transitive thermodynamic tournament built of irreversible processes does not contain a cycle of length 3, or in other words the transitive thermodynamic tournament is acyclic and contains no directed thermodynamic cycles. This statement supplies the alternative shaping of the Second Law of Thermodynamics.

CRediT authorship contribution statement

Nir Shvalb - Writing – review & editing, Writing – original draft, Mark Frenkel - Writing – review & editing, Writing – original draft, Investigation; Formal analysis; Shraga Shoval - Writing – review & editing, Writing – original draft, Supervision; Edward Bormashenko - Writing – review & editing, Writing – original draft; Methodology, Investigation, Formal analysis, Conceptualization.

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Appendix A. Procedure enabling ordering of the thermodynamic states suitable for the Ramsey analysis.

The states available for the thermodynamic system of the constant are supplied in **Table 1A**. The pressure and volume of the states are ordered as follows: $P_1 > P_2 > P_3$; $V_1 < V_2 < V_3$. The thermodynamic states are summarized in Table 1A.

Table 1A. Thermodynamic states available to the thermodynamic system of the constant mass

	P_1	P_2	P_3
V_1	$P_1 V_1$	$P_2 V_1$	$P_3 V_1$
V_2	$P_1 V_2$	$P_2 V_2$	$P_3 V_2$
V_3	$P_1 V_3$	$P_2 V_3$	$P_3 V_3$

Some of transitions between these states will be thermodynamically attainable a some of them are non-attainable. The complete Ramsey graph depicted the states is shown in Figure 1A. Red solid lines depict possible transitions and blue ones demonstrate “forbidden” ones.

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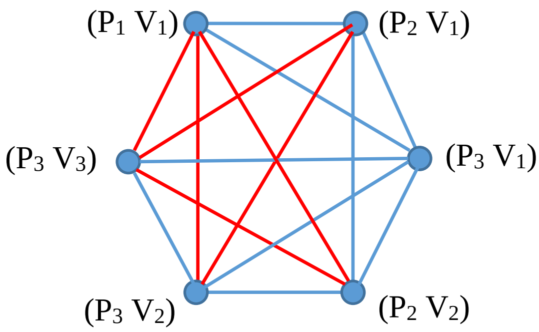

Figure 1A. The map of thermodynamic states available for the constant mass thermodynamic system is depicted; $P_1 > P_2 > P_3$; $V_1 < V_2 < V_3$. Red lines connect the states which are attainable by the thermodynamic process. Blue lines connect the states which are unattainable by the thermodynamic process.

Available $(P_1, V_1) \to (P_2, V_2) \to (P_3, V_3)$ and forbidden $(P_1, V_1) \to (P_2, V_1) \to (P_3, V_1)$; $(P_3, V_1) \to (P_2, V_2) \to (P_3, V_2)$; $(P_3, V_3) \to (P_3, V_1) \to (P_3, V_2)$ and $(P_2, V_1) \to (P_3, V_1) \to (P_2, V_2)$ cycles are recognized. The available cycle containing five points is also recognized.

Now we construct the complete graph built of the states: (P_1, V_1), (P_1, V_2), (P_2, V_1), (P_1, V_2), (P_3, V_2), (P_3, V_1) and (P_2, V_2),

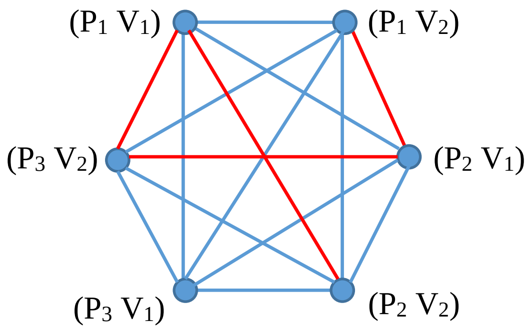

Figure 2A. The map of thermodynamic states available for the constant mass thermodynamic system is depicted; $P_1 > P_2 > P_3$; $V_1 < V_2 < V_3$. Red lines connect the states which are attainable by the thermodynamic process. Blue lines connect the states which are unattainable by the thermodynamic process.

In this case, we have no available cycles; however, we have 7 forbidden cycles, for example $(P_1, V_1) \to (P_2, V_1) \to (P_3, V_1)$; $(P_1, V_1) \to (P_1, V_2) \to (P_3, V_1)$ and $(P_2, V_1) \to (P_3, V_1) \to (P_2, V_2)$.

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According to pressure and volume of the states order and Eq. 1 the cycles are thermodynamically available, when the indices related to pressure and volume decrease and increase simultaneously.