The "virial theorem" derived from Lazare Carnot's mechanics. Its role of principle for the kinetic theory of gases

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Abstract: In textbooks the virial theorem plays a subordinate and lateral role. Its historical origin and derivation are here recalled. An alternative derivation is offered from Lazare Carnot's mechanics, which a previous paper showed to be a more appropriate basic theory than Newton's mechanics for the kinetic theory of gases. Being related to the energy balance, the virial theorem is more appropriately considered as the main principle of an energetic foundation of the kinetic theory of gases, as already Linsday ingenuously has suggested in the 50's.

Keywords: Virial theorem, Lazare Carnot's mechanics, Newton's mechanics, energy balance, foundations of kinetic theory of gases, Linsday

1. Introduction

The kinetic theory of gases (KTG) was built through a long and uneven historical path. In the "Conclusion" of his account on the history of KTG Mendoza has sadly stressed the following consideration:

> The outstanding feature of this story is that – like the dynamical theory of heat – the kinetic theory of gases had first to break the grip of an abstruse and authoritative mathematical theory before the simple basic physical ideas could be accepted. These difficulties should, perhaps, be presented in their proper perspectives in our teaching textbooks (Mendoza 1961, p. 39).

It is easy to recognize in the accused theory Newton's mechanics, which most theorists had predicted to be capable to include all others possible theories.

Eventually, a stable theory was achieved by Maxwell's papers after the mid of 19^{th} Century. In 1860 paper he clearly illustrated the theory constituting the basis of KTG, i.e. the theory of the collision of elastic bodies. Actually, a century and half before, Leibniz (1698, p. 129) had suggested this theory; but its suggestion was ignored because most scholars considered one law, i.e. the conservation of energy, as not always valid (e.g. in the case of collisions of hard bodies; in that times a hard body was considered as the ideal model of a body in order to analyse collisions). This ignorance forced the theorists to take a long theoretical detour. In a previous paper (Drago 2014) I showed that, rather than Newton's formulation, L. Carnot mechanics, i.e. the accomplishment of Leibniz' contributions to mechanics, results to be the appropriate foundation for the usual version of KTG. Unfortunately, also L. Carnot's formulation was ignored for a long time.

In the history of KTG a next decisive step was represented by Clausius' 1870 paper, introducing the "virial theorem" (VT). At present time this result is considered as an addition to a theory already well-formulated. I will discuss: 1) its better derivation, whether L. Carnot's mechanics is more appropriate than Newton's mechanics; 2) the foundations of KTG, i.e. whether this "theorem" is sufficient to built this theory.

2. Derivation of the virial theorem from Newton's continuous equation of motion

Let us recall the history of VT, which all textbooks about either Mechanics or Statistical Mechanics present in a cursorily way.[1]

In 18l2 Clausius' mechanistic conception of heat had led him to suspect VT. Eight years later, he published the paper proving this theorem (Clausius 1870). In VT the kinetic energy is taken in mean; it is equal to the value of the virial, which is defined as the half product of the position coordinates of each particle of a gas with the force acting on it:

$$<\Sigma 1/2mv^2> = - 1/2<\Sigma f.r>$$

(Clausius obtained VT also in the case of all forces deriving from a potential).

Clausius' proof was reiterated almost literally by (Brush 1976, Vol. 2, sect. 11.4).[2] This author adds that: 1) the equation was well known long before, but only Clausius has justified it in a mathematical way; 2) the crucial step of the proof is an integration by parts of a term – the main term *mvr*, where *m* is the mass, *v* the velocity, *r* the position of the particle and an under script is understood for each component of the system – is set equal to zero because its time integral over a long time is in mean very little;[3] 3) Clausius has exploited his theorem not for obtaining new state equations of gases in more cases than the ideal gas, rather «in connection with his more general discussion of the relationship between thermodynamics and mechanics».

van der Waals has exploited VT for obtaining the state equation of an imperfect gas. At present VT is applied in order to obtain the equation of imperfect gas also in more difficult cases.

We conclude that Clausius' VT played a crucial role in completing the KTG.

[1] See for instance (Levi Civita, Amaldi 1922, Vol. II, pp. 424-425), (Goldstein 1959, pp. 82-85). Incidentally, Ladera and Alomà y Pilar Leòn (2010) suggest several applications to Physics' teaching at University's level.

[2] (Brush 1961, p. 598 fn. 14) lists all old papers concerning the VT.

[3] The latter mathematical step of the proof is the same as in Lagrange's foundation of his formulation of mechanics (apart the fact that here the integral is exactly null because the integration interval is null).

3. Lazare Carnot's formulation of mechanics as an alternative to Newton's formulation

In the above the derivations all start by applying to an elementary component of the gas Newton's second law. Unfortunately, it is customary to call in a generic way "mechanics" each set of formulas related to the mechanical realm and then it is attributed to Newton. Instead, there exist at least two formulations of mechanics, Newton's and Carnot's. A previous paper (Drago 2014) has shown that the remaining part of KTG is more properly derived from L. Carnot's formulation of mechanics, rather than Newton's theory.[4] We repeat the essentials of this formulation as it is presented in his main book on the subject (Carnot 1803).

First of all, one has to recall that L. Carnot declared in the preface of his book that his formulation depends on the principle of virtual works (PVW) suitably accommodated in order to deal with collision phenomena (Carnot 1803, sect.s 128-130). In fact, this principle is independent from Newton's mechanics (Drago 1993).

In his second book on mechanics Carnot illustrated the physical experiences supporting this principle. Then he considered its particular case of Torricelli's principle for a system of connected bodies which are subject to gravity. He generalized past evidence for the PVW, considered by him as a methodological principle.

Actually, he could proceed along a different theoretical path.

1. To assume as a methodological principle the impossibility of a perpetual motion (this statement was stressed by him; but he wanted to prove it, rather than assume it).

2. By considering a complex mechanical system including constraints (his usual theoretical situation) to state that no positive work can be produced by the constraints, otherwise a perpetual motion would be possible: $\Sigma\, Rds \geq 0$, where R represents a constraint's reaction, s a displacement and an underscript is understood.

3. Under this condition, the sum of the virtual works of the acting forces have to be positive or null: $\Sigma\, F^a ds \leq 0$. This is the usual formula for this principle.

4. According to both L. Carnot and D'Alembert a force F means a mere short denotation of the product ma, where a is the acceleration and m the mass. Rather than a force, Carnot considered mv, where v is the velocity. Carnot considered as the basic situation a collision of bodies; a collision changes the velocity of a body according to the equation $W = V + U$, where W is the velocity before, V the velocity after, and the U the loss of velocity in consequence of the collision (Carnot 1803, sect. 130). In this notations the PVW is represented by the following formula: $\Sigma\, mUVcos\ UV \geq 0$.

5. Although ignoring the vector calculus, he correctly represented the three velocities on a triangle, to which he applied his celebrated formula, called of the cosine. By adding the masses and summing up on all particles of a gas, one obtains $\Sigma\, mW^2 = \Sigma\, mV^2 + \Sigma\, mU^2 + 2\, \Sigma\, mUVcos\ UV$. But the last term is null owing to the principle of virtual works. The result is the balance of energy: $\Sigma\, mW^2 = \Sigma\, mV^2 + \Sigma\, mU^2$. The term in U represents either kinetic energy, or potential energy or other forms of energy.

Carnot has considered the following two cases:

[4] Landau and Lifschitz (1960, pp. 22-24) derives it from the Lagrangian, which is less appropriate to the task because this formulation makes use of AI.

1) the collision of plastic bodies; in such a case the final velocities are all equal to a final velocity V; this velocity times the sum of mU is null because the latter term is null. The result is what he called the first fundamental equation.

2) He considered a geometric motion (i.e. a motion which in the given configuration of the constraints is reversible); he has multiplied it with ΣmU and in the two cases of translational and rotational motion he has respectively obtained, through calculations of simple algebra, the other two invariants, i.e. the momentum and the momentum of momentum.

4. L. Carnot's formulation and KTG

At glance, Lazare Carnot's mechanics is more appropriate to the physical situation of a gas than Newton's for four reasons:

1) Its main equation describes the basic phenomenon inside a gas, i.e. the discrete collisions of the elementary components of the gas, considered as elastic bodies, just as the particles of a gas behave; instead Newton's equation ignores as inexistent the collisions; it would be appropriate to the situation if the particles were subjected to continuous forces of interaction.

2) It shares the same philosophical attitude – i.e. to see as a whole a complex system – which is apparent in all applications of VT, e.g. to find the state equation of a gas.

3) The introduction of a mean operation is at all unjustified in Newton's abstract (metaphysical) framework; instead in the Carnotian attitude it may be considered as an additional expedient for solving the basic problem of the theory. In addition, a mean value may be considered to be a doubly negated proposition: "It is <u>not</u> <u>false</u> that the value is …", i.e. a proposition belonging to intuitionist logic; which is the same logic on which L. Carnot's mechanics is based, as all other theories aiming to solve a basic problem.

4) From the mathematical viewpoint, the derivation of VT from Newton's mechanics agrees with constructive mathematics only if the time integration is on a uniformly continuous function, which is not a case owing to the discrete variations caused by the collisions. Hence, this derivation belongs to an AI mathematics; while the simple operations of L. Carnot's formulation clearly agree with constructive mathematics, hence PI.

Moreover, VT is aimed to obtain gas equations; hence its theory is a problem-based one. In sum, the choices an appropriate derivation of VT relies on *the problem-based organization of the theory (PO)* and *the potential infinity* (*PI)*; these choices are the same choices of Carnot's mechanics and moreover they are alternative to the basic choices of Newton's mechanics – i.e. a deductive theory from few axioms and the use of the actual infinity of the infinitesimal analysis.

5. An alternative derivation of the "virial theorem"

Let us notice that Clausius wanted to offer calculations according to the Newtonian theoretical attitude. The same attitude to conform to the old paradigm is manifest in all the papers of that time (e.g. Maxwell's ones), owing to the reverential respect for the English genius. The theoretical physicists have maintained a distance from the well-known cultural origin of the subject, i.e. the Leibniz's viewpoint as well as his theory of collision of elastic bodies and his energy conservation (Drago 2014).

Let us recall that Newton's theoretical framework did not include the energy balance.[5] It can be derived only when the force F is a conservative one, i.e. in the case it can be derived from a potential; in mathematical terms, only when the differential form in the three spatial coordinates $dL=F.ds$ is an exact differential. This is a very particular situation. When the form is not exact, one can however search an integrating factor ρ such that dL/ρ is exact. Only in some particular case this move is possible. Yet, in the case such ρ exists, one has to recall that in thermodynamics the similar operation leads to consider instead of the heat, Q, the entropy, $\int dQ/T$, i.e. a completely different magnitude; with respect to it Q is an anthropomorphic magnitude, whereas the entropy is a state variable. The introduction in mechanics of a magnitude $\int dL/\rho$ means to consider it as a state variable while the work L becomes an anthropomorphic magnitude; hence a balance of energy is no more assured and hence the perpetual motion is allowed.

The usual way to remedy to this impossibility is to consider the energy balance in Newton's framework by appealing to the very particular case of the conservative forces, as if they were the only ones in nature. Lagrange was the first to mislead; he wrote that the case of conservative forces was "properly" the only one in mechanics: «… it is properly the case of nature» (Lagrange 1988, p. 32). An excellent text of history of mechanics has covered this incorrect proposition by changing that word in "probably": «… it is probably the case of nature» (Dugas 1950, p. 328).

Actually the above two formulations of mechanics are incommensurable owing to the differences in the two couples of choices. The very rare case of conservative forces is not enough to give a general translation between them; it is only a very narrow bridge. The ignorance of this fact is a source of theoretical confusion. Indeed, this fact has constituted a hindrance for KTG theorists, because they did not perceive that the most natural way to obtain VT is to start from L. Carnot' mechanics, based on (both the PVW and) the energy balance. A textbook (Levi Civita, Amaldi 1923, vol. II, cap. V, p. 424-425) deals with VT as an exercise (no. 8) concerning the PLV. The authors show that in the virial definition ds may be equivalently considered as the distance between two molecules mutually exchanging F. Their product then gives a particular case of all virtual works considered in the PVW; hence the virial derives from it. One can add that this kind of ds may be considered as a geometric motion, because (first definition of geometric motion) its inverse is possible, and (second definition of this motion) it does not change the mutual

[5] Without referring to the energy balance R.B. Linsday (1941, pp. 2-9) has characterized in an excellent way the nature of the Newtonian theoretical framework as well as its radical difference from both statistical mechanics and KTG.

interaction. Hence, apart the averaging operation, VT derives from both PVW and L. Carnot's formulation. One more short way for the same derivation can be suggested.

In Carnot's first book on mechanics (Carnot 1783) the Theorems of sect.s 24-26 describe the kinetic energy balance; the theorem of sect. 42 the balance of work and kinetic energy; this is the most simple form of the VT, i.e. the equality between the kinetic energy with the potential energy.

At this point the general form of the VT is derived through one simple step; it is enough to consider the mean on all the particles – this is the very novelty of VT – of the magnitudes in the energy balance.

Clausius has considered this relationship as relevant in order to establish VT:

> The theorem of the equivalence of *vis viva* and work can then be expressed very simply; and in order to exhibit distinctly the analogy between this theorem and that respecting the virial, I will place the two in juxtaposition:
>
> (1) The sum of the *vis viva* and the ergal [potential energy] is constant.
>
> (2) The mean of *vis viva* is equal to the virial.[6]

We conclude that from both a technical viewpoint and a foundational viewpoint Lazare Carnot's formulation represents the correct basic theory for obtaining VT.

Viceversa, the conclusive result of the historical process of KTG's theoretical building, i.e. VT, leads to re-evaluate L. Carnot's theoretical framework, which was alternative to Newton's mechanics.

6. Two independent foundations of the kinetic theory of gases?

VT is more than a single law, rather it works as a general principle, from which it is possible derive at least the state equation of all kinds of gas. Let us put the question: Can the KTG be built on the VT?

In fact, (Linsday 1941, chap. V) has founded KTG on VT. From the virial equation he derives the state equation of a perfect gas, as an instance of all equations for any kind of gas. In his subsequent book (Linsday 1951, p. 184) he hence stated that VT:

> can be used as the starting point for the kinetic theory of gases.

If the principle from which the entire theory is derived, VT, derives from the energy balance, Newton's mechanics is put definitely aside.

At this point a historical question is important: Why the derivation of VT from L. Carnot's equations was ignored although it was of a great relevance for the KTG? I see two reasons:

[6] See the English translation of Clausius' paper in (Brush 1965-66, p. 175).

1) Along two centuries the energy balance was denied as a general law.

2) This balance was relegated to the applications to complex systems as machines, and hence to engineers' practice. This balance was neglected even by the historians for a long time. Eventually a paper (Kuhn 1959) has re-constructed its difficult historical path performed before its recognition as a general law. A more detailed historical account (Scott 1970) has illustrated a long theoretical struggle between the two theoretical attitudes, one based on the conservation of energy and the other one on the Newtonian atomism.

This balance was re-evaluated by the energetists in the last quarter of the 19^{th} Century as the basic principle of a new theory of mechanics, that they planned in alternative to Newton's one. Eventually this attempt failed since it was recognized that the balance is a one-dimensional equality, whereas Newton's second law is a three dimensional equality. But in L. Carnot's mechanics it adds to the energy balance the conservation of momentum and also the conservation of momentum of momentum, hence this formulation enjoys three equations. Hence, the energetists failure was caused by their ignorance of L. Carnot's mechanics.

Even more surprisingly, Mach has ignored this theory, although it played a very important role in history of physics; according to Sadi Carnot's words (Carnot 1824, p. 8), from it originated thermodynamics, which Mach maintained to be the most important theory for the foundations of the entire theoretical physics (Mach 1896).

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