The kinetic theory of gases was unwarily derived from Huygens-Leibniz-Carnot's formulation of mechanics

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Abstract: The historical development of the kinetic theory of gases will be examined under the light of an alternative in its basic theory of mechanics, i.e. either Newton's formulation – built on hard bodies located in fixed point and mutually interacting through continuous forces –, or Huygens-Leibniz-L. Carnot's one – built on moving elastic bodies, subjected to the principle of virtual velocities. The latter one was misunderstood along two centuries and re-discovered some decades ago. It will be proved that the historical process of the birth of the kinetic theory of gases was highly influenced by the theoretical conflict between the two formulations. Eventually, the latter formulation resulted to be the suitable one for building the kinetic theory of gases. The celebrated Brush's account of this history will result to be biased in order to attribute to only Newton's formulation the foundational origin of the new theory, so much to cancel any theoretical divergence.

Keywords: Kinetic theory of gases, Alternative formulation of mechanics, Incommensurability.

1. Introduction

Previous papers presented a quick analysis of this theoretical divergence through the basic notions pertaining to each of the two formulations of mechanics (Drago, Saiello 1995a; Drago, Saiello 1995b). Indeed, KTG (Kinetic Theory of Gases) does not deal with Newton's basic notions, i.e. force, accelerations or trajectories; moreover, its space is not absolute but no more than the volume of a container and the time is not absolute but a merely discrete variable with two-values only, i.e. before and after. As a trivial consequence, the mathematical tools which are usual in Newton's mechanics - the differential equations on the two continuous variables space and time –, here are lacking. Rather, the basic variables are the velocity, the momentum and the energy, just the fundamental variables of Huygens-Leibniz-L. Carnot's (henceforth HLC) formulation. Consequently, only the HLC formulation offers the appropriate conceptual base for KTG.

Here, this first suggestion will be elaborated by means of an analysis of both the formal and historical developments of the KTG. To this aim the attention will be addressed to the few papers which determined its birth. As first, Boyle's paper (Boyle 1660), although it is a merely verbal one. Then Newton's one (Newton 1687), although it is linked to an incorrect conception of a gas; Herapath's three papers (Herapath 1821, 1836 and 1847) are too cumbersome and involved with respect to the achievements they suggest, they can be dismissed without loss of generality. Only the papers by Daniel Bernoulli (1738), Clausius (1857, 1858, 1870), Maxwell (1860) deserve an accurate inspection.

In the next section I will quickly present the basic issues of both the Newton's mechanics and the alternative formulation, i.e. the HLC's. In sections 3-6 I will examine the more relevant papers of the KTG. In the final section it will be remarked that the resulting account relies on both the notions of incommensurability of the two formulations and their radical variations in the meanings of the common basic notions. This account is very different from the received one, in particular Brush's, which is biased by a pro-Newton attitude, so much to obscure the great theoretical distance between Newton's mechanics from the KTG and thus to cancel the divergence.

2. Newton's formulation and Huygens-Leibniz-Carnot's formulation

Newton based his formulation of mechanics on the continuous variables – mainly, space time and forces – , all conceived as idealistic notions (absolute space, absolute time, force-cause). It is rightly remembered that the law $f=ma$ never was written by Newton; it was stated the first time in Euler's writings. The same holds true for the systematic application of the differential equations to physics. However, Newton implicitly applied both this law and such kind of equations to several cases. This fact linked Newton's physics to a mathematics relying on the actual infinity (AI) of the infinitesimals. Moreover, he organised the theory as a whole in a deductive way from three axioms-principles only (AO); from which, once they are translated in differential equations of the infinitesimal analysis, the wanted laws of the phenomena at issue are derived. Let us recall that Newton's mechanics dominated the entire theoretical physics along two centuries and more.

HLC formulation is quickly presented. Leibniz's program for building a theoretical mechanics avoided force-causes, because "it is necessary to explain facts by means of facts". He puts as basic features of his theory the contingent propositions (and implicitly, non-classical logic), the principle of sufficient reason, the impossibility of perpetual motion.

First Huygens suggested the laws of the impact of elastic bodies; however, then Leibniz wrote them at best in an unpublished manuscript which is surprisingly modern; it verbally states several results concerning the various kinds of conservation (even the :conservation of energy in general).[1]

1. Principle of the relativity of motion: $x-y = -(x'-y')$;
2. Conservation of the total momentum: $mx+My = mx' + My'$;

[1] This point was first recognized by Dugas (1950, pp. 460-520), Leibniz (1698), Costabel (1960), Drago (2001), Drago (2003, pp. 122-131). A detailed illustration of the historical relevance of notions of HLC is given by the book by Scott (1970).

3. Conservation of kinetic energy: $mx^2+My^2 = mx'^2 + My'^2$. where m and M are the masses of respectively the two bodies, v and V the velocities and v' and V' the same magnitudes after the impact. This phenomenon is considered by Leibniz as the basic one for explaining any other mechanical phenomenon.

Huygens-Leibniz's laws lacked of the notion of potential energy, the conservation of the momentum-of-momentum, the treatment of the impact of inelastic bodies and a comprehensive principle regulating a general theory of all mechanical phenomena, the representation of a continuous phenomenon as the limit of a series of discrete phenomena.

Daniel Bernoulli stated the principle of virtual velocities in the year after Leibniz's death. Almost seven decades after, Lazare Carnot accomplished this program (Carnot 1783; Carnot 1803). At his time Carnot's formulation of mechanics was well-known; but afterwards, owing to its focus on mechanical machines it was recognised as no more than the beginnings of technical physics. It was re-evaluated fifty years ago (Gillispie 1971; Scott 1970; Grattan-Guinness 1990, 2, §5.2.6; Drago 2004; Bellini *et al.* 2007); first of all it was remarked that L. Carnot intended for "machines" all kinds of communication of motions; hence his formulation of mechanics enjoys the widest theoretical generality.

His theory of mechanics is based on the relativity of motion, the impact of elastic bodies, action-reaction and a generalisation of the principle of virtual velocities[2] (unfortunately presented by L. Carnot after his 2nd equation which was obscurely justified). From it, by dismissing any idea of causality, both the impact of all kinds of bodies and the invariants of motion, i.e., momentum, m.-of-m., and energy, are drawn through merely algebraic-trigonometric techniques applied to a relational space and a time of the kind before-after.

3. The relevance of this alternative formulation for the KTG

The differences between the two formulations of mechanics concern the history of the KTG inasmuch as at the conceptual level their basic notions present the following dichotomies:

- in mathematical terms: continuous scheme of description/ discrete scheme;
- in material terms: fluid/atoms.

If the atoms are chosen, one more dichotomy appears:

[2] Lagrange' mechanics too derives from the principle of virtual velocities, but it argues in a different way than Carnot's and moreover it makes use of AI in mathematics. (Capecchi, Drago 2005; Drago 2008). More in general, all theories which are derived from the principle of the virtual works – as L. Carnot's mechanics is – do not consider causality.

- fixed atoms/colliding atoms.

The latter case gives one more dichotomy, since the ideal model of the body impact may be:

- hard body/elastic body.

Notice that *only in the last case the conservation of energy* and, more in general, the principle of virtual velocities *hold true*.

About the first two dichotomies, Newton's mechanics, or, better, the Newton-Euler's mechanics, chose the former alternatives; whereas the HLC formulation chose the latter alternatives. In addition, Newton considered not only a continuous scheme but also atoms; which however were considered hard and fixed.

Notice that the elementary level of the mathematics qualifies L. Carnot's theory as making use of the potential infinity only (PI). Moreover, he lucidly suggested that there exist two alternative organization of mechanics, i.e. the "empirical" one (I mean: one based on a problem, OP) and the "rational" (i.e. the deductive one, OA) (Carnot 1783, pp. 101-103; Carnot 1803, p. xiii). Its divergence from Newton's formulation thus is traced back to their respective two choices on these two basic dichotomies concerning respectively the organisation of the theory and the mathematics. Resulting both choices at variance, these two theories correspond to two incommensurable models of a scientific theory.

But by taking in account L. Carnot's formulation, the history of mechanics results to be – contrarily to a deeply rooted and widespread prejudice for a unclear development of a unique paradigm –, a development of an essentially pluralistic kind, characterised by two different lines of development, i.e. the dominant one of the Newtonian paradigm (AO and IA) (Drago 1988; Drago 1996; Drago 2001) and the minority one of L. Carnot's theory (PO and PI).[3]

4. D. Bernoulli's hypothesis of the impacts of elastic molecules: some results on gases

Let us now consider the history of the birth of the KTG in this new historical framework. In 1660 R. Boyle stated a first quantitative result of KTG, although in merely verbal terms (Boyle 1660). His work was summarised by Brush through the following words:

> A qualitative atomic theory of the 'spring' of air – i.e. the property of resisting compression by exerting pressure on a surface in contact with it – is proposed […] Each [gaseous] body is like a little spring, which is bent or rolled up, but also try to stretch itself out again. This tendency to expand is characteristic not only of air that has been compressed, but also of the ordinary air in the atmosphere, which has to

[3] Already some scholars suggested a similar dichotomic development in the history of mechanics (Brown 1965; Dugas 1950, Livre III; Brunschvicg 1949, Livre XIII).

> support the weight of a column of air of many miles in height above it. In support of this theory, the experiment of Pascal is mentioned [by Boyle] […] (Brush 1965, p. 43).

Subsequently, Newton wanted to build a new theory on Boyle's results according to his universal program of research; which planned

> from the phenomena of motion to investigate the forces of nature and from these forces to demonstrate the other phenomena […] for I am induced by many reasons to suspect that they [the natural phenomena] may all depend upon certain forces by which the particles of bodies, by some causes hitherto unknown, are either mutually impelled towards one another, and cohere in regular figures, or are repelled and recede from one another (Newton 1687, Preface).

In Prop. XXIII Th. XVIII of *Principia* he obtained Boyle's law by conceiving the gas as "a fluid composed of particles fleeing from each other", owing to the actions of forces that are "inversely proportional to the distances of the centres". Hence, he interpreted Boyle's idea of the "spring" of air in terms of external forces acting on the particles; which are fixed on their locations in the space and are perfectly hard bodies – so that e.g. they do not bounce.

By equating the speed of sound in the air to the square root of the derivative of the density on pressure, he obtained (in the isothermal hypothesis) an approximated value of this velocity. But, owing to his model of the perfectly hard body, he unrecognised the law of energy conservation. Of course, these Newton's hypotheses could not give reason of the several phenomena pertaining to the KTG.

As a Leibniz's follower, Daniel Bernoulli applied to a gas confined in a vessel Leibniz's ideas, which are the same of the modern ones; i.e., a gas is composed by innumerable particles which mutually interact through elastic collisions (Bernoulli 1738). He argued in mathematical terms through the two notions, the weight of the particles and their collective impacts on a piston (Brush 1965, p. 61). No calculations of the conserved quantities have been performed, although they were implicitly assumed. Brush summarised his work by the following words:

> Daniel Bernoulli introduced a gas model in which an indefinitely large number of similar [elastic] particles of diameter *d* and speed *v* move in a closed container of volume *V* supporting a piston with pressure *P* by their impacts. The average distance between particles is *D*. The temperature *T* is a function of *v*. He showed that
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> 1. for variations of *P* and *V* at constant *T*, Boyle's law PV = constant holds in the limit $d/D \to 0$;
> 2. corrections to Boyle's law can be estimated for finite d/D, and might be checked against experimental data at high pressures if such were available;
> 3. if the speed of the particles is varied at constant volume, the pressure is proportional to v^2;
> 4. it is possible to define a temperature scale by using the equation $PV = CT$, where C = constant. In that case *T* would be proportional to v^2 (Brush 1983, p. 30).

In the previous page of Brush's book one more result Bernoulli's is recalled, i.e. the interpretation of Gay-Lussac's law.

It is manifest that the birth of KTG cannot be attributed to Boyle, who offered a mere hint, and Newton either, since he obtained few results from a patently wrong viewpoint; but rather to Daniel Bernoulli, who stated from correct hypotheses very important results linking microscopic world with the macroscopic one. But his paper was ignored and then re-discovered not before a century.

5. The introduction of both energy conservation and probability (Clausius' and Maxwell's papers)

In 1845 a paper by Waterstone revived the model of an elastic gas. But was rejected by the Royal Society with the appraisal "Nothing but nonsense". It stood unpublished along fifty years. Eventually the chemist Kroenig wrote a paper in the year 1856, i.e. some years after the birth of the first principle of thermodynamics which opposed the model of hard bodies, unable to give reason of it. Kroenig

> deduced the ideal-gas law from the simplest assumption of perfectly elastic spheres moving parallel three perpendicular axes with a common velocity. [… It] gave a rather elementary discussion of the molecular velocities and specific heats of gases but did not make any calculations or comparisons with experiment (Brush 1965, p. 23).

Just after 1857, Clausius wrote a paper where he conceived a gas as innumerable molecules mutually interacting through essentially elastic collisions. Instead of considering – as usual before him – the internal interactions only, he added the interactions with the vessel. He argued in terms of the "force" on the piston; however this notion is correctly defined as the result of the innumerable weak impacts of the molecules (Brush 1965, pp. 128-9). Brush summarised as follows the several important results obtained by Clausius:

> By considering collisions of molecules of mass m against the wall of a container of volume v, assuming that all n molecules move with velocity u, Clausius shows that the pressure of the gas is equal to ($mnu^2/3v$). The absolute temperature is proportional to ($\frac{1}{2}nmu^2$). The actual [mean] velocities of gas molecules can be calculated in this way; for example, at the temperature of melting ice, the velocity of an oxygen molecule is, on the average, 461 metres per second.
> The ratio of the *vis viva* of translatory motion to the total *vis viva* is found to be equal to $3(\gamma'-\gamma)/2\gamma$, where γ is the specific heat of the gas at constant volume (for unit volume) and γ' is specific heat at constant pressure. For air, $\gamma/\gamma' = 1.421$, and hence this ratio is 0.6315 (Brush 1965, pp. 111-112).

Notwithstanding these great improvements in conceiving ever more features of molecules, the Newtonian idea of the hard body persisted in Clausius' mind; so that he tried to conciliate the two notions through the last advancements of the chemical theory

– i.e. the distinction between atom and molecule –; so to conceive a body which at the same time is a "rigid", i.e. hard,[4] body and an elastic body:

> I am also of opinion that vibrations take place within the several masses in a state of progressive motion. Such vibrations are conceivable in several ways. Even if we limit ourselves to the consideration of the atomic masses solely, and regard these as absolutely rigid, it is still possible that a molecule, which consists of several atoms, may not also constitute an absolutely rigid mass, but that within it the several atoms are to a certain extent moveable, and thus capable of oscillating with respect to each other.
> It may also remark, that by thus ascribing a movement to the atomic masses themselves, we do not exclude the hypothesis that each atomic mass may be provided with a quantity of finer matter, which, without separating from the atom, may still be moveable in its vicinity.
> […] For brevity I will call the latter the *motion of the constituents* (Brush 1965, pp. 113-114).

Notwithstanding his cumbersome model of a molecule, Clausius' calculations successfully made use of the conservation laws; hence, his treatment was compatible with the notion of elastic body. He applied not only the conservation of the momentum – a law holding true for all kinds of bodies –and the law of translational energy conservation to the KTG – as Kroenig had done – , but also the other forms of energy – the rotational one and even that of an unknown matter surrounding the molecules – so that he considered the balance of the total energy pertaining to a molecule (an anticipation of the equipartition theorem). At the end of the paper he declared that his treatment was aimed to achieve the completeness:

> We must conclude, therefore, that beside the translatory motion of the molecules as such, the constituents of these molecules perform other motions, whose *vis viva* also forms a part of the contained quantity of heat (Brush 1965, p. 134).

This improvement resulted to be a decisive one.

A second paper in 1858 (Clausius 1858) replied to some objections he had received; the mean velocity of a molecules seemed exaggerated; in particular, the mutual diffusion of two gases seemed to disprove his previous results. In his answer, Clausius added a new feature to his previous model of a molecule: a Boscovichian force which for a great distance of the molecule from the centre is attractive and it is repulsive for a short distance. Hence, he mixed in an opportunistic way impacts and forces. The curious Clausius' way of theorizing shows the great philosophical resistance to definitely accept Leibniz's model of elastic molecules. Remarkably, first he applied the notion of probability, however to a single molecule, for obtaining its mean free path.

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[4] As it is well known in Statics a body which support a pressure of whatsoever intensity is called "rigid". By trespassing this notion to the dynamical realm, one obtains the notion of a "hard" body, i.e. a body which preserves its shape irrespectively of the intensity of the received impulse. In Clausius' quotation the adjective "rigid" is intended in the dynamical realm; hence a name "hard" would be more appropriate.

A clear conception of the whole subject was offered by Maxwell's 1860 paper (Maxwell 1860). At just its starting, he declared which ideas of mechanics constituted his theoretical base; (time before/after, space as volume), impact, velocity, momentum, kinetic energy, conservation of momentum and conservation of energy (in the II part of the paper he obtained also the momentum-of-momentum).

He called "elastic" the bodies and their impacts, except for three times (one time at the beginning of the paper p. 150; and two times in the final p. 171, as reprinted in Brush 1965, pp. 148-171), when he called the molecules also "hard", although the two adjectives are incompatible. Were the superfluous mentions of the adjective "hard" a homage to the old Newton's idea?

The organization of the contents of the paper is interesting. It is composed by 23 problems and their solutions. Hence, his detachment from Newton's theoretical tradition concerned also the organization of the theory.

The first problem asks the velocity of two elastic bodies after a collision; their final velocities are obtained by applying the conservation of the momentum (with respect to the centre of mass of the system) through a unusual geometrical construction. The problem III applies the conservation of energy for obtaining the bodies' velocities after the impact. Therefore, the second and third Huygens-Leibniz's laws of the elastic impact have been obtained by Maxwell, notably through new mathematical methods.

After a part II devoted to the diffusion of gases, in the part III of the paper Maxwell extends the theory to a more general model of the molecules; no more perfect spheres, but bodies of whatsoever form; so that he has to take in account one more conservation law, i.e. that of the momentum-of-momentum (Brush 1965, p. 167).

Through calculations on this conservation and the two conservations of both momentum and energy he obtains the solution for the new kinds of molecules (Brush 1965, pp. 168-169). It is remarkable that by the way he obtains – in contrast to Newton's absolute time – the relativity of the motion of the two colliding bodies, Hence, his paper reiterated exactly all Huygens-Leibniz's laws, but without recalling their historical paternity.

It is remarkable that through the problem to find out "the probability of the direction of the velocity after the impact lying between given limits", in the I part the second proposition introduces a new notion (Brush 1965, p. 151). The new notion has been already useful in the resolution of the III problem (Brush 1965, p. 152). The resolutions of the first four problems constitute the base of his theory. All the well-known results follow, the celebrated velocity distribution included.[5]

Far to be a mere mathematical instrument, the notion of probability carries on a philosophy. It is aimed to put a remedy to our ignorance of the exact situation. In this sense the notion of probability represents a methodological principle aimed to solve the problem of accepting a priori our ignorance of the exact values. As a modal word, probability is equivalent to a doubly negated proposition; hence, it introduces that non-

[5] He obtained also a divergence with the experimental data about specific heats, which was resolved later by quantum theory (Brush 1983, p. 66).

classical logic which underlies a problem-based organization. In sum, Maxwell approached very closely a PO theory.[6]

6. The basic principle: Clausius' virial theorem

The TKG acquired a full autonomy when in 1870 Clausius applied the notion of probability to the conservation of the energy at the atomic level. The theorem of virial, by mixing together the notion of work with that of mean, is a characteristic notion of the new theory. The virial theorem establishes a balance between the virial of the system of the moving particles and the mean over time of the kinetic energy of the same system.

$$\sum \frac{m}{2}\overline{v^2} = -\frac{1}{2}\sum \overline{(X\,x + Y\,y\; Z\,z\,)}.$$

In such a way the notion of probability is no more an instrumental notion of the KTG, but it is included as a fundamental notion. Let us remark that the virial theorem concerns a constrained body, as a gas confined by the vessel in a given volume is; moreover, it is a generalization of the law of energy conservation; at last it is an application of the principle of the impossibility of a perpetual motion.

The same holds true for a machine subjected to the principle of virtual velocities. One may conclude that this Clausius' advancement constitutes the counter-part of the basic theoretical principle upon which is based the HLC theory.

We conclude that, apart the notion of probability, all the above characteristic features of the final KTG are at odd with all those of Newton's mechanics; on the contrary, they are exactly those founding the HLC mechanics. As a whole, the historical development of the KTG was an obscure and tiring process of re-discovering the theoretical relevance of the HLC formulation of mechanics. By ignoring it, both Clausius and Maxwell had to invent anew the basic issues of this formulation.

7. The implications of the incommensurability of KTG with the Newtonian paradigm

Which basic choices characterise the resulting theory, KTG?

It may seem that Boyle's question – is a gas composed by an infinite number of particles? – requires a choice on the kind of infinity. However, no one theorist suggested for

[6] In order to instantiate the kind of inference process that he called 'abduction', the philosopher Peirce alleged two scientific examples only; i.e. Kepler's way to arrive to his first law, concerning the orbits of the planets, and the KTG (Fann 1970, p. 22). Indeed, Peirce refers to KTG at least in a long comment and in two cursorily remarks [Peirce 1931-1958, respectively (2.639) (7.220) and (8.60)]. In the first one Peirce remarks that Boyle's paper "represented [to his contemporaries] a unfounded hypothesis"; but after the year 1850, KTG appeared as "a deduction of the [more relevant] mechanical theory of heat" (Peirce 1931-1958, 7.220); where "mechanical" is intended by Peirce according to Newton's theory of mechanics (Peirce 1931-1958, 2.639). These remarks are a meagre basis for a definite answer to the question whether in this case Peirce implicitly suggested an alternative way to build a theory through his abduction, as he did elsewhere (Drago 2014).

the number of particles the actual infinity, but only a potential infinite. Hence, KTG's mathematics results of a constructive kind, relying on the choice for PI.[7]

About the kind of organization of the theory, KTG received both its basic hypotheses (collisions among elastic bodies) and laws from the Huygens-Leibniz's theory of impact. In this sense its principles are a priori principles; thus, its organisation results to be an AO. However, KTG was not a mere prolongation of the previous theory since it added the notion of probability, as playing an essential role in the distribution of the velocities and, even more importantly in the virial theorem. It introduced to a PO theory.

In sum, the basic choices of the KTG on the kind of organization is the AO when the problem of the theory is considered in an instrumental way and the virial theorem is considered a theorem; it is the PO when its problem is considered as unattainable by our direct knowledge and the virial equation – obtained through the methodological principle of the probability – plays the role of the basic principle of the theory. Therefore, the theory belongs to either the Cartesian MST or the Carnotian MST; anyway it is at odd with the Newtonian MST owing to the different choice on the kind of infinity; or, in formal terms, the kind of mathematics. Hence KTG and the Newtonian MST are mutually incommensurable.

Unfortunately, in the history of physics this philosophical novelty of KTG was ignored. The historians noticed no more than the postponement of the origin of the KTG along at least one century the common opinion on this delay was that the paradigmatic role played by Newton's formulation obstructed the birth of KTG. Actually, this obstruction was a consequence of an incommensurability with the Newtonian MST (Brush 1965). By ignoring any rival formulation to Newton's, the historians did not suggest satisfying explanations. Rather, they misinterpreted KTG as a mere instrumental theory, and even worse as derived from Newtonian mechanics.[8]

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[7] The model of a gas as a set of interacting molecules seems deny the impossibility of a perpetual motion. Given this impossibility, why such molecules do not collapse into a rest state? Of course the thermal equilibrium of the gas with the walls implies that a continuous flux of energy from the latter ones to the gas; hence, the motion of the gas is perpetual but only because the system is open to inward energy which supplies the loss of internal energy of the gas.

[8] Brush's so accurately detailed account is explicitly at all pro-Newton's paradigm (Brush 1965, p. 21). More balanced is Dugas (1950). Scott's book (1970) is illuminating on all radical variations of meaning of the basis notions of KTG.

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