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Atom and aether in nineteenth-century physical science

Alan F. Chalmers

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Abstract This paper suggests that the cases made for atoms and the aether in nineteenth-century physical science were analogous, with the implication that the case for the atom was less than compelling, since there is no aether. It is argued that atoms did not play a productive role in nineteenth-century chemistry any more than the aether did in physics. Atoms and molecules did eventually find an indispensable home in chemistry but by the time that they did so they were different kinds of entities to those figuring in the speculations of those natural philosophers who were atomists. Advances in nineteenth-century chemistry were a precondition for rather than the result of the productive introduction of atoms into chemistry.

Keywords Atoms · Aether · Chemical formulae · Scientific realism

Introduction

When the chemist Wilhelm Ostwald dropped his opposition to atoms early in the twentieth century he cited J. J. Thomson's experiments on cathode rays as one of the decisive factors that led him to change his position. Thomson's experiments were possible because of nineteenth-developments in electrical and vacuum technology and electromagnetic theory that owed nothing to atomic theories of matter from Democritus through Boyle, Gassendi and Newton and beyond, nor to Dalton's notion of the atom as the fundamental constituent of matter.[1] The electron that was to be crucial for a scientific version of atomism that could adequately accommodate chemical bonding resulted from experimental investigation of specific phenomena in the laboratory rather than as a culmination of centuries of

[1] For an account of Thomson's experiments see Smith (2001).

A. F. Chalmers (✉)
Philosophy Department, Flinders University, P.O. Box 2100, Adelaide 5001, Australia
e-mail: alan.chalmers@flinders.edu.au

philosophical speculation about atoms as fundamental components of the material world. There is a stark contrast between the atoms of contemporary science and atoms proposed as the ultimate constituents of the material world in various philosophies from Leucippus and Democritus onwards.

As even Ostwald came to concede, atoms did eventually find a place in the science of chemistry. In this article I wish to stress the extent to which that accomplishment came as the result of specific experimental research and not as a culmination of philosophical speculation about atoms. Successes in nineteenth-century chemistry were one of the pre-conditions for, rather than the result of, the productive incorporation of the atom into chemistry. I seek to highlight this point by drawing a comparison between the status and fate of the aether and of the atom in nineteenth-century physical science. We now understand a sense in which the successes of wave optics and electromagnetism in the nineteenth century were independent of assumptions about the aether that typically accompanied theorizing in those areas. By drawing analogies between the status of the aether in nineteenth-century physics and the atom in nineteenth-century chemistry I seek to illustrate the sense in which the successful incorporation of the atom into chemistry was a twentieth-rather than a nineteenth-century achievement. It was not out of the question for much of the nineteenth century that the atom would not suffer the same fate as the aether came to do.

My critical analysis of the status of the atom in nineteenth-century chemistry is not motivated by a positivist–style opposition to theories that go beyond the phenomena by postulating the existence of unobservable entities. The assumption, central to modern chemistry at least since Lavoisier, that elements exist in their compounds, an assumption that I am certainly not wishing to question, goes beyond what is observable. Further, the gases whose discovery helped to make Lavoisier's innovations possible are not directly observable, and if the sense of 'observable' is weakened to make it possible to say that they are then it is likely that the atoms and molecules of modern chemistry will be observable on similar grounds.

The recognition that light waves and other electromagnetic radiation involve fluctuating electromagnetic fields that exist in their own right and are not states of some underlying medium ran counter to materialist or realist intuitions that informed general accounts of the nature of material reality including the simple mechanical properties that were attributed to atoms. Twentieth-century developments in quantum mechanics ran counter to them too. Reading the eventual vindication of atomism as a victory for realism encourages the thought that the account of reality offered by the mechanical philosophy and the updated versions that succeeded it were somehow on the right lines. This paper suggests to the contrary that atomism constituted no more a victory for realism than the banishment of aether mechanisms underlying optical and electromagnetic phenomena constituted a defeat.

Science vs philosophy

It is nowadays uncontroversial to note that there is a qualitative distinction between claims made about reality by scientists and by philosophers. The former are meant to be empirical in a sense that the latter are not. Scientific claims are meant to be borne out by observation and experiment to a degree that would be unlikely to eventuate were they false. Philosophical claims about reality are metaphysical in the sense that they go beyond what can be so justified. They are accommodated to, rather than confirmed by, empirical evidence.

The modern separation of, and recognition and articulation of the difference between, science and metaphysics cannot be uncritically projected onto the past. However, the beginnings of the separation and distinction and their recognition were already present in the seventeenth century. Boyle, for instance, distinguished between claims, such as those he made about the 'spring' of the air, defended by his air-pump and other experiments and used to explain the workings of barometers, on the one hand, and his mechanical philosophy, which claimed that, at rock bottom, material reality consists of nothing but portions of impenetrable matter with an unchanging shape and size and a degree of motion or rest, on the other.[2] Three decades later Newton, in the *Principia*, defended his mechanics and its application in astronomy on the grounds that it could be 'derived from the phenomena'. He specified and employed the law of gravity in the *Principia* admitting that he could not explain gravity. When Lavoisier formulated his chemical theory a century later he defined chemical elements in terms of the limits of chemical division and dissociated his chemistry from the atomism of his collaborator Laplace. I am not being entirely anachronistic to pose the question of the extent to which chemical atomism of the nineteenth century constituted science as opposed to philosophy or metaphysics.

Atomism in nineteenth-century chemistry

Newton transformed the mechanical philosophy by introducing force into its fundamental ontology. However, the eighteenth-century Newtonian project of understanding chemistry by reference to inter-atomic force laws was unproductive as far as eighteenth-century chemistry is concerned, a case made in detail by Arnold Thackray (1970). Lavoisier's notion of an element as a component of compounds that cannot be decomposed by chemical means served to productively transform experimental chemistry in a way that bypassed atomism. According to a common view, it was John Dalton's theory, proposed in the first decade of the nineteenth century, which constituted the first productive introduction of atoms into the science of chemistry. I regard this view as in need of severe qualification. Little of the undoubted progress made in nineteenth-century chemistry can be attributed to atomic theories. Consequently, that success cannot be regarded as constituting a strong case for atomism. Fruitful introduction of atoms into chemistry was a twentieth-century achievement.

Dalton's atomic theory emerged in the context of physical problems and bore the marks of those origins. Forces between atoms varying inversely as their separation accounted for Boyle's law for gases while spheres of caloric surrounding each atom had implications for thermal phenomena such as specific heats of gases. These speculations failed to make productive contact with experiment and Dalton's modifications of them became incoherent.[3] Once we drop the physics from Dalton's atomism, as his contemporaries soon learnt to do, we are left with the basic chemical thesis. Each chemical element has least parts that are all alike and which combine in simple and characteristic ways to form the least parts of compounds. This chemical atomism yields the laws of constant, multiple and reciprocal proportions, the first already accepted on experimental grounds when Dalton published his theory in 1808 and the others soon vindicated by a range of experiments. The laws of proportion, supplemented

[2] For the distinction between Boyle's mechanical philosophy and his experimental science see Chalmers (1993).

[3] For a more detailed appraisal of the status of Dalton's chemistry see Chalmers (2005).

by the law of combining volumes of gases discovered experimentally by Gay Lussac in 1809, became a basic and indispensable part of chemistry thereafter.

The price that was paid for ridding Dalton's atomism of its problematic physical content was that the theory failed to yield testable consequences other than the laws of proportion. Those contemporaries of Dalton, such as Humphry Davy, who were wary of Dalton's speculations about atoms, could dispense with the latter and simply adopt the laws of combining weights and volumes as fundamental guides to their experimenting. Because Dalton's atomism, shorn of its problematic physics, ascribed no properties to atoms other than their relative weights, the theory was incapable of guiding experiment in directions that were not available to those working with the laws of proportion alone. Dalton's theory could explain the laws of proportion but there was no evidence independent of the laws of proportion that it was the right explanation.[4]

There is reason to believe that Jacob Berzelius saw the situation pretty much as I have outlined it here when he introduced formulae into chemistry as a device for capturing the essence of Dalton's theory. The symbols in those formulae can be taken in a modern way as symbolizing atoms, so that H_2O for water indicates that two atoms of hydrogen combine with one of oxygen to form a least part of water. An atomic weight of 16 for oxygen relative to hydrogen yields the experimentally-confirmed proportion of 8:1 for the weight of oxygen relative to hydrogen in water. But the symbols in formulae do not have to be interpreted as referring to atoms. Any portion of hydrogen whatsoever can be chosen as the standard and the 'atomic weight' of another element determined in terms of the weight of that element that combines with the reference portion of hydrogen.[5] It is this latter interpretation that accords best with how chemists determined relative atomic weights in the laboratory. They worked with weights and volumes rather than atoms. Berzelius (1813, p. 359) recommended his formulae on the grounds that they captured, and gave a simple and convenient way of representing, facts about combining weights and volumes without a commitment to atomism. This is not to say that Berzelius was unsympathetic to atomism. At the time he introduced his formulae he was already developing an atomic theory of his own based on electrostatic attractions. But Berzelius (1815, p. 123) was careful to distinguish these 'conjectures' put forward as 'ideal speculations' from the experimentally-determined facts about combining weights and volumes.

Formulae as introduced into inorganic chemistry by Berzelius in the second decade of the nineteenth century were little more than convenient devices for summarizing facts about the composition of compounds and relative combining weights that could be represented by other means. This was to change dramatically when formulae were introduced into organic chemistry late in the 1820 s, as Ursula Klein (2003) has shown in detail. Formulae were to prove their worth in organic chemistry when they were adapted to describe properties over and above combining weights. A distinction was made between empirical formulae and rational formulae. Empirical formulae indicate only elemental constitution and, in conjunction with a table of atomic weights, relative combining weights. Rational formulae involve some ordering of the symbols that reflect properties that go beyond the relative weights of the elements. I illustrate with an example that abstracts from the historical detail.

[4] Paul Needham (2004) shares my skepticism about the degree to which Dalton's atomism was explanatory but goes further than I do to claim that the theory did not even explain the laws of proportion.

[5] Chemical formulae and atomic weights were underdetermined by experiments on combining weights and volumes, which were compatible, for example, with a relative atomic weight of 8 for oxygen and a formula of HO for water. But the need to confront that problem was present whether or not one interpreted formulae in terms of atoms.

The simplest formula for acetic acid consistent with the relative weights of carbon, oxygen and hydrogen in it is CH_2O. This empirical formula is unable to capture the fact that hydrogen in acetic acid can be replaced by an equal volume of chlorine in four different ways, yielding four distinct compounds. Three of those compounds are acids similar to acetic acid but involving a replacement of volumes of hydrogen by equal volumes of chlorine that stand in the ratio 1:2:3. A fourth compound resulting from the replacement of hydrogen by an equal volume of chlorine is not an acid at all, but a salt. These experimental facts can be accommodated by doubling the numbers in the formula and rearranging the symbols, so that the formula becomes $C_2H_4O_2$, rearranged to read $C_2H_3O_2H$. The experimental facts can now be readily understood in terms of the replacement of one or more of the hydrogens by chlorine, with three chloro-acetic acids represented as $C_2H_2ClO_2H$, $C_2HCl_2O_2H$ and $C_2Cl_3O_2H$ and the salt, acetyl chloride, as $C_2H_3O_2Cl$.

Rational formulae were employed in organic chemistry to classify chemical compounds, to indicate what could be substituted for what, and to trace chemical reactions by means of equations. The action of acids became understood in terms of hydrogen replacement. Polybasic acids, producing two or more series of salts, were understood as possessing two or more replaceable hydrogens. The demands put on rational formulae, that they signify a range of chemical properties and track chemical reactions via equations, were to result in a virtually unique set of formulae up to the task by around 1860, as Alan Rocke (1984) has shown. The under-determination of formulae and atomic weights was overcome by chemical means. Rational formulae were further developed into the structural formulae of Kekulé exploiting a new property that chemists had learnt to apply to chemical elements, namely, valency. The structures became three dimensional to accommodate optical activity and stereo-chemistry. The advances in organic chemistry brought about by use of formulae were dramatic and undeniable, as the emergence of the synthetic chemical industry bore witness.

Chemical formulae and atomism

The fact that there is no simple identification of the productive use of chemical formulae of the kind described in the previous section and the acceptance of atomism is indicated by the eruption of the so-called ‘atomic debates’ conducted at meetings of the British Association around 1870, documented in Brock (1967). Whilst most physicists were comfortable with hypotheses concerning atoms, the majority of chemists were more cautious. Edward Frankland, one of the main contributors to the construction of the notion of valency, referred to atoms as “a kind of ladder to assist the chemist”[6] . Just a few years earlier Kekulé (1867, p. 304) had declared that the “question whether atoms exist or not has but little significance in a chemical point of view”. According to the historian David Knight (1992, p. 120) “chemists were almost all atomists” but then qualifies his claim by observing that they recognized this assumption as an “optional extra” when pressed. Even Stanislao Cannizzaro, a supporter of atomism in chemistry, resisted the identification of the structure exhibited in formulae with the arrangements of atoms in space.[7]

[6] Cited in Brock (1967, p. 21).

[7] Cannizzaro (1910, p. 42), in the famous paper of 1858 in which he used vapor density and specific heat measurements to fix relative atomic weights, was careful not to commit himself to the claim that rational formulae which distinguished the acidic from other hydrogen in organic acids represented arrangements of atoms in space, indicating that “without touching the disposition of the atoms within the molecule of acids, I only wish to indicate distinctly the part which is not changed in the transformation of the acid into its corresponding salts”.

Some of the ambivalence apparent in the writings of the chemists can be clarified by employing the distinction stressed by Alan Rocke (1984, pp 10–15) between physical atomism and chemical atomism. Most chemists resisted identifying the symbols in chemical formulae with indivisible physical atoms interacting via Newtonian forces and with good reason. Such assumptions offered no useful guidance to the chemist. Chemical atoms involved the weaker assumption that the symbols in chemical formulae refer to the least parts of chemicals, that is, those that cannot be broken down further by chemical means. It is presumed that chemical atoms have properties distinctive of the elements they are least parts of and are responsible for them combining in the way that they do. These properties of atoms are not specified in advance by embedding them in some physical theory but are to be discerned as a result of chemical research. Valency can be interpreted as one such property.

Kekulé is best interpreted as a chemical atomist. In the paragraph following the one containing his denial of the relevance of the atom for chemistry he proceeded to declare his belief that "*chemical atoms exist*, provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses". He made it clear that he regarded one of the fruits of chemical atomism to be the development of the concept of valency (which Kekulé referred to as 'atomicity"). That concept makes it possible to see how complex molecules are built up from chemical atoms as the basic building blocks. Radicals are a secondary concept, which themselves possess a valency in a derivative sense. The methyl radical, CH3, for example, possesses a valency of one because one of the four valencies of carbon remain unsatisfied. Valency also makes possible a clarification of the notion of substitution. One chemical atom or groups of chemical atoms can only be substituted for an atom or group of atoms with the same valency.

Although I cannot deny that many chemists involved in the advancement of organic chemistry in the nineteenth century were chemical atomists I insist that there was a rationale for those that declined to commit to atomism at all. In my previous section I indicated how formulae could be interpreted in terms of combining portions rather than combining atoms. Chemical formulae indicate crucial features of the structure of compounds they are formulae of, but that structure did not have to be an atomic structure. The formula for acetic acid discussed above identifies a structure capable of accounting for the various ways in which it can combine with chlorine whether there are atoms or not. The success of organic chemistry did not constitute a compelling case for atomism and those chemists of the time who resisted atomism need not be branded as misguided positivists. It should also be observed that chemical atomism was distinct from the atomism that was part of the philosophical tradition. The former was postulated for reasons internal to chemistry, and the properties of chemical atoms other than their relative weight were left open until they could be added as a result of further scientific research.

A strong case for the redundancy of the atom in nineteenth-century chemistry was made at the turn of the century by Pierre Duhem.[8] Much of his case I can endorse. However, I take issue with Duhem in a crucial respect. Duhem's critique of atomism was couched in terms of a philosophical position that denied that science was capable of probing behind the phenomena to explain them. He was of the opinion that atomism must be excluded from science in principle. I, by contrast, argue that progress in chemistry for most of the nineteenth century owed little or nothing to atomism and that a compelling case for it had yet to be made. Such a case was eventually made, and the beginnings of it were already in place by the time Duhem published his book.

[8] See Needham (2002) for an English translation.

More than one of the physicists involved in the atomic debates referred to above remarked, in effect, 'why doubt the existence of atom; you might as well doubt the existence of the aether'.[9] It is, of course, ironic from a modern point of view that a case for atomism was supported by comparison with a case for the aether, since there is no aether. I hold that the comparison is a fair one, and draw the conclusion that the case for atoms was weak. There was no guarantee until late in the nineteenth century that atoms would not go the way of the aether.

The aether in nineteenth-century physics

To an increasing extent, from Fresnel's work of the 1830 s onwards, the case for the wave theory of light became compelling. Optical phenomena such as reflection, refraction, interference, diffraction and polarization were explained in a quantitative as well as qualitative way and novel phenomena were predicted. Most physicists took the wave theory to imply that light waves are transverse waves in a mechanical aether. That is, most physicists were mechanists. They presumed that the material world is a mechanical world, not in the sense of the seventeenth century mechanical philosophers such as Boyle but in a broader sense that included Newtonian forces in its ontology. This assumption, that the world is a mechanical world governed by Newton's laws, became generalized in the second half of the nineteenth century with the Lagrangian and Hamiltonian formulations of mechanics, a move that implied a special ontological status for mechanical energy. From a mechanistic point of view light waves had to be mechanical waves. They had to be waves in a mechanical medium, and, because the waves were transverse, the medium had to be elastic. From the mechanistic point of view the wave theory of light implied an elastic aether. Further, since light travels with a finite velocity reaching us from distant stars, the whole of space is filled with this aether.

Here is how John Tyndall (1889, pp. 131–132), a British physicist who was not alone in drawing an analogy between the case for atoms and for the aether as I am doing, saw the case for the aether in 1870.

> Let us make such a medium [the aether] our starting point, and endowing it with one or two other necessary properties, let us handle it in accordance with strict mechanical laws. Let us carry our results from the world of theory into the world of sense and see whether our deductions do not issue in the very phenomena of light which ordinary knowledge and skilled experiment reveal. If in all the multiplied varieties of those phenomena, including those of the most remote and entangled description, this fundamental conception always brings us face to face with the truth, if no contradiction to our deductions from it be found in external nature, but on all sides agreement and verification; if, moreover, as in the case of Conical Refraction, and in other cases, it has actually forced upon our attention phenomena which no eye has previously seen, and no mind has previously imagined, such a conception must, we think, be something more than a mere figment of the scientific fancy. In forming it, that composite and creative power, in which reason and imagination are united has, we believe, led us into a world no less real than that of the senses, and of which the world of sense itself is the suggestion and justification.

[9] For details see Brock (1967, pp. 22–23).

Tyndall went so far as to suggest that the case for the aether was on a par with if not stronger than, the case for other minds.

From the mid 1860 s James Clerk Maxwell attempted to extend the application of the aether into electromagnetism. He aimed to explain electromagnetic phenomena as the manifestation of stresses and motions in a mechanical aether and met with significant success. As well as being able to reproduce known electromagnetic phenomena the theory was able to explain light. Waves of light in Maxwell's theory were the propagation of mutually perpendicular electric and magnetic fields, the latter corresponding to stresses and vortices in the aether respectively. The theory successfully predicted the equality of the ratio of the electromagnetic and electrostatic units of charge and the velocity of light and also the equality of the square of the refractive index of a material and the product of its dielectric constant and magnetic permeability. The theory also predicted that fluctuating currents should radiate, although Maxwell himself was not aware of this. The novel consequences of Maxwell's theory stemmed from his introduction of the so-called displacement current. This current was equal to the rate of change of the displacement, D, in an insulating medium, that vector being related to the electric field, E, by the equation $D = \varepsilon E$, where ε represents the dielectric constant of the medium. There was no strong evidence for the reality of the displacement current until the experiments that led to the first production of radio waves from electrical oscillations by Heinrich Hertz in 1888. FitzGerald was not alone in interpreting Hertz's experiments as clinching the existence of the aether. "Henceforth", he wrote, "I hope no learner will fail to be impressed with the theory-hypothesis no longer-that electromagnetic actions are due to a medium pervading all known space, and it is the same medium as the one by which light is propagated".[10]

Early in the twentieth century Einstein challenged the place of the aether in optics and electromagnetism. He challenged adherents to an aether to indicate some phenomenon where motion with respect to the aether, as opposed to motion of systems relative to each other, made a difference to an experimental outcome. Failure to successfully meet Einstein's challenge was to become a reason to drop the aether. In the resulting reformulation of electromagnetism the electric and magnetic fields are not the states of anything. They are primitives, as is the charge on the electron.

Comparing the fate of atom and aether

One of the lessons to be learnt from the transformations that took place in physical science in the opening decades of the twentieth century is, or should be, that mechanistic notions of the deep structure of the material world are seriously misleading. Such notions, as they figured in natural philosophy from Democritus to the nineteenth century, proved to be poor guides about the structure of the material world and needed to be transcended. The idea that light waves needed to be waves in some material medium, seemingly a commonplace in the nineteenth century, gave way to the idea that light waves involve the propagation of electric and magnetic fields that are primitive. In retrospect, at least, the assumption of an undulatory theory of light was crucial for progress, whereas the assumption of the underlying aether was redundant as far as such progress is concerned. With respect to electromagnetism, the path that led to Maxwell introducing the crucial displacement current in fact owed little to the mechanical models of the aether which Maxwell presented

[10] As cited in Hunt (1991, p. 160).

as underlying electromagnetic phenomena.[11] The fact that fluctuating displacements give rise to magnetic fields just as currents through a wire do was something that physicists just had to get used to. It was necessary to shed the mechanistic intuitions that fueled the assumptions about an aether underlying optical and electromagnetic phenomena. The electric field has the symmetry of an arrow and the magnetic field the symmetry of a spinning disc. But there is no stretched or spinning matter to account for this as the Maxwellians presumed. The fields are continuous and primitive. They posses their structure all the way down, as it were.

I suggest that for most of the century the place of the atom in chemistry was analogous to that of the aether in optics and electromagnetism. Atoms could be bracketed off from chemistry just as the aether could from optics and electromagnetism without loss of empirical content. Given the evidence available, it was not out of the question that chemical substances were continuous, possessing the structure denoted by chemical formulae all the way down. Few chemists saw it that way, some taking an agnostic line with respect to the existence of atoms and others treating them as an 'optional extra'. But then, few nineteenth-century physicists recognized the dispensability of the aether.[12]

By the turn of the nineteenth century, evidence for atomism in chemistry independent of the successful application of chemical formulae was mounting. The success of the kinetic theory of gases, culminating in its dramatic confirmation by Jean Perrin's experiments on Brownian motion left little room for doubting the existence of atoms and molecules. The success of the kinetic theory could not be preserved if atoms and molecules were bracketed off as they could be in nineteenth-century chemistry. But it is worth stressing that, whilst the kinetic theory made it possible to identify the weights of atoms and molecules, doing so did not do much to aid or alter chemistry. It did not help chemists attribute properties to atoms that were needed for them to do chemical work. The twentieth century was well under way before the role of the electron in chemical bonding bore fruit.

Concluding remarks

Atomism was eventually vindicated and found an indispensable home in twentieth-century experimental chemistry. Accompanying this occurrence was the banishment of aether mechanisms in optics and electromagnetism and the treatment of fields and charge as primitives. The message I wish to draw from this is the extent to which the structure of the world as revealed by science is something that needs to be learnt via the progress of that science. Whether phenomena are explicable by underlying mechanisms or not, and if they are, what character those hidden mechanisms possess, is something that needs to be learned. Science has revealed itself to be capable of revealing much about the structure of material reality that goes far beyond what could possibly have been foreseen by those such as the mechanical philosophers who had constructed philosophical characterizations and defenses of atomism. Indeed, the methods of experimental science have proved to be so potent that it has displaced natural philosophy as the discipline to which one turns for the best answers to questions about the deep structure of reality. What is more, the kinds of answers are markedly different in many respects from those that had been anticipated by

[11] For detail on the relationship between Maxwell's electromagnetic theory and his mechanical aether models see Chalmers (1986); Chalmers (2001).

[12] Ernst Mach was a possible exception. He subscribed to an undulatory theory of light but declined to hypothesize about an aether.

natural philosophers. Properties such as the spin of the electron have no correlates in the philosophical systems that spawned philosophical atomism and the path to that conception passed through detailed problems in physics and chemistry and solutions to them through experiment. I fear that viewing twentieth-century confirmation of the existence of atoms as a vindication of centuries of speculations about them will lend credence to the idea that Democritus and the mechanical philosophers such as Boyle were on the right track, a conception that obscures the vital distinction between the philosophical methods employed by those philosophers, which have proved to be poor tools for probing the structure of material reality, and the methods of experimental science, which have proved to be potent tools capable of revealing a material reality differing starkly from anything Democritus could possible have anticipated.

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