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ARTICLE

Moving Molecules Above the Scientific Horizon: On Perrin's Case for Realism

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Abstract This paper aims to cast light on the reasons that explain the shift of opinion—from scepticism to realism—concerning the reality of atoms and molecules in the beginning of the twentieth century, in light of Jean Perrin's theoretical and experimental work on the Brownian movement. The story told has some rather interesting repercussions for the rationality of accepting the reality of explanatory posits. Section 2 presents the key philosophical debate concerning the role and status of explanatory hypotheses c. 1900, focusing on the work of Duhem, Stallo, Ostwald, Poincaré and Boltzmann. Section 3 examines in detail Perrin's theoretical account of the molecular origins of Brownian motion, reconstructs the structure and explains the strength of Perrin's argument for the reality of molecules. Section 4 draws three important lessons for the current debate over scientific realism.

Keywords Atomism · Hypothesis · Scientific realism · Jean Perrin · Brownian movement · Metaphysics

1 Introduction

Heinz Post (1968) drew a useful distinction between two types of atomic theory in the late nineteenth century: what he called "essentially atomic theories", which do allow the determination of Avogadro's number, (the number of molecules in a gram-molecule of a

In an earlier paper on Perrin, I focused mostly on Peter Achinstein's reconstruction of Perrin's argument. This paper has now appeared in *Philosophy of Science Matters* (edited by G. Morgan) by Oxford University Press. The present paper has a much broader scope. It sets Perrin's argument within a wider discussion about the status and nature of hypotheses and draws some conclusions for the current debate over scientific realism. Many thanks to Steven French, Juha Saatsi and an audience in the History and Philosophy of Science Seminar at Leeds as well as to Antigone Nounou, Vassilis Sakellariou and the participants of my Jean Perrin graduate seminar for useful comments and discussions. Thanks are also due to two anonymous referees of *JGPS*.

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gas) and those that do not. The atomic hypothesis—the key assumption of which was that matter is discontinuous—entailed that atoms should be countable; hence, the determination of Avogadro's number was a key plank in its defence. For, among other things, the determination of this number would allow the determination of other atomic properties, e.g., the size of molecules. There had been many attempts to determine Avogadro's number (cf. Brush 1968a, b), notably by William Thomson (1870), who used four ways to estimate it and who actually declared that the atomic hypothesis thereby received "a high degree of probability". But all this did not really sway the balance in favour of the atomic conception of matter (especially as this was captured by the kinetic theory of gases).

The incessant and irregular agitation of small particles suspended in a liquid, which came to be known as Brownian movement because it was first identified as such by the botanist Robert Brown in 1828, was destined to play a decisive role in the wider acceptance of the atomic conception. By 1900, as Brush (1968a, b) and Nye (1972) document, Brownian motion (visible only through a microscope) had already received a lot of attention among scientists. There was a widespread view that it was due to molecular movements, though there was neither a proper theory to explain it nor serious experimental confirmation of it. Léon Gouy argued in 1888 that the random motion of the suspended Brownian particles was due to the co-ordinated movement of the liquid molecules. He noted that the random motion of the suspended particles makes manifest the internal agitation of the liquid. Significantly, he also eliminated a number of other potential explanations of Brownian movement (e.g., that the movement was due to convection currents or to the illumination of the particles by the microscope or other external causes). But all this amounted to nothing like a proper *theory* which unveiled the atomic basis (the quantitative mechanism) of the Brownian movement.

Two important things happened in the first decade of the twentieth century which, as Nye (1976, 266) put it, led to "a completely renovated atomic hypothesis". One was Einstein's theory of Brownian motion in 1905, which provided for an explanatory mechanism of it based on the molecular kinetic theory; the other was Jean Perrin's theoretical and experimental work, which yielded a very accurate determination of Avogadro's number. In Perrin's hand, Avogadro's number became an invariant and indispensable feature in explanations of various and diverse phenomena.

Indeed, between roughly 1908 and 1912, there was a massive shift in the scientific community in favour of the atomic conception of matter. The importance of Perrin's own work is nicely captured by the following observation, made by André Lalande (1913, 366–367) in his annual essay on the philosophy in France for the year 1912:

> M. Perrin, professor of physics at the Sorbonne, has described in *Les Atomes*, with his usual lucidity and vigour, the recent experiments (in which he has taken so considerable a part) which prove conclusively that the atoms are physical realities and not symbolical conceptions as people have for a long time been fond of calling them. By giving precise and concordant measures for their weights and dimensions, it is proved that bodies actually exist which, though invisible, are analogous at all points to those which we see and touch. An old philosophical question thus receives a positive solution.

This brief and matter-of-fact announcement expressed a rather widely shared sentiment on the European continent that Perrin's experimental work had clinched the issue of the reality of atoms. When Perrin received the Nobel Prize for physics in 1926, it was noted in the presentation speech by Professor C W Oseen that he "put a definite end to the long struggle regarding the real existence of molecules".

The aim of this paper is to cast light on the reasons that explain the shift of opinion concerning the reality of atoms and molecules in the beginning of the twentieth century, in light of Perrin's theoretical and experimental work on the Brownian movement. The story told will have some rather interesting repercussions concerning the scientific realism debate and the rationality of accepting the reality of explanatory posits. Section 2 will present the key philosophical debate concerning the role and status of explanatory hypotheses c. 1900, focusing on the work of Duhem, Stallo, Ostwald, Poincaré and Boltzmann. Section 3 will examine in detail Perrin's theoretical account of the molecular origins of Brownian motion and will reconstruct the structure and explain the strength of Perrin's argument for the reality of molecules. Section 4 will draw some lessons for the current debate over scientific realism.

2 The Role and Status of Explanatory Hypotheses c. 1900

By 1900, the atomic conception of matter was the battleground for a number of controversies—both scientific and philosophical. Lack of space does not allow me to present the various takes on these controversies in any detail.[1] Hence, I will move straight to what I take it to be the heart of the *philosophical* controversy. This will set the stage, the intellectual milieu, within which Perrin's work was done and received.

Towards the end of the nineteenth century, there was a popular view that there was a tension in the employment of hypotheses in science—especially, of explanatory hypotheses, such as the atomic one. On the one hand, they seemed to be indispensable in science in the sense that their employment resulted in the most conspicuous, economical and efficient organisation and classification of empirical laws and observable phenomena. Let's say that hypotheses were perceived to be *instrumentally indispensable*. On the other hand, they have had various epistemic characteristics that made them suspicious, if not simply problematic: they were uncertain, underdetermined by the evidence, transcending experience (both horizontally—that is, involving ordinary inductive leaps—and vertically—that is, assuming new kinds of stuff in order to get explanations), and revisable. Let's say that hypotheses were perceived to be *epistemically precarious*. The tension was resolved in two principal ways. The first was to rid hypotheses of any cognitive value: they are mere instruments for organisation and predictions. The second was to look for ways in which hypotheses could gain in epistemic strength: ways in which they overcome the status of *pure* hypotheses. It was within this second way that Perrin's strategy was developed. And it was quite successful as a doubt-removing strategy precisely because it tallied with the 'epistemological openness' that characterised a number of philosophically-minded scientists (including Perrin himself).

In the rest of this section, I will discuss these two ways to remove the tension by looking at the relevant arguments of five key participants in the philosophical controversy concerning the atomic conception of matter.

2.1 Duhem: Explanation as Metaphysics

Duhem was the most stringent advocate of the first way. He was perhaps the first to pose the problem in genuine philosophical terms: the problem with hypotheses was that they

[1] The interested reader should look at the following: Post (1968), Nye (1976), Gardner (1979), Krips (1986), Nyhof (1988), and de Regt (1996).

were meant to be explanatory and explanation was a venture into metaphysics. The notion of metaphysics at play here was thoroughly Kantian: metaphysical knowledge was 'knowledge beyond experience'. And yet, hypotheses are incredibly useful in science—a point on which Duhem never wavers. He credits Cartesians with the thought that hypotheses are indispensable and blames them for having advanced hypotheses with a specific content, viz., about invisible entities. At the same time, he credits Newtonians with the thought that science should stick to the empirical and the observable and blames them for having restricted the scientific method to ordinary induction (refraining from hypotheses). The atomic hypothesis was supposed to be the kind of hypothesis that should be avoided or be used in a purely symbolic fashion. Energetics, on the other hand, was supposed to be the right kind of hypothesis: it was based on general principles (like the principle of conservation of energy) which have had an experimental basis but were not arrived at inductively; these principles, as Duhem put it, were "pure postulates or arbitrary decrees of reason" (1913, 233). Duhem places the problem of hypotheses within a genuinely philosophical framework by specifying that the very aim of science (exemplified in energetics) had nothing to do with the "revelation of the true nature of matter" but everything to do with the establishment of general rules under which experimental laws are subsumed. If science aims neither at explanation nor at inductive generalisation, the atomic conception of nature is simply doomed from the start, even if one might have hoped that there *could* be an empirical basis for it.

In fact, Duhem (1892) had tried to articulate his opposition to *chemical* atomism by developing a phenomenological theory of chemical composition based on the notions of equivalent weights (as opposed to atomic weights) and valence (as opposed to atomicity). Even though part of his motivation for this was to avoid some of the (empirical) problems faced by the atomic theory (cf. 1892, 173–176), an important role in his endeavour was played by his thought that by avoiding hypotheses of a certain sort, he could avoid various metaphysical worries that plagued the atomic conception of matter, e.g., what kind of element is an atom and why is it indivisible? He thereby thought he could ensure the autonomy of chemistry from metaphysics (1892, 177)—a theme that was further explored in relation to physical theory in general in his (1906). He concluded in his characteristic up-front-ness: "let us never trust hypotheses for an instant, and in particular let us never attribute a body and a reality to the abstractions that the weakness of our nature imposes on us" (1892, 177).

Duhem's critique of hypotheses was based on a certain understanding of *explanation*—which equated it with positing unobservable entities and structures and with reducing the behaviour of observable entities to them and their own laws of behaviour. This was not accidental, of course. The atomic hypothesis was precisely the kind of hypothesis that complied with the foregoing account of explanation. His own conception of science was such that the search for explanation of the sort just noted was simply outside the scope of science, since it was taken to be characteristic of metaphysics. In a certain sense, then, Duhem was simply begging the *philosophical* question against atomism.

Duhem never admitted the atomic hypothesis as an established scientific theory, even though he outlived Perrin's work on it. He insisted till the bitter end that "hypotheses are *not* assumptions about the very nature of material things", but have "as their sole aim the economical condensation and classification of experimental laws" (1906, 219). And yet he famously took it that as science advances, and as, in particular, theories are unified and yield novel predictions, they tend to become "natural classifications". The kinds of consideration involved in Duhem's argument for conceiving theories as natural classifications were—very clearly—explanatory; and precisely because of this, Duhem insisted that they fall outside of what he took it to be the proper method of science. It may well be argued, contrary to Duhem, that it is *part and parcel* of science and its method to rely on explanatory considerations in order to form and defend rational belief. But even if this were to be left to the one side, it would still remain puzzling that Duhem never took it to be the case that the atomic conception of matter tended towards a natural classification. He remained convinced (see his 1913, 238) that energetics would win the argument against atomism. If anything, then, it would be energetics that would tend towards a "natural classification"; a prospect that was never to come true.

2.2 Stallo: Explanation as Reduction to the Familiar

An alternative way to resist atomism on philosophical grounds had been canvassed by the German-American philosopher John Bernard Stallo (1888).[2] Stallo raised explicitly the epistemic issue of when a hypothesis has the right to graduate to being true (or nearly true, at any rate) and put forward a set of criteria that were destined to become standard features of hypothesis-appraisal. As he (1888, 85) put it:

> Confessedly the atomic theory is but a hypothesis. This in itself is not decisive against its value; all physical theories properly so called are hypotheses whose eventual recognition as truths depends upon their agreement with the canons of logic, upon their congruence with the facts which they serve to connect and explain, upon their conformity with the ascertained order of Nature, upon the extent to which they approve themselves as trustworthy anticipations or previsions of facts verified by subsequent observation or experiments, and finally upon their simplicity, or rather their reducing power.

Internal coherence, empirical adequacy, entailment of novel predictions, simplicity, unifying power: these are, of course, the usual theoretical virtues that speak in favour of the truth of a scientific hypothesis, according to the standard realist view of science. But Stallo intended to *defeat* the atomic hypothesis precisely on these grounds! The body of his (1888) is an attempt to show that the basic tenets of the atomic theory *fail* all of these criteria. Stallo was aware of the fact that the prospects of the atomic hypothesis were tied to the prospects of the kinetic theory of gases, since it was there that it fared a lot better as an explanation of a variety of facts. His chief argument was that, seen as an essential part of the kinetic theory of gases, the atomic hypothesis fails as an explanation of the empirical facts. Why? Stallo took it that science should aim at explanation. Moreover, he (1888, 105) took it that explanation is unification, which is effected by showing that the *explanandum* is partially or totally identical with the *explanans*. This sounds very promising, since it might well leave room for showing that empirical laws are instances of theoretical laws—those of the kinetic theory of gases in particular. But this door was closed off for Stallo because he added a *further* requirement, viz., that the *explanans* must be already known (familiar with) in experience. Hence, explanation is reduction to the familiar (cf. 1888, 106). It follows that the kinetic theory is *not* genuinely explanatory.

There is an obvious retort to Stallo's stance, viz., that this reduction to the familiar will fail to meet the theoretical virtues he himself had put forward as signs of the epistemic maturity of a hypothesis. In other words, unless the explanatory hypothesis involves positing unfamiliar entities (such as atoms and molecules), it won't be able to satisfy in a

[2] Stallo's book *The Concepts and Theories of Modern Physics* was first published in 1882 and was translated into French in 1884 and into German in 1901.

rigorous way the foregoing criteria. He is certainly aware of this objection: an explanation (unification) might be best achieved by showing that apparently distinct phenomena have a feature in common on the condition that they also share "some other feature not yet directly observed, and perhaps incapable of being observed" (1888, 111). For instance, several optical phenomena had been unified by the undulatory theory of light (that light consists of undulations) on the further assumption of the luminiferous ether ("an all-pervading material medium, of a kind wholly unknown to experience, as the bearer of the luminar undulations"). Stallo's retort is an expected one: the real unifier (the actual *explanans*) is the *real* (that is, the observable) entity (the undulations) and not the *fictitious* entity (the ether). Another obvious reply to Stallo is that light vibrations are not quite observable! Hence the line between the real and the fictitious is not quite the line between the visible and the invisible. If indeed light undulations are given to us in experience, they are given to us in a very different way from which tables and chairs are given to us.

What Stallo seems to have in mind here (as seen from the text that immediately follows the points already made) is what Mach later on assumed as a valid principle of commitment to unobservable tokens of an *observable type* of entity. Mach—who was influenced by Stallo and wrote a very favourable forward to the German translation of Stallo's (1888)—introduced a principle of continuity, according to which: "Once we have reached a theory that applies in a particular case, we proceed gradually to modify in thought the conditions of such case, as far as it is at all possible, and endeavour in so doing to adhere throughout as closely as we can to the conception originally reached" (1893, 168). It was this principle that allowed him to say that invisible vibrations can be real (though invisible), while atoms cannot be. For Mach (1893, 587) assuming invisible vibrations is legitimate if, by this assumption, one can anticipate and detect several effects which should be attributed to the presence of vibrations, e.g., certain tactile impressions. The admission of the existence of invisible vibrations is warranted by the fact that their positing is "serviceable and economical". It helps systematise, organise and anticipate various phenomena. Supposing that some entities exist even if they are invisible "makes experience intelligible to us; it supplements and supplants experience" (ibid.). The principle of continuity underwrites this commitment because in the process of accepting *invisible* vibrations, the concept of vibration did not change. Nor were vibrations infested with properties unlike those possessed by tokens of them already observed. Atoms, however, were taken to violate this principle. Atoms were given properties which "absolutely contradict the attributes hitherto observed in bodies".[3]

This line of argument would be congenial to Stallo (who found an instance of it in Jevons—cf. 1888, 111) but it would not be enough to turn the balance against atoms. For if unobservability is not, on its own, a ground for suspicion, and if supposed fictitious entities—despite their radical difference from those given in experience—play an important role in establishing "an agreement between the phenomena" ("real" and "observable" as Stallo puts it), then in what sense are they *really* fictitious? Recall from above that Stallo did allow that a hypothesis might graduate to truth, provided the relevant criteria are satisfied. What is more, Stallo was quite impressed by Whewell's consilience of

[3] Mach's views of atomism underwent a radical change from an early acceptance of the atomic conception of matter to a later full rejection and (perhaps) to an even later endorsement of it. Part of the reasons that Mach developed an enmity to atoms was that he took them to be Kantian things-in-themselves. This attribution rendered them unreal because—ultimately—outside space and time, while at the same time made the *concept* of 'atom' useful because it facilitated the mathematical representation of the phenomena. For a summary of Mach's views, see my (1999, chapter 2). Among the many papers on Mach on atomism, I'd single out those by Brush (1968a, b) and Bachtold (2010).

induction—which is typically effected by positing entities of different (and typically unobservable) kind. He (1888, 115) was certainly aware of the gist of Whewell's argument, viz., that a hypothesis gets extra credit from being able to yield *novel* predictions ("the great merit of successful previsions"). His reply to this is rather puzzling. He (1888, 116) says:

> When an hypothesis successfully explains a number of phenomena with reference to which it was constructed, it is not strange that it should also explain others connected with them that are subsequently discovered.

Unless there is an ontological connection between the old and the new phenomena, it *is* strange that the hypothesis successfully predicts the new ones. And there is no reason to take this possibility seriously (that is, the ontic connection) unless we take the content of the hypothesis seriously as providing the link between the known and the novel phenomena. Interestingly, this is exactly what Duhem famously thought when he said that this "clairvoyance" of scientific theories would be unnatural to expect—it would be a "marvellous feat of chance"—if "the theory was a purely artificial system" which "fails to hint at any reflection of the real relations among the invisible realities" (1906, 28).[4]

2.3 Ostwald: Definite and Measurable Quantities

Energetics was a research programme advanced by Wilhelm Ostwald among others. Positively put, it was a programme for developing a scientific theory of matter that was based on phenomenological thermodynamics and the principle of conservation of energy as a fundamental generalisation. But it was also based on a quite explicit philosophical agenda, viz., that the aim of science was to advance theories that refrained from what was widely called "the atomo-mechanical" image of the world. In his (1896, 596), Ostwald stated the following as the aim of science:

> To set realities, demonstrable and measurable magnitudes, in definite relations with one another, so that when one is given the other will follow—that is the purpose of science, and it cannot be fulfilled by the substitution of any hypothetical figure, but only by the demonstration of the mutual dependencies of measurable magnitudes.

His polemic on "scientific materialism"—which was based on the mechanics of atoms—had as one of its pillars the foregoing view of science, its other pillar being a disdain towards hypotheses. And yet, it was obvious to Ostwald that even energetics required hypotheses and that the very principle of conservation of energy (as well as others involved in the theory such as that the various forms of energy are characterised by two factors: intensity and quantity) was itself a hypothesis. He (1907) resolved this problem by adopting a mixed view which rested on a distinction between good hypotheses (what he called 'prototheses') and bad hypotheses (for which he reserved the term 'hypothesis'). Hypotheses were taken to be unverifiable assumptions about inaccessible entities. Prototheses were taken to be, by and large, experimental assumptions about "unknown relations between accessible quantities". Prototheses were supposed to be necessary for the development of scientific theories and were refineable and replaceable by more accurate

[4] It would be unfair to Stallo to claim—as I have not—that all of his criticism of the atomic conception of matter was philosophically-driven. He did put together a compendium of various scientific anomalies (centrally: the specific heats anomaly) that the kinetic theory of gases faced and did try to argue that the kinetic theory "has none of the characteristics of a legitimate physical theory" (1888, 126).

assumptions—mostly due to further experimental work. We can safely say that prototheses were taken to have theoretical parameters that were determinable by further research and experimentation.

This division might well have helped Ostwald in legitimising the use of some hypotheses, but it merely re-frames and does not resolve the problem of the *cognitive status* of hypotheses. The difference, if any, between the principle of conservation of energy and the atomic hypothesis is one of degree. For a start, energy is no less unobservable than atoms. In his attempt to deal with problems like this, Ostwald (1907, 408) introduced an important criterion concerning the cognitive status of hypotheses—one that was destined to show why the atomic hypothesis (as developed and tested by Perrin) could change cognitive status. Ostwald noted that energy—perhaps unlike atoms when he was making these points—was a "measurable quantity" and that—more generally—*definiteness* and *measurability* were conditions such that, once met, they could change the status of a hypothesis. Here (1907, 500) is a long but important quotation:

> When expressions or notations of magnitudes which cannot be observed and measured and for which we can substitute no definite and empirically determinable value, occur in a formula by means of which some physical relations are to represented, we have to deal with a hypothesis. For the task of the exact sciences is to establish the reciprocal relation of measurable and demonstrable quantities, or in other words to find the mathematical forms or functions by which these quantities are interrelated, so that one of them can be calculated when the others are given. (…) As long as a single magnitude appears which is not susceptible to measurement, we cannot consider the assumed [functional] condition as proven.

Note that the aim of science remains the same as noted above. And yet, it is now much clearer that attributing definite and measurable properties to a posited entity is a presupposition for gaining knowledge of it and that this presupposition can be met by otherwise invisible entities. Definite and measurable properties is a way to show that the posited entity is not in causal isolation. Ostwald does not quite put it like this, but he *almost* says this when he adds: "not being susceptible to measurement is only another expression for the fact that nothing at all depends upon this thing" (1907, 501–502).

Ostwald's conversion to atomism was perhaps the most vocal. Already in 1908, in the preface of the third edition of his *Outlines of General Chemistry* he noted:

> … [T]he agreement of the Brownian movements with the requirements of the kinetic hypothesis, established by many investigators and most conclusively by J. Perrin, justify the most cautious scientist in now speaking of the experimental proof of the atomic nature of matter. The atomic hypothesis is thus raised to the position of a scientifically well-founded theory, and can claim its place in a textbook intended as an introduction to the present state of out knowledge of General Chemistry (1912, vi).

He then went on to present the atomic hypothesis in relation to the Brownian movement and spoke of "the final proof of the grained or atomistic-molecular nature of matter (…) after a fruitless search during a whole century" (1912, 483–484). As it will become clear when we discuss Perrin's work, atoms came to meet the requirements of definiteness and measurability that Ostwald had put forward. In his recollection of the reasons why he changed his mind, Ostwald (1912, 485) stressed that until the work of Perrin there was "no experimental proof" of the atomic conception of matter.

2.4 Poincaré: from Indifference to Reality

Poincaré's acceptance of the atomic conception of matter signifies in the clearest way what was already there in Ostwald and we might call 'epistemological openness'—that is, willingness to admit that hypotheses can change cognitive status: from being merely useful and fertile to being true, or largely so.

In his address to the 1900 International Congress of Physics in Paris, Poincaré claimed that the atomic hypothesis, viz. the hypothesis that matter has a discontinuous structure, is "indifferent", that is, useful as a device of computation or for providing "concrete images" which help scientists fix their ideas (1900, 10). From this, Poincaré noted, there is no reason to conclude "the real existence of atoms".

Four year later, in his address at the St Lewis International Congress of Arts and Science, Poincaré made some special reference to the Brownian movement and to Gouy's account that it was the product of collisions with the molecules of the liquid. The apparent problem was that the explanation of Brownian motion by reference to the kinetic theory of gases (and the concomitant atomic hypothesis) led to the violation of the second law of thermodynamics—one of the principles that Poincaré thought were central in his physics-of-principles. This time, however, Poincaré did not repeat his previous claims about indifferent hypotheses. Instead, he declared that the matter should be handed over to the experimenters and, until they pass on a judgement, to "quietly continue our work, as if the principles were still uncontested" (1906, 617).

And then again in 1912, in a lecture delivered at the French Society of Physics, Poincaré famously spoke of the experimental proof of the reality of atoms: "the atoms are no longer a convenient fiction; it seems, so to speak, that we can see them since we know how to count them" (1913, 89). What really made the difference for Poincaré was Perrin's experiments on the Brownian motion: the shift of the atomic hypothesis from the status of an indifferent hypothesis to the status of a true description of reality was centred around what Poincaré took it to be its experimental verification by Perrin. Here (1913, 90) is a long but beautiful quotation:

> The brilliant determinations of the number of atoms computed by Mr Perrin have completed the triumph of atomism. What makes it all the more convincing are the multiple correspondences between results obtained by entirely different processes. Not too long ago, we would have considered ourselves fortunate if the numbers thus derived had contained the same number of digits. We would not even have required that the first significant figure be the same; this first figure is now determined; and what is remarkable is that the most diverse properties of the atom have been considered. In the processes derived from the Brownian movement or in those in which the law of radiation is invoked, not the atoms have been counted directly, but the degrees of freedom. In the one in which we use the blue of the sky, the mechanical properties of the atoms no longer come into play; they are considered as causes of optical discontinuity. Finally, when radium is used, it is the emissions of projectiles that are counted. We have arrived at such a point that, if there had been any discordances, we would not have been puzzled as to how to explain them; but fortunately there have not been any. The atom of the chemist is now a reality (…).

Poincaré took very seriously the fact that hypotheses are indispensable in science (1900, 8) but he went one to distinguish between three types of hypotheses. The first type included all those assumptions that make mathematical physics possible, e.g., certain idealisations and simplifications, principles of symmetry and the like. The second type—which Poincaré called ‘indifferent’—has a similarity with the first in that it includes assumptions that ease calculations. But they are significantly different from the first type in that the same results—or predictions—can also be achieved, perhaps in a more cumbersome fashion, by their negations. Poincaré used the atomic conception of matter as an example of an indifferent hypothesis. The core of the atomic conception of matter was that matter was discontinuous, that is that it had a granular structure: it consisted of a huge—but not infinite—number of particles in constant motion subject to mechanical laws. So the rival hypothesis—indifferent too—was that matter was continuous. The third kind of hypothesis is what he called “true generalisations” (1900, 10), which are subject to experimental confirmation or disconfirmation.

Implicit in Poincaré’s distinction is the claim that the real generalisations (which included Maxwell’s laws and other highly theoretical ones) could be accommodated within either of the pair of indifferent hypotheses—if only with varying degrees of complexity. But then it is equally implicit in his thought—and was made explicit later on—that indifferent hypotheses are the kind of hypotheses that can change cognitive status: they can become empirical in the sense that they might well be amenable to experimental test (part of which might be that other established empirical generalisations are no longer embedded within either the hypothesis or its negation). In his (1900, 16) he outlined how this is possible by noting that the kinetic of gases has revealed a “true relation”, which, without the kinetic theory, “would be deeply hidden”, viz., the relation between the pressure of gases and osmotic pressure (that is, that the law of the osmotic pressure follows from the kinetic theory). Interestingly, this theory-mediated fact that was established by Boltzmann and impressed Poincaré the most was essentially used in Perrin’s theoretical account of the Brownian movement.

Poincaré did share with many others a certain disdain for metaphysics, and with Duhem, in particular, the thought that science will never be able to have in view how things are-in-themselves. And though he did not equate explanation with metaphysics, he was very sceptical—to say the least—about searching for explanations that posit unobservable entities, and in particular mechanical explanations in terms of atoms-in-motion obeying the laws of mechanics. He took it that science progresses by establishing general principles and by showing that there is continuity (mostly formal-mathematical continuity) in the transition from old principles to new ones. He nonetheless came to accept the atomic conception of matter, at least in its essentials. A prime reason for this was that he thought it incredible that a hypothesis leads to *novel* predictions as a matter of chance. Novel predictions require explanation—the unexpected requires explanation. This is a principle that Poincaré abided by throughout his career (see 1900, 7 & 8 for one of the many occurrences of this principle in his *oeuvre*). There is, actually, a particular case in which Poincaré thought that this Principle is compelling: when “experience reveals a coincidence which could have been anticipated and could not be due to chance, and particularly when a numerical coincidence is involved” (1913, 90). When an otherwise unexpected coincidence is anticipated and explained by a hypothesis, this “ceases” to appear to us as hypothesis (cf. 1913, 89). And this is precisely what Poincaré thought happened with the atomic conception of matter c. 1912. In fact, apart from Perrin’s determination of Avogadro’s number, Poincaré also thought that the kinetic theory of gases had already the impressive success of explaining a coincidence, viz., that the laws of the gases, the laws of the dilute solutes and the laws obeyed by the free electrons in metals are the *same*: they all follow from the basic hypotheses of the theory. Actually, Perrin extended these laws to cover emulsions too, and this extension was essential to his explanation of the molecular origins of Brownian movement.

2.5 Boltzmann: Hypotheses are not Just Milk Cows

It was mainly Boltzmann—one of the founders of the modern atomic conception of matter and of the kinetic theory of gases, in particular—who saw very clearly that explanatory role is an important factor in the evaluation of hypotheses and that some explanations are better than others. Boltzmann (1900) took to heart Maxwell's critique of the Hypothetico-Deductive method: a hypothesis is not true just because its deductive consequences are empirically confirmed. There is always the possibility of alternative hypotheses that do the business and there is always need for fresh evidence in favour of the chosen hypothesis. In detailing the various forms of resistance to the atomic conception of matter, Boltzmann focused his attention not so much on energetics but on what he aptly called "phenomenologists", that is those scientists (including the early Planck) who were opposed to the explanation of the visible in terms of the invisible. According to the phenomenologists, the aim of science was to "write down for every group of phenomena the equations by means of which their behaviour could be quantitatively calculated" (1900, 249). The theoretical hypotheses from which the equations might have been deduced were taken to be the scaffolding that was discarded after the equations were arrived at. For phenomenologists, then, hypotheses are not unnecessary or useless—rather they have only a heuristic value: they lead to stable (differential) equations and *that's it*.

Boltzmann's reaction was that it was simply an illusion on the part of the phenomenologists to think that by doing all this they do not go beyond experience. The chief reason why this is so is that all scientific representation involves idealisation and this ubiquitous feature of science goes far beyond what is given in experience. Besides, Boltzmann thought, the further science is removed from experience, "the broader the survey we obtain, the more surprising the facts we discover" (1900, 251). There is a price though for this broader survey, viz., that the further we go away from experience, "the greater the likelihood of our going astray". So the dilemma is not between staying within experience and transcending it. This is illusory. The real issue is trying to *secure*—epistemically—our going beyond experience.

How is this done? Boltzmann made two rather critical points. The first was related to an attempt to neutralise the "historical principle" employed by the phenomenologists, viz., that hypotheses are essentially insecure because they tend to be abandoned and replaced by others, "totally different" ones. Against this "historical principle", Boltzmann argued that despite the presence of "revolutions" in science, there is enough continuity in theory change to warrant the claim that some "achievements may possibly remain the possession of science for all time" (1900, 253). Besides, if the historical principle is correct at all, it cuts also against the equations of the energeticists and the phenomenologist's. The second point made by Boltzmann was that the empirical successes of certain hypotheses (and in particular of the kinetic theory of gases) and the fact that these successes could not have been attained in any other way warrants the claims that these hypotheses "deserve calculation and not antagonism" (1900, 255).

This last point, of course, does not imply—as it stands—that there is reason to take empirically successful hypotheses to be true. But the overall tone of Boltzmann's argument suggests that he took it that the atomic hypothesis was essentially correct. Boltzmann was fully aware of the anomalies that this hypothesis faced (e.g., the specific heats anomaly); as he was aware that the molecules must have had an internal structure. So further evidence was certainly required. But, as he stressed in his (1906, 599), the atomic conception of matter has given "a better explanation of the previously known facts, it inspired new experiments and permitted the prediction of unknown phenomena". Besides, it has provided a unified framework for the study of all forms of matter (cf. 1901, 73 & 76).

It seems that Boltzmann's major concern c. 1900—when he felt that the atomic conception of matter was losing ground—was not so much to defend its truth but rather to (a) make vivid its usefulness and (b) leave open the route from its being useful to its being true (cf. his 1901). But he was quite clear that the battlefield for the atomic hypothesis would be a rather conclusive proof of the discontinuity of matter (cf. his 1906, 600). Boltzmann did not live to see Perrin's work on the discontinuous structure of matter. Around 1900 he still had to do a lot of work to persuade the community that the atomic hypothesis was not just a "milk cow", as he nicely put it.[5]

2.6 The End of a Philosophical Journey

The way I have tried to chart the terrain on which the philosophical battle for the atomic conception of matter was fought c. 1900 has refrained from using well-known philosophical labels to describe the views of the main protagonists. Their views, it is by now clear I hope, were quite complex to be captured by simple and all-encompassing labels. Still, I take it that the interpretative line I have used shows something useful, viz., that the stance towards explanatory hypotheses was not uniform and rigid. In fact, it considerably influenced the scientists' verdict on the fate of the atomic conception of matter. To put it a bit crudely, the Stallo-Duhem-Mach line on the role and status of explanatory hypotheses did not leave much room for accepting the atomic conception of matter as by and large true—even after critical evidence had been gathered in its favour. The Ostwald-Poincaré-Boltzmann line (despite the very significant differences in the overall outlook of these three) was characterised by a certain epistemological openness. It is true that c. 1900, the atomic hypothesis needed quite a lot of work to graduate from hypothesis to truth. But then again, were this work to be done, it could so graduate!

The tension with which I started this section—the tension between the instrumental indispensability of hypotheses and their epistemic precariousness—could not be resolved unless the atomic conception of matter started to meet some of the requirements that were

[5] Max Planck's case is very instructive. He also started as an anti-atomist (in the 1890s) and insisted, in rivalry with Boltzmann, on the usefulness of a continuous conception of matter. He advocated thermodynamics as distinct from atomism. It was his ground-breaking work on the black-body radiation and the quantization of energy that made him more favourable towards the atomic conception of matter, as he had to rely on an atomistic-statistical model for the explanation of the black-body radiation (cf. Krips 1986). It is also noteworthy, however, that Perrin's work on the Brownian motion played some important role in shifting Planck towards atomism. In a public lecture in Berlin in 1910, he noted "(…) indeed, in the elucidation of the so-called Brownian movement, it [the kinetic theory of gases] has provided the direct, so to speak concrete, justification for its existence, and this has been its supreme triumph. In brief, it can be said that, in heat, chemistry, and electron theory, the kinetic theory of the atom is no longer merely a working hypothesis, but a lasting and established theory" (1960, 31). In a rectorial lecture in 1914 in the University of Berlin he was even more explicit (referring to the Brownian motion): "These molecules, themselves invisible, continually collide with particles floating around them (which are visible in a microscope) and are impelled along irregular paths. The final theoretical proof of the correctness of this explanation was first given quite recently, when Einstein and Smoluchowski, obtained statistical laws governing the distribution of density, the velocities, the mean free paths, and even the rotations of the microscopic particles, and these laws were most strikingly confirmed quantitatively in all details, particularly through the experimental work of Jean Perrin. There can be no doubt now, in the mind of the physicist who has associated himself with inductive methods, that matter is constituted of atoms (…) (1960, 63). Certain relevant aspects of Planck's methodological perspective are highlighted by Krips (1986). One particularly apposite consideration is Planck's claim that atoms emerged as the invariant elements of various theoretical models of the phenomena (cf. 1960, 42).

necessary for it to change cognitive status. It had to become more precise and, in particular, it had to be such that the magnitudes attributed to molecules became definite and measurable. It could then be put to a more definite test. The philosophical moral, however, should be obvious: the instrumental indispensability of hypotheses need not be in tension with an enhanced epistemic status they might achieve. Hypotheses can and do change cognitive status.

It is precisely within this intellectual milieu that Perrin started his own theoretical endeavours concerning the atomic conception of matter.

3 Perrin and the Atomic Conception of Matter

Perrin started his career with important experimental work on the cathode rays, showing in 1895 that they are negatively charged particles.[6] When it comes to the atomic hypothesis itself, his own attitude towards it exemplifies the general attitude we have noted above: a movement from the utility of the atomic hypothesis to its truth. Perrin's case is, then, in itself instructive as to the examination of reasons that engender and justify this shift.

3.1 Explaining the Visible by the Invisible

Perrin's first paper on the atomic conception of matter was published in 1901 in *Revue Scientifique* under the title: the molecular hypotheses. Ten years later, he published another paper (1911) in the same journal with the title: the reality of molecules. The conclusion of this article was that "the objective reality of molecules" had been demonstrated. What had happened in between?

In (1901, 449), he took it that, by and large, the debate about the molecular hypothesis—that is the debate about whether matter is continuous or discontinuous—has had a "uniquely philosophical character" and as such the choice between the two approaches was a matter of "taste". The issue could not yet be dealt with experimentally. Perrin did favour the atomic conception, but he was adamant that even though numerous of its consequences had been experimentally confirmed and even though these did not follow from the alternative hypothesis (of continuity), still "we will not perhaps have the right to say that the molecular hypothesis is true, but we will know at least that it is useful".[7] The atomic hypothesis remained "one of the more powerful tools of research" invented by human reason. Perrin presented the rudiments and the successes of the kinetic theory of gases and stressed that the law of the corresponding states that was established by van der Waals was a "triumph" of the theory. But he did also claim that for the acceptance of the atomic conception as something more than useful, the determination of the number of molecules and of their diameter was required.

In his textbook on Physical Chemistry of 1903, he contrasted two methods for doing science: the inductive, which proceeds by analogy and generalisation, and the intuitive-deductive, which consists "in imagining a priori matter to have a structure that still escapes our imperfect senses, such that its knowledge permits *deductive* predictions about the

[6] The classic and still unparalleled biography of Perrin is by Nye (1972).

[7] Perrin did stress, already in 1901, that the molecules of gases are composed of atoms and that the atoms have internal structure. But from the point of view of the kinetic theory of gases—and the fundamental claim that matter was discontinuous—the difference between molecules and atoms was not particularly important insofar as they were both treated as particles in constant motion.

sensible properties of the universe" (1903, viii). The latter method fosters "the illusion of a satisfactory explanation" (…) of "the visible in terms of the invisible, even when [it does not] lead to the discovery of new facts".

Perrin was sensitive to the fact that for many of his contemporaries the atomic hypothesis was a venture into metaphysics. Surprisingly, he added: "I do not forget that the sensation is the only reality". This would seem to condemn the atomic hypothesis from the start. Yet, Perrin made two important comments on the claim above. The first is that "[Sensation] is the only reality, on the condition that to the actual sensations all *possible* sensations are added". This is important because he thought that the atomic hypothesis could, in the end, be rooted in sensations. How this could be possible is illustrated by the second comment he made, in which he drew an analogy between molecules and microbes—the latter did become the object of 'possible sensation' via the microscope. Here is how he put it:

> One would certainly have been able, without the aid of the microscope, to arrive at the thought that contagious diseases were due to the multiplication of very small living beings. One, guided by these ideas a priori, would have been able to discover almost all of the Pasteurian technique. One would have thus followed deductive science and cured the contagious diseases, but following a way condemned by the supporters solely of the inductive method, until the very day in which the microscope had proved that the microbe hypothesis expressed several possible sensations. Here then is an indisputable example of a structure which could escape our senses and the knowledge of which allows anticipation of certain properties which are [to our senses] directly accessible.

Note that Perrin does not complain about the unobservability of atoms (or of microbes). Nor is his point that microscopes render them directly observable. Rather, his point is that explanatory reasons cannot constitute the *sole* ground for accepting the reality of a hypothesised explanatory posit.

By the time he wrote *Les Atomes*, he had become a more ardent defender of the intuitive-deductive method. In the preface, he (1916, vii) noted:

> To divine in this way the existence and properties of objects that still lie outside our ken, *to explain the complications of the visible in terms of invisible simplicity* is the function of the intuitive intelligence which, thanks to men such as Dalton and Boltzmann, has given us the doctrine of Atoms. This book aims at giving an exposition of that doctrine.

However, even then, he very much hoped that there will be some day in which atoms will be "as easy to observe as are microbes today", though for him the use of microscope is within the "realm of experimental reality" (1916, x). The point that needs to be appreciated is that for Perrin science should proceed by refusing to limit itself "to the part of the universe we actually see" (1916, xii) and that the best way to achieve this is to aim at explanation-by-postulation, that is by aiming to explain the visible in terms of the invisible.

3.2 Setting the Stage for an *Experimentum Crucis*

Perrin's more technical work is collected in his *Brownian Movement and Molecular Reality*, which appeared in French in 1909 and was translated into English in 1910. In this book, he makes almost no methodological remarks, but I shall attempt to reconstruct the structure of his argument for the reality of molecules in a way that his methodology is clearly brought out. The key point of his strategy is this (1910, 7):

> Instead of taking this hypothesis [the atomic hypothesis] ready made and seeing how it renders an account of the Brownian movement, it appears preferable to me to show that, possibly, it is logically suggested by this phenomenon alone, and this is what I propose to try.

Perrin takes it that the atomic hypothesis has some initial plausibility, which is grounded in the fact that it remains the only serious admissible explanation of Brownian movement. Reviewing the work of Gouy and others, he suggests that several potential causes of the movement can be safely eliminated and that, in particular, the cause of the movement is internal and not external (cf. 1910, 6). This kind of eliminative approach paves the way for rendering the standard atomic explanation of Brownian movement "by the incessant movements of the molecules of the fluid" the only serious admissible explanation. This is not enough to render it true or probable; and yet, by the end of his reasoning, Perrin does think that it is probable *and* true. This happens because Perrin succeeded in showing that Brownian movement *is* an instance of molecular movement and hence it obeys the laws of the molecular movement. Hence, it can be used to (a) determine Avogadro's number and (b) to specify the individuating properties of molecules and atoms, such as their mass and dimensions (cf. 1910, 49–51). Avogadro's hypothesis, as Perrin (1910, 10) put it, is this: "Any two gram-molecules contain the same number of molecules". As noted in the Introduction, there had been a number of estimations of it before Perrin embarked on the project of its determination. What was really gained by Perrin's approach?

Perrin was looking for a phenomenon which could allow him to determine directly Avogadro's number. His theoretical construction proceeds as follows. Let us suppose we have a uniform emulsion (all granules are identical) in equilibrium, which fills a vertical cylinder of cross section *s*. Consider a horizontal slice contained between the levels <h, h + dh>, where this slice is enclosed between two semi-permeable pistons—they are permeable to the molecules of water but impermeable to the granules. Each piston is subjected to osmotic pressure by the impact of the granules it stops. This slice does not fall; hence there must be an equilibrium between the force that tends to move it upwards (viz., the difference of the osmotic pressures) and the force that tends to move it downwards (viz., the total weight of the granules less the buoyancy of the liquid). Having estimated both forces, Perrin arrives at the equation of the distribution of the emulsion

$$2/3W\log(n_0/n) = \varphi(\Delta - \delta)gh \tag{1}$$

where W is the mean granular energy, φ the volume of each granule, Δ its density, δ the density of the intergranular liquid and n and n_0 respectively the concentrations of the granules at the two levels separated by height h. The task then is to measure all magnitudes other than W; hence, to determine W (cf. 1910, 24).[8]

The equation of distribution describes an exponential law. It shows that the concentration of the granules decreases in an exponential way as a function of the height: the concentration is denser towards the bottom of the cylinder and rarer towards its top. This is exactly what happens with the distribution of the density of air: the barometric pressure

[8] It is of significance that, as Perrin (1910, 24, note) stresses, the equation of distribution of emulsion was arrived at independently—and by different means—by Einstein and Smoluchowski. What he observed, and they did not, was that Eq. 1 could furnish a crucial experiment for the molecular theory of Brownian movement.

decreases exponentially as a function of the height. It is this analogy that allows Perrin to justify an important assumption he makes, viz., that the mean granular energy W of the particles in Brownian motion is equal to mean molecular energy W'. In other words, he argued that the Brownian particles behave as large molecules and hence obey the laws of the gases. Indeed, the first few sections of his (1910) aim to motivate this claim. The mean kinetic energy W' of the molecules of a gram-molecule of a gas is a function of Avogadro's number N. It is equal to $(3R/2N)T$, where T is the absolute temperature of the gas and R is the constant of the perfect gases (cf. 1910, 19). Hence,

$$W' = (3R/2N)T. \tag{2}$$

Perrin relied on van't Hoff's proof that the invariability of energy (viz., that the mean kinetic energy is the same for all gases at the same temperature) holds *also* for the molecules of dilute solutions and generalised it to all fluids, including emulsions. Given this generalisation, he (1910, 20) could note that

> not only (…) each particle owes its movement to the impacts of the molecules of the liquid, but further (…) the energy maintained by the impacts is on average equal to that of any one of these molecules.

The claim that "the mean energy of translation of a molecule [is] equal to that possessed by the granules of an emulsion"—that is that $W = W'$—is crucial. It paved the way for calculating the granular energy in terms of molecular magnitudes. Accordingly, Perrin thought that the road was open for an *experimentum crucis*: either $W = W'$ or $W \neq W'$ and given that both W and W' could be calculated, we might have "the right to regard the molecular theory of this movement as established" (1910, 21).

Being an extremely skilful experimenter, Perrin managed to prepare suitable emulsions of a gum called 'gamboge' and mastic, with spherical granules of radius α. Equation 1 thus becomes

$$2/3W\log(n_0/n) = 4/3\pi\alpha^3(\Delta - \delta)gh. \tag{1'}$$

Here again, all magnitudes but W are measurable. Determining the ratio (n_0/n) was quite demanding, but Perrin used the microscope to take instantaneous snapshots of the emulsion. Determining the value α of the radius was even more demanding, but Perrin used three distinct methods to achieve this, one relying on Stokes's equation (capturing the movement of a sphere in a viscous fluid), and two without applying this equation (using, instead, a *camera lucida*). These calculations were in impressive agreement, which led Perrin to conclude, among other things, that the otherwise controversial application of Stokes's equation (because it was meant to apply to continuous fluids) was indeed legitimate.

When all was said and done,[9] Perrin was able to calculate the granular energy W (which is independent of the emulsion chosen). If $W = W'$, there is a direct prediction of Avogadro's number N from Eqs. 1 and 2, that is:

[9] Perrin presents in painstaking detail the various ways in which he manipulated the emulsions that he studied and his various attempts to establish concordances between the values of the properties of the Brownian particles (cf. 1910, §§15–22). At one point he described how he had to wait for 2 or 3 days for various protozoa to die that had developed in an emulsion which had not been rendered aseptic. The bacteria "fell inert to the bottom of the preparation" (1910, 41). For an illuminating discussion of the use of the ultramicroscope by Perrin, cf. Bigg (2008).

$$(RT/N)\log(n_0/n) = 4/3\pi\alpha^3(\Delta - \delta)gh$$

and

$$N = 3RT\log(n_0/n)/4\pi\alpha^3(\Delta - \delta)gh. \tag{1''}$$

This prediction could then be compared with known calculations of N based on the kinetic theory of gases, e.g., that by van der Waals's ($N = 6.10^{23}$) (cf. 1910, 44). Perrin made a number of experiments and concomitant calculations and the agreement was always impressive. As he (1910, 46) put it: "[I]t is manifest that these values agree with that which we have foreseen for the molecular energy. The mean departure does not exceed 15% and the number given by the equation of van der Waals does not allow for this degree of accuracy".

Perrin became immediately convinced that "this agreement can leave no doubt as to the origin of Brownian movement". "[A]t the same time", he said, "*it becomes very difficult to deny the objective reality of molecules*". What convinced him, he (1910, 46; 1916, 105) says, was that on any other hypothesis (better, on the negation of the atomic hypothesis), the expected value of N from the study of the movement of granules suspended in a liquid would be either infinite or zero—it would be infinite if all granules actually fell to the bottom of the vessel, and zero if the fall of the granules was negligible. Hence, on the hypothesis that matter is continuous, the probability that the predicted value of N would be the specific one observed would be zero; on the contrary, this probability is high given the atomic hypothesis. This, Perrin noted, "cannot be considered as the result of chance".[10]

As if his own approach was not enough, Perrin went on to report on a number of other calculations of Avogadro's number, including from: the measurement of the coefficient of diffusion; the mobility of ions; the blue colour of the sky (the diffraction of the sunlight by the atmospheric molecules); the charge of ions; radioactive bodies; the infra-red part of the spectrum of the black-body radiation. Though all these calculations were less accurate than his own, he took it that this "miracle of concordance", as he called it, put beyond doubt the reality of molecules. Avogadro's number emerged as an "essentially invariant" element of

[10] A distinct part of Perrin's work on the molecular explanation of Brownian motion was related to his attempt to verify experimentally Einstein's theory of diffusion. Einstein had presented his work on the "movement of small particles suspended in a stationary liquid" in (1905). Based on the existence of a dynamic equilibrium between osmotic forces and viscous forces, he was able to derive the coefficient of diffusion of the suspended (Brownian) particles as a function of the coefficient of viscosity of the liquid and the size of the suspended particles. He was then able to calculate the square of the mean displacement of the suspended particles (due to their collision with the liquid molecules) as a function of the diffusion coefficient and the time and from this, to derive a theoretical prediction of Avogadro's number N. But Einstein relied on an important statistical assumption, viz., that the motion of the suspended particles was completely irregular—corresponding to a stochastic process—and, hence that the displacements of the particles could be captured by a normal probability distribution which determined the number of particles which are displaced by a given distance in each time interval (cf. 1905, 14–16). Though Perrin could have stopped with his own determination of Avogadro's number, he took it upon himself to verify Einstein's assumption by suitable experiments (1910, §31). Einstein's theoretical prediction had been put to the test c. 1906 and it had been found to be in conflict with experimental findings. Based precisely on his account of the molecular origin of the Brownian movement, Perrin could argue that Einstein's theory was either based on some unnoticed unjustified assumption or that the experiments that were used to test it were not accurate (cf. 1910, 58–59). Indeed, further experiments he and his assistant M Claudesaigues performed—trying to measure the displacement of granules of known diameter—confirmed Einstein's theory. Hence, Perrin could assume that the previous experiments on Einstein's theory must have been wrong (cf. 1910, §29). Perrin's calculation of Avogadro's number based on Einstein's theory was in good agreement with his own. Perrin offers a very detailed discussion of Einstein's theory and his own experimental verification of it in his 1911 Solvay conference paper (cf. 1912, 189–216). For a fine discussion of Einstein's 1905 paper, see Renn (2005).

various ways to represent the structure of matter (1910, 74). The multiple determinations of Avogadro's number by different means and in seemingly distinct areas was an important element in Perrin's strategy for proving the reality of molecules, since it was the key to proving the invariance of the molecular properties. Given that the access to the molecules was only indirect—and given Perrin's insistence that their magnitudes should be definite and measurable—it was important to be shown that these magnitudes are essentially invariant irrespective of the observable phenomena that leads to their calculation.[11]

Here then is his conclusion:

> I think it impossible that a mind, free from all preconception, can reflect upon the extreme diversity of the phenomena which thus converge to the same result, without experiencing a very strong impression, and I think it will henceforth be difficult to defend by rational arguments a hostile attitude to molecular hypotheses, which, one after another, carry conviction, and to which at least as much confidence will be accorded as to the principles of energetics (1910, 91).

3.3 The Objective Reality of Molecules

What then is the logical structure of Perrin's argument? Note well his claim that he was after a crucial experiment for the reality of atoms. Of course, there are no crucial experiments, *stricto sensu*. But as Poincaré has put it, an experiment can condemn a hypothesis, even if it does not—strictly speaking—falsify it. Perrin's argument was precisely meant to condemn the denial of the atomic hypothesis—which, of course, is not to say that he intended to condemn energetics. As we have just seen, he did think (and he had already noted this in his 1903) that energetics need *not* imply the denial of the atomic hypothesis, viz., that matter is continuous.

I take it that given the details of the presentation above, Perrin's reasoning is best reconstructed by means of a probabilistic argument. Given his theoretical model, Perrin has made available two important probabilities, viz.

$$\text{Prob}(n = N/AH) = \text{very high}$$
$$\text{Prob}(n = N/-AH) = \text{very low}$$

That is, the probability that the number of molecules in a gram-molecule of a gas (including an emulsion, which does behave as a gas) is equal to the Avogadro number N given the atomic hypothesis is very high, while the probability that the number of molecules is equal to the Avogadro number given the denial of the atomic hypothesis is very low. These two likelihoods (in the technical sense of the term) can be used to specify the Bayes factor f.

$$f = \text{prob}(n = N/-AH)/\text{prob}(n = N/AH)$$

Bayes's theorem states

$$\text{prob}(AH/n = N) = \text{prob}(n = N/AH)\text{prob}(AH)/\text{prob}(n = N)$$

where

[11] A version of this point is made by de Broglie (1945, 11).

$$\text{prob}(n = N) = \text{prob}(n = N/AH)\text{prob}(AH) + \text{prob}(n = N/-AH)\text{prob}(-AH).$$

Using the Bayes factor, Bayses's theorem becomes this:

$$\text{prob}(AH/n = N) = \text{prob}(AH)/(\text{prob}(AH) + f\,\text{prob}(-AH)).$$

Perrin's argument then can be put thus:

1. f is very small.
2. $N = n$ is the case.
3. prob(AH) is not very low.
4. Therefore, prob($AH/n = N$) is high.

Premise 1 (that f is very small) is established by the body of Perrin's demonstration, which shows that given the denial of the atomic hypothesis, it is extremely unlikely that the Avogadro number has the specific value it does (that is, that the number of molecules in a gram molecule of a gas is equal to Avogadro's number).

Premise 2 is established by a series of experiments involving different methods and different domains.

Premise 3 is crucial, since it is required for the probabilistic validity of Perrin's argument. It specifies the prior probability of the atomic hypothesis and without the prior probability the argument noted above would commit the base-rate fallacy. Perrin's preparatory eliminative work had aimed to show that, by eliminating several alternative potential explanations of Brownian movement, the atomic hypothesis had gained at least some initial plausibility which was reflected in its being given some non-zero prior probability of being true.[12]

The following might, actually, be stressed. There is a rare case in which the prior probability of a hypothesis does not matter, and this is when the Bayes factor is zero. This happens when just one hypothesis can explain the evidence. Then, we can dispense with the priors. If the Bayes factor is zero, no matter what prob(AH) is, the posterior probability prob($AH/n = N$) is unity. And the Bayes factor is zero if prob($n = N/-AH$) is zero. Recall Perrin's wording: "That, in the immense interval [0, infinity] which a priori seems possible for N, the number should fall precisely on a value so near to the value predicted, certainly cannot be considered as the result of chance" (1910, 46; cf. also 1916, 105). This is *almost* tantamount to saying that his experiments established that prob($n = N/-AH$) = 0.

This kind of claim would (and does) explain Perrin's confidence that the atomic hypothesis has been "established"; that he has offered "a decisive proof" of it (1916, 104). Admittedly, there is room for manoeuvre here, since it *might* be argued that prob($n = N/-AH$) has, after all, a small finite value. In that case, some reliance on the prior probability prob(AH) is inevitable and the usual philosophical dialogue would kick off: How are the priors fixed? Are they fully objective? If not, is the case for the reality of atoms strong?

Instead of entering this dialogue now, I will simply state that prior probabilities express reasonable degrees of belief, which supervene on certain causal and explanatory qualities

[12] Is there any reason to take the suggested probabilistic reconstruction of Perrin's argument as being Perrin's own? There is some interesting circumstantial evidence, coming mostly from the fact that Émile Borel—who was Perrin's close friend and colleague and teacher of his son, Francis—was an expert on probability theory and had actually made explicit reference to Bayes's theorem in his (1914). Borel (1914, 99) explicitly associated Bayes's theorem with the case of finding the probability of the causes (given their effects) and stressed that there is need to specify the a priori probability of the cause, though he admitted there was uncertainty as to how a priori probabilities were estimated. Borel did make many references to Perrin's statistical methods in his (1914).

of a given hypothesis.[13] In fact, in the case we examined, the prior probability of the atomic conception of matter was fixed by applying causal-eliminative reasoning to the various hypotheses that might have explained the origins of the Brownian movement.[14]

3.4 Removing the Scaffolding?

But didn't Perrin end up his (1910) with the strange claim that the reference to molecules was dispensable? Indeed, he (1910, 91) stressed the following:

> Lastly, although with the existence of molecules or atoms the various realities of number, mass, or charge, of which we have been able to fix the magnitude, obtrude themselves forcibly, it is manifest that we ought always to be in a position to express all the visible realities without making any appeal to elements still invisible. But it is very easy to show how this may be done for all the phenomena referred to in the course of this Memoir.

And then he proceeded to show how the very reference to Avogadro's number could be eliminated. Consider any two laws in which N features as a constant (e.g., Einstein's diffusion equation and the law of the distribution of radiation) and take their pure functional form. "The one", Perrin says,

[13] The whole issue is subtle, of course. But I think scientific realists have unnecessarily conceded the point—if they in fact have—that *either* prior probabilities should be fixed in a fully objective and logical manner (God-given? based on purely logical or synthetic a priori principles like the Principle of Indifference?) or else they are purely subjective and idiosyncratic and therefore useless in the defence of the rationality of belief in theories. Prior probabilities can be whimsical, but they need not be. They can be based on judgements of plausibility, on explanatory considerations prior to the collection of fresh evidence and other such factors, which—though not algorithmic—are quite objective in that their employment does and should command rational agreement.

[14] There have been a number of discussions-cum-reconstructions of the structure of Perrin's reasoning. I cannot discuss them here in any detail. But I will present a very brief (and sketchy) summary of them and hint to their major shortcomings. A fully developed account of the philosophical reconstructions of Perrin's argument has to wait for a different occasion. Part of the reason why there are many varied readings of Perrin's argument is that the various interpreters focus on different *parts* of Perrin's argumentative strategy. Wesley Salmon (1984) has argued that Perrin's reasoning was an instance of 'a common cause argument', where the reality of molecules is taken to be the common cause displayed in the various ways to calculate Avogadro's number. The chief problems with this reconstruction is that (a) it does not adequately explain Perrin's own contribution to the confirmation of the atomic hypothesis, since most of the ways to calculate Avogadro's number were known (and they were in agreement) before Perrin brought them together in his books; and (b) it is not clear in what sense exactly the molecules are the common cause of the agreement perceived in the various calculations of Avogadro's number. Nancy Cartwright (1983) has argued that Perrin's reasoning was an instance of the inference to the most likely cause. But from the fact that the correlated phenomena (the phenomena that allow the determination of Avogadro's number) have a cause, it does not follow what this cause is; in particular, it does not follow that the cause is the incessant motion of the molecules. Deborah Mayo (1986) focuses her attention on Perrin's verification of Einstein's theory and argues that classical error-statistics captures Perrin's reasoning. This might well be right when it comes to explaining Perrin's attempt to secure Einstein's assumption of the random distribution of the mean displacements of the Brownian particles, but fails to explain the reasoning behind Perrin's own account of Brownian motion. Richard Miller (1987) has argued that Perrin's reasoning was based on topic-specific truisms, for example that the Brownian movement is in need of a causal explanation, and that the molecular collisions offer this explanation. But these topic-specific truisms were available before Perrin; hence we do not have an explanation of why it was *Perrin's* determination of Avogadro's number that tilted the balance in favour of the atomic conception of matter. Peter Achinstein (2001) has offered the most sophisticated reconstruction of Perrin's reasoning to date, trying to come to terms with the details of Perrin's own demonstration of the cause of the Brownian motion. I offer a criticism of Achinstein's account in my (2011). For a criticism of van Fraassen's (2009) recent account of Perrin's strategy, see my (forthcoming).

> expresses this constant [Avogadro's number] in terms of certain variables, a, a′, a″, …,
> $N = f[\mathrm{a}, \mathrm{a}', \mathrm{a}'', \ldots]$;
> the other expresses it in terms of other variables b, b′, b″, …,
> $N = g[\mathrm{b}, \mathrm{b}', \mathrm{b}'', \ldots]$.
> Equating these two expressions we have a relation
> $f[\mathrm{a}, \mathrm{a}', \mathrm{a}'', \ldots] \equiv g[\mathrm{b}, \mathrm{b}', \mathrm{b}'', \ldots]$,
> where only evident realities enter, and which expresses a profound connection between two phenomena at first sight completely independent, such as the transmutation of radium and the Brownian movement (1910, 91–92).

This way to proceed might well suggest that, in the end, Perrin wanted to show that the molecular hypothesis is eliminable: a scaffolding that may well be removed after connection between empirical phenomena have been established. Note, for one, that the 'evident realities' which enter into the functional relations thus established are not merely observable magnitudes or properties of observable entities. For instance, the diameter of the Brownian particles or the wave-length of emitted light are not observable. They are, however, determinate and measurable and this is what Perrin insisted on. More importantly, however, Perrin did not take it that the possibility of eliminating the constant N implied that molecules could be dispensed with. In (1910, 92) he noted that the discovery of functional relations such as the above—which could not have been established without the atomic hypothesis—mark "the point where the underlying reality of molecules becomes part of our scientific consciousness".

And if this had left any doubt to his reader about his commitments, in a subsequent publication in which he also presented *verbatim* the same idea of establishing functional relations among "evident realities" he (1912, 250) added:

> But, under the pretence of rigour, we will not make the mistake to throw thus out of our equations the elementary magnitudes that allowed ourselves to obtain them. This would not be to remove a scaffolding that has become useless to the finished structure; it would be to mask the pillars that that have made its skeleton and beauty.

And in his *Les Atomes*, he put the point in a similarly graphical way:

> But, under the pretence of rigour, we will not make the mistake to avoid the intervention of the molecular elements in the enunciated laws that we would not have obtained without their assistance. This would not be to uproot a useless stake from a thriving plant; it would be to cut the roots that nourish it and make it grow.[15]

The choice of contrast by Perrin is very suggestive: scaffolding vs pillars and stake vs roots. Neither pillars nor roots can be removed without destroying whatever is supported by them.

4 Lessons for Scientific Realism

Let me tie the various threads of this long study together and draw some general lessons for scientific realism.

[15] My translation from p. 284 of the French edition of *Les Atomes* (Flammarion, 1991). The rendering of this passage in the English translation of the book (1916, 207) is mistaken.

Hypotheses in science are indispensable but epistemically precarious. Hypotheses—especially explanatory hypotheses that posit unobservable entities—have to earn their right to graduate to truths (or near truths, anyway). But they should be granted this right by a spirit of epistemological openness, which allows scientists to change their minds when decisive evidence in favour of (or against) a hypothesis becomes available—evidence that meets ordinary scientific criteria of relevance and strength. This openness is contrasted to, typically philosophically-motivated, stances which take it to be the case that there are no circumstances under which hypotheses can change cognitive status and gain in credibility.

The change of cognitive status is enabled when an explanatory hypothesis implicates entities (magnitudes) with definite and measurable properties amenable to experimental control. It is boosted when there are 'miracles of concordances', that is when the various predictions drawn from it are so accurate and concordant that they cannot reasonably be taken to be a matter of chance—as both Poincaré and Perrin stressed. It is secured when the posited entities and their properties are essentially invariant elements of various theoretical representations. These can be taken to be doubt-removing strategies which explain the change of epistemic attitude towards an explanatory hypothesis and underwrite the acceptance of the reality of entities that were initially taken to be ontically suspicious. They constitute reasons such that, once available, they are seen as conclusive by the active participants in scientific debates about the reality of invisible entities.

Here, then, are three general lessons for the scientific realism debate that this study has driven home.

4.1 Causal Role Matters

To introduce the first, let us recall Perrin's early (1903) hope to make molecules the objects of "possible sensations". In his (1916, 105) he claims:

> The objective reality of the molecules therefore becomes hard to deny. At the same time, molecular movement has not been made visible. The Brownian movement is a faithful reflection of it, or, better, it is a molecular movement in itself, in the same sense that the infra-red is still light.

Perrin's point here is precisely that size does not matter, but causal role does! Like Pasteur before him, Perrin did place the molecules firmly within the laboratory, grounding their causal role and offering experimental means for their detection and the specification of their properties—even though, the molecules *themselves* did not become visible. This is of great significance because it becomes clear that Perrin's argument should be compelling for anyone who does not take it that strict naked-eye observability is a necessary condition for accepting the reality of an entity. It should also be compelling for anyone who thinks that causal role is a criterion for accepting the reality of an entity—irrespective of whether some instances of this entity are observable, while others are not. Recall Perrin's claim that the movement of the Brownian particles was a "faithful reflection" of the molecular movement, since the differed from molecules only in size and exemplified the very motion in which molecules were engaged. It then becomes clear why Perrin's argument could offer compelling reasons to almost everyone but Duhem, who took a very hard line on observability and denied the very call for explanation-by-postulation.

By the same token, it becomes clear that the real issue about the so-called theoretical entities is not their (un)observability, but rather their causal accessibility. Under favourable circumstances, causal accessibility can be seen as a kind of 'observation by proxy'. But what Perrin brought home was the claim that explanatory posits become causally accessible only if they are attributed definite and measurable properties. It is precisely this feature that renders claims about them open to empirical confirmation. What Ostwald aptly called "the scientific horizon" is not fixed and immovable; claims that were once below it can and do move above it. What facilitates this change is not that some suspicious entities become visible, but rather that some entities that are initially posited solely on the basis of explanatory considerations enhance their explanatory role: claims about them become definite and measurable; their causal role is established experimentally; they become, *qua* invariant elements, the locus of unification of disparate phenomena.

4.2 Context Matters

Perrin's case for the reality of molecules is rather exceptionally strong. Whether, however, it is really exceptional or not it is not easy to tell, because the second lesson of this study should be that commitment to the reality of certain explanatory posits should be made on the basis of the *strength* of the evidence there is for them.

Perrin's case highlights a general claim that I have been advancing lately, viz., that commitment to the reality of specific explanatory posits is a matter that depends on the context. As I have argued in my (2009), there are two types of evidence that are brought to bear on the truth of scientific hypothesis (and which inform judgements of prior probability and of confirmation). The first type is what I call *first-order evidence* and is related to whatever evidence scientists have in favour of a hypothesis. In Perrin's case, this evidence includes the several methods of determination of Avogadro's number, the evidence that goes into fixing a non-zero prior probability to the atomic hypothesis (e.g., the evidence that the cause of Brownian movement is internal to the fluid) etc. The second type of evidence, what I call *second-order evidence*, comes from the track record of scientific theories and/or meta-theoretical (philosophical) considerations that have to do with the reliability of scientific methodology. This, for instance, is evidence that many past explanatory hypotheses have been abandoned, or that there have been alternative potential explanations of some phenomena that came to be accepted later on etc. This kind of (historical-philosophical) evidence does not concern particular scientific theories but science as a whole. It is the kind of evidence that, for instance, motivates the pessimistic induction. I have claimed in my (2009), that the proper philosophical task is to balance these two kinds of evidence and that this balancing is context-dependent.

We have seen that both kinds of evidence played important—though generally conflicting—roles in the assessment of the cognitive status of the atomic conception of matter. In particular, both kinds of evidence were in use in assessing whether the atomic conception could and should change status from an instrumentally indispensable hypothesis to truth. Roughly put, the evidence that favoured the molecular origin of the Brownian movement was pitted against evidence for what Boltzmann aptly called the 'historical principle' of radical theory change, or claims about the explanatory-cum-metaphysical status of the atomic conception. Perrin's case shows how the context can settle issues of balance. His case for the molecular origin of the Brownian movement is so strong that the first-order evidence for the reality of molecules takes precedent over the second-order evidence there might be for being sceptical or instrumentalist about explanatory posits. The fact—if it is a fact—that other explanatory hypotheses have failed in the past is rendered irrelevant, in this context, by the strength of the first order evidence. The point is not that meta-theoretic or philosophical considerations do not get into the evidential balance sheet. Rather, it is that in certain contexts, they are trumped by the detailed and well-supported explanation of the phenomena to be explained.

4.3 Essential Truth Matters

Finally, the third lesson. The foregoing study suggests that after Perrin's achievements, it became *unreasonable* to defend the superiority of the molecular theory without defending its truth. That the evidence for the atomic hypothesis was indirect—that is, via its confirmation, as opposed to direct observation—does not imply that this evidence was insufficient. On the contrary, after a point and in the given context of balancing first-order and second-order evidence, resistance to the atomic hypothesis was solely based on philosophical dogma. Let's be careful here. My point is *not* that philosophical dogma is unreasonable. Rather, it is that adhering to philosophical dogma in the face of mounting scientific evidence against its basic presuppositions is unreasonable. It flies in the face of what I have called 'epistemological openness'.

But does Perrin's case show that the atomic conception is *true*? What it *does* show is that an essential component of it—viz., the discontinuous structure of matter—is true. It also shows how certain properties of the constituents of matter have been rendered definite and measured. In addition, it shows that Avogadro's number consolidated the unity of the atomic conception of matter: it was its essentially invariant element. Hence, the atomic conception was essentially true. This commitment left it open that it required further development and elaboration. For instance, it was already known to the advocates of the atomic conception back then that the molecules were made of atoms and that the latter had an internal structure.[16] Hence, it was known to them that various assumptions that helped the modelling of various phenomena on the basis of the atomic conception (e.g., that molecules were perfectly elastic spheres, and others) were wrong and needed refinement and/or replacement. All this is as it should be. As I argued many years ago (cf. my 1999), commitment to the truth of a theory is not an all-or-nothing matter. Progress and convergence do not require that theories capture the whole truth and nothing but the truth. The atomic conception of matter, in its essentials, has become a stable and permanent part of our evolving scientific image of the world.

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[16] There are a number of philosophical issues related to individuation, identity and countability of microscopic entities that are relevant to the arguments examined in this paper, whose discussion has to wait for a different occasion. However, the following should be stressed. Even if we were to fully accept that atoms lose their individuality for good, according to quantum mechanics, it does not follow from this that Avogadro's number loses its status as a significant invariant since, ultimately, it is the cardinal number of a collection of atoms and this can be had and calculated independently of whether or not the atoms in this collections can be individuated. In fact, we can follow French and Krause (2006) and think of Avogadro's number as a perfectly legitimate quasi-cardinal (see their Q19 on p. 286) of a quasi-set.

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